

A STUDY ON THE SYNTHESIS OF LITHIUM CARBONATE (Li<sub>2</sub>CO<sub>3</sub>) FROM WASTE ACIDIC SLUDGE

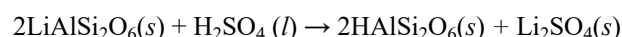
In this study, the synthesis of lithium carbonate (Li<sub>2</sub>CO<sub>3</sub>) powder was conducted by a carbonation process using carbon dioxide gas (CO<sub>2</sub>) from waste acidic sludge based on sulfuric acid (H<sub>2</sub>SO<sub>4</sub>) containing around 2 wt.% lithium content. Lithium sulfate (Li<sub>2</sub>SO<sub>4</sub>) powder as a raw material was reacted with CO<sub>2</sub> gas using a thermogravimetric apparatus to measure carbonation conditions such as temperature, time and CO<sub>2</sub> content. It was noted that carbonation occurred at a temperature range of 800°C to 900°C within 2 hours. To prevent further oxidation during carbonation, calcium sulfate (CaO<sub>4</sub>S) was first introduced to mixing gases with CO<sub>2</sub> and Ar and then led to meet in the chamber. The lithium carbonate obtained was examined by inductively coupled plasma–mass spectroscopy (ICP-MS), X-ray diffraction (XRD) and scanning electron microscopy (SEM) and it was found that of lithium carbonate with a purity above 99% was recovered.

*Keywords:* Lithium carbonate, thermogravimetric apparatus, lithium sulfate, carbon dioxide

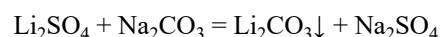
## 1. Introduction

Lithium is a light and rare reserved metal in the earth. It is a new energy material and strategic metal, and has been used in a wide range of fields such as ceramics, the aerospace industry, nuclear energy, batteries, pharmaceuticals and metallurgical industry in recent years [1-3]. Recently, lithium-ion batteries have received great interest because the multi-electron reaction of lithium is important to realize a high specific capacity for electrode material. Lithium carbonate (Li<sub>2</sub>CO<sub>3</sub>) is a raw material for lithium conductor synthesis and has good electrochemical inertness, and thus is considered an appropriate component for the manufacture of the protective layer of cathode [4-6]. High purity Li<sub>2</sub>CO<sub>3</sub> is widely used in lithium-ion batteries, and it is mostly produced from lithium mineral such as spodumene (Li<sub>2</sub>O·Al<sub>2</sub>O<sub>3</sub>·2SiO<sub>2</sub>), which is contained in the second-largest source of lithium, pegmatites [7-9]. The traditional extraction of lithium from sources containing spodumene is the sulfuric acid method, which requires two main steps, leaching by sulfuric acid solutions, which yields a lithium sulfate solution, and carbonation for lithium carbonate [10-12]. The sulfuric acid process is based on the high reactivity of β-spodumene by calcination at 1100°C and is mixed and roasted with concentrated sulfuric acid (H<sub>2</sub>SO<sub>4</sub>) at 250°C, and consequently the hydrogen in the sulfuric acid is replaced by lithium ions to generate lithium sulfate (Li<sub>2</sub>SO<sub>4</sub>)

and insoluble ore gangue [8,13]. Several studies concerning the extraction of lithium from spodumene were conducted in the 20th century, but those methods were dismissed due to low lithium yield, high temperature and long duration [7,14]. Therefore, the sulfuric acid process is widely researched nowadays. The reaction of the sulfuric acid follows the equation below:



The second main step, carbonation, is commonly precipitated by the reaction of sodium carbonate [10,11,13,15] according to the following equation:



At present, South Korea has been importing lithium raw materials for manufacturing lithium-ion batteries; therefore, it is necessary to establish a stable resource supply system for the survival of domestic industries in the competitive global market. For resources, many studies have been conducted domestically on lithium recycling and recovery of lithium from waste material and seawater, but commercialization of the recovery and production of lithium is still difficult at the current technology level [16-19]. In Korea, the lithium waste recycling process has been investigated in several studies to recover the lithium from several types of waste including waste lithium batteries and solutions containing spodumene using traditional extraction methods

<sup>1</sup> PUKYONG NATIONAL UNIVERSITY, DEPARTMENT OF METALLURGICAL ENGINEERING, BUSAN, 48513, KOREA

\* Corresponding author: jpwang@pknu.ac.kr



such as acid leaching and chemical precipitation [19-23]. After sulfuric acid leaching, most research has been conducted on the precipitation of lithium using soda ash ( $\text{Na}_2\text{CO}_3$ ) due to different systems of reactive crystallization between solutions of lithium sulfate and sodium carbonate to obtain lithium carbonate and sodium sulfate, as shown in the above reaction.

Although carbonation using soda ash is a widely recognized  $\text{Mg}^+$ ,  $\text{Na}^+$ , and  $\text{SO}_4^{2-}$  has been concerned common impurities in commercial process.  $\text{Li}_2\text{CO}_3$ , and sodium sulfate is also generated as a byproduct during the precipitation of lithium carbonate [14,20,21].

Therefore, rather than the conventional processes such as acid leaching and chemical precipitation, this study suggested an eco-friendly, low cost and simple process of recovering valuable metals and was conducted to produce lithium carbonate using a thermal reaction with  $\text{CO}_2$  gas from lithium sulfate. The effects of temperature, reaction time, stirring time and mixing ratio were carefully considered to recover lithium carbonate effectively. It was found that lithium carbonate was easily separated from impurities by water leaching and vacuum filtration, respectively. The recovered specimen was examined by inductively coupled plasma-optical emission spectrometry (ICP-OES) and its purity was found to be 94.53% with a lithium concentration of 10.21wt.%.

## 2. Experimental method

### 2.1. Experimental materials

In this study, lithium sulfate ( $\text{Li}_2\text{SO}_4$ ) and lithium sulfate ( $\text{Li}_2\text{SO}_4$ ) reagent were used as experimental materials. Fig. 1 and Table 1 show the results of phase analysis and component analysis of the raw materials used in the study. X-ray diffraction (XRD) analysis was conducted for phase analysis, and energy dispersive X-ray spectroscopy (EDS) and inductively coupled plasma (ICP) analysis were conducted for chemical component analysis. As a result of XRD analysis, it was confirmed that

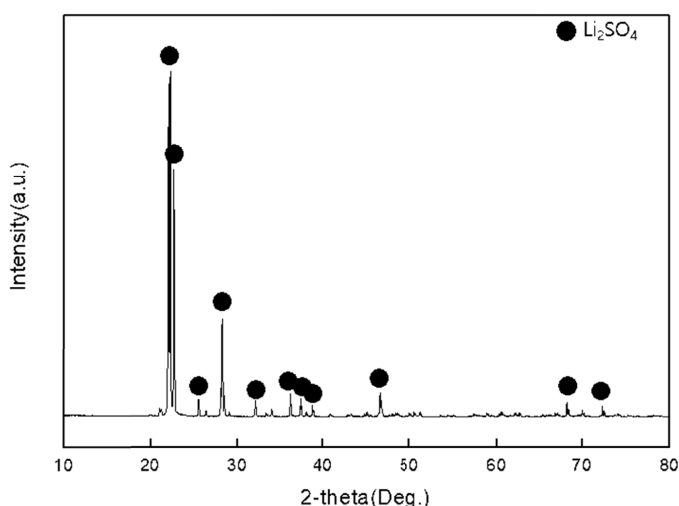


Fig. 1. XRD pattern of sample of lithium sulfate  $\text{Li}_2\text{SO}_4$

the raw materials were present in the form of  $\text{Li}_2\text{SO}_4$ . And as a result of component analysis, it was confirmed that the content of Li, S and O was 10.8wt%, 36.25wt%, and 63.75wt%, respectively.

TABLE 1

Chemical composition of sample of  $\text{Li}_2\text{SO}_4$  powder

| Type                     | EDS (wt.%) |       | ICP (wt.%) |
|--------------------------|------------|-------|------------|
|                          | O          | S     | Li         |
| $\text{Li}_2\text{SO}_4$ | 63.75      | 36.25 | 10.8       |

### 2.2. Thermogravimetric analysis

Thermogravimetric analysis (TGA) was conducted to confirm the possibility of phase change with temperature of lithium sulfate ( $\text{Li}_2\text{SO}_4$ ). In  $\text{CO}_2$  gas (300cc/min) atmosphere, a thermogravimetric change experiment of lithium sulfate ( $\text{Li}_2\text{SO}_4$ ) was conducted at temperatures from 30°C to 990°C at a temperature elevation rate of 5°C/min, and the results are shown in Fig. 2. It was confirmed that weight decreased at 800°C ~ 900°C, and the phase change of lithium sulfate ( $\text{Li}_2\text{SO}_4$ ) powder is expected to occur at 800°C ~ 900°C.

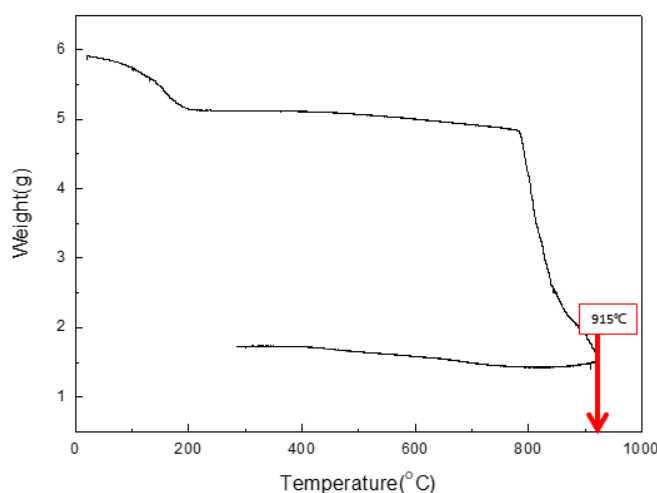
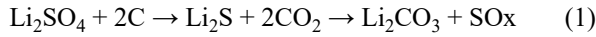


Fig. 2. TGA curve of  $\text{Li}_2\text{SO}_4$  according to various heating temperatures from 30 to 990°C under  $\text{CO}_2$  atmosphere

### 2.3. Carbonation

Carbonation was conducted to change  $\text{Li}_2\text{SO}_4$  phase into  $\text{Li}_2\text{CO}_3$  in the lithium sulfate ( $\text{Li}_2\text{SO}_4$ ) powder. A cubicle was used as an experimental apparatus, and a schematic diagram of the furnace is shown in Fig. 3. During the experiment, a white lubrication releasing agent was applied using an SUS crucible to prevent the sample from being adsorbed in the crucible, and 30 g of the sample was used. It is expected that phase change will occur through the thermal reaction between lithium sulfate powder and  $\text{CO}_2$  gas at high temperature according the reaction formula below.



$$\Delta G^*_{800\sim 900^\circ\text{C}} \leq 0 \quad (2)$$

Based on the TGA measurement results, the temperature was reduced at a rate of 5°C/ min at a temperature condition of 800-900°C. Carbon powder was added to change the lithium sulfate (Li<sub>2</sub>SO<sub>4</sub>) phase into Li<sub>2</sub>S, and lithium sulfate powder and carbon powder were added at ratios of 1:1, 1:2, and 1:4. Experiments were conducted in a CO<sub>2</sub> gas atmosphere (300cc / min), and reaction time was set to three conditions of 1 hour, 2 hours, and 3 hours.

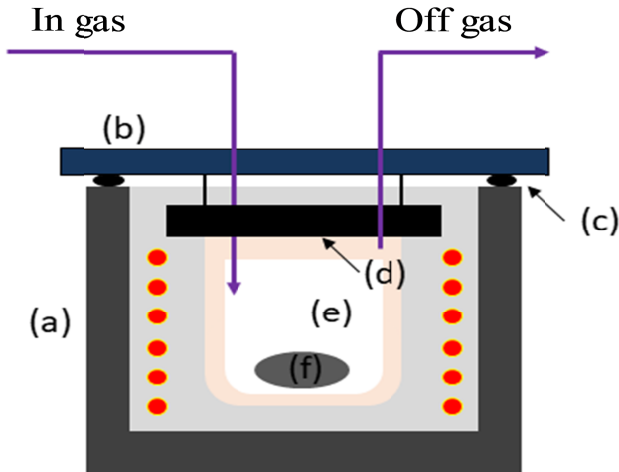


Fig. 3. Schematic diagram of experimental apparatus for carbonation

### 2.4. Water Leaching

Water leaching was conducted to remove residual carbon powder after phase change from lithium sulfate powder. Using the property of Li phase being soluble in water and the property of carbon powder being insoluble in water, Li was separated from carbon powder. As shown in Table 2 below, in Li phase Li<sub>2</sub>CO<sub>3</sub>, solubility increases as the water temperature decreases, and carbon powder is insoluble in water. It is judged that the solubility of Li<sub>2</sub>CO<sub>3</sub> increases as the temperature decreases because the reaction of Li<sub>2</sub>CO<sub>3</sub> solution in water is an exothermic reaction. Therefore, water leaching in low temperature water is considered to be advantageous. For water leaching, experiments were conducted under the following conditions: ratios of 1:10, 1:20 and 1:30 between powder and distilled water at normal distilled water temperature; and water leaching time of 1 hour, 2 hours, and 3 hours.

TABLE 2

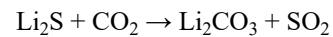
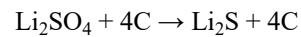
Differences in solubility in water between Li<sub>2</sub>CO<sub>3</sub> and carbon powder

| Materials           | Li <sub>2</sub> CO <sub>3</sub> | Carbon Powder |
|---------------------|---------------------------------|---------------|
| Solubility in Water | 1.54 g/100 mL (0°C)             | Insoluble     |
|                     | 1.32 g/100 mL (20°C)            |               |
|                     | 1.00 g/100 mL (60°C)            |               |
|                     | 0.72 g/100 mL (100°C)           |               |

## 3. Results and discussion

### 3.1. Carbonation

To confirm phase change after the carbonation of lithium sulfate powder, XRD analysis was conducted, and the results according to temperature conditions are shown Fig. 4. As a result of XRD analysis, it was confirmed that phase change did not occur at 800°C and complete phase change occurred at 900°C. The experimental results confirmed that the optimum temperature condition for carbonation reaction was 900°C. This reaction can be conducted with continuous equations:



Based on the reactions stated, lithium sulfate first reacted with carbon, leading to lithium sulfide.

Lithium sulfide can meet carbon dioxide to finally transform into lithium carbonate. The two reactions might occur simultaneously to fabricate lithium carbonate from lithium sulfate.

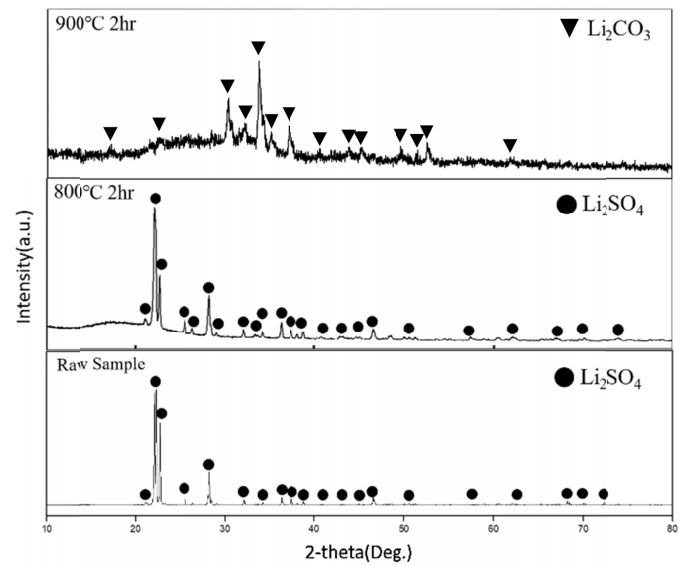


Fig. 4. XRD pattern comparison between raw sample and after carbonation at temperatures of 800°C and 900°C.

After deriving the optimum temperature conditions, experiments were conducted to derive the optimum carbon powder content. The results were analyzed by XRD, and are shown in Fig. 5. As a result of XRD analysis, it was confirmed that phase change occurred at ratios of 1:1, 1:2, and 1:3, and the optimum carbon content was 1:1.

After deriving the optimum condition for the addition of carbon, experiments were conducted to derive the optimum reaction time. The results were analyzed by XRD, and are shown in Fig. 6. As a result of XRD analysis, it was confirmed that complete phase separation did not occur at 1 hour, and complete phase change occurred at 2 hours.

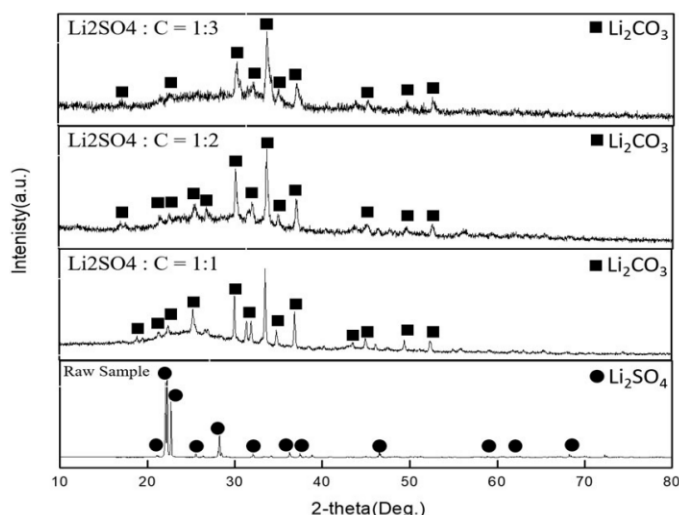


Fig. 5. XRD pattern comparison between the raw material and after carbonation with carbon powder at ratios of 1:1, 1:2 and 1:3.

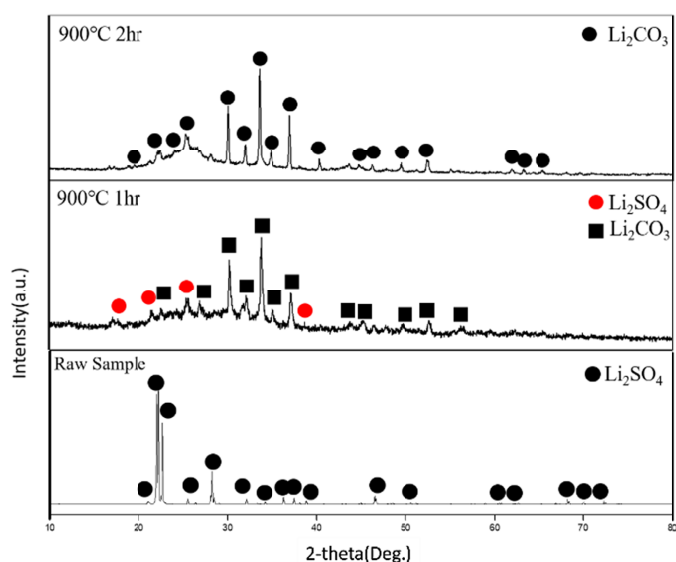


Fig. 6. XRD pattern comparison between the raw material and after carbonation for 1 and 2 hours

### 3.2. Water Leaching

After carbonation, water leaching was conducted using the difference in solubility between  $\text{Li}_2\text{CO}_3$  and carbon powder. Lithium carbonate exhibits low water solubility for an alkali metal carbonate. The solubility decreases with increasing temperature. Lithium carbonate may be dissolved in water by conversion to a hydrogen carbonate. Releasing carbon dioxide by heating the solution of lithium hydrogen carbonate causes reprecipitation of the lithium carbonate. To investigate the effect according to the ratio between the sample and distilled water, experiments were conducted by stirring for 3 hours under three conditions of 1:10, 1:20, and 1:30, and the results are shown in Table 3. As a result, Li component appeared in the powder after vacuum filtration at ratios of 1:10 and 1:20, and no Li component was detected at the 1:30 ratio. Based on the experimental results,

1:30 was derived as the optimum ratio between the sample and distilled water.

TABLE 3

Li content in powder after vacuum filtration

| Type        | ratio 1:10 | ratio 1:20 | ratio 1:30 |
|-------------|------------|------------|------------|
| Li contents | 2230 ppm   | 139 ppm    | N/D        |

To investigate the effect of the water leaching time, experiments were conducted under three conditions of 1 hour, 2 hours, and 3 hours, and the results are shown in Table 4. As a result of the experiment, Li component was detected in the powder after vacuum filtration when stirred for 1 hour and 2 hours and Li content was not detected when stirred for 3 hours, which confirmed that  $\text{Li}_2\text{CO}_3$  phase was completely eluted.

TABLE 4

Li content in powder after vacuum filtration (stirring time 1 h, 2 h, 3 h)

| Type       | 1 h      | 2 h     | 3 h |
|------------|----------|---------|-----|
| L contents | 2119 ppm | 380 ppm | N/D |

Finally, the lithium content in the recovered lithium solution was analyzed by ICP, and the results are shown in Table 5. ICP analysis results confirmed the lithium content of wt%. In comparison with the raw material, lithium carbonate ( $\text{Li}_2\text{CO}_3$ ) solution with a recovery rate of 94.53% and purity above 99% was recovered.

TABLE 5

Li content in solution after water leaching

| Type        | $\text{Li}_2\text{CO}_3$ Solution |
|-------------|-----------------------------------|
| Li Contents | 10.21wt%                          |

## 4. Conclusions

This study was intended to concentrate lithium carbonate and recover it from lithium sulfate through carbonation with the aim of producing lithium carbonate through dry thermal reaction rather than wet thermal reaction.

1. The optimal conditions of lithium sulfate ( $\text{Li}_2\text{SO}_4$ ) phase change through carbonation were a 1:1 ratio between lithium sulfate and additive carbon powder; reaction temperature of 900°C; and reaction time of 3 hours.
2. The optimum conditions of water leaching after carbonation were a 1:30 ratio between powder and distilled water, and a leaching time of 3 hours.
3. From the lithium solution finally recovered through carbonation and water leaching, a lithium carbonate solution with a recovery rate of 94.53% and a lithium concentration of 10.21wt.% were recovered.

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