Recycling of production residues from primary lithium batteries

M. Kahl, S. Pavón, M. Bertau

Institute of Chemical Technology, TU Bergakademie Freiberg, Freiberg, Saxony, 09599, Germany
Keywords: lithium, recycling, production residue, oxidation
Presenting author email: martin.kahl@chemie.tu-freiberg.de

Introduction

Energy storage systems based on lithium, lithium-ion or lithium polymer are currently the best technology and main driving force behind the growing demand of lithium. (Martin 2017, Ziemann 2018). Moreover, Li batteries are the main market of lithium and represents 65 % of the world supply. (Jaskula 2020) Recently Li supply gets increasing attention because the e-mobility is becoming an alternative to conventional combustion engine vehicles.

In 2019, world demand accounts for 77,200 t of Li or 411,000 t LCE (lithium carbonate equivalents) (Jaskula 2020). Estimations for 2027 show an ongoing trend in demand, with a consumption of up to 1,000,000 LCE (188,000 t Li). (Roskill 2020) Global Li reserves amount to 17 million tons, but supply has been classified as critical because 88 % of its production comes from Australia, Chile and China (Jaskula 2020). Consequently, the EU-Commission declared lithium as critical raw material (European Commission 2020) and therefore, the recycling of this metal from secondary sources like End of Life (EoL) products and production residues has become essential.

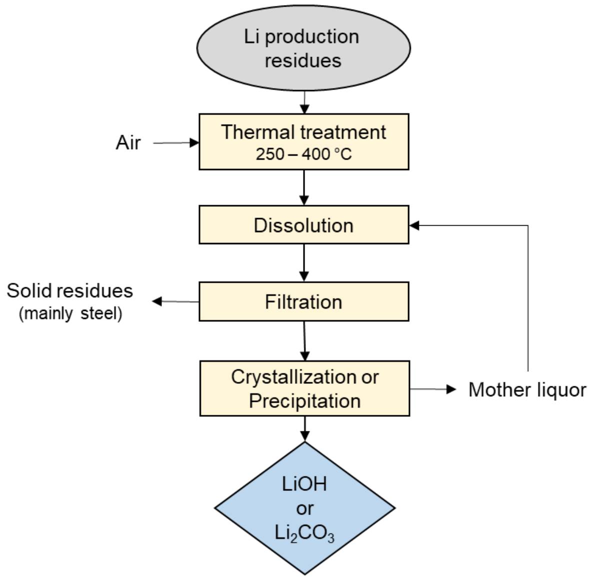

Figure 1. Recycling process scheme of production residues from primary lithium batteries.

The production residues of primary lithium battery production are currently considered as waste and disposed in landfills. However, they are a valuable source for Li recycling due to their availability in industrial countries and high Li content but high purity demands for Li battery grad (≥99.5 %) and high reactivity towards air, prevent the direct reuse of the Li metallic. Hence, the recovery of Li as Li_2CO_3 or LiOH from aqueous solution is proposed (see Figure 1). The challenge is the handling of high energy release during dissolution in water (32 MJ/kg Li) and H_2 generation. To circumvents both problems, an oxidation reaction of Li to Li_2O before dissolution by using mid temperature is proposed, which reduced energy release up to 70 %. The current work focusses on the oxidation reaction and the optimization of process conditions.

Materials and Methods

Residues of lithium battery production were supplied by FNE Entsorgungsdienste Freiberg GmbH and stored under Ar atmosphere. The sample preparation consists of cutting the samples to a uniformly size directly before oxidation. Oxidation of samples was performed in a muffle furnace (LVT 15/11 Nabertherm corp., Germany) and the residues were leached using 50 mL of 3 M HNO_3 for 15 min to prevent precipitation of $Fe(OH)_3$. The Li concentration of the leachate was analysed by atomic emission spectrometry with inductively coupled plasma (ICP-OES, Optima 4300 DV, Perkin Elmer, Corporation, Waltham, USA). X-ray diffraction (XRD) analyses (D8 DISCOVER, Bruker, Corporation, Billerica, USA) will be used for characterization of the obtained product.

Results & Discussion

The production residues of primary lithium batteries have a high Li-content (~50%), therefore representing a valuable waste from which this critical raw material can be recovered and recycled. Furthermore, the purity of these residues after dissolution in water is ≥ 99.8%. Hence, the production of high pure Li compounds from this secondary source is promising.

The samples were composed by punching residues with 46.8±1.32 % Li contaminated with 21.0 ±0.7 % of stainless steel and 15.3±0.84 % of plastics. It is expected that the temperature, residence time and sample mass have a significant influence on the oxidation performance and thus on the Li-conversion. Li oxidizes readily under air atmosphere forming a variety of Li compounds such as Li_2O, Li_3N, Li_2CO_3 and LiOH. However, for a complete oxidation at room temperature, 48 h are needed. But this residence time can be drastically reduced by increasing the temperature up to 400 °C.

The temperature has a great influence on Li-content (see Figure 2.a), reaching a maximal conversion at 400 °C. The influence of residence time and sample mass on the Li-conversion was lower compared to the obtained by varying the temperature. Whereas increasing temperature and residence time maximize Li-conversion, the sample mass seems to have a negative influence on Li-conversion (Figure 2.b) because increasing the sample mass results in enhanced sintering and decreased surface volume ratio.

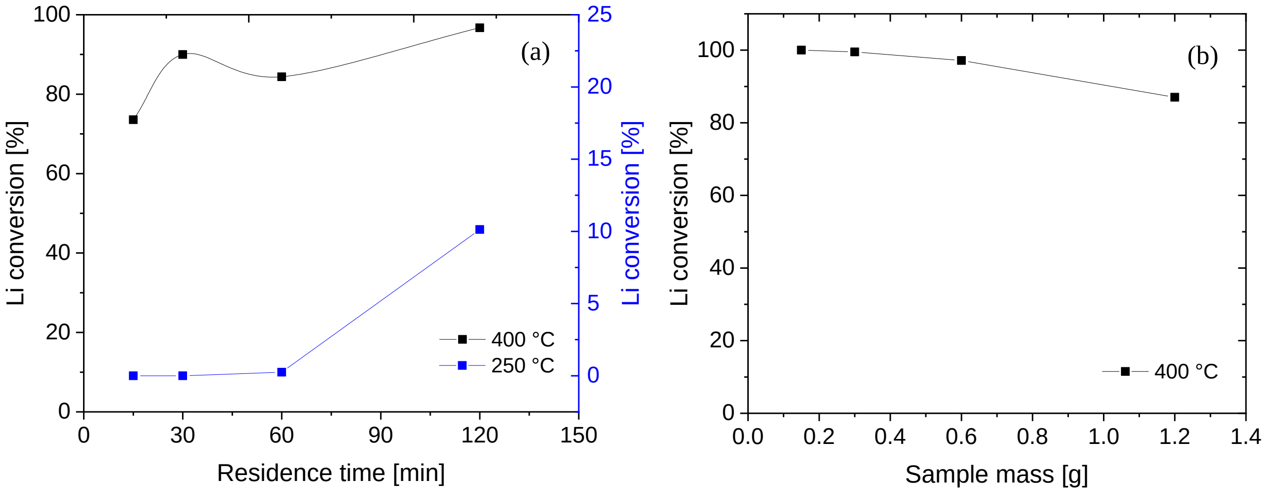

Figure 2. Effect of temperature and time on Li-content using 0.3 g of sample (a) and effect of the sample mass on Li content at 400 °C (b).

The Li-conversion by the oxidation reaction will be optimized using a 3^3 Box Behnken experimental design (see Table 1). This design of experiments allows the evaluation of the significance of each factor and the influence of their correlations on the Li-conversion. Furthermore, an optimal oxidation conditions will be obtained as well as a mathematical model equation which enables the assessment of the Li-conversion at any desired point within the examined factor levels.

Table 1. Factors and factor levels in the experimental design.

Factors		Factor levels		
		-1	0	+1
A	Temperature [°C]	250	325	400
B	Residence time [min]	15	30	45
C	Sample mass [g]	0.30	0.75	1.20

Conclusions

Production residues of primary lithium batteries represent a valuable resource for lithium recycling due to their high Li-content and purity (≥ 99.8 %) after dissolution. The Li metallic on these residues is oxidized to Li_2O and Li_3N reducing energy release at least in 70 % during dissolution. The temperature has a great influence on Li-conversion whereas other factors such as residence time or sample mass have not a significant effect. To sum up, the proposed process which contains a thermal treatment on the oxidation stage is suitable to reduce energy release during the Li metallic dissolution. Therefore, the process will be optimized by using a statistical design of experiment which allows the determination of a Li-conversion optimum.

EUROPEAN COMMISION, Critical Raw Materials Resilience: Charting a Path towards greater Security and Sustainability, Brussels, **2020**.

B. W. Jaskula, Mineral Commodity Summaries 2020, **2020**.

G. Martin, L. Rentsch, M. Höck, M. Bertau, Energy Storage Materials **2017**, 6, 171–179.

Roskill, Lithium Outlook to 2030, 17th Edition, available at https://roskill.com/market-report/lithium/ **2020.**

S. Ziemann, D. B. Müller, L. Schebek, M. Weil, Resources, Conservation and Recycling **2018**, 133, 76–85.