Article

Purification of Lithium Carbonate from Sulphate Solutions through Hydrogenation Using the Dowex G26 Resin

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Received: 11 October 2018; Accepted: 12 November 2018; Published: 15 November 2018

Abstract: Purification of lithium carbonate, in the battery industry, is an important step in the future. In this experiment, the waste lithium-ion batteries were crushed, sieved, leached with sulfuric acid, eluted with an extractant, and finally sulphate solutions were extracted, through selective precipitation. Next, sodium carbonate was first added to the sulphate solutions, to precipitate lithium carbonate (Li_2CO_3). After that, lithium carbonate was put into the water to create lithium carbonate slurry and CO_2 was added to it. The aeration of CO_2 and the hydrogenation temperature were controlled, in this experiment. Subsequently, Dowex G26 resin was used to remove impurities, such as the calcium and sodium in lithium carbonate. Moreover, the adsorption isotherms, described by means of the Langmuir and Freundlich isotherms, were used to investigate the ion-exchange behaviors of impurities. After removing the impurities, the different heating rate was controlled to obtain lithium carbonate. In a nutshell, this study showed the optimum condition of CO_2 aeration, hydrogenation temperature, ion-exchange resin and the heating rate to get high yields and purity of lithium carbonate.

Keywords: lithium carbonate; sulphate solutions; hydrogenation; ion-exchange; purification

1. Introduction

In the early industrial development, lithium (Li) was used in many industries. For example, lithium acted as a fluxing agent in the ceramic industry and as a deoxidizer and dechlorination agent in the metallurgical industry. In addition, lithium has attracted more and more attention, worldwide, in the recent years, because of its application in the battery industry [1,2]. Lithium is mainly supplied to electronic industrial products, especially the power battery market. Lithium-ion batteries (LIBs) are widely used in electric vehicles and hybrid vehicles, due to their high energy density and high tolerance of a wide range of temperatures [3,4].

According to the report of the US Geological Survey [5–9], the market for lithium is mainly 39% for the battery industry, 30% for the ceramics and glass industry, and 8% for the lubrication industry. Lithium is usually extracted from brine [10–12] and mineral [13] and the world's annual crude lithium production is about 35,000 tons. Among all countries, Australia and Chile are the largest and second largest crude lithium exporters, respectively. In order to meet the needs of the battery industry, lithium production increased by, approximately, 12% in 2016. It is expected that the lithium-ion battery industry will flourish in the future and the demand for lithium metal will become more and more urgent. The refore, it is important to recycle lithium metal or its compounds from LIBs.

It not only achieves the goal of waste reduction but also improves the secondary resource utilization of waste LIBs.

In the LIBs, lithium, cobalt (Co), nickel (Ni), and manganese (Mn) are the main materials that are needed to recycle. Among them, Lithium is usually obtained in the form of lithium carbonate. Lithium carbonate has become a very important material in recent years. The global demand for lithium carbonate has gradually increased, due to its versatility, and the price will rise significantly in the future [14]. According to the report of Sociedad Quimica y Minera de Chile, the demand for lithium carbonate will increase six hundred thousand tons to eight hundred thousand tones. For industrial activities, lithium carbonate is not only used as cathode materials in the LIBs but is also used to create other compounds, such as lithium chloride (LiCl), lithium bromide (LiBr) and lithium oxide (Li₂O). LiCl, LiBr, and Li₂O all can be raw materials for other industries. For example, LiBr can be used as an absorbent and a refrigerant. On the other hand, in the medical industry, lithium carbonate can also be used as a treatment for bipolar disorder [15,16]. Due to the unlimited development of lithium carbonate, a lot of countries try various methods to purify lithium carbonate to apply in different industries.

In the purification process, the methods used mainly are the causticization method, electrolysis, recrystallization, hydrogenation–decomposition, and the hydrogenation–precipitation method [17]. As the hydrogenation–decomposition method generates little waste of materials and solutions and can achieve a higher purification of lithium carbonate, it was chosen for this experiment. During the decomposed process, calcium and lithium, both, separate out in the form of carbonates, due to their common properties of precipitation with an increase in temperature. In addition, sodium is also a critical problem in the purification process. To deal with these problems, the ion-exchange resin was chosen to remove the impurities. Comparing the literature, it could be observed that as a resin, IRC-748 has a great adsorption efficiency on Ca²⁺, but insufficient efficiency on Na⁺; Dowex G26 has the better effect on both Ca²⁺ and Na⁺. In order to reduce the impurities, efficiently, Dowex G26 was used in this experiment. To sum up, the hydrogenation–decomposition method and the Dowex G26 resin were used to get a high purity of the lithium carbonate.

2. Materials and Methods

2.1. Materials

The sulphate solutions came from a recycling LIBs waste cathode materials, which were done by previous research; their content is shown in Table 1 [18]. Sodium carbonate (Na₂CO₃) was purchased from Nihon Shiyaku Reagent, Tokyo, Japan (NaCO₃, 99.8%), for the chemical precipitation. CO₂ was purchased from Air Product and Chemical, Taipei, Taiwan (CO₂ ≥ 99%), to carry out the hydrogenation–decomposition method. Dowex G26 was obtained from Sigma-Aldrich (St. Louis, MO, USA) and was used as a strong acidic cation exchange resin, to remove impurities. Multi-elements ICP standard solutions were acquired from AccuStandard, New Haven, Connecticut State, USA. The nitric acid (HNO₃) and sulfuric acid (H₂SO₄) were acquired from Sigma-Aldrich (St. Louis, MO, USA) (HNO₃ ≥ 65%) (H₂SO₄ ≥ 98%).

Table 1. The metal composition of leach liquor.

Element	Ni	Li
Concentration (ppm)	130 ppm	8000 ppm

2.2. Equipment

The materials were analyzed by energy-dispersive X-ray spectroscopy (EDS; XFlash6110, Bruker, Billerica, MA, USA), X-ray diffraction (XRD; DX-2700, Dangdong City, Liaoning, China), scanning electron microscopy (SEM; S-3000N, Hitachi, Tokyo, Japan), and inductively coupled plasma optical emission spectrometry (ICP-OES; Varian, Vista-MPX, PerkinElmer, Waltham, MA, USA). In order to

control the hydrogenation temperature and heating rate, a thermostatic bath (XMtd-204; BaltaLab, Vidzemes priekšpilsēta, Rīga, Latvia) was used to heat the lithium carbonate slurry and the lithium bicarbonate solutions. On the other hand, a stainless-steel machine which was a closed, eight hundred milliliters cylinder, was designed, in which CO₂ could be added from the top. Moreover, an electric blender was appended to make the CO₂ dissolve into the lithium carbonate slurry. To calculate the amount of CO₂ aeration, Flowmeter (GP5700; SIARGO, Lexington, MA, USA) was used in this experiment.

2.3. Experimental Procedures

2.3.1. Chemical Precipitation

The metal which was dissolved in the liquid phase was selectively precipitated, in the solid phase, by the chemical reaction in this process. The lithium was precipitated by carbonate sodium as shown in Equation (1).

The lithium carbonate was recovered after filtration and washed with hot water, to remove the residual impurities. In this procedure, lithium carbonate would precipitate when the temperature increased. However, the content of nickel ion would decrease intensely. Due to the different characteristics of solubility, the composition of lithium carbonate would change, as well. Table 2 shows the metal composition of the lithium carbonate obtained, after the chemical precipitation by inductively-coupled plasma optical emission spectrometry (ICP-OES; Varian, Vista-MPX, PerkinElmer, Waltham, MA, USA).

Table 2. The composition of lithium carbonate.

Element	Lithium Carbonate	Ca ²⁺	Na ⁺	SO ₄ ^{2−}
Content (%)	98%	0.15%	1.5%	0.35%

2.3.2. Lithium Carbonate Slurry

Enough lithium carbonate was obtained in order to make lithium carbonate slurry, in the first process. However, the amount of the water would affect the hydrogenation and decomposition processing. If the amount of water was low, it would not be possible to add enough CO₂ to the slurry. If there was too much water, it would cause more energy consumption in the decomposition procedure. On account of these conditions, 10 g lithium carbonate with 400 milliliters of deionized water were mixed to make our lithium carbonate slurry.

2.3.3. Hydrogenation Processing

After making the lithium carbonate slurry, it was first put into the thermostatic bath to maintain its temperature. Subsequently, it was poured into the aeration and stirring device and the CO₂ was added into it. Equation (2) shows the reaction for the dissolution of the CO₂ into the slurry.

In this procedure, the CO₂ aeration and hydrogenation temperature were controlled and the pressure was kept at 0.2 MPa. The parameters for the CO₂ aeration (1 L–2.5 L) and hydrogenation temperature (26.5 °C–30 °C) were set up. The initial weight of lithium carbonate and deionized water was 410 g. On adding the CO₂ into the slurry, it turned into the lithium bicarbonate solution. However, it still had some lithium carbonate, which did not change into lithium bicarbonate. By filtering the remain lithium carbonate solid, we could weigh the lithium bicarbonate solutions. At last, the value we got the yields of the lithium bicarbonate solutions and this has been shown in this study.

2.3.4. Ion-Exchange

Dowex G26 is a strongly acidic resin which was used to exchange cations ions efficiently. Dowex G26 was used to remove the Ca^{2+} and Na^{+} which were the two most abundant impurities in the lithium bicarbonate solutions, in this process. The adsorption isotherms, described by means of the Langmuir and Freundlich isotherms, were used to investigate the ion-exchange behaviors of Ca^{2+} . With the parameters of pH value, the Ca^{2+} , and Na^{+} adsorption efficiencies were compared, without high pH values, because the Ca^{2+} would precipitate when it combined with OH^{-} . On the other hand, the effect of the reaction time was also compared. The parameters of the ion-exchange experiments, the pH values (1–8) and reaction times (2 min–1024 min), were set. After removing the impurities, the content of the lithium bicarbonate solutions was investigated in this study.

2.3.5. Decomposition Processing

After removing the impurities in the lithium bicarbonate solutions by Dowex G26, lithium carbonate was needed to precipitate from the lithium bicarbonate solutions. Equation (3) shows the reaction through which the lithium carbonate was acquired, by heating the lithium bicarbonate solutions.

The heating rate was an important factor to control the impurities in this procedure. If the heating rate was too high, the lithium carbonate crystal would contain other ions. If the heating rate was too low, the energy consumption would increase. In order to compare the effect of the heating rate, the solutions were put into a thermostatic bath, the parameters ($0.5\text{ }^{\circ}\text{C}/\text{min}$ – $1\text{ }^{\circ}\text{C}/\text{min}$) were set up and the solutions were heated to $90\text{ }^{\circ}\text{C}$. The whole process of experiment is shown in Figure 1.

Figure 1. The outline of the purification process for lithium carbonate from sulphate solutions.

3. Results and Discussion

3.1. Hydrogenation Processing

3.1.1. Effect of CO₂ Aeration

The effect of CO₂ aeration was investigated with a range of 1 L–2.5 L. The result of Figure 2 shows that 1 L, 2 L, 2.25 L, and 2.5 L of aeration had the lower yields and the 1.75 L had the highest

yield. By Equations (4) and (5), if CO_2 was insufficient, the HCO_3^- was insufficient as well. However, if the CO_2 was excessive, the HCO_3^- turned back into CO_3^{2-} and caused the yields of the lithium bicarbonate solutions to decrease. The optimum aeration of the CO_2 , in the condition of 10 g lithium carbonate with 400 mL H_2O , was 1.75 L, due to these conditions.

Figure 2. The yields of lithium bicarbonate solutions with different CO_2 aeration.

3.1.2. Effect of Hydrogenation Temperature

The hydrogenation temperature was investigated from 26.5 °C–30 °C. As the hydrogenation process was a reversible reaction, the slurry temperature played an important role, even if it only had a little change. Figure 3 shows the yields of the parameter. As seen in the figure, 27.5 °C was the optimum parameter with the highest yield. In the lower temperature, the solubility of lithium carbonate was high but the reaction was too difficult to be in progress. If the temperature was higher, the solubility of lithium carbonate was low and the reverse reaction became faster to make lithium bicarbonate turn back into lithium carbonate. However, the effect of hydrogenation temperature on purity was only a little because it was irrelevant to the precipitation of impurities.

Figure 3. The yields of lithium bicarbonate solutions with different hydrogenation temperatures.

3.2. Ion-Exchange

3.2.1. Isothermal Adsorption Models

In this study, the different initial concentrations of Ca^{2+} (10, 20, 50, 100, 200 and 400 ppm) and the relationship between C_e (concentration of adsorbate in the liquid when adsorption is in equilibrium) and q_e (equilibrium adsorption capacity of the adsorbent), were used to create the isothermal adsorption curve (Figure 4). From the results, the saturated adsorption amount was 80 mg/g.

In order to get a high accuracy of the adsorption model, Langmuir and Freundlich equations were used to create the figures. Equation (6) and Figure 5 show the Langmuir equation [19] and indicate that they use the relationship between C_e and C_e/q_e , to get the maximum adsorption capacity q_m and adsorption equilibrium constant K_L . On the other hand, Equation (7) and Figure 6 show the Freundlich equation [20] and indicate that they use the relationship between $\ln C_e$ and $\ln q_e$, to get the empirical constant n and the adsorption equilibrium constant K_F . By R^2 in Figures 5 and 6, the adsorption behavior of Dowex G26 fits with the Langmuir model. It showed that the resin has a uniform adsorption position, on the surface.

$$\frac{C_e}{q_e} = \frac{C_e}{q_m} + \frac{1}{q_m K_L} \quad (6)$$

$$\ln q_e = \ln K_F + \frac{1}{n} \ln C_e \quad (7)$$

Figure 4. Isothermal adsorption curve of Ca^{2+} .

Figure 5. Langmuir isothermal adsorption curve.

Figure 6. Freundlich isothermal adsorption curve.

3.2.2. Effect of the pH Value

In order to test the parameters (pH 1–8), the concentration ratio of Ca^{2+} and Na^{+} were set 1 and 10 mg/L, which were based on the concentration of lithium bicarbonate solutions. Figure 7 shows that the relationship between the pH value and the adsorption efficiency of Ca^{2+} and Na^{+} . In the figure, pH 6 and pH 7 had the optimum adsorption efficiency. As the pH value of the lithium bicarbonate solution was near 7 (7.32–7.38), pH 7 was chosen to be the parameters in this experiment.

Figure 7. Adsorption efficiency on Ca^{2+} and Na^{+} with pH value.

3.2.3. Effect of Reaction Time

The influence of reaction time was investigated to see that the longer the reaction time, fewer was the adsorption efficiency of the resin. Figure 8 shows that the adsorption efficiencies were similar at 2 min to 16 min of reaction time. However, after 16 min, the values got lower drastically. The reason was that some Li^{+} was adsorbed by resin and caused the precipitation of Ca^{2+} and Na^{+} . In order to minimize the adsorption of Li^{+} , 4 min was chosen to be our reaction time.

After getting the optimum parameters of the Dowex G26, the lithium bicarbonate solutions were purified, and the data are shown in Table 3.

Table 3. The composition of lithium bicarbonate solutions.

Element	Li^{+}	Ca^{2+}	Na^{+}	SO_4^{2-}
Content (%)	99.475%	0.015%	0.5%	0.01%

Figure 8. Adsorption efficiency on Ca^{2+} and Na^{+} with reaction time.

3.3. Decomposition Processing

The Effect of Heating Rate

The heating rate was the most important parameter of the yields and impurity. If the heating rate was high, it would cause impurities such as Na^{+} to be wrapped by lithium carbonate. The impurities precipitated would have an increase in yields and a decrease in purities. In Figure 9 it can be seen that the experiment with resin had only a small change of purity because the impurities were already eliminated by the Dowex G26, at the beginning. The highest yield was at 1°C of the heating rate because the impurities precipitated, and the highest purity was at 0.5°C .

After the ion-exchange and the hydrogenation-decomposition, the lithium carbonate was enriched and separated from the calcium and sodium (as seen in Table 4). By concentrating and heating, the XRD and SEM analysis of the metal oxides were shown in Figures 10 and 11. There was no impurity phase detected and the ICP analysis also showed that the purity of lithium carbonate was almost 99.9%.

Table 4. The element content of the lithium carbonate after the hydrogenation–decomposition and the ion-exchange.

Element	Li^{+}	Ca^{2+}	Na^{+}	SO_4^{2-}
Content (%)	99.9%	0.005%	0.095%	N.D.

N.D.: Not-detected.

Figure 9. The yields and purities of the heating rate with resin.

Figure 10. XRD analysis.

Figure 11. SEM analysis.

4. Conclusions

This study proposed a hydrometallurgical way to recover lithium carbonate, effectively, from the sulphate solutions. Calcium and sodium could be separated, effectively, with pH 7 and a 4 min reaction time in the ion-exchange step. In the hydrogenation–decomposition procedure, yields were the highest with 1.75 L of CO₂ aeration, 27.5 °C of hydrogenation temperature, and 1 °C of the heating rate; purity was highest with a 0.5 °C heating rate, with the Dowex G26 resin. With these conditions, the lithium carbonate product could be acquired by the drying treatment, at 90 °C and its purity and recovery rate were almost 99.9% and 87.6%. In comparison with other methods, this method produced less waste and energy consumption, less use of chemicals, and could efficiently purify the lithium carbonate from the sulphate solutions.

Author Contributions: Supervision, W.-S.C. and H.-J.H.; Writing–original draft, C.-H.L.; Writing–review & editing, C.-H.L. and H.-J.H.

Funding: This research was funded by NCKU Research & Development Foundation (106S281).

Acknowledgments: We are pleased to acknowledge the support of the Laboratory of Resources Circulation (LRC) at National Cheng Kung University.

Conflicts of Interest: The authors declare no conflict of interest.

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