Recycling of Lithium-Ion Battery Cells – Modelling the Crushing and Mixing Process

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Abstract. A variety of different process routes have been established for the recycling of lithium-ion batteries. To compare and optimize these routes effectively, a high process understanding is important. To take a closer look at the mechanical processes used for the recycling, models for the various sub-processes will be developed. This work focus on the modelling of the crushing of lithium-ion batteries in a cutting mill and the subsequent drying of the material in a mixing device. These models must consider the complex material behaviour of the crushed battery materials as well as the initial conditions of the materials within the battery cell. For example, the primary particle size distribution of the individual materials in the battery prior to the first comminution in the cutting mill is unknown. Based on these conditions, the first process step was described as a black-box model. Using this initial model, the input conditions for the subsequent process steps can be determined, enabling the development of physical models such as population balances for the subsequent processes.

1. Introduction

The recycling of Li-ion batteries is becoming increasingly important due to the rising demand of electric cars and the request for more independence from global raw materials markets. Therefore, a range of recycling processes have been implemented in industry. Especially in the context of the recycling of end-of-life batteries, there are several ways to recover the valuable materials via mechanical, hydrometallurgical or pyro-metallurgical process routes. The processing via a mechanical process chain, which this work focuses on, contains several comminution and separation steps. For these comminution and separation operations, various processes can be used as well as different process sequences, which can both affect the recovery rates. One way of recycling Li-ion batteries is based on the LithoRec process [1] shown in Fig. 1. First, the cells or modules are crushed in a shredder. The shredded battery fragments are than dried and stressed in a mixing and drying unit bevor the heavy parts of the cells such as the casing are removed using a zig-zag-sifter. After the electrolyte evaporation and separation of the heavy components, the remaining fragments consist mostly coated and uncoated electrode foils as well as separator foils and the detached black mass. These fragments can be stressed a second time to increase the yield of black mass in the subsequent screening step. A cutting mill or an impact mill can be used for this second comminution. At the end of the process chain the separator foils are removed from the copper and aluminum foils using a second air classification.

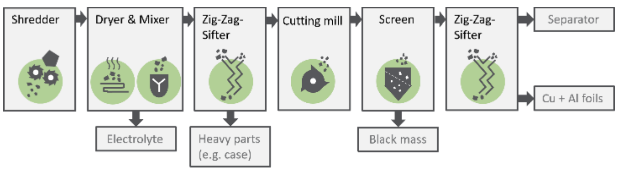

Figure 1. Mechanical process chain based on LithoRec [1]

A high process understanding and a large database are important to optimize a process chain and compare it with other recycling routes. To get this large database, the dynamic flowsheet simulation is beneficial. With this simulation it is possible to investigate the influence of several operating parameters of the single processes as well as the influence of these parameter changes on the subsequent processes and finally on the mass recovery of the different battery materials, whereby the so-called black mass (anode and cathode coating) represents the most valuable fraction. For the simulation, it is essential to develop process models that can be used in corresponding simulation software like Dyssol. In this work the focus is on the modelling of the first two process steps (crushing the cells and mixing/drying the fragments) and the required series of experimental studies.

2. Experimental

To develop the process models, a large database is required in advance. Accordingly, parameter studies are conducted for each individual process step. A key challenge here is the complex mixture of materials used in the battery cells. For this reason, the same type of

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cylindrical battery cells, whose cell composition is known from cell analysis [2], was consistently used for experimental data (exp. data) collection. To minimize the impact of fluctuating process conditions on data collection, the experiments were initially conducted on a laboratory scale. To do this, the battery cells were first crushed in a cutting mill. After comminution, the fragmented material was analyzed using analytical sieving. The material with a particle size of less than 500 µm was defined as black mass. The parameter study, which compared different bottom screen sizes of the cutting mill and different rotational speeds, showed an increase in black mass recovery at higher rotational speeds and with smaller screen sizes. Since small amounts of other materials can also end up in the <500 µm mesh fraction, the black mass was also analyzed using X-ray fluorescence (XRF) to determine the levels of impurities from Cu, Fe, and Al components. This shows a corresponding increase in impurities in the BM as the screen size decreases (Fig. 2), though there is only a slight change at varying speeds.

To investigate the subsequent mixing and drying step, a standard setting was selected in the cutting mill for cell crushing (700 rpm, 10 mm bottom mesh size). The crushed material was further processed in the mixing and drying unit at different circumferential speeds and at different drying temperatures. To ensure a sufficient data set for subsequent modeling, different processing times were also examined in this step in order to characterize the change in the particle size distribution (PSD) of the individual materials over time. While the change in drying temperature had no significant effect on black mass recovery, increasing the mixer's circumferential speed resulted in a higher black mass yield. However, the proportion of impurities in the black mass is also increasing. The mixing process has a significantly greater impact on the impurity content in the black mass than the cutting mill process, even at lower circumferential speeds (Fig. 2). However, after subtracting the proportion of impurities from the total mass of the black mass fraction, there is still a net recovery of about 90% of the black mass present in the cell.

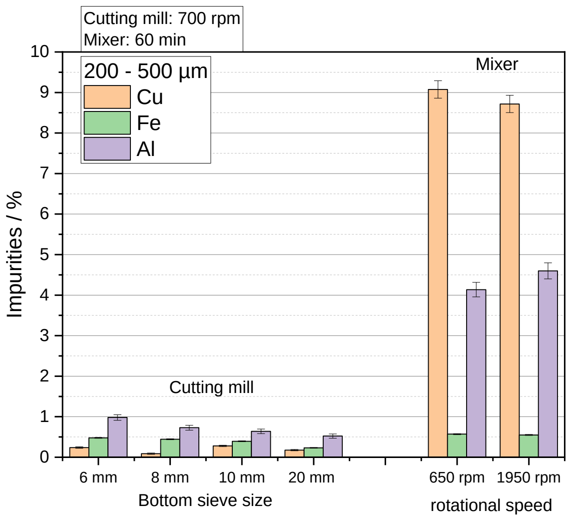

Figure 2. XRF Analysis of impurities in the black mass

3. Modelling

Models for the individual process steps will be developed based on the experimentally determined data. These models will be used to calculate the incoming and outgoing material flows. This primarily requires data on the size distributions of the individual materials. On this basis, the mass flows of the individual materials and, consequently, the recovery rates can be determined during subsequent separation processes. In addition to the particle size distribution, the proportion of black mass detached from the electrode foils is another important factor. Only the black mass detached from the foils can be separated later; furthermore, residual coating on the foils influences the material behaviour during separation processes such as sifting processes.

3.1. Crushing of battery cells

In the cutting mill, the first crushing of the whole cells into individual fragments is carried out. Since the process starts with crushing entire battery cells, the primary particle size distribution of the battery materials inside is not known. For this reason, a black-box model is used for the first process step. In the chosen modelling approach, the resulting particle size distributions following the comminution process are described using Weibull distributions (Eq. (1)).

$$Q_3\left(\frac{x}{d_s}\right) = 1 - e^{-\left(\lambda * \left(\frac{x}{d_s}\right)\right)^k} \quad (1)$$

These Weibull-Distributions have two material specific parameters λ and k. Furthermore, it includes the bottom screen mesh size of the mill d_s. This allows calculating the resulting particle size distribution for each material component depending on the used bottom screen size [3]. In Fig. 3 these results for different screen sizes are shown for Cu foil compared to the experimental data.

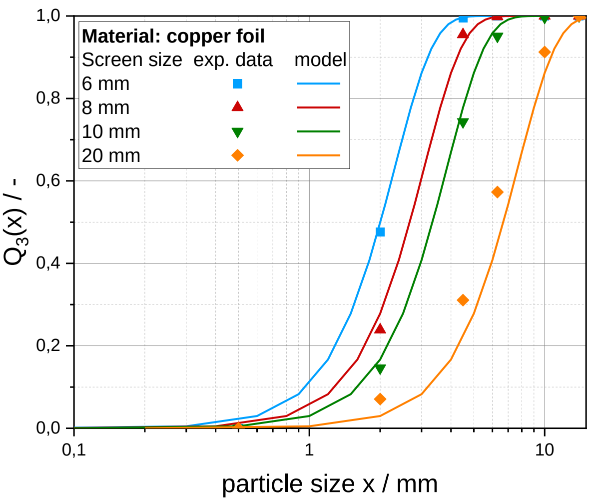

Figure 3. PSDs for Cu foil, exp. data and Weibull-model

3.2. Mixing and drying process

Contrary to the first cell crushing step, for the mixing and drying process, the initial particle size distribution of the individual materials is known. As a result, working with a black-box model is no longer necessary. Changes in the particle size distributions can be modelled here using a population balance model (Eq. (2)).

$$\frac{dm_i}{d_t} = \sum_{j=i}^{i_{max}} S_j b_{ij} m_j - S_i m_i \qquad (2)$$

The corresponding breakage functions S and distribution functions b for this balance equation must be determined individually for each material. This requires data on the temporal changes in particle size distributions during the mixing process. A challenge in this determination is the mutual influence of the materials on one another. The larger, heavy housing components have an abrasive effect on, for example, the coated foils and can cause additional stress here, meaning that the fracture functions cannot be determined from individual material tests.

Using the population balance equations, it is possible to display the particle size distributions over time (Fig. 4). Calculating the particle size distributions is one of the most important steps in modelling, as these provide the basis for the subsequent separation processes and thus, for example, allow us to estimate the expected yield of black mass after the sieving process. In addition, by analysing changes in the particle size distribution of other materials, such as copper and aluminium foils, the proportion of these materials in the <500 µm fraction can be determined, thereby also providing information about the purity of the black mass fraction.

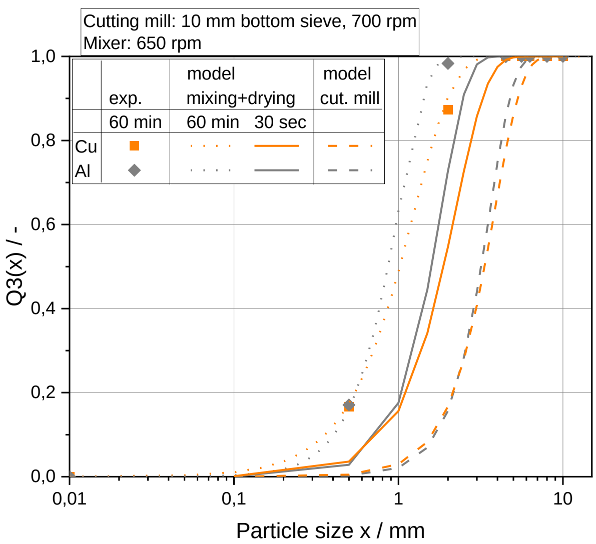

Figure 4. Modelled PSDs for Cu/Al foil after crushing and different mixing times compared to experimental data

4. Summary

The mechanical recycling of Li-Ion batteries consists of several comminution and separation steps. Due to the complicated material behaviour, it is often not possible to use literature models for most process steps. Thus, models must be developed or existing models must be adapted to the present material system consisting of foil materials, powders, and solid metal components.

While the cells are initially crushed in the first process step with partial detachment of the black mass from the foils, the second process step significantly increases the delamination of the black mass due to the additional stress applied by the mixer during material drying.

For modelling purposes, the various battery components must be considered separately. For each material, separate models or functions are created to calculate the resulting particle size distribution. By analysing the changing size distributions, it is possible to calculate the expected material recovery rates in the separation processes, such as the recovery rate of the valuable black mass and the proportion of impurities from other battery components in this size range.

By combining these models with other process models, an entire process chain can be represented through simulations, thereby reducing the need for time-consuming experimental studies and thus provides an efficient way to compare and optimize processes and process chains.

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