Recycling of LiPF$_6$ from lithium-ion battery black mass

B.F. Hansel$^1$, S. Pavón$^{1,2}$, C. Pätzold$^1$, M. Bertau$^{1,2}$

$^1$Institute of Chemical Technology, Technische Universität Bergakademie Freiberg, Freiberg, Saxony, 09599, Germany
$^2$Fraunhofer Institute for Ceramic Technologies and Systems IKTS, Fraunhofer Technology Center for High-Performance Materials THM, Freiberg, Saxony, 09599, Germany

Keywords: recycling, lithium, fluorine, electrolyte.
Presenting author email: bastian-fabien.hansel@chemie.tu-freiberg.de

Introduction

Lithium-ion batteries (LIBs) have become indispensable in electric mobility sector in recent years. However, already established industrial recycling processes (e. g. Umicore-, Sony-Sumitomo-, Toxo- or Recuply-process) are focused on the recovery of metals such as Co or Ni instead of Li. (Velázquez-Martínez et al. 2019) Due to the increasing demand and political competition for global Li deposits, a change in this trend is expected.

In most cases, the raw material of LIB-recycling is the solid black mass and no attention has been given to the recovery of electrolyte compounds. This electrolyte, which consists of highly valuable Li-salts (usually LiPF$_6$) in an organic matrix, accounts for up to 20 wt.-% of the total battery for an electric vehicle unit. In addition, the electrolyte contributes for about 9% of the LIB-costs due to the valuable conducting salts. (Thompson et al. 2020) The high cost of these unusual Li-salts is attributed to the complex production process. For this reason, an approach to electrolyte utilization while preserving the valuable anion species is of high economic importance. This is realized by the COOL-process 2.0 (Figure 1).

The COOL-process, a leaching using supercritical CO$_2$, is a future-directed process in terms of circular resources chemistry, circular economy as well as zero-waste concepts. All these aspects are the key points to cover the present and future society necessities. The increased LIB-demand is attributed to their high energy-storage capacity and energy density, low self-discharge effects and heavy metal content. As evidence of the importance and paradigm shift for e-mobility, 4.5 billion LIBs were manufactured in 2021. (Velázquez-Martínez et al. 2019) Furthermore, an increase can be expected in the near future due to the ongoing electrification of passenger and cargo transportation vehicles.

The current work is focused on the improvement of this approach, COOL-process 2.0, which includes the separation and recovery of such Li electrolyte salts from the main battery components. The work already performed presents promising results for the recovery of LiPF$_6$, ignored by other processes, even if the goal of complete LiPF$_6$ recovery has not yet been achieved.

Materials and Methods

The set-up for the recovery of LiPF$_6$ consists mainly of a heating and cooling zone. In the heating zone, 1 mL of 1 mol/L LiPF$_6$-ethylene carbonate/dimethyl carbonate (50 vol.-%:50 vol.-%, battery grade, Sigma Aldrich) is heated by a tube furnace up to 200 $^\circ$C. The sample is placed in an unglazed combustion boat and seated in a ceramic tube. During heating, the LiPF$_6$ decomposition gas is carried away by dried N$_2$ with variable flow rate. The decomposition gas is absorbed by 20 mL of a dried mixture (50 vol.-%:50 vol.-%) of ethylene carbonate (98 %, Sigma Aldrich) and dimethyl carbonate (> 99.8 %, Carl Roth). To minimize the HF formation during recovery, the solvent drying process (water content < 20 mg/kg) with 3A molecular sieves is carried out in a N$_2$-filled glove box. This procedure requires pre-drying of the industrial grade ethylene carbonate in a vacuum desiccator.

Figure 1: COOL-process 2.0 of LIB black mass by implementing Li-salt recovery from electrolyte.
conventional three-necked round-bottomed flask is used as an absorption reactor, which can be cooled down up to -20 °C. The excess gas is led into a Ca(OH)₂ scrubber.

For validation the recovered LiPF₆-containing solutions were analyzed by ion chromatography (anion separation, conductivity detector, eluent: 2.3 mmol/L Na₂CO₃, 2.2 mmol/L NaHCO₃, 25 % acetonitrile). Due to the use of an unspecific conductivity detector the PF₆⁻-quantification is carried out using matrix-matched KPF₆ (99 %, p. a., VWR) standards.

**Results and Discussion**

The thermal recovery optimization of the most used electrolyte salt LiPF₆ is investigated by using synthetic model systems. Because of the strong heterogeneity of LIB-electrolytes, a constant sample composition is recommended to reach sufficient accuracy of the preliminary statistical optimization data.

The results obtained by ion chromatography depicted in Figure 2 disclose the successful recovery of LiPF₆. Since the PF₆⁻-anion interacts strongly with the separation column (high retention time), it can be differentiated from foreign ions with sufficient accuracy. The high exchange capacity of the used column and the separation at room temperature results in the observable intense tailing effect of the PF₆⁻-peak. The variation in retention time is caused by the absence of a column oven and, in the case of the PF₆⁻-peak, by the additional high retention times. Regarding PF₆⁻-quantification and the non-specific conductivity detector, the preparation of matrix-matched KPF₆ standards was established as part of the work already performed. Without optimization, a maximum PF₆⁻-recovery for the LiPF₆ solution of 77 % was achieved.

**Conclusion**

The recovery of LiPF₆ from a model solution, which simulates the electrolyte of LIBs, was achieved by thermal separation. This approach shows an alternative for electrolyte recycling from batteries, which maintains PF₆⁻-species in the resource cycle. Thus, contributing to a circular economy and implementing the zero-waste concept. In terms of Li recycling, the opportunity of utilization up to 20 wt.-% of a LIB cell, as part of the COOL-process 2.0, leads to both green and ongoing maximization of Li recovery. Apart from economic benefits, this includes the environmental protection, due to the controlled handling of LiPF₆. Especially in the context of scaling up the COOL-process 2.0, this is of particular importance.

However, due to a various number of possible side reactions (by-products are shown in Figure 2) the optimization of LiPF₆ separation and recovery is not a trivial one. Hence, further research is focused on the variation and subsequent optimization of different process conditions (e. g. oven temperature, cooling temperature, heating time, N₂-flowrate, gas separation).

**Acknowledgements**

Financial support by the German Federal Ministry of Education and Research (Grant nr. 03XP0332B) is gratefully acknowledged.

**References:**


Thompson, Dana L.; Hartley, Jennifer M.; Lambert, Simon M.; Shiref, Muez; Harper, Gavin D. J.; Kendrick, Emma et al. (2020): The importance of design in lithium ion battery recycling – a critical review. In: Green Chem. 22 (22), S. 7585–7603. DOI: 10.1039/D0GC02745F.