Selective Recovery of Lithium from different spent Lithium-Ion Batteries

R. Mende[1], D. Kaiser[1], M. Bertau[1]

[1] Institute of Chemical Technology, TU Bergakademie Freiberg, Freiberg, Saxony, 09599, Germany

Keywords: black mass, Li_2CO_3, sc-CO_2, lithium-ion batteries.
Presenting author email: doreen.kaiser@chemie.tu-freiberg.de

Introduction

Since electric vehicles produce significantly less CO_2 than conventional vehicles, especially when combined with renewably generated electricity, electromobility is the key to climate-friendly mobility worldwide and unavoidable in order to achieve the politically set climate targets. The share of electric vehicles registered worldwide is steadily increasing. Coupled with an increasing demand for electric vehicles is a growing need for lithium-ion batteries (LIBs), the production of which in turn requires a wide range of raw materials like aluminum, cobalt, copper, lithium, manganese and nickel. To be able to cover this demand, as well as for economic and ecological reasons, efficient recycling processes of the spent LIBs is necessary.

The known processes for recycling spent LIBs focus on the recovery of cobalt and/or nickel. The other valuable metals are only partially recovered or not recovered at all. Lithium in particular is not economically recycled in the conventional processes. It is different with the COOL-process presented here (figure 1). The key step of this process is the leaching of the LIBs with supercritical CO_2 (sc-CO_2), which allows a selective mobilization of the lithium. The remaining residue contains the remaining valuable metals, which can all be recovered by subsequent acid digestion and liquid-liquid extraction (Kaiser et al. 2021; Pavón et al. 2021).

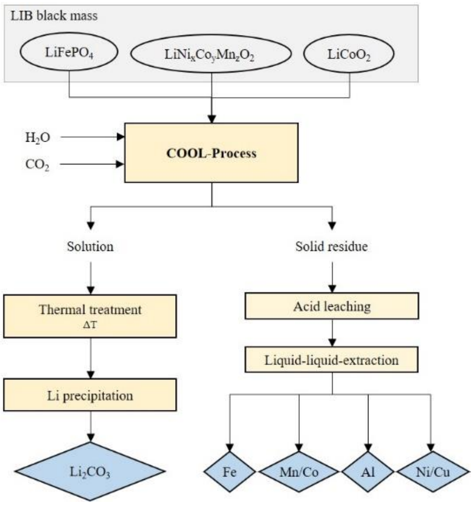

Figure 1 *Flowsheet of the COOL-process for recycling spent LIBs (adapted of (Kaiser et al. 2021; Pavón et al. 2021).*

Another advantage of the COOL-process is that different lithium containing raw materials can be processed simultaneously. Thus, different LIB types can be processed, a unique feature of all known LIB recycling processes. This fact significantly improves the economic efficiency of LIB recycling. Battery research is still ongoing, which is why more and more different battery types will exist on the market in the future. A sorting process is connected with a large sorting effort, which is very costly and can only be done manually. Simultaneous processing of different types of batteries is therefore intended to make recycling considerably easier. All products of the COOL-process can be fed back to the production of new LIBs, thus closing the material cycles. This makes the COOL-process a prime example of an efficient and sustainable circular economy. This paper focused on the selective recovery of lithium from various black masses of different spent LIB-types.

Material and Methods

All experiments for lithium mobilisation were done in a Hastelloy autoclave (Berghof BR-500). For this purpose, black mass was suspended in 400 mL water (11-33 g/L; 500 rpm), heated with a heating rate of 5 K/min (150-230 °C) and treated with CO_2 after reaching the target temperature (100 bar). After completion of the desired reaction time (2-4 h) the reaction mixture was cooled down to $T < 30$ °C under pressure and subsequently decompressed to normal pressure. Afterwards the suspension was filtered and the leachate was analyzed by ICP-OES (Co, Mn, Al, Fe, Ni) and AAS (Li). The dried solid residue, after being digested in aqua regia, was also analysed by ICP-OES and AAS.

For precipitation of Li_2CO_3 a part of the digestion solution was concentrated at 100 °C by a factor of 40. The solid product was filtered and washed with deionized water. The purity of the product was analysed by AAS after dissolving in 1%(v/v) HNO_3.

Results and Discussion

Using one black mass (type $LiNi_xCo_yMn_zO_2$) as an example, a statistical design of experiments (DOE; 3^3 Box-Behnken Design) was used to optimize the experimental parameters for selective leaching of lithium. As a result of the DOE, the following conditions for maximum Li mobilization were determined: temperature 230 °C, residence time 4 h, 11 g black mass per L water. Under these conditions a maximum Li mobilisation of 94.5 wt.% could be achieved. These pre-optimized experimental conditions were transferred to other black masses. It was found that regardless of the battery type, the optimum digestion conditions are similar, which allows simultaneous processing. A novelty on the market of battery recycling processes.

The Li dissolved by the COOL-process could be isolated as lithium carbonate (Li_2CO_3) by precipitation after thermal treatment without any addition of chemicals like soda. The isolated Li_2CO_3 is characterized by a high purity (>99.8 %), which already corresponds to that of battery grade without any cleaning steps, which in turn enables direct recycling to battery production. This is made possible by the fact that during leaching with sc-CO_2 only a small co-mobilization of the accompanying elements takes place. Only for aluminum was a co-leaching of more than 1 % observed. Figure 2 shows the results of co-mobilization for two different black mass types ($LiNi_xCo_yMn_zO_2$ and $LiFePO_4$).

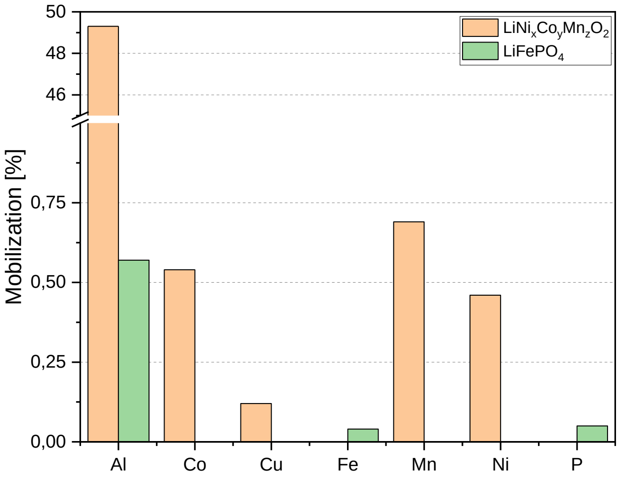

Figure 2 *Co-mobilization of Al, Co, Cu, Fe, Mn, Ni and P during COOL-process of two different black mass types. The leaching conditions were: 230 °C, 100 bar, 4 h, 11 g/L*

Conclusion

An efficient process for recycling spent LIBs must be highly adaptable due to the variety of different battery types. This criterion is clearly met by the COOL-process. This process allows a unification of various black masses and enables a selective mobilization of lithium. The leaching of black mass (11 g/L) with supercritical CO_2 at 230 °C and 100 bar for 4 hours mobilized up to 94.5 wt.% of the containing lithium into the digestion solution. Afterwards, the dissolved Li could be precipitated as lithium carbonate (Li_2CO_3) by simple precipitation without the addition of further reagents. The crude product obtained in this way is already of battery quality due to the low co-mobilization of other accompanying substances and can thus be fed into battery production without further conditioning. This makes the COOL-process an ideal way of closing material cycles (circle economy). Since the process does not involve the addition of expensive or even toxic reagents, the COOL-process is also very sustainable and efficient from both economic and ecological point of view. In addition, the process enables the material use as well as chemical storage of the greenhouse gas CO_2, which improves the carbon footprint. Since all plant components can be operated using regeneratively produced electricity, this approach completely eliminates the use of fossil raw materials, which contributes significantly to achieving the climate targets.

References

Kaiser D, Pavón S, Bertau M (2021) Chemie Ingenieur Technik 93:1833–1839. https://doi.org/10.1002/cite.202100098

Pavón S, Kaiser D, Bertau M (2021) Chemie Ingenieur Technik 93:1840–1850. https://doi.org/10.1002/cite.202100101