Selective Electrolyte Recovery from spent Li-Ion Batteries using Sub – and Supercritical Carbon Dioxide Technology

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The electrolyte is a crucial component for the cell performance of a Li-Ion battery (LiB) during its life-time. The nonaqueous electrolyte is a multicomponent system consisting of a conductive salt, mainly $LiPF_6$, organic carbonate solvents and additives. A combination of both non-polar and polar organic solvents is generally used for a high dissociation of the conductive salt while achieving low viscosity [1]. 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 environmental and toxic emissions (HF, etc.) [2]. The residual electrolyte in the black mass is problematic due to the presence of the organic electrolyte solvents. Secondary streams coming from the recycling plants are then considered to be hazardous. This represents a technical and financial burden for the recycling companies.

To fill the gap in the battery recycling process, we developed a sub- and supercritical carbon dioxide (sc-CO_2) extraction process to selectively recover the electrolyte from spent LiBs. Sc-CO_2 extraction technologies are already heavily employed in the food, beverage, pharmaceutical, and cosmetic industry. Sc-CO_2 is formed once the pressure and temperature of CO_2 exceed its critical point of 31°C and 73.8 bar. In the so-called supercritical state, CO_2 exhibits excellent mass-transfer characteristics, and its solvent properties can be fine-tuned to adjust its physicochemical characteristics by varying pressure and/or temperature. However, CO_2 is an ineffective solvent for high molecular weight polymers and ionic compounds of high polarity under readily achievable pressure and temperature conditions. By adding a co-solvent or a modifier, however, the solubility properties of sc-CO_2 can be significantly improved [3]. Therefore, sc-CO_2 in addition to a suitable co-solvent can be used to selectively recover the polar electrolyte components, i.e., lithium hexafluorophosphate ($LiPF_6$) and ethylene carbonate (EC).

Critical process parameters, like pressure and temperature, and extraction times were investigated to understand their relation on the extraction efficiency of the polar electrolyte components i.e., $LiPF_6$ and EC by supercritical CO_2 and cosolvent system. The composition and purity of the extracts were analyzed qualitatively and quantitatively. The process exhaust stream was continuously analyzed to track the potential formation of the $LiPF_6$ decomposition products.

The results showed that sc-CO_2 in combination with an aprotic co-solvent is a suitable approach to extract the polar electrolyte components in high purities. Furthermore, the decomposition of the conductive salt, $LiPF_6$, was minimized with the selective sub- and sc-CO_2 extraction process during the battery recycling.

References

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