

## PURIFICATION OF LITHIUM COMPOUNDS FOR APPLICATION IN ENERGY STORAGE DEVICES

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PIBIC/CETEM period: August 2015 to July 2016

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### Abstract

Lithium compounds with high-purity chemical specifications are key-materials in the new energetic sustainability era; their most important applications aim towards storage of great amount of energy, replacing fossil combustibles and promoting the use of solar energy inclusively during the night periods. A simple purification process for the lithium hydroxide and carbonate compounds is proposed in this paper in an economically viable and sustainable procedure, envisaging subsequent application in the production of rechargeable lithium-ion batteries for portable devices, electric vehicles batteries and energy storage devices in industrial scale. The referred process is based on knowledge and application of the solubility properties of the involved substances, on a series of consecutive washings and filtrations for the lithium carbonate, and solubilization and precipitation of impurities for the lithium hydroxide, in order to eliminate impurities with low-loss of the material of interest. Basic equipment was used, hence reducing process cost and increasing its viability.

**Keywords:** lithium hydroxide, lithium carbonate, purification, Li-ion battery.

## PURIFICAÇÃO DE COMPOSTOS DE LÍTIO PARA APLICAÇÃO EM DISPOSITIVOS DE ARMAZENAMENTO DE ENERGIA

### Resumo

Compostos de lítio com especificações químicas de alto teor de pureza são materiais chave na nova era de sustentabilidade energética; suas aplicações mais importantes visam o armazenamento de grande quantidade de energia, substituindo as fontes combustíveis fósseis e promovendo a utilização de energia solar, inclusive durante o período da noite. É proposto neste trabalho um processo simples para a purificação dos compostos carbonato e hidróxido de lítio de maneira economicamente viável e sustentável, prevendo sua posterior aplicação na produção de baterias recarregáveis de íon-lítio para aparelhos portáteis, baterias para veículos elétricos e para armazenadores de energia em escala industrial. O processo em questão baseia-se no conhecimento e aplicação das propriedades de solubilização das substâncias envolvidas, em uma sequência de lavagens e filtrações consecutivas do carbonato de lítio, e processos de solubilização e precipitação de impurezas para o hidróxido de lítio, a fim de eliminar as impurezas com baixa perda do material de interesse. Foram utilizados equipamentos básicos, reduzindo assim o custo do processo e aumentando sua viabilidade.

**Palavras chave:** hidróxido de lítio, carbonato de lítio, purificação, baterias de íon-Li.

## 1. INTRODUCTION

In the last decades, it has been increasingly visible the rising lithium demand in the international market [MORENO, L., 2013]. Lithium appears under several forms in nature, mostly as chlorides and oxides, and can be found in deserts – which account for the largest world reserves of this element/metal (Salar de Atacama, in Chile; Salar del Hombre Muerto, in Argentine; Salar de Uyuni, in Bolivia; and others in China) – in the sea water, in hectorite clay, and in pegmatites like spodumene (main source of lithium in Brazil, Australia and Canada), lepidolite and amblygonite [MORENO, L., 2013].

Lithium is the lightest of all metals, of density approximately half that of water, besides having enormous electrochemical potential [JEPPSON D. W., 1978]. Due to these characteristics, lithium has become a strategic material for the new generation, being the most adequate and used for rechargeable lithium-ion batteries production, which store energy for portable electronic devices. Recently, lithium has been highlighted for its usage in the composition of high-energy storage devices and electrical vehicles batteries (EVB), which require both high energetic power and lightness. As a result of its particular properties, its renowned applications in energy storage and the fact of not being considered as a pollutant if discarded correctly and/or recycled, lithium has been considered for many as the best alternative to fossil fuels and has been henceforth called “white petroleum” [STTAFORD, J., 2016].

In spite of all this technological and economic potential, currently, Brazil produces only technical grade lithium compounds, in other words, lithium with lower purity chemical specifications than required for the production of rechargeable batteries, including vehicles ones, being then used mostly in the production of high-performance lubricant greases, common practice since the 1940s [MORENO, L., 2013], aluminum, ceramics and glass. In this panorama, it is indispensable that Brazilian lithium industry takes part in this wide, favourable and in development market. In order to make this possible, this work aims for the implementation of a viable and economical alternative for the purification of lithium compounds (carbonate and hydroxide) in industrial scale, as to insert Brazil in this field, and increasing the competitiveness of the national industry, mainly in electronic devices and electrical vehicles batteries field.

## 2. OBJECTIVES

To test and provide a purification process for lithium compounds (carbonate and hydroxide) that can be adapted to the Brazilian industrial process, targeting the opening of doors for the entry of the country in the lithium global market.

## 3. METODOLOGY

For both purification processes, the materials and equipment used were: porcelain mortar with pestle; watch glass for material weighing; analytical balance; 100 mL and 2 L graduated cylinders; 250 mL, 1 L and 2 L beakers; 2L inox steel pan; hotplates with magnetic stirring; mechanical stirrer; 1 L kitasato; Büchner funnel; quantitative filter paper; stove (for lithium carbonate); refrigerator (for lithium hydroxide); thermocouple and quicksilver thermometer; distilled water;  $\text{BaCl}_2 \cdot 2\text{H}_2\text{O}$  (purity of 99%); lithium carbonate ( $\text{Li}_2\text{CO}_3$ ) with purity at 98.50%; lithium hydroxide mono-hydrate ( $\text{LiOH} \cdot \text{H}_2\text{O}$ ) with purity at 54.77%. The lithium compounds used are technical grade and were supplied by Companhia Brasileira de Lítio (CBL). A methodology was employed for each compound, based on the solubility of involved substances as shown in Fig. 1:

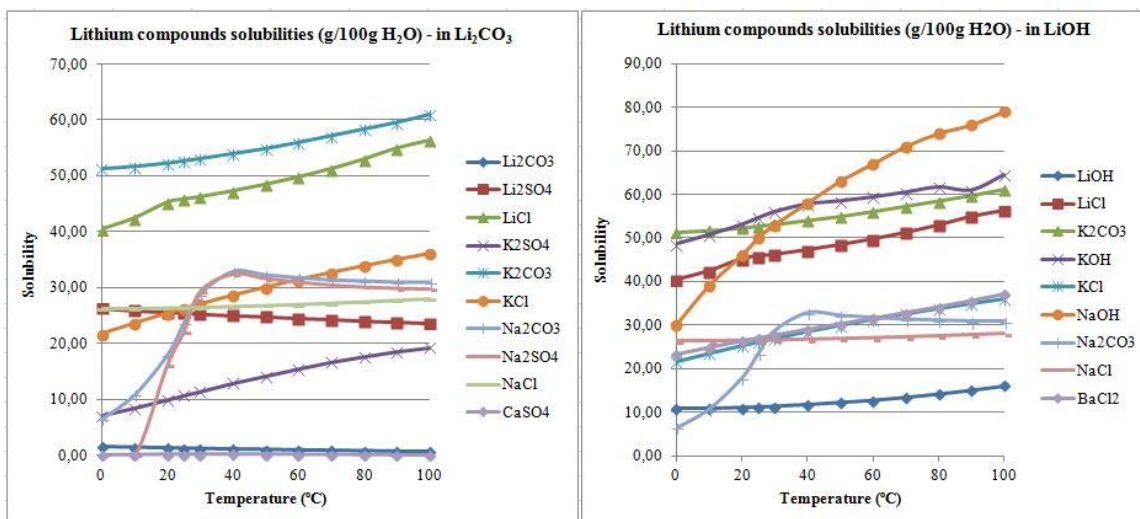


Fig.1: Solubility behaviour of lithium compounds in  $\text{Li}_2\text{CO}_3$  and  $\text{LiOH}$ .

### 3.1. Lithium carbonate

The objective was to reach a minimum purity value of 99.50% of Li for this compound, which is the minimum value required for lithium-ion batteries production. Tests of purification were performed, with five samples of approximately 55 g for each test. These samples were weighed on the analytical balance and dried on the stove (at  $100^\circ\text{C}$ ) until a constant weigh was obtained (therefore, all moisture was removed). The samples were crushed on the mortar and the resulting powder measured and weighed once more, as to grant approximately 50 g of sample mass (chosen based on the process). The first test used a 1:1  $\text{Li}_2\text{CO}_3$  to water ratio, while the other tests used a 1:2  $\text{Li}_2\text{CO}_3$  to water ratio. This process was developed by Gustavo Daniel Rosales, a former researcher of the lab, and this work utilized it as one of its purification methods as well as tried to improve the purification rate, which was achieved.

The sequences of washings and filtrations used in this process are exposed in reduced form on Fig 2. The final solids are marked in a blue circle while the liquors are marked in orange.

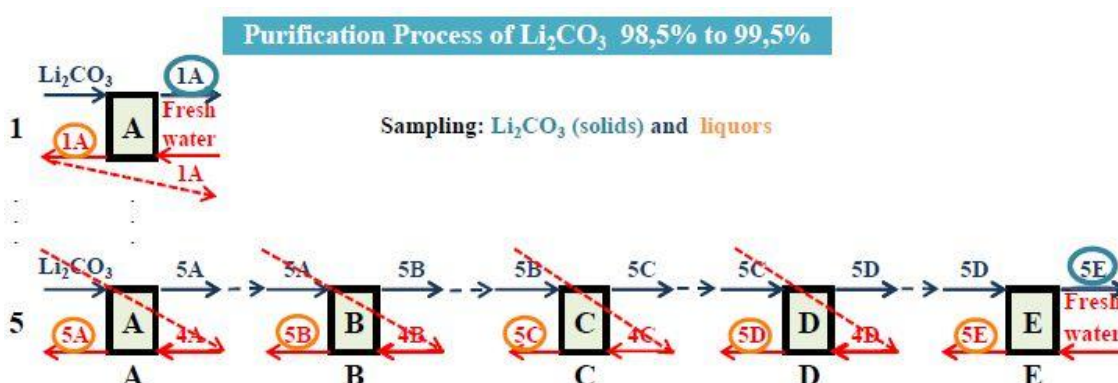


Fig.2: Lithium carbonate simplified purification diagram (original by Rosales, G).

The stages of washing of the  $\text{Li}_2\text{CO}_3$  were performed in beaker, with magnetic stirring and under temperature of approximately  $90^\circ\text{C}$  for 15 minutes. The temperature was fixed in order to allow the minimum solubility of  $\text{Li}_2\text{CO}_3$  possible, without reducing the solution volume due to water evaporation.

As shown in Fig. 2, the wash water at the end of each washing-filtration step is reused in the following washing stages. This promotes the saturation of the input solution in relation to lithium, in the case of reutilized wash water, for as previously mentioned and observed on Fig.1,  $\text{Li}_2\text{CO}_3$ , solubility decreases with temperature rise, besides the fact of the input solution being saturated in lithium, further reducing its loss by solubilization during the washing. Samples of 1 mL were removed from the output wash water for analyses, as were samples from the solids at the end of each stage, where these have undergone impurities detection analysis.

### 3.2. Lithium hydroxide

This process objective was to eliminate the ions  $\text{CO}_3^{2-}$ , lithium hydroxide's main impurity (measured in terms of total carbon with LECO determination, then converted to  $\text{CO}_2$  terms), in order to obtain a compound of purity equal or higher than 56.5%. For that purpose, a calculated mass of  $\text{BaCl}_2 \cdot \text{H}_2\text{O}$  was added to a solution of  $\text{LiOH} \cdot \text{H}_2\text{O}$  in order to form  $\text{BaCO}_3$ , an extremely insoluble compound, then removing it by filtering the solution. More  $\text{BaCO}_3$  precipitate can eventually be formed by increasing  $\text{LiOH} \cdot \text{H}_2\text{O}$  concentration through evaporation of the water of the solution, therefore, a series of evaporations and filtrations were performed as to remove any formed precipitate from the solution.

## 4. RESULTS AND DISCUSSION

The tests performed for the purification of  $\text{Li}_2\text{CO}_3$  exhibited results consistent with ones previously achieved through the same method. The use of a watch glass over the beaker mouth to reduce the loss of water through evaporation proved to be a valid implementation for its use improved the purification ratio. The results for this purification process are shown on Table 1.

**Table 1: Results of  $\text{Li}_2\text{CO}_3$  purification process (1:2  $\text{Li}_2\text{CO}_3$  to water ratio).**

RESULTS								
Content/Sample	Purified 1	Purified 2	Purified 3	Purified 4	Purified 5	Tech. Grade	FMC BG	Rockwood BG
$\text{Li}_2\text{CO}_3$ wt%	99,74	99,76	99,76	99,76	99,77	98,84	99,5 min	99,80
Cl wt%	$8,15 * 10^{-5}$	$8,29 * 10^{-5}$	$8,19 * 10^{-5}$	$8,48 * 10^{-5}$	$8,61 * 10^{-5}$	$1,00 * 10^{-5}$	0,01 max	-
$\text{SO}_4^{2-}$ wt%	0,26	0,24	0,24	0,24	0,23	0,38	0,1 max	0,05
Na wt%	$1,22 * 10^{-5}$	$1,24 * 10^{-5}$	$1,23 * 10^{-5}$	$1,27 * 10^{-5}$	$1,29 * 10^{-5}$	0,15	0,05 max	0,065
K wt%	$1,22 * 10^{-5}$	$1,24 * 10^{-5}$	$1,23 * 10^{-5}$	$1,27 * 10^{-5}$	$1,29 * 10^{-5}$	-	-	-
Ca wt%	$8,15 * 10^{-5}$	$8,29 * 10^{-5}$	$8,19 * 10^{-5}$	$8,48 * 10^{-5}$	$8,61 * 10^{-5}$	0,03	0,04 max	0,016
Fe wt%	$2,45 * 10^{-5}$	$2,49 * 10^{-5}$	$2,46 * 10^{-5}$	$2,54 * 10^{-5}$	$2,58 * 10^{-5}$	8,00	5 max	0,001

The analysis of the samples from the purification process used for  $\text{LiOH} \cdot \text{H}_2\text{O}$  provided the results shown in Table 2, where significant reduction of  $\% \text{CO}_2$  (0,44%  $\rightarrow$  0,06%) is perceived. With such reduction, the methodology used can be considered efficient, though battery grade was not reached.

**Table 2: Results of  $\text{LiOH} \cdot \text{H}_2\text{O}$  purification process**

Samples	%LiOH
$\text{LiOH} \cdot \text{H}_2\text{O}$ (tech grade product report)	54,77
$\text{LiOH} \cdot \text{H}_2\text{O}$ (Post-treatment)	55,15

## 5. CONCLUSIONS

The results obtained show that it is possible to purify  $\text{Li}_2\text{CO}_3$  to comply with the requirements needed for battery grade compounds and to drastically reduce the contamination of  $\text{LiOH}\cdot\text{H}_2\text{O}$  by  $\text{CO}_2$ . It is possible then, to conclude that this work can be implemented on a larger scale since it follows the principles of hydrometallurgy, which allow scale-up procedures without mishaps.

## 6. ACKNOWLEDGMENTS

Before anything else, I am very grateful for the opportunity of this research grant given to me by CNPq, for without it this work wouldn't have been possible. I also thank my advisor Paulo F. A. Braga and other CETEM employees for all the support throughout this year, CETEM for the infrastructure given, COAM for the analysis of my samples, and Guilherme Moreira and Caroline Gonçalves, research colleagues, for the support during the realization of tests and writing of this paper.

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