Solvent Extraction of Electrolyte Compounds in the Recycling of Lithium Ion Batteries

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The extraction of lithium hexafluorophosphate from lithium ion batteries with organic solvents is a promising possibility to remove the conducting salt and recover organic compounds. The influence of temperature onto degradation and extraction was investigated. Multi-stage cross-flow extractions have been performed with dimethyl carbonate as extractant and a combination with a second set of extractions with water. The experiments have been performed in a stirred vessel with 0.5 L volume in inert gas atmosphere. The samples have been analyzed by ion chromatography. After five stage extraction with dimethyl carbonate and three stages with water including drying the fluoride loading in the fine fraction smaller 200 µm was 166 mg fluoride per kg solid material.

1. Introduction

Recycling lithium ion batteries from traction systems is a global challenge with increased importance due to their increasing distribution and limited lifespan. Previous recycling processes focused on the recovery of metals e.g. cobalt, nickel and lithium by hydrometallurgical and pyro metallurgical methods [1–7]. In the collaborative research project LithoRecII, a comprehensive recycling process for lithium ion batteries to recover value compounds and to minimize the risk potential due to the chemical compounds was investigated. The electrolyte is a mixture of conducting salt lithium hexafluorophosphate ($LiPF_6$) and organic carbonates and represents about 20 % of the mass of a single battery cell. These compounds were captured by a solvent extraction with dimethyl carbonate, in following abbreviated as DMC, one of the constituents of the electrolyte mixture. Being a low-boiling organic solvent, it could be removed in a drying process. This allows the subsequent recovery steps to be conducted with reduced risk and effort. The preparation of batteries for extraction in recycling includes the collection, discharging and shredding in nitrogen atmosphere. The solvent is evaporated after extraction by drying and prior to the recovery of precious metals e.g. lithium, cobalt and manganese by mechanical, hydrometallurgical and pyro metallurgical processes. The conducting salt $LiPF_6$ is decomposing in equilibrium reaction and is likely to react to hydrofluoric acid in presence of water as shown in equation 1. [8–18]

$$LiPF_6 \rightarrow LiF + PF_5 \rightarrow LiF + 2\,HF + POF_3 \qquad (1)$$

The further hydrolysis of POF_3 results in three equivalents HF and phosphoric acid according to [19,20]. For the recovery of the conducting salt and organic compounds from electrolyte the extraction with super-critical carbon dioxide and combination with solvents e.g. acetonitrile was the only alternative which has been studied [21].

2. Experimental

2.1 Battery material

The electrolyte compounds of the batteries are the conducting salt and organic carbontes. The cells for characterization experiments have been Panasonic CGR 18650 CH, cylindric cells with electric charge of 2250 mAh and nominal voltage of 3.6 V. After discharging the cells were grinded at the Institute for Particle Technology (TU Braunschweig, Braunschweig, Germany) in the “Battery analysis mill”, a modified SM 200 cutting mill (Retsch, Haan, Germany), in nitrogen atmosphere and packaged immediately under inert gas atmosphere. The battery mass of a single cell was 42.64 g on average before the grinding and 37.79 g afterwards. The composition of the batteries was assumed to be a mixture of DMC (40 %), ethylmethyl carbonate (20 %), propylene carbonate (10 %) and ethylene carbonate (EC) (30 %) with 1,18 mol $LiPF_6$/L electrolyte. The salt concentration was determined by the Münster Electochemical Energy Technology centre (MEET) (WWU Münster, Münster, Germany). For each of the experiments in section 3.1 a single cell was used and for the experiment in 3.2 two cells were used.

2.2 Stirred vessel

For the extraction experiments a Versoclave 3 (Büchi Glas Uster, Uster, Switzerland) stirred vessel with 0.5 L was used. The temperature was measured internally by a PT-100, the connected cryostat is a CC 405 (Peter Huber Kältemaschinenbau GmbH, Offenburg, Germany). The stirred vessel was in a housing made of PMMA and alumina profiles. The whole vessel was made from stainless steel. The housing was flushed with nitrogen and the vessel was filled with argon. Most of the experiments were conducted at a pressure of 2 bar absolute or slightly higher. For the extraction kinetics a pneumatic sample system was used to take samples during the experiment from the center of the vessel using internal pressure.

2.3 Ion chromatography

The focus for analysis was the determination of hexafluorophosphate concentration and fluoride, one of the decomposition products. For this reason the ion chromatograph 881 Compact IC pro in combination with a 919 IC Autosampler plus (Deutsche Metrohm GmbH & Co. KG, Filderstadt, Germany) was used. The ion chromatography and accessory was controlled by using Metrohm MagIC Net software. All columns were distributed by Metrohm (Deutsche Metrohm GmbH & Co. KG, Filderstadt, Germany). A linear matrix elimination was integrated with an external 6-port-valve (VICI Vlaco Instruments Co. Inc., Schenkon, Switzerland). The flow rate of eluent was 0.7 mL/min and a temperature of 55 °C was set in the column oven. The composition of eluent was 0.7 L ultrapure water, 0.3 L acetonitrile, 10 mL 1 M sodium carbonate and 2 mL 1 M sodium hydrogen carbonate. The eluent was degassed before use. For the calibration fluoride and phosphate standards (Merck KGaA, Darmstadt, Germany) and $LiPF_6$ salt 1 M dissolved in a mixture of DMC and EC supplied by the MEET (MEET, University Münster, Münster, Germany) were employed. The samples were diluted with DMC for the extract analysis and with ultrapure water. From the anion chromatography result for hexafluorophosphate (PF_6^-) the mass of $LiPF_6$ was calculated. The hexafluorophosphate and fluoride mass loading in the fine fraction was analyzed by the dispersion of 0.5 g fine fraction of raffinate in 100 mL ultrapure water. The fine fraction was produced by drying of the raffinate and sieving with Alpine e200 LS (Hosokawa Alpine AG, Augsburg, Germany) with 200 µm sieve mesh. A sample from solution was taken, filtered and used for ion chromatography.

2.4 Parameters for single stage extraction with DMC

The experiments were performed with solvent to solid mass ratio of 7.5, DMC as solvent and a single Panasonic 18650 cell for each experiment. The stirrer speed was set to 50 rpm. Samples were taken after 1, 3, 5, 10, 15 and 30 minutes. Samples from extract were analyzed by ion chromatography.

2.5 Parameters for multi-stage extraction with DMC

Four cross-flow extraction stages with DMC as extractant have been performed. The extract was separated from stirred vessel after 30 minutes and fresh solvent was added. The temperature was set to 20 °C and the stirrer speed was 50 rpm. The solvent to solid mass ratio for the first stage was 10 and 7.5 for the following stages. The raffinate was dried at 105 °C for three days. Afterwards the fluoride and hexafluorophosphate loading were determined by dissolving the fine fraction in ultrapure water as described in 2.3.

2.6 Settings for combination of multi-stage extractions using DMC and water

The set consisted of five extraction stages with DMC, drying, three extraction stages using water as extractant followed by drying and sieving. The extraction time per stage was 30 min. The temperature for the extractions with DMC was set to 20 °C and for the extractions with water 80 °C were set. The solvent to solid mass ratio for DMC was 5 and for water 10. The stirrer speed was 50 rpm. Two Panasonic 18650 batteries with 84.4 g overall mass have been used for DMC extraction and 30 g from the dried raffinate were used for second part of extractions. Sampling was performed as described in 2.5.

3. Results and Discussion

3.1 Single stage extractions with DMC

In single stage extractions the influence of the extraction temperature was determined. The temperatures were set to 10, 20, 30 and 40 °C. In Figure 1 the mass fractions of the conducting salt $LiPF_6$ in the extract are displayed over extraction time. For 10 °C, 20 °C and 30 °C the $LiPF_6$ mass fraction in the extract increases continuously over time, while for 40 °C it increases in the first 15 minutes and decreases thereafter. Additionally, the extracted $LiPF_6$ content is maximum for 20 °C while it decreases with increasing extraction temperature. While the increase from 10 °C to 20 °C may be attributed to an increase in solubility the drop in the $LiPF_6$ content indicates a degradation of $LiPF_6$ at higher temperatures. While the chromatograms for 10 °C and 20 °C only show minor peaks indicating degradation, the chromatograms for 30 °C and 40 °C showed significant peaks for fluoride and unidentified peaks presumably resulting from decomposition. The following multi-stage extractions with DMC have therefore been performed at 20 °C to achieve the optimum combination of minimum degradation and highest solubility.

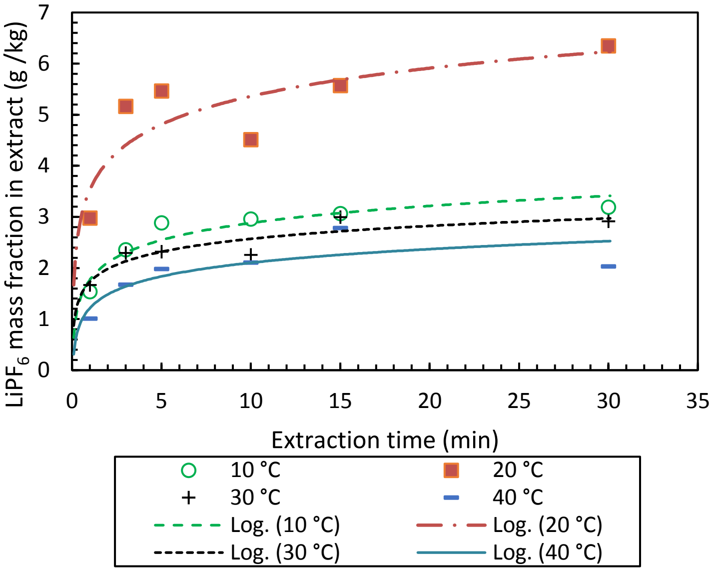

Figure 1. Influence of extraction temperature with logarithmic fits for extraction with DMC.

3.2 Multi-stage extractions with DMC

For the reduction of conducting salt as source for toxic decomposition products multi-stage cross-flow extractions with DMC were used. A four stage extraction was employed to decrease $LiPF_6$ contaminations in solid material for hydrometallurgic processing. The mass fractions for fluoride and $LiPF_6$ in the extract, the cumulated extracted mass of conducting salt and extraction efficiencies are shown in Table 1. Fluoride was only detected in the first stage. The hexafluorophosphate mass fraction decreases after each stage with the maximum mass fraction of 3.106 g PF_6^- per kg extract after first stage and minimum of 0.021 g per kg extract after fourth stage. The extracted mass of $LiPF_6$ after first stage is 1.154 g and after fourth stage 0.007 g. The mass of $LiPF_6$ is calculated based on the composition of the samles and each extract at the end of stage. After fourth stage the cumulated mass of $LiPF_6$ in extract was 1.323 g. The extracted mass per stage decreases significantly and therefore it is assumed that the fresh solvent primarily dilutes the remaining solvent in raffinate. The remaining solvent is approximately 1 kg solvent per kg solid. The extraction efficiency $Y_{\text{extr, LiPF6 in solution}}$ for dissolved $LiPF_6$ based on the overall mass of conducting salt in extract in reference to overall mass of conducting salt in solution from extract and liquid fraction of raffinate is calculated as shown in equation 2.

$$Y_{extr,\, LiPF_6 in\, solution} = \frac{\sum m_{LiPF_6\ in\ extract}}{\sum m_{LiPF_6\ in\ extract} + m_{LiPF_6\ in\ raffinate\ in\ last\ stage}} \qquad (2)$$

The effect of degradation of conducting salt is included by the mass of $LiPF_6$ in the solid after the drying as shown in equation 3 for the extraction efficiency for overall $LiPF_6$ $Y_{\text{extr, LiPF6 from extract + solid}}$. Therefore, the mass of $LiPF_6$ in fine fraction has been included and also the degraded part of the conducting salt from the complete hydrolysis. Equation 4 presents calculation for the mass of $LiPF_6$ in solid. For $LiPF_6$ the mass loading in fine fraction is multiplied with mass of fine fraction. The degradation reaction is also taken into account by calculating the mass of conducting salt assuming complete hydrolysis as described in [19] and complete traceability of fluoride. The fine fraction of solid from the raffinate has been analysed by extraction with ultrapure water as described in section 2.3 Ion chromatography. No loading with fluoride und hexafluorophosphate was assumed for coarse fraction. For the recovery of high value metal compounds the fine fraction is relevant and therefore the coarse fraction is separated after drying. The sieving with a 200 µm mesh resulted in fractions with similar weight.

$$Y_{extr,\, LiPF_6\, from\, extract+solid} = \frac{\sum m_{LiPF_6\, in\, extract}}{\sum m_{LiPF_6\, in\, extract} + m_{\,LiPF_6\, in\, solid}} \tag{3}$$

$$m_{\,LiPF_6\, in\, solid} \;=\; X_{g,LiPF_6} \bullet m_{Fine\, fraction} + X_{g,F^-} \bullet \frac{\widetilde{M}_{LiPF_6}}{6\,\widetilde{M}_{F^-}} \bullet m_{Fine\, fraction} \tag{4}$$

The key parameters for recovery processes of value materials from lithium ion batteries are represented by the fluoride and hexafluorophosphate loading in the fine fraction of raffinate after drying process. The fluoride loading was 3558 mg fluoride per kg fine fraction of solid phase and 233 mg PF_6^- per kg. The remaining PF_6^- was not expected after the extraction and drying for three days at 105 °C. The extraction of dissolved $LiPF_6$ was highly sucessful, while 7 % of the conducting salt remained as $LiPF_6$ or in decomposed form in the solid material. A further reduction of fluoride loading in solid was required and therefore the experiment in section 3.3 was performed.

Table 1 Mass fractions of anions in extract, cumulated extracted mass $LiPF_6$ and extraction efficiencies for four stages at 20 °C.

Extraction stage	Fluoride mass fraction in extract (g/kg)	PF_6^- mass fraction in extract (g/kg)	$LiPF_6$ mass extracted per stage (g)	$LiPF_6$ mass extracted cumulated (g)	Accumulated extraction efficiency based on $LiPF_6$ in solution $Y_{extr,\, LiPF6\, in\, solution}$	Accumulated extraction efficiency based on $LiPF_6$ in extract and solid including degradation $Y_{extr,\, LiPF6\, from\, extract\, +\, solid}$
1	0.047	3.106	1.154	1.154	0.8717	0.8111
2	0.000	0.415	0.138	1.293	0.9762	0.9083
3	0.000	0.078	0.024	1.317	0.9944	0.9253
4	0.000	0.021	0.007	1.323	0.9993	0.9299

3.3 Combination of multi-stage extractions using DMC and water

For the further reduction of fluoride loading in solid material after extraction with DMC and drying a second set of multi-stage cross-flow extractions using water as extractant were performed. The solubility for LiF is higher in water than in DMC [22]. The results for the extraction of LiF with DMC are shown in Table 2 and show similarities to data in Table 1. Fluoride is only detectable in extract from the first stage. The mass fraction of PF_6^- and mass of extracted $LiPF_6$ decrease with rising number of extraction stages. The loading of fluoride was 1093 mg fluoride per kg and 218 mg PF_6^- per kg solid phase after extraction with DMC.

Table 2 Mass fractions of anions in extract, cumulated extracted mass $LiPF_6$ and extraction efficiencies for five stages at 20 °C.

Extraction stage	Fluoride mass fraction in extract (g/kg)	PF_6^- mass fraction in extract (g/kg)	$LiPF_6$ mass extracted per stage (g)	$LiPF_6$ mass extracted cumulated (g)	Accumulated extraction efficiency based on $LiPF_6$ in solution $Y_{extr,\ LiPF6\ in\ solution}$	Accumulated extraction efficiency based on $LiPF_6$ in extract and solid including degradation $Y_{extr,\ LiPF6\ from\ extract\ +\ solid}$
1	0.019	6.646	2.460	2.460	0.8295	0.8125
2	0.000	0.899	0.391	2.852	0.9615	0.9418
3	0.000	0.179	0.075	2.926	0.9867	0.9665
4	0.000	0.058	0.023	2.950	0.9945	0.9741
5	0.000	0.033	0.013	2.963	0.9991	0.9786

The extraction with water was performed with a higher solvent to solid ratio than the extractions with DMC in this section. Table 3 shows the a decrease of fluoride mass in extract with rising number of stages and while after the first stage the mass fraction of hexafluorophosphate decreases the value stays constant for second and third stage. The extraction efficiency for fluoride $Y_{extr,\ F^-}$ was calculated as the mass of fluoride in extract in relation to extracted mass of fluoride and fluoride mass in fine fraction as shown in equation 5. The fluoride mass in solid was also determined by the extraction in ultrapure water and in reference to fine fraction of solid.

$$Y_{extr,F^-} = \frac{\sum m_{F^-\ in\ extract}}{\sum m_{F^-\ in\ extract} + m_{F^-\ in\ fine\ fraction\ of\ solid}} \qquad (5)$$

The analysis of the solid material after drying and sieving showed no loading with hexafluorophosphate and 166 mg fluoride per kg solid material. Therefore, the reduction of fluoride and PF_6^- was successfully performed. $LiPF_6$ was degraded completely after drying. The extraction efficiency for fluoride shows the possibility of further reduction.

Table 3 Mass fractions of anions in extract for three stages of extraction with water at 80 °C.

Extraction stage	Fluoride mass fraction in extract (g/kg)	PF_6^- mass fraction in extract (g/kg)	Accumulated extraction efficiency for F^- based on fluoride in extract and in solid
1	0.194	0.018	0.8017
2	0.026	0.005	0.9379
3	0.003	0.005	0.9575

4. Conclusions

The extraction of the conducting salt lithium hexafluorophosphate from lithium ion batteries using the organic extractant dimethyl carbonate is accompanied by degradation at elevated temperatures. The optimum temperature for extraction is 20 °C. The reduction of conducting salt by multi-stage cross-flow extractions with dimethyl carbonate was demonstrated successfully, but traces were still present in raffinate and furthermore higher loadings with fluoride. Therefore, a combination of a set of extractions with dimethyl carbonate, drying and a second set of extractions with water was tested. As a result the conducting salt was completely removed below detection limit. The loading of fluoride was reduced to 166 mg fluoride per kg fine fraction of solid raffinate.

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