Extraction of Organic Carbonate Based Electrolytes with Supercritical Carbon Dioxide for a High Efficient Recycling of Lithium-Ion Batteries

Martin Grützke, Xaver Mönnighoff, Martin Winter and Sascha Nowak*

University of Münster, Institute of Physical Chemistry, MEET - Battery Research Center
Corrensstraße 46, 48149 Münster, Germany

Portable electronics like cellphones, camcorders and mp3-players as we know them nowadays would not be imaginable without lithium-ion batteries (LIBs). They are the energy storage device of choice due to the high energy density and high reversibility without a memory effect. LIBs are also the most promising technology for electric and hybrid vehicles.[1] It is expected that the amount of produced traction batteries will strongly increase in the next years.

LIBs are a complex mixture of several chemicals which contain for example heavy metals. Besides the limited amount and the increasing costs of the raw material, the protection of the environment is a basic reason to focus on the recycling of LIBs. Therefore, a recycling procedure with the highest possible recovery rate should be developed. The already existing recycling procedures for LIBs are only focusing on the solid parts of the batteries. The recovery of volatile compounds like the organic carbonates which serve as the solvent of the electrolyte, or electrolyte additives has never been applied in the industry. New methods for the separation of the electrolyte from the other battery parts have to be developed to increase the recovery rate.

Extraction of the battery scrap with solvent is conceivable. Another approach is the extraction with supercritical fluids like for example supercritical carbon dioxide (sc CO_2). This method is faster, more selective and efficient compared to extraction with solvent.[2-3] Moreover, no sample pre-concentration or clean-up process is necessary.[4]

We wanted to know if the extraction of non-aqueous battery electrolytes for LIBs is possible with sc CO_2. Thus, we did a simple proof of principle experiment. Six layers Freudenberg 2190 separators (polyethylene fleece, 6 x 6 cm^2) were soaked with LP30 (dimethyl carbonate - DMC, ethylene carbonate - EC, 1:1; 1 mol/L $LiPF_6$) and stirred in an autoclave with sc CO_2 for one hour. The extracted electrolyte was collected afterwards and analyzed by gas and ion chromatography (GC-MS and IC). A recovery rate of about 75% could be achieved. Degradation products of the conducting salt were detected only in small amounts. The concentration of $LiPF_6$ and EC slightly increased (quantified by IC and GC), while the concentration of DMC decreased. No degradation products could be detected with GC-MS which confirms the mild extraction conditions.

The recovery rate should be enhanced. Thus, we installed a conventional sc CO_2 extraction system whereby through-flow experiments are possible. The equipment and the conditions were optimized regarding extraction time and recovery rate. We achieved a recovery rate of over 80% of the electrolyte for shredded traction batteries. The extract mainly consists of DMC, EMC, EC and cyclohexyl benzene (analyzed by GC-MS).

These results verify that the extraction of organic carbonate based electrolytes for LIBs is not only possible out of separators but also out of complex mixtures of shredded traction batteries. The concentrations of the extracted compounds in the extract depend on the particular adsorption properties of the extracted material. Consequently, extraction with sc CO_2 is a suitable method for the separation of the electrolyte from other battery parts and could be applied in the recycling process of lithium-ion batteries.

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*to whom correspondence should be addressed:

sascha.nowak@uni-muenster.de