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# Lithium Recovery by Precipitation from Impure Solutions – Lithium Ion Battery Waste

**Abstract:** The present work introduces the results obtained when hydrochloric acid leaching solutions were investigated with the aim of recovering the lithium present in industrial battery waste. The lithium-rich solution after HCl leaching for battery waste contains major impurities such as iron, nickel, cobalt, manganese, aluminum, and copper. This composition was used as a model system to prepare a synthetic solution for lithium recovery by precipitation. The precipitation results indicated that the feeding rate of carbonate and stirring rate had an effect on particle size distribution. Uniform particles were obtained with a semi-batch process. A faster carbonate feeding rate can result in a smaller particle size due to the high supersaturation degree and chemical reaction rates.

Keywords: Lithium battery waste, Lithium carbonate, Precipitation

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## 1. Introduction

Lithium is a considerable and important element since major industrial products such as lithium carbonate, lithium chloride, lithium bromide, and butyl lithium are closely related to our daily life, environmental safety, and mental health [1]. Lithium-ion batteries (LIBs) are attracting attention as they are increasingly being used in mobile phones, computers, and cameras thanks to their various advantages in energy storage including high energy density, modest weight, long cycle life, and no memory effect. Consequently, a huge amount of LIBs are being produced to meet the demand of this tremendous consumption [2], resulting in environmental pollution and material wastes as well as metal loss from the circular economy, when insufficiently treated. It is commonly known that spent lithium ion batteries contain valuable metals/metal oxides, organic chemicals, metallic shells, and plastics in abundance. Thus, the recovery and recycling of lithium is attracting great attention among scientists and engineers regarding environmental protection and economic benefits [3-6].

Lithium carbonate is an inorganic salt that is used in a variety of applications, such as catalysts, and also in ceramics and pharmaceuticals. Recovery of lithium as lithium carbonate salt by precipitation is a commonly used method of recovery performed after leaching and recovery unit processes. For instance, Nayl et al. [7] and Zhang et al. [8] reported on an acidic leaching process and subsequent precipitation of Li<sub>2</sub>CO<sub>3</sub> with the addition of soda ash. Different compounds can be recovered at different pH values, which indicates that pH has a significant impact on the leaching and precipitation process. The leaching rate is affected by many factors such as reaction time, acid concentration, reductants present and reaction temperature [9]. Margarido et al. [10] described the carbonate pressure leaching technology to obtain Li<sub>2</sub>CO<sub>3</sub> which can save energy and chemicals. However, the particle size, crystal shape, and purity of Li<sub>2</sub>CO<sub>3</sub> depend on various parameters such as temperature, concentration, pH, and impurities [11]. Additionally, waste raw materials are in general more heterogeneous and complex [12] than well-defined primary raw materials,

emphasizing the importance of considering the effect that impurities can have on Li production process.

The work presented here aimed at achieving a combined process to recover lithium by leaching and precipitation. LIB waste processing using hydrochloric acid has been investigated in several studies [8, 13] and it has been proven to be an efficient lixiviant. Strong HCl concentrations have been used in the prior research, subsequently causing strongly acidic solutions. Due to the complexity of battery chemistry, several elements are prevalent in LIBs, most importantly cobalt, lithium, nickel, manganese, aluminum, copper, and iron [14]. This variation is caused by the use of different active materials in batteries. Aluminum and copper are found in current collectors. Chemicals such as LiCoO<sub>2</sub>, LiMnO<sub>2</sub>, LiFePO<sub>4</sub>, and Li-NMCO<sub>2</sub> (nickel-manganese-cobalt) are commonly used as active materials [15]. In recovering lithium via carbonate precipitation, it is therefore mandatory to purify the solution from other metals due to the otherwise commonly known, adverse formation of metal hydroxide and carbonate during the neutralization of the solution.

Fractional precipitation, followed by evaporation, is a straightforward way to achieve a relatively pure lithium-rich solution. The described method enables fractional removal of different elements based on their solubility at different pH levels; however, ultra-pure separation at any stage is not possible by this method only. Therefore, in this study a synthetic lithium-rich chloride solution containing metal impurities was prepared in order to investigate the crystallization phenomena in the solution.

## 2. Materials and methods

# **2.1 Product liquid solution (PLS)**

The lithium-containing solution for the Li<sub>2</sub>CO<sub>3</sub> precipitation experiments was prepared by dissolving industrially collected, crushed, and sieved LIB waste. The cobalt-rich fraction of the battery waste, provided by an industrial operator, was used as the raw material, which is shown in Fig. 1. The analysis for the metals (Li, Co, Cu, Mn, Ni, Fe) present in the crushed LIB waste was performed by using flame atomic absorption spectroscopy (FAAS, Varian AA240). Exceptionally, inductively coupled plasma atomic emission spectroscopy (ICP-OES, Perkin Elmer 7100 DV, USA) was used in the analysis of aluminum (Al).

## (Figure 1)

LIB waste was leached using 4 M HCl. After each experiment, the leachates were filtered by vacuum filtration with a Büchner funnel and flask. The resulting leachates were combined in a sealable polymer container, hereinafter called the product liquid solution (PLS).

The recovered PLS was acidic. In order to conduct solution purification for the lithium recovery stage, the solution was neutralized by using sodium hydroxide (97% NaOH, Caelo) and sodium carbonate (>99.5% Na<sub>2</sub>CO<sub>3</sub>, Fluka). Neutralization was performed in two steps; first with sodium hydroxide and then with sodium carbonate, ensuring maximal removal of the other metals as either hydroxide or carbonate. After the purification by neutralization, the resulting PLS was analyzed for metal content by using FAAS and ICP-OES. This resulting solution can be considered to have a representative ratio of lithium to impurities after hydrometallurgical processing of industrially crushed LIB waste. Based on the analysis of PLS, the solution contained approx. 1.2 g L<sup>-1</sup> of lithium and a minor amount of impurities, the Li/Co ratio being approx. 100 whereas the Li/Ni,

Li/Mn, Li/Fe, Li/Cu and Li/Al ratios were all one order of magnitude higher, at about 1000. In the current study, the synthetic solutions used in the Li<sub>2</sub>CO<sub>3</sub> precipitation were prepared by mimicking the composition of this PLS. However, it is highly probable that the absolute concentrations of metals will be higher in an industrial process solution.

# 2.2 Precipitation of lithium carbonate

# 2.2.1 Materials

The synthetic solution was prepared with an analytical reagent grade of lithium chloride (purity  $\geq$  99%, Merck), cobalt chloride hexahydrate ( $\geq$  97 %, VWR), copper chloride dehydrate ( $\geq$  99.6 %, VWR), nickel chloride hexahydrate ( $\geq$  98 %, Merck), aluminum chloride hexahydrate ( $\geq$  99 %, Fluka), manganese chloride tetrahydrate ( $\geq$  98 %, J.T. Baker), and iron chloride hexahydrate ( $\geq$  98 %, Sigma-Aldrich). An analytical grade of sodium carbonate (Sigma-Aldrich) with a purity of  $\geq$  99 % was selected and used to precipitate lithium carbonate.

# 2.2.2 Experimental methods

In order to recover lithium, the leaching solution has to be concentrated in order to precipitate as much  $Li_2CO_3$  as possible. Zhu et al. [11] reported that the lithium recovery rate increased significantly with an increase in lithium concentration, especially when it was in the range of 5 to 20 g L<sup>-1</sup>. Therefore, a synthetic solution whose concentration was much denser than the leaching solution was prepared, mimicking the expected real solution, resulting in the solution composition shown in Tab. 1. The concentration ratio of Li between the synthetic solution and PLS was twentyfold. The pH of the prepared solution was then adjusted to 10 with 1 M NaOH in order to minimize the impurities of the final product. Some initial precipitates with a brown color formed due to the addition of NaOH solution, indicating that the precipitates were composed at least in part of iron. In addition, some amorphous substance may have formed during this step since it was necessary to use 0.45 µm micro filters to remove the brown precipitates. A clear filtrate was obtained after filtering out the initial precipitates, which was then used in the following precipitation process.

# (Table 1)

In each experiment, 50 mL of filtrate solution was placed in a 250 mL jacketed reactor (inner diameter 65 mm) equipped with a thermostat (Lauda RK 8 CS). Four baffles were located symmetrically in the reactor to promote efficient mixing and prevent vortex formation. The temperature of the solution was controlled with a thermostat. A pitch blade turbine (diameter 20 mm) with four blades was used as a stirrer. All the experiments were carried out at 50 °C since this was the optimal temperature reported in the literature [11]. When the solution achieved the target temperature, a saturated Na<sub>2</sub>CO<sub>3</sub> solution was prepared and pumped into the reactor with a metering and transfer pump (Watson Marlow 323) at different flow rates of 3, 8, and 16 mL min<sup>-1</sup>(residence time 27, 10, and 5 min, respectively). The total amount of saturated Na<sub>2</sub>CO<sub>3</sub> solution was 81 mL. A schematic representation of the experimental setup is shown in Fig. 2. After the addition of Na<sub>2</sub>CO<sub>3</sub> solution, the whole system was kept mixed at 50 °C for 1 h. Finally, the crystals were filtered with a Büchner funnel and dried at 50 °C overnight in an oven.

(Figure 2)

Besides the semi-batch precipitation processes, two batch experiments were carried out at a mixing rate of 750 and 850 rpm using the same procedures to compare the difference between these two process modes.

## 2.2.3 Characterization

The product from each batch was examined by X-ray powder diffraction (XRD, Brucker D8). Cu-Ka ( $\lambda$ =1.5418 Å), operating at 40 kV, with 40 mA used as a radiation source. The diffraction data were recorded for 2 $\theta$  in the range of 10° – 70° with an increment rate of 0.02°. The particle size distribution of the crystals was analyzed with a Malvern Mastersizer 3000 laser particle size analyzer. Ethanol (96%, technical, VWR) was used as the background since the solubility of Li<sub>2</sub>CO<sub>3</sub> in water is relatively high. The morphologies and surface features were photographed with an optical microscope. The detailed morphology of the precipitates was examined with a Zeiss (LEO) 1450VP scanning electronic microscope (SEM). ICP-OES was used to observe the purity of the final products.

## 3. Results and discussion

A synthetic solution, the concentration of which was twenty times higher than the leaching solution, was prepared in the current research. In industrial processes, evaporation is commonly applied in order to concentrate product liquid solution prior to crystallization of battery chemical salts from metal solutions. If the leaching solution is concentrated by evaporation, the recovery rate of lithium can be increased after precipitation [11] and the organic compounds present can be evaporated to some extent [16].

The final crystals obtained from the present study were Li<sub>2</sub>CO<sub>3</sub>, identified by XRD. Fig. 3 presents the pure white crystals and typical XRD patterns obtained, which agreed well with the reference data JCPDS 22-1141 [17]. This indicates that mainly lithium carbonate was precipitated in the studied solutions. The shape of the XRD peaks indicates that the Li<sub>2</sub>CO<sub>3</sub> was well crystallized. The morphology of the final product analyzed by optical microscope is illustrated in Fig. 4. The crystals obtained from semi-batch precipitation were uniform, whereas more agglomerates were formed during the batch process. Furthermore, precipitates were also examined by SEM to illustrate the morphology of the crystals in detail. In Fig. 5 it can be seen that the Li<sub>2</sub>CO<sub>3</sub> crystals are flower-shaped spherical particles, which is impossible to ascertain from optical microscope images alone. Kallman et al. [18] reported that the morphology of commercial Li<sub>2</sub>CO<sub>3</sub> had flocculent spherical particles, which differed from the particles obtained from the current work. The reason for the morphology difference may be due to the existence of different impurities, which can have an impact on nucleation and crystal growth during precipitation. Gao et al. [19] found that the precipitated Li<sub>2</sub>CO<sub>3</sub> formed massive agglomerates of numerous primary sheets with a median diameter of 10.64 µm. Their agglomerates had petals as part of a flower-shaped crystal, akin to the results obtained in the present work; however the morphology is different. This may be due to the formic acid that was utilized in leaching and neutralization before precipitation in their study. A similar phenomenon was observed in SEM analysis, suggesting that aggregated particles had precipitated from the batch process, as shown in Fig. 5d. Well-shaped crystals can be obtained from the semi-batch process, as illustrated in Figs. 5a-5c.

(Figure 3)

(Figure 4)

### (Figure 5)

In the present work, three feeding rates of 3, 8, and 16 mL min<sup>-1</sup> (residence times of 27, 10, and 5 min, respectively) and two rotation speeds of 750 and 850 rpm were used. Fig. 6 shows the particle size distribution of  $Li_2CO_3$  obtained from the three feeding rates and the batch precipitation process at stirring rates of 750 rpm and 850 rpm. It can be seen that a narrow particle size distribution was always obtained with the semi-batch precipitation process for both mixing rates, whereas the batch process resulted in a wide particle size distribution. The difference between the particle size distributions was caused by the use of the semi-batch process, which was easier to control. Moreover, the particle size increased slightly with a decrease in feeding rates, indicating that a higher feeding rate will lead to higher supersaturation, which accelerates the chemical reaction rate and precipitation process. Meanwhile more nuclei were generated with higher supersaturation, resulting in the formation of small particles. Similar trends in particle size distribution were obtained for both the mixing rates studied. These results are consistent with the morphology of the crystals shown in Figs. 4 and 5.

#### (Figure 6)

The major impurities commonly found in lithium ion batteries of the selected precipitates were determined by ICP-OES. The chemical composition of the precipitates, as shown in Tab. 2, indicates that the element Li was mainly present in the white solids, which is consistent with the results of XRD. The biggest impurities present in the lithium carbonate precipitates were Cu (approx. 0.1 mg/g) and Fe (approx. 0.08 mg/g). It is clear that the purity of the Li product vs. Co had increased 47 times from the synthetic solution and 13 times vs. Mn. It can be concluded that a relatively high precipitate purity could be reached with the proposed precipitation method. As supposed by Swain [20], the purity and yield could be improved by adjusting the pH of the lithiumconcentrated solution with two steps. The reason is that other divalent metals can be precipitated out as hydroxide form at around pH 12 based on theoretical prediction, so that lithium can remain in the solution. After that, Li<sub>2</sub>CO<sub>3</sub> can be precipitated in the maximum amount after adjusting the solution to pH 14. This method could be considered in a future study as a certain amount of divalent metal impurities were observed in the present study. Moreover, Volkova et al. [21] reported that Li<sub>2</sub>CO<sub>3</sub> has higher stability than the other lithium salts, such as LiCl, LiNO<sub>3</sub>, and Li<sub>2</sub>SO<sub>4</sub>, when stored in air, suggesting that recovery of lithium as lithium carbonate can be a favorable process route for Li recycling. Furthermore, the yield can be increased with the introduction of ethanol and by raising the precipitation temperature [21]. These factors have to be taken into account in further research.

(Table 2)

### 4. Conclusions

A lithium-rich PLS was prepared from industrial battery waste. The PLS was treated in a fractional precipitation process in order to produce a model PLS for synthetic solutions. This purified PLS had major element impurity concentration ratios to lithium of approx. 1:10 (Li:Co) and 1:1000 (Li:Ni, Li:Mn, Li:Fe, Li:Cu, Li:Al). A synthetic solution for the precipitation of lithium carbonate was prepared that mimicked these ratios in the solution.

Lithium was successfully recovered as Li<sub>2</sub>CO<sub>3</sub> salt by the precipitation process and vacuum filtration from the synthetic leaching liquor. The semi-batch process yielded a narrow particle size

distribution and uniform crystals whereas the batch precipitation process resulted in agglomerate formation. The results show that the feeding rate has an impact on the particle size distribution of  $Li_2CO_3$ . Moreover, rotation speed also has an influence on particle size distribution. The particle size decreased with an increase in rotation speed, especially for the batch process. An increase in the stirring rate may have reduced the effect of residence time on particle size distribution. Therefore, similar particle size distributions were obtained, allowing for relatively short crystallization times. Small particles were obtained with a higher feeding rate due to the higher supersaturation and faster chemical reaction. The particles formed have flower-like spherical crystals. A high purity  $Li_2CO_3$  solution could be further used as a washing liquid to obtain much purer lithium carbonate.

The methodology presented in the current research work illustrated the potential value and provided a valuable basic reference for further investigating the precipitation of lithium carbonate from industrial lithium wastes. Meanwhile, the combination of leaching and precipitation could be employed as an efficient way to recover lithium as a pure product. Furthermore, the recovery of Ni and Co could also be performed using the precipitation method in an appropriate pH range.

### 5. Acknowledgements

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### 6. References

[1] B. Swain, Sep. Purif. Technol. 2017, 172, 388-403. DOI: 10.1016/j.seppur.2016.08.031

[2] D. Larcher, J-M. Tarascon, *Nature Chemistry* 2015, 7, 19 – 29. DOI: 10.1038/nchem.2085

[3] H.D. Miser, R.E. Steven, O.A. Ogunseitan, *Environ. Sci. Technol.* **2013**, *47*, 5495-5503. DOI: 10.1021/es400614y

[4] T. Hoshino, Fusion Eng. Des. 2013, 88, 2956-2959. DOI: 10.1016/j.fusengdes.2013.06.009

[5] X.P. Chen, C.B. Luo, J.X. Zhang, J.R. Kong, *ACS Sustain. Chem. Eng.* **2015**, *3*, 3104-3113. DOI: 10.1021/acssuschemeng.5b01000

[6] Y. Yang, S.M. Xu, Y.H. He, *Waste Manage*. **2017**, *64*, 219-227. DOI: 10.1016/j.wasman.2017.03.018

[7] A.A. Nayl, R.A. Elkhashab, Sayed M. Badawy, M.A. El-khateeb, *Arab. J. Chem.* **2017**, *10*, S3632-S3639. DOI: 10.1016/j.arabjc.2014.04.001

[8] P.W. Zhang, T. Yokoyama, O. Itabashi, T.M. Suzuki, K. Inoue, *Hydrometallurgy* **1998**, *47*, 259-271. DOI: 10.1016/S0304-386X(97)00050-9

[9] C. Peng, J. Hamuyuni, B.P. Wilson, M. Lundström, *Waste Manage*. **2018**, In Press. DOI: 10.1016/j.wasman.2018.02.052

[10] F. Margarido, N. Vieceli, F. Durão, C. Guimarães, C.A. Nogueira, *Comun. Geol.* **2014**, *101*, 795-798. (http://www.lneg.pt/download/9655/41\_2904\_ART\_CG14\_ESPECIAL\_II.pdf)

[11] S.G. Zhu, W.Z. He, G.M. Li, X. Zhou, X.J. Zhang, J.W. Huang, *Trans. Nonferrous Met. Soc. China* **2012**, *22*, 2274-2281. DOI: 10.1016/S1003-6326(11)61460-X

[12] Pratima Meshram, B.D. Pandey, T.R. Mankhand, *Waste Manage*. **2015**, *45*, 306-313. DOI: 10.1016/j.wasman.2015.05.027

[13] M. Contestabile, S. Panero, B. Scrosati, J. Power Sources, 2001, 92, 65-69. DOI: 10.1016/S0378-7753(00)00523-1

[14] M. Aaltonen, C. Peng, B.P. Wilson, M. Lundström, *Recycling* **2017**, *2* (4), 20. DOI: 10.3390/recycling2040020

[15] Lithium Process Chemistry: Resources, Extraction, Batteries, and Recycling (Eds: A. Chagnes, J. Swiatowska), Elsevier Science, **2015**.

[16] J. Jamdová, P. Dvořák, J. Kondás, L. Havlák, *Ceramics–Silikáty* **2012**, *56*(*1*), 50-54. (https://www.irsm.cas.cz/materialy/cs\_content/2012/Jandova\_CS\_2012\_0000.pdf)

[17] Y.Z. Sun, X.F. Song, J. Wang, J.G. Yu, Cryst. Res. technol. 2011, 46(2), 173-177. DOI: 10.1002/crat.201000532

[18] J.S. Kallman, S. dePiero, S. Azevedo, H.E. Martz, *Proc. SPIE* **2014**, *9020*, Computational Imaging XII. DOI: 10.1117/12.2048876

[19] W.F. Gao, X.H. Zhang, X.H. Zheng, X. Lin, H.B. Cao, Y. Zhang, Z. Sun, *Environ. Sci. Technol.* **2017**, *51*, 1662-1669. DOI: 10.1021/acs.est.6b03320

[20] B. Swain, J. Chem. Technol. Biotechnol. 2018, 93, 311-319. DOI: 10.1002/jctb.5332

[21] T.S. Volkova, V.V. Rudskikh, V.A. Orlova, I.G. Tananaev, *Russ. J. Appl. Chem.* **2015**, *88*(9), 1388-1394. DOI: 10.1134/S1070427215090025

#### **Tables:**

Li	Со	Al	Ni	Fe	Mn	Cu	
23.995	0.137	0.006	0.026	0.018	0.019	0.014	

**Table 1.** Composition of synthetic solution (g L<sup>-1</sup>).

**Table 2.** Results of ICP-OES analysis of selected precipitates (mg g<sup>-1</sup>).

Sample	Li	Со	Al	Ni	Fe	Mn	Cu
3 ml min <sup>-1</sup> , 750 rpm	164	0.02	< 0.02	< 0.05	0.07	0.01	0.10
16 ml min <sup>-1</sup> , 750 rpm	157	0.03	< 0.02	< 0.05	0.09	0.01	0.10
batch, 750 rpm	163	0.03	< 0.02	< 0.05	0.09	0.01	0.09

### **Figure legends:**

Fig. 1 Mechanically processed mixed lithium ion battery waste, containing most of the active electrode materials.

Fig. 2 Scheme of experimental setup.

Fig. 3 Photo (a) and XRD pattern (b) of products of Li<sub>2</sub>CO<sub>3</sub> obtained from precipitation process.

**Fig. 4** Optical microscope image of  $Li_2CO_3$  obtained from semi-batch with residence time of 5 min (a) and batch process (b).

**Fig. 5** SEM images of  $Li_2CO_3$  crystals obtained from semi-batch process with residence time of 27 min (a), 10 min (b), and 5 min (c), and batch process (d).

**Fig. 6** Particle size distribution of  $Li_2CO_3$  obtained from semi-batch (residence time 27, 10 and 5 min) and batch precipitation process at 50 °C and 750 rpm (a), and 850 rpm (b).

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A Li-rich solution was obtained from a hydrochloric acid leaching process for real industrial battery waste, which was used as a model system to prepare a synthetic solution to recover lithium by precipitation. Lithium carbonate was successfully recovered from an impure mimic solution. Narrow and uniform crystals were obtained from a semi-batch process.





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