

Recycling of LiPF₆ from lithium-ion batterie black mass

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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-, Toxco- or Recuplyprocess) 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 LiPF₆) 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 CO₂, 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 LiPF₆, ignored by other processes, even if the goal of complete LiPF₆ recovery has not yet been achieved.

Materials and Methods

The set-up for the recovery of LiPF₆ consists mainly of a heating and cooling zone. In the heating zone, 1 mL of 1 mol/L LiPF₆-ethylene carbonate/dimethyl carbonate (50 vol.-%:50 vol.-%, battery grade, Sigma Aldrich) is heated by a tube furnace up to 200 °C. The sample is placed in an unglazed combustion boat and seated in a ceramic tube. During heating, the LiPF₆ decomposition gas is carried away by dried N₂ 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 N₂-filled glove box. This procedure requires pre-drying of the industrial grade ethylene carbonate in a vacuum desiccator. A

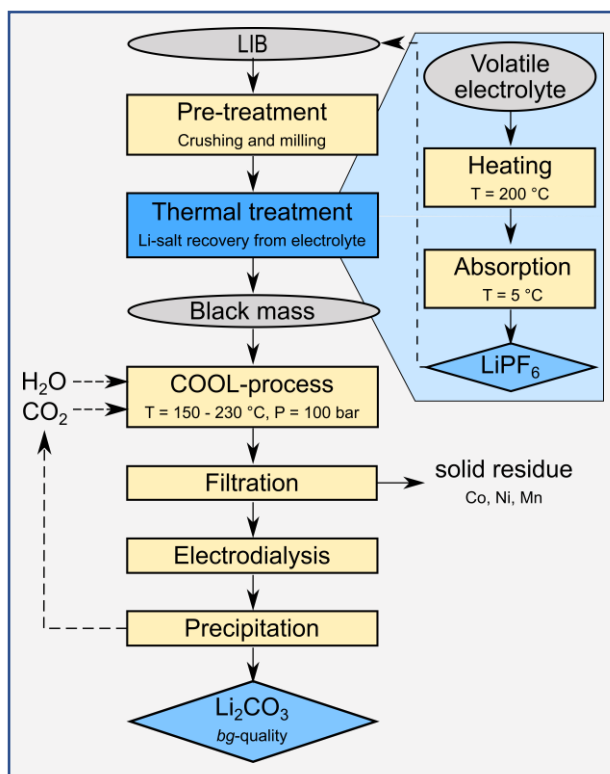


Figure 1: COOL -process 2.0 of LIB black mass by implementing Li-salt recovery from electrolyte.

conventional three-necked round-bottomed flask is used as an absorption reactor, which can be cooled down up to $-20\text{ }^{\circ}\text{C}$. The excess gas is led into a $\text{Ca}(\text{OH})_2$ scrubber.

For validation the recovered LiPF_6 -containing solutions were analyzed by ion chromatography (anion separation, conductivity detector, eluent: $2.3\text{ mmol/L Na}_2\text{CO}_3$, $2.2\text{ mmol/L NaHCO}_3$, 25% acetonitrile). Due to the use of an unspecific conductivity detector the PF_6^- -quantification is carried out using matrix-matched KPF_6 (99% , p. a., VWR) standards.

Results and Discussion

The thermal recovery optimization of the most used electrolyte salt LiPF_6 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 LiPF_6 . Since the PF_6^- -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 PF_6^- -peak. The variation in retention time is caused by the absence of a column oven and, in the case of the PF_6^- -peak, by the additional high retention times. Regarding PF_6^- -quantification and the non-specific conductivity detector, the preparation of matrix-matched KPF_6 standards was established as part of the work already performed. Without optimization, a maximum PF_6^- -recovery for the LiPF_6 solution of 77% was achieved.

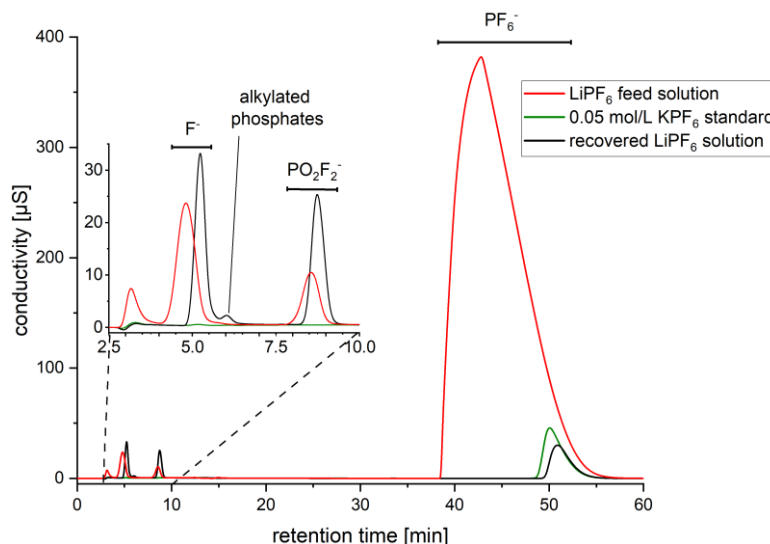


Figure 2: Ion chromatogram of the recovered and feed LiPF_6 solutions. KPF_6 standard concentration correlates with the maximal possible PF_6^- -concentration regarding an absorber volume of 20 mL .

Conclusion

The recovery of LiPF_6 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 PF_6^- -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 $20\text{ wt.}\%$ 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 LiPF_6 . 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 LiPF_6 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, N_2 -flowrate, gas separation).

Acknowledgements

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