

## Development of a Sub- and Supercritical Carbon Dioxide Extraction Process for the Selective Recovery of the Electrolyte from spent Li-Ion Batteries

**N. Zachmann<sup>\*</sup>, M. Petranikova, B. Ebin**

*Chalmers University of Technology, Department of Chemistry and Chemical Engineering, Industrial Material Recycling, S-412-96, Sweden*

*\*Corresponding author: zachmann@chalmers.se*

Research and industry focus on the electrolyte composition design to improve the performance, safety, lifetime and cost of the LiB cell. The electrolyte, however, receives little attention in the LiB end-of-life stage. In the lab-scale and industrialized recycling strategies, the recycling of the electrolyte is seldomly considered as they focus mainly on the recycling of the valuable cathode active material transition metals (Li, Co, Mn, Ni) and the current collector materials (Al, Cu). Thereby, the electrolyte either decomposes and/or evaporates (uncontrollably) causing a risk of immeasurable toxic and environmental emissions (HF, etc.) [1]. In the produced black mass during the common recycling steps, the remaining electrolyte is problematic due to the presence of the organic electrolyte solvents. Secondary streams coming from the recycling plants are then considered to be hazardous and represent a technical and financial burden for the recycling companies.

It is evident that an alternative technique must be implemented to fully recover the electrolyte from the spent LiBs, as traditional methods. In this study, an innovative sub- and supercritical carbon dioxide (sc-CO<sub>2</sub>) extraction process to recover the electrolyte from spent LiBs was developed to fill the gap in the battery recycling process. The nonaqueous electrolyte is a multicomponent system consisting of a conductive salt, mainly LiPF<sub>6</sub>, organic carbonate solvents and additives. Mainly, a combination of both non-polar and polar organic solvents is used for a high dissociation of the conductive salt while achieving low viscosity [2]. The excellent mass-transfer characteristics of sub- and sc-CO<sub>2</sub> and its easily adjustable solvent properties under the variation of pressure and temperature can be potentially used to selectively recover the non-polar electrolyte components with high efficiency and purity [3].

We determined the effects of the critical process parameters, pressure, temperature, and static and dynamic extraction times on the selective extraction of the non-polar components of the electrolyte i.e., dimethyl carbonate (DMC), ethyl methyl carbonate (EMC), from spent LiBs. The composition of the extracted product was analyzed qualitatively and quantitatively by attenuated total reflection- Fourier-transform infrared spectroscopy (ATR-FTIR), Gas Chromatography-Mass Spectrometry (GC-MS) and Inductively Coupled Plasma - Optical Emission Spectrometry (ICP-OES). The process exhaust stream was continuously analyzed by FTIR and the impact of the process on the active cathode material for subsequent recycling steps for the recovery of the valuable transition metals was studied by X-Ray diffraction analysis (XRD).

The results showed that the CO<sub>2</sub> density, determined by the process pressure and temperature, is the significant factor for a selective separation of the non-polar electrolyte solvents DMC and EMC, in high purity. Analysis of the process exhaust gas indicated that the innovative selective sub- and sc-CO<sub>2</sub> extraction process eliminates the formation of hydrogen fluoride (HF) and phosphoryl fluoride (POF<sub>3</sub>) which originate from the LiPF<sub>6</sub> decomposition during the battery recycling process. Finally, analysis of the active cathode material indicated that the process conditions had no impact on the active material structure and hence the proposed toxic-emission-free process has no limiting effect on subsequent recycling strategies of the valuable metals.

### References

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