

Recovery of iron phosphate and lithium carbonate from sulfuric acid leaching solutions of spent LiFePO_4 batteries by chemical precipitation

Chen Jing ¹, Thanh Tuan Tran ², Man Seung Lee ¹

¹ Department of Advanced Materials Science & Engineering, Institute of Rare Metal, Mokpo National University, Chonnam 534-729, Korea

² Faculty of Biological, Chemical and Food Technology, Can Tho University of Technology, Can Tho City 900000, Vietnam

Corresponding author: mslee@mokpo.ac.kr (M.S. Lee)

Abstract: The recycling of lithium and iron from spent lithium iron phosphate (LiFePO_4) batteries has gained attention due to the explosive growth of the electric vehicle market. To recover both of these metal ions from the sulfuric acid leaching solution of spent LiFePO_4 batteries, a process based on precipitation was proposed in this study. Since ferric and ferrous ions coexisted in the leaching solution, all the ferrous ions were first oxidized to ferric ions by adding H_2O_2 to the leaching solution. About 99% iron(III) was recovered as iron phosphate by adjusting the solution pH to 2 at 25 °C for 30 mins. After the precipitation of iron phosphate, the remaining Li(I) in the filtrate was recovered as lithium carbonate by precipitation with Na_2CO_3 as a precipitant. Addition of acetone to the filtrate at room temperature greatly enhanced the precipitation percentage of Li(I). Moreover, solid Na_2CO_3 was better than Na_2CO_3 solution in precipitating Li(I). About 95% of lithium ions was recovered as carbonate precipitates under the optimum conditions: solution pH = 11, 3.0 molar ratio of solid Na_2CO_3 to Li(I), 7/5(v/v) volume ratio of acetone to the filtrate, 25 °C, 300 rpm for 2 hrs.

Keywords: spent LiFePO_4 battery, leaching solution, precipitation, lithium, iron

1. Introduction

The increasing demand for lithium iron phosphate (LiFePO_4) batteries, driven by the growing electric vehicle (EV) and renewable energy sectors, has led to a growth in the generation of spent LiFePO_4 batteries. It was announced by Build Your Dreams (BYD) company in November 2023 that lead-acid batteries would be completely replaced by LiFePO_4 batteries (BuildYourDreams 2023). A significant challenge in meeting the growing demand for LiFePO_4 batteries is the increased price of the metal components, especially lithium. It was reported that lithium demand is expected to increase from about 500,000 tonnes of lithium carbonate equivalent (LCE) in 2021 to about 3-4 million tonnes by 2030 (Marcelo 2022). In March 2022, the price of lithium carbonate (Li_2CO_3) exceeded US \$ 75,000 per ton (Marcelo 2022). Iron(III) phosphate (FePO_4) is a valuable raw material for the production of LiFePO_4 batteries (Chen et al. 2022). Therefore, the recycling of lithium carbonate and iron phosphate from spent LiFePO_4 batteries presents concurrent environmental and economic advantages.

The recovery of the metals from spent LiFePO_4 batteries using sulfuric acid leaching has drawn much attention as a viable and effective recycling method (Li et al. 2017). Lithium ions, ferrous iron, ferric iron, sulfate, and phosphate ions are present in the solution when the cathode powders of spent LiFePO_4 battery are leached with H_2SO_4 solution (Song et al. 2021). The separation of two metal ions from the leaching solutions can be achieved by using several operations such as chemical precipitation, solvent extraction, and ion exchange (Hubicki and Kołodziejka 2012; Korkisch 2013). Metal separation in large scale operation was possible with chemical precipitation whose key benefits are excellent efficiency and easy operation (Nie et al. 2014; Fu and Wang 2011). In general, ferrous and ferric ions are present in the acidic leaching solutions of LiFePO_4 batteries. Therefore, ferrous ions are oxidized to ferric ions which can be separated by precipitation of FePO_4 or iron hydroxide ($\text{Fe}(\text{OH})_3$) over Li(I) from the leaching solution (Mahandra and Ghahreman 2021). In precipitation, the precipitation pH can be calculated by

inserting the concentration of ferric ion into the solubility products of FePO_4 or $\text{Fe}(\text{OH})_3$. Sodium carbonate (Na_2CO_3) and sodium phosphate (Na_3PO_4) are used to precipitate lithium ions from the leaching solution of spent LiFePO_4 batteries (Wu et al. 2022). The precipitation conditions for lithium ions are relatively stringent compared to iron ions owing to the lower concentration of $\text{Li}(\text{I})$. Carbonate and phosphate ions are basic and thus they can be protonated, resulting in a decrease in their effective concentrations. Therefore, the precipitation of $\text{Li}(\text{I})$ is done in alkaline solutions. Solvent extraction method could be used to obtain high-purity metals from acidic leaching solutions (Wilson et al. 2014). Some researchers used di-(2-ethylhexyl) phosphoric acid (D2EHPA) to extract $\text{Fe}(\text{III})$ over $\text{Li}(\text{I})$ from the leaching solution (Jin et al. 2014). However, it is difficult to completely strip the iron(III) from the loaded D2EHPA when the concentration of iron(III) in the loaded organic is high (Tran et al. 2019). Dioctyl phthalate (DOP) and tributyl phosphate (TBP) could be used as an extractant for the separation of $\text{Li}(\text{I})$ (Ji et al. 2016). Ion exchange was employed to separate $\text{Li}(\text{I})$ and iron ions (Fukuda 2019). However, the occurrence of resin contamination and some problems in its application on a large scale limits the employment of ion exchange. Therefore, there are few cases of practical application for the recovery of iron and lithium from spent LiFePO_4 batteries with most experiments still in the development stage.

Considering some advantages of precipitation as a separation operation, this study focused on investigating the chemical precipitation for the recovery of iron and lithium from H_2SO_4 leaching solutions of spent LiFePO_4 batteries. Most of the iron in the leaching solution was recovered as iron phosphate by control of solution pH. The addition of organic solvent to the filtrate after the separation of iron ions showed a favourable effect on the enhancement of the precipitation of lithium carbonate. Higher precipitation percentage of $\text{Li}(\text{I})$ was obtained under ambient temperature. The optimum conditions for the precipitation of the metal compounds from the leaching solutions of LiFePO_4 batteries were obtained. This study demonstrated the feasibility of recovering lithium and iron compounds with high purity from spent LiFePO_4 batteries. Due to its simplicity and ease of operation, this process is not only effective on a laboratory scale but also for industrial-scale application. This has significant implications for the large-scale processing of spent batteries and resource recovery.

2. Experimental

2.1. Chemicals and reagents

All chemicals and reagents employed in this work were purchased from Daejung Chemical & Metals Co., Korea. Sodium hydroxide (NaOH , > 97%) and sulfuric acid (H_2SO_4 , > 95%) solutions were prepared by dissolving or diluting with doubly distilled water. Hydrogen peroxide (H_2O_2 , > 30%) was employed as an oxidizing agent. Sodium carbonate anhydrous (Na_2CO_3 , > 99.0%) was employed as a precipitant. Organic solvents such as acetone ($\text{C}_3\text{H}_6\text{O}$, > 99.8%) and ethanol ($\text{C}_2\text{H}_6\text{O}$, > 94.5%) were added to the aqueous solution to enhance the precipitation efficiency of $\text{Li}(\text{I})$ in these experiments. All the chemicals were used without any purification.

2.2. Experimental procedure and analytical methods

2.2.1. Preparation of the leaching solution of spent LiFePO_4 batteries containing iron and lithium

In our previous study (J. Chen et al. 2023), complete dissolution of iron and lithium from the spent LiFePO_4 cathodes by sulfuric acid solution was obtained under the following conditions: 1.5 mol/L H_2SO_4 , 100 g/L pulp density, 25 °C, 60 min and 300 rpm stirring speed. The concentrations of the metal ions and phosphate ions were determined by ICP-OES (Inductively coupled plasma optical emission spectroscopy, Spectro Arcos, Cleve, Germany). Titration of the leaching solution indicated that iron ions existed as $\text{Fe}(\text{II})$ and $\text{Fe}(\text{III})$ ions (Skoog et al. 2013). In order to oxidize $\text{Fe}(\text{II})$ to $\text{Fe}(\text{III})$, hydrogen peroxide was added to the leaching solution as an oxidizing agent. The composition of the pregnant leach solution (PLS) after oxidation with H_2O_2 is shown in Table 1.

2.2.2. Precipitation of iron and lithium from the leaching solution

Precipitation experiments were performed in a 100 mL beaker by using a magnetic stirrer (WiseStir MSH-20D, Daihan Scientific Co., Korea) to control stirring speed, reaction temperature and time.

Precipitation of Fe(III) as FePO_4 was done by varying solution pH with NaOH solution. Then solid Na_2CO_3 or Na_2CO_3 solution was added to the filtrate to precipitate Li_2CO_3 in the presence of acetone or ethanol. In the precipitation experiments, adequate amount of the precipitant was added to the leaching solution (20 mL) after the oxidation of Fe(II). The precipitates, FePO_4 and Li_2CO_3 were separated from the solutions with the filter paper (ADVANTEC No. 2, 110 mm, 100 circles, Toyo Roshi Kaisha, Ltd.) under atmospheric pressure. The pH of the solutions before and after precipitation experiments was measured by a pH meter (Orion Star A211, Thermo Fisher Scientific, Waltham, Massachusetts, USA) and electrode (Orion 8102BNUWP ROSS Ultra pH/ATC Triode). The morphology of the precipitates was identified by SEM (UHR field emission scanning electron microscope, UHR FE-SEM, SU-70, Hitachi, Japan). The concentration of Fe(III) and Li(I) in the aqueous solutions was measured by ICP-OES. The precipitation percentage of Fe(III) or Li(I) was calculated by Eq. (1):

$$\text{Precipitation percentage (\%)} = \frac{m_i - m_i^*}{m_i} \times 100\% \quad (1)$$

where m_i and m_i^* are the masses of Fe(III) or Li(I) in the aqueous solution before and after the precipitation experiments, respectively.

Table 1. The composition of the sulfuric acid leaching solution of spent LiFePO_4 batteries after being oxidized with H_2O_2

Composition	Li(I)	Fe(III)	P
g/L	4.57	37.30	18.90

3. Results and discussion

3.1. Selective precipitation of Fe(III) over Li(I) from the solution

3.1.1. Effect of solution pH

As presented in Table 1, the concentration of Fe(III), Li(I) and total P in the stock solution was 37.30, 4.57, and 18.90 g/L, respectively. From the total concentration of P, the concentration of phosphate ion (PO_4^{3-}) can be calculated to be 57.96 g/L. The solubility products of $\text{Fe}(\text{OH})_3$, FePO_4 and $\text{FePO}_4 \cdot 2\text{H}_2\text{O}$ at 25°C are 2.79×10^{-39} , 1.3×10^{-22} and 9.91×10^{-16} , respectively (Speight 2005; Yang et al. 2022). The precipitation pH of these compounds can be calculated by inserting the concentration of Fe(III) and phosphate ions into the solubility products. Calculated results indicated that FePO_4 can be precipitated when solution pH is higher than 0.02, while solution pHs higher than 1.21 and 2.3 are required to precipitate $\text{Fe}(\text{OH})_3$ and $\text{FePO}_4 \cdot 2\text{H}_2\text{O}$, respectively. Since solution pH is the most important variable in the precipitation of Fe(III), solution pH was varied from 1 to 5 by adding NaOH solution. Reactions were carried out at 25 °C for 30 min at a stirring speed of 300 rpm. The precipitation percentage of the components in the oxidized leaching solution is shown in Fig. 1. The precipitation percentage of Fe(III) increased from 44 to over 99% as solution pH rose from 1 to 2 and then remained constant for further increase of solution pH, whereas that of Li(I) was lower than 1%. It was noticeable that the co-precipitation of phosphate ions was observed, which was ascribed to the precipitation of FePO_4 .

When solution pH is higher than 1.21, precipitation of $\text{Fe}(\text{OH})_3$ can occur. In general, ferric hydroxides are gelatinous and thus have a strong tendency to adsorb some metal ions. In our experimental ranges, the precipitation behaviour of Fe(III) and phosphate ions was similar. Since the precipitation percentage was calculated on the basis of the mass of the elements, the molar ratio of iron to phosphate in the precipitates of Fe(III) was calculated from the change in the masses of iron and phosphorus. When solution pH was 2.0, the precipitation percentage of Fe(III) and phosphate ions was 99% and 95%, respectively. The molar ratio of Fe(III) to phosphate ion in the precipitate obtained from solution pH = 2.0 was unity, indicating that most of the precipitates consisted of FePO_4 . Our data indicated that FePO_4 would be selectively precipitated over $\text{Fe}(\text{OH})_3$. This can be ascribed to the difference in the ionic charge and concentration between phosphate and hydroxide ions. Although the solubility product of $\text{Fe}(\text{OH})_3$ is much smaller than that of FePO_4 , the concentration of phosphate ion is much higher than that of hydroxide ion when solution pH is 2.0. Moreover, the ionic charge of the phosphate ion is 3, while that of the hydroxide ion is one. Therefore, the interaction between Fe(III) and

phosphate would be much stronger than that between Fe(III) and hydroxide ions. The SEM micrograph of the precipitates from solution pH of 2.0 is shown in Fig. 2. This material is characterized by a spongy structure with some degree of agglomeration. The morphology of the precipitates is consistent with that of the iron phosphate reported in the published paper (Qian et al. 2012). The purity of the iron precipitates recovered at 25 °C and pH = 2.0 was 99%. The precipitation of Li(I) in Fig. 1 (less than 1%) might be ascribed to the adsorption of Li(I) on the precipitates of Fe(III). The precipitation reaction of FePO_4 can be represented as Eq. (2) (Yang et al. 2022).

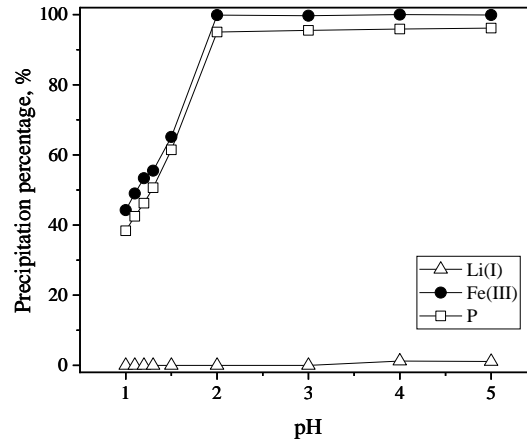
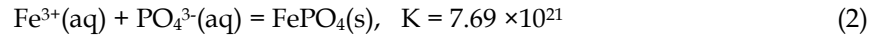


Fig. 1. The effect of solution pH on the precipitation of Fe(III) and Li(I) from the oxidized leaching solution. (Conditions: 30 min reaction time, 25 °C temperature, 300 rpm stirring speed)

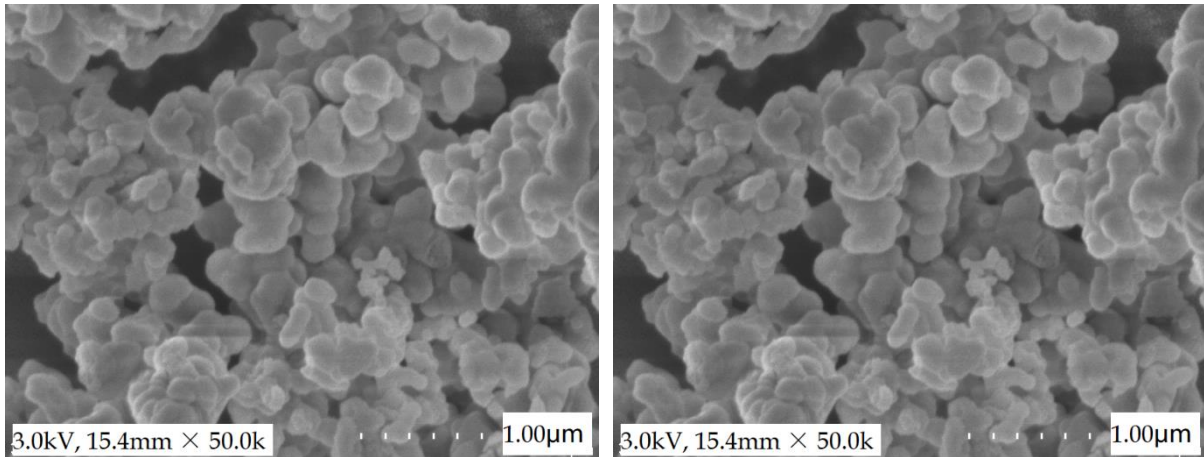


Fig. 2. The FE-SEM micrographs of the precipitates of iron(III) phosphate recovered from the solution

3.1.2. Effect of temperature on Fe(III) precipitation

When the concentration of Fe(III) in the solution becomes lower, the super-saturation degree of Fe(III) would be decreased and thus the critical radius for the nucleation of ferric phosphate precipitates would be increased. Therefore, it is difficult to completely precipitate Fe(III) in the feed solution. The concentration of Fe(III) in the solution after precipitation experiments at solution pH = 2 was 30 mg/L at ambient temperature. The solubility product of FePO_4 and $\text{Fe}(\text{OH})_3$ would decrease as reaction temperature increases (Zhang et al. 2017; Liu and Millero 1999). Therefore, the effect of temperature on the precipitation of the metal ions in the leaching solution was investigated by varying temperature from 25 °C to 95 °C for 30 min at a stirring speed of 300 rpm. Fig. 3 shows that there was no significant difference (around 0.04%) in the precipitation percentage of the metal ions as the reaction temperature increased to 95 °C. Therefore, the optimum conditions for the precipitation of FePO_4 from the feed solution were selected to be pH = 2, 25 °C, 300 rpm, and 30 min.

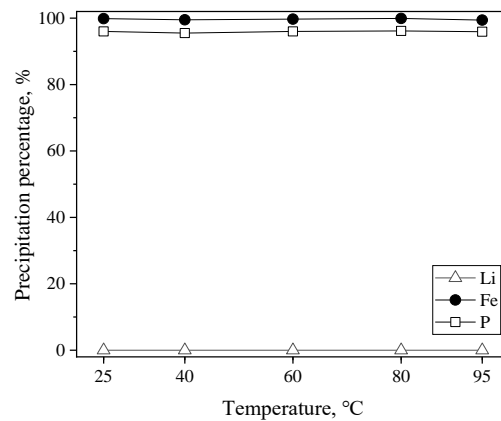
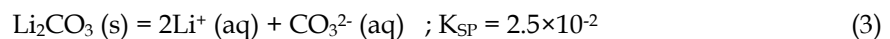


Fig. 3. The effect of temperature on the precipitation of Fe(III) from the solution. (Conditions: pH = 2.0, 30 min reaction time, 300 rpm stirring speed)

3.2. Precipitation of Li(I) from the filtrate after separation of Fe(III)

3.2.1. Effect of volume ratio of organic solvents to the filtrate containing Li(I)

The filtrate after the separation of Fe(III) from the oxidized leaching solution contained 2.87 g/L Li(I), Na(I), and a small amount of Fe(III) (about 30 mg/L). In general, the recovery of Li(I) from the filtrate is possible by precipitating Li(I) as lithium carbonate or lithium phosphate, as represented in Eqs. (3) and (4):



Although the solubility of Li_3PO_4 is much smaller than that of Li_2CO_3 , Li_2CO_3 precipitate is an important lithium material and has a wide range of industrial applications. Moreover, Li_2CO_3 can be easily converted into LiOH compared to Li_3PO_4 (Kim 2008). As a precursor for batteries, LiOH has better structural properties and electrochemical performance than Li_2CO_3 and other lithium compounds (Dahlkamp et al. 2024). Therefore, the precipitation of Li(I) as Li_2CO_3 from the filtrate by using Na_2CO_3 was investigated. In general, the solubility of solids would be decreased as the dielectric constants of the solutions are lowered. Therefore, acetone (dielectric constant = 21.01) and ethanol (dielectric constant = 24.6) were added to the filtrate to facilitate the precipitation of Li_2CO_3 (Tran et al. 2022). The precipitation experiments were carried out by varying volume ratio of organic solvent to the filtrate from 1/5 to 7/5 and other parameters were kept at 1.5 molar ratio of Na_2CO_3 to Li(I), 300 rpm, 25 °C, solution pH = 11 and 2 hrs reaction time. Fig. 4 shows that the precipitation percentage of Li(I) increased as the volume ratio of the organic solvent to the filtrate rose. Moreover, a higher precipitation percentage of Li(I) was obtained with acetone than with ethanol because the dielectric constant of acetone is lower than that of ethanol. Namely, the precipitation percentage of Li(I) increased from 6 to 91% for acetone and from 1 to 85% for ethanol in the experimental ranges.

3.2.2. Effect of temperature

The solubility product of Li_2CO_3 at 60 and 80 °C is 2.0×10^{-4} and 8.9×10^{-5} , respectively, indicating that it decreases with increasing temperature (Cai et al. 2018). Therefore, to increase the precipitation percentage of Li(I) from the filtrate, precipitation experiments were done by varying reaction temperature from 25 to 95 °C at a stirring speed of 300 rpm and solution pH = 11 for 2 hrs. In these experiments, acetone was added to the filtrate at 7/5 (v/v) volume ratio of acetone to the filtrate and the molar ratio of Na_2CO_3 to Li(I) was fixed at 1.5. Fig. 5 shows the precipitation percentage of Li(I) increased from 91 to 96% as the temperature rose from 25 to 95 °C. Since the boiling point of acetone is 56 °C, the evaporation loss of acetone would be comparable when the reaction temperature is higher than 50 °C (Chang et al. 2009). Moreover, the effect of temperature on Li_2CO_3 precipitation was also investigated in the absence of acetone under the same reaction conditions. Fig. 6 shows that the highest precipitation percentage (41%) of Li(I) was obtained at 95 °C, indicating that the addition of acetone to

the filtrate is of importance in enhancing the precipitation of Li(I). Therefore, the reaction temperature of 25 °C in the presence of acetone was employed in further studies.

Addition of acetone or ethanol would have a favorable effect on the precipitation of Li(I) by decreasing the dielectric constant of the resulting solution. However, the decrease in the concentration of Li(I) owing to the increased solution volume would have a negative effect on the precipitation because the super-saturation degree of Li(I) is lowered. From the obtained results, the optimum volume ratio of acetone to the filtrate was considered to be 7/5 (v/v).

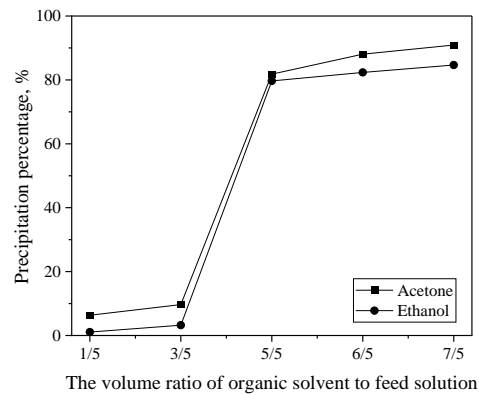


Fig. 4. The effect of the volume ratio of organic solvent to the filtrate on the precipitation of Li(I). (Conditions: pH = 11, 2 hrs reaction time, 25 °C temperature, 300 rpm stirring speed, 1.5 for the molar ratio of solid Na_2CO_3 to Li(I))

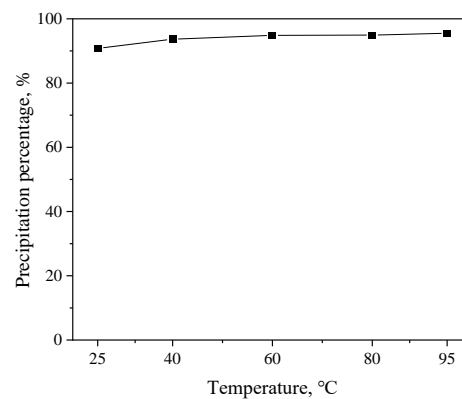


Fig. 5. The effect of temperature on the precipitation of Li(I) from the filtrate. (Conditions: pH = 11, 2 hrs time, 300 rpm stirring speed, 7/5 (v/v) acetone to the filtrate, 1.5 for the molar ratio of solid Na_2CO_3 to Li(I))

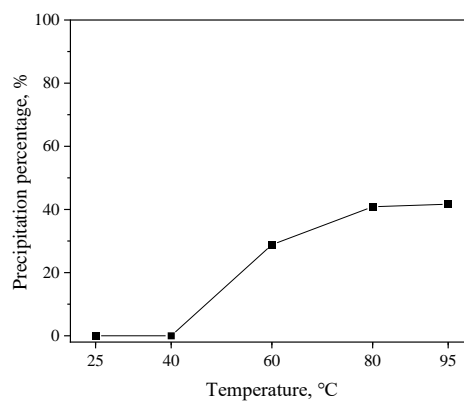


Fig. 6. The effect of temperature on the precipitation of Li(I) from the filtrate in the absence of acetone. (Conditions: pH = 11, 2 hrs reaction time, 300 rpm stirring speed, 1.5 for the molar ratio of solid Na_2CO_3 to Li(I))

3.2.3. Effect of molar ratio of solid Na₂CO₃ to Li(I)

To increase the precipitation percentage of Li(I) from the filtrate, the molar ratio of Na₂CO₃ to Li(I) was increased from 1.5 to 3.0 and the volume ratio of acetone to the filtrate was fixed at 7/5 (v/v). All reactions were carried out at 25 °C with 300 rpm stirring speed and solution pH = 11 for 2 hrs. As shown in Fig. 7, the precipitation percentage of Li(I) increased from 91 to 95% when the molar ratio of Na₂CO₃ to Li(I) was increased from 1.5 to 3. Therefore, the precipitation percentage of Li(I) was improved by 5% when the molar ratio of Na₂CO₃ to Li(I) was increased from 1.5 to 3.

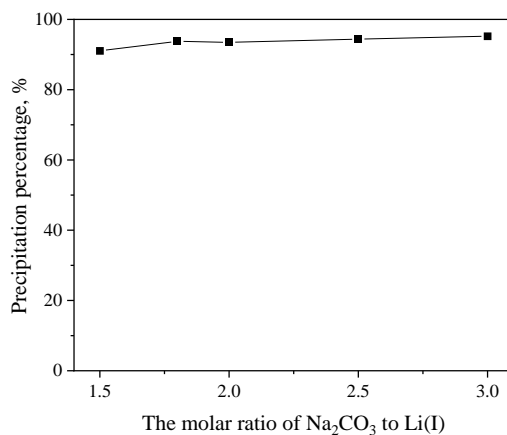
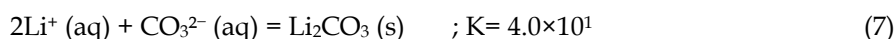
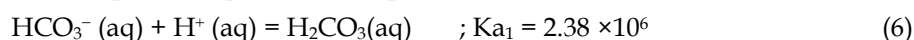
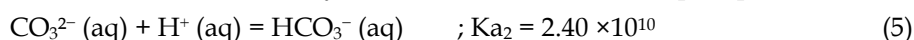


Fig. 7. The effect of solid Na₂CO₃ dosage on the precipitation of Li(I) from the filtrate in the presence of acetone. (Conditions: pH = 11, 2 hrs reaction time, 25 °C temperature, 300 rpm stirring speed, 7/5 (v/v) of acetone to the filtrate)

3.2.4. Effect of the physical state of Na₂CO₃ and reaction time

To consider the effect of reaction time on the precipitation percentage of Li(I) from the filtrate, reaction time was varied from 1 to 3 hrs. In these experiments, the molar ratio of Na₂CO₃ to Li(I) was fixed at 3 and the volume ratio of acetone to the filtrate was controlled to 7/5 (v/v). Experiments were done at 25 °C and a stirring speed of 300 rpm from the solution with pH = 11. In precipitation, one of the most important variables is the concentration of target metal ions because the critical radius for nucleation of the precipitates would be decreased with the super-saturation degree. In precipitation of Li₂CO₃, either solid Na₂CO₃ or Na₂CO₃ solution can be employed as a precipitant. Na₂CO₃ solution would have a positive effect on the precipitation of Li₂CO₃ owing to favourable reaction kinetics in liquid solutions. However, addition of Na₂CO₃ solution would lead to a decrease in the concentration of Li(I), which would have a negative effect on the precipitation of Li(I). Therefore, the effect of the addition of solid Na₂CO₃ or solution on the precipitation percentage of Li(I) was also compared. In Fig. 8, the precipitation percentage of Li(I) reached 95.2% by solid Na₂CO₃, while that was 83.0% by Na₂CO₃ solution in the experimental ranges. Carbonate ions are a strong base and have a strong tendency to be protonated. As represented in Eqs. (5) and (6), carbonate ions are easily protonated, resulting in a decrease in its concentration which can take part in precipitation reaction of Li(I). When solution pH is 11, the concentration of hydrogen ions is negligible. Thus, most of the Na₂CO₃ added to the solution exists as carbonate ions which can precipitate Li(I) according to Eq. (7). Therefore, when Na₂CO₃ solution is employed as a precipitant, it is important to control solution pH in order to maintain the effective concentration of carbonate ion. By contrast, when solid Na₂CO₃ is introduced to the filtrate with pH = 11, the dissolved carbonate ion can directly react with Li(I) ions to form precipitates



From the obtained results, 2.0 hrs reaction time was enough for Li(I) precipitation with solid Na₂CO₃. Thus, the optimum conditions for the precipitation of Li(I) from iron-free filtrate were 3.0 for the molar ratio of solid Na₂CO₃ to Li(I), 7/5 (v/v) volume ratio of acetone to the filtrate, 300 rpm stirring speed,

25 °C temperature, solution pH = 11 and 2 hrs. Under these optimum conditions, the precipitation percentage of Li(I) was 95.2%. **Fig. 9** shows the SEM images of Li_2CO_3 powders obtained by precipitating with solid Na_2CO_3 under the above conditions. The morphology of lithium carbonate is a multiply rounded plate shape with a relatively flat surface and exists in clusters. The appearance of the precipitates shows an agglomeration state, which is in good agreement with the reported data (Shin et al. 2022).

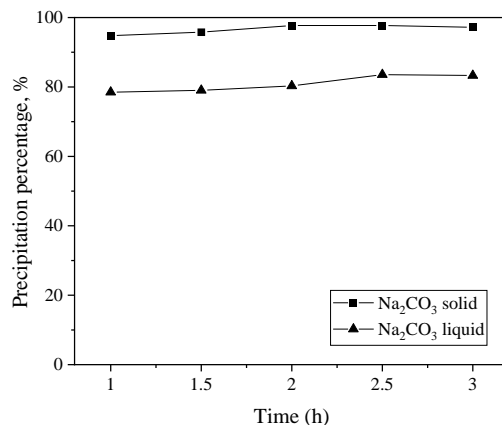


Fig. 8. The effect of time and the form of Na_2CO_3 on the precipitation of Li(I) from the filtrate. (Conditions: pH = 11, 25 °C temperature, 300 rpm stirring speed, 7/5(v/v) of acetone to the filtrate, 3.0 for the molar ratio of Na_2CO_3 to Li(I))

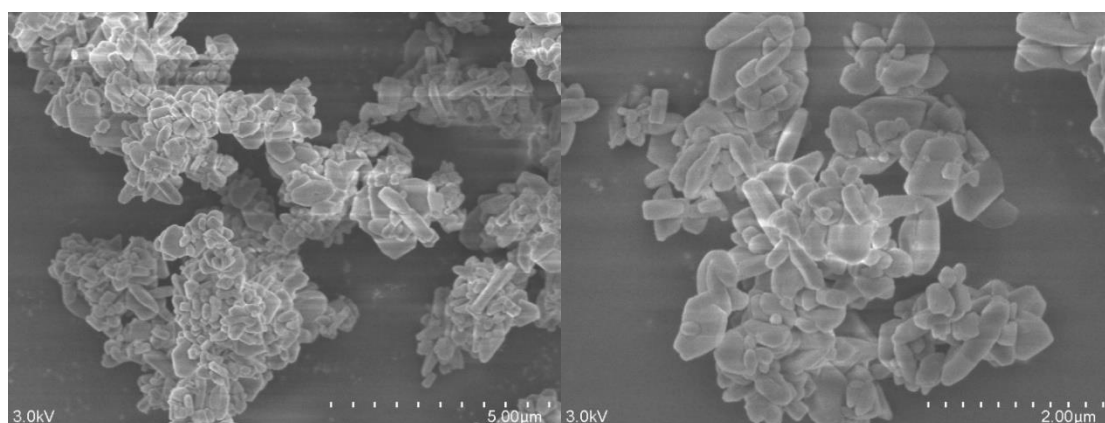


Fig. 9. The FE-SEM micrograph of the precipitates of lithium carbonate recovered from the filtrate after the separation of iron

3.3. Integrated procedure

From the obtained results, a procedure was proposed for the recovery of Li(I) and Fe(III) compounds from the H_2SO_4 leaching solution of spent LiFePO_4 batteries using the precipitation method. Firstly, most of Fe(III) present in the leaching solution is recovered as FePO_4 by adjusting solution pH to 2 at 25 °C. After the separation of Fe(III), the pH of the filtrate containing Li(I) is increased to 11 and Li_2CO_3 is recovered by using solid Na_2CO_3 as a precipitant in the presence of acetone at 25 °C. This process shows some advantages: (1) simple and quick operation; (2) recovery of Fe(III) and Li(I) compounds with high purity, (3) saving chemical and energy consumption due to the reactions done at room temperature. A complete loop of spent LiFePO_4 battery recycling can be accomplished by using the precipitates of FePO_4 and Li_2CO_3 in the production of LiFePO_4 batteries.

4. Conclusions

A hydrometallurgical process was proposed for the recovery of lithium carbonates and iron phosphates from the sulfuric acid leaching solutions of spent LiFePO_4 batteries. In sulfuric acid solutions, iron ions

existed as ferrous and ferric ions and thus ferrous ions were first oxidized to ferric ions by using H_2O_2 as an oxidizing agent. When the pH of the oxidized solution was increased to 2, most of the iron was precipitated as FePO_4 . The optimum conditions to precipitate iron phosphate were solution pH = 2, 30 min at 25 °C. After recovery of iron phosphate, precipitation experiments of Li(I) from the filtrate were done by investigating the effect of some variables, such as reaction time and temperature, the addition of organic solvent, the nature of Na_2CO_3 as a precipitant. Presence of acetone or ethanol showed a positive effect on the precipitation of Li_2CO_3 . Addition of solid Na_2CO_3 was more effective than that of Na_2CO_3 solution in precipitation of Li_2CO_3 . About 95% of Li(I) ions from the iron-free filtrate with solution pH = 11 was precipitated in the form of Li_2CO_3 under the following conditions: 3.0 molar ratio of solid Na_2CO_3 to Li(I), 7/5 (v/v) volume ratio of acetone to the filtrate, 2 hrs reaction time, 300 rpm stirring speed, and 25 °C temperature.

Acknowledgments

This work was supported by the Technology Innovation Program (Development of Material Component Technology) (Project number: 20011183) funded by the Ministry of Trade, Industry & Energy (MOTIE, Korea).

References

- AZEVEDO, M., BACZYŃSKA, M., HOFFMAN, K., KRAUZE, A., 2022. *Lithium is the driving force behind electric vehicles, but will supply keep pace with demand New technologies and sources of supply can fill the gap*. McKinsey & Company, <https://www.mckinsey.com/industries/metals-and-mining/our-insights/lithium-mining-how-new-production-technologies-could-fuel-the-global-ev-revolution>.
- BUILDYOURDREAMS., 2023. *Taking the lead in eliminating lead-acid start batteries, BYD is far ahead again this time*. edited by SOHO, https://sports.sohu.com/a/736401212_119208.
- CAI, W., CHEN, R., YANG, Y., YI, M., XIANG, L., 2018. *Removal of SO_4^{2-} from Li_2CO_3 by Recrystallization in Na_2CO_3 Solution*. Crystals. 8(1), 19.
- CHANG, Y., LEE, J., WU, S., CHEN, C., SHU, C., 2009. *Elevated pressure and temperature effects on flammability hazard assessment for acetone and water solutions*. J. Therm. Anal. Calorim. 95 (2), 525-534.
- CHAVES, E. S., DOS SANTOS, E. J., ARAUJO, R. G., OLIVEIRA, J. V., FRESCURA, V. L. A., CURTIUS, A. J., 2010. *Metals and phosphorus determination in vegetable seeds used in the production of biodiesel by ICP OES and ICP-MS*. Microchem. J. 96 (1), 71-76.
- CHEN, B., LIU, M., CAO, S., CHEN, G., GUO, X., WANG, X., 2022. *Regeneration and performance of LiFePO_4 with Li_2CO_3 and FePO_4 as raw materials recovered from spent LiFePO_4 batteries*. Mater. Chem. Phys. 279, 125750.
- DAHLKAMP, J. M., QUINTERO, C., VIDELA, Á., ROJAS, R., 2024. *Production processes for LiOH – A review*. Hydrometallurgy 223, 106217.
- FU, F., WANG, Q., 2011. *Removal of heavy metal ions from wastewaters: A review*. J. Environ. Manage. 92 (3), 407-418.
- FUKUDA, H., 2019. *Lithium extraction from brine with ion exchange resin and ferric phosphate*. Doctoral dissertation, University of British Columbia.
- HUBICKI, Z., KOŁODYŃSKA, D., 2012. *Selective removal of heavy metal ions from waters and waste waters using ion exchange methods*. Ion Exch. Technol. 7, 193-240.
- JI, L., HU, Y., LI, L., SHI, D., LI, J., NIE, F., SONG, F., ZENG, Z., SUN, W., LIU, Z., 2016. *Lithium extraction with a synergistic system of dioctyl phthalate and tributyl phosphate in kerosene and FeCl_3* . Hydrometallurgy. 162, 71-78.
- JIN, Y., MA, Y., WENG, Y., JIA, X., LI, J., 2014. *Solvent extraction of Fe^{3+} from the hydrochloric acid route phosphoric acid by D2EHPA in kerosene*. J. Ind. Eng. Chem. 20 (5), 3446-3452.
- J., CHEN, T., T., TRAN, M., S., LEE., 2023. *Recovery of pure lithium phosphate from sulfuric acid leaching solutions of spent LiFePO_4 batteries by solvent extraction and chemical precipitation*. J. Min. Metall., Sect. B.
- KIM, K. J., 2008. *Recovery of Lithium Hydroxide from Spent Lithium Carbonate using Crystallizations*. Sep. Sci. Technol. 43 (2), 420-430.
- KORKISCH, J., 2013. *Modern methods for the separation of rarer metal ions*. Elsevier.
- KOSMULSKI, M., MACZKA, E., JARTYCH, E., ROSENHOLM, J. B., 2003. *Synthesis and characterization of goethite and goethite-hematite composite: experimental study and literature survey*. Adv. Colloid Interface Sci. 103 (1), 57-76.
- LI, H., XING, S., LIU, Y., LI, F., GUO, H., KUANG, G., 2017. *Recovery of Lithium, Iron, and Phosphorus from Spent LiFePO_4 Batteries Using Stoichiometric Sulfuric Acid Leaching System*. ACS Sustainable Chem. Eng. 5 (9), 8017-8024.

- LIU, X., MILLERO, F. J., 1999. *The solubility of iron hydroxide in sodium chloride solutions*. *Geochim. Cosmochim. Acta* 63 (19), 3487-3497.
- MAHANDRA, H., GHAREMAN, A., 2021. *A sustainable process for selective recovery of lithium as lithium phosphate from spent LiFePO₄ batteries*. *Resour., Conserv. Recycl.* 175, 105883.
- MASAMBI, S., DORFLING, C., BRADSHAW, S., 2016. *Comparing iron phosphate and hematite precipitation processes for iron removal from chloride leach solutions*. *Miner. Eng.* 98, 14-21.
- NIE, Z. R., MA, L. W., XI, X. L., 2014. *"Complexation-precipitation" metal separation method system and its application in secondary resources*. *Rare Met.* 33 (4), 369-378.
- QIAN, L., XIA, Y., ZHANG, W., HUANG, H., GAN, Y., ZENG, H., TAO, X., 2012. *Electrochemical synthesis of mesoporous FePO₄ nanoparticles for fabricating high performance LiFePO₄/C cathode materials*. *Microporous Mesoporous Mater.* 152, 128-133.
- SHIN, J., JEONG, J. M., LEE, J. B., CHO, H. J., KIM, Y. H., RYU, T., 2022. *Preparation of lithium carbonate from waste lithium solution through precipitation and wet conversion methods*. *Hydrometallurgy.* 210, 105863.
- SKOOG, D. A., WEST, D. M., HOLLER, F. J., CROUCH, S. R., 2013. *Fundamentals of Analytical Chemistry*. Cengage Learning.
- SONG, Y., XIE, B., SONG, S., LEI, S., SUN, W., XU, R., YANG, Y., 2021. *Regeneration of LiFePO₄ from spent lithium-ion batteries via a facile process featuring acid leaching and hydrothermal synthesis*. *Green Chem.* 23 (11), 3963-3971.
- SPEIGHT, J. G., 2005. *Lange's Handbook of Chemistry, Sixteenth Edition*. 16th ed. New York: McGraw-Hill Education.
- TRAN, T. T., IQBAL, M., LEE, M. S., 2019. *Comparison of the extraction and stripping behavior of iron (III) from weak acidic solution between ionic liquids and commercial extractants*. *Korean J. Met. Mater.* 57(12), 787-794.
- TRAN, T. T., SON, S. H., LEE, M. S., 2022. *Recovery of High-Purity Lithium Compounds from the Dust of the Smelting Reduction Process for Spent Lithium-Ion Batteries*. *Korean J. Met. Mater.* 60 (4), 291-300.
- WILSON, A. M., BAILEY, P. J., TASKER, P. A., TURKINGTON, J. R., GRANT, R. A., LOVE, J. B., 2014. *Solvent extraction: the coordination chemistry behind extractive metallurgy*. *Chem. Soc. Rev.* 43 (1), 123-134.
- WU, X., MA, J., WANG, J., ZHANG, X., ZHOU, G., LIANG, Z., 2022. *Progress, Key Issues, and Future Prospects for Li-Ion Battery Recycling*. *Glob Chall.* 6 (12), 2200067.
- YANG, L., FENG, Y., WANG, C., FANG, D., YI, G., GAO, Z., SHAO, P., LIU, C., LUO, X., LUO, S., 2022. *Closed-loop regeneration of battery-grade FePO₄ from lithium extraction slag of spent Li-ion batteries via phosphoric acid mixture selective leaching*. *Chem. Eng. J.* 431, 133232.
- ZHANG, T., LU, Y., LUO, G., 2017. *Effects of temperature and phosphoric acid addition on the solubility of iron phosphate dihydrate in aqueous solutions*. *Chin. J. Chem. Eng.* 25 (2), 211-215.