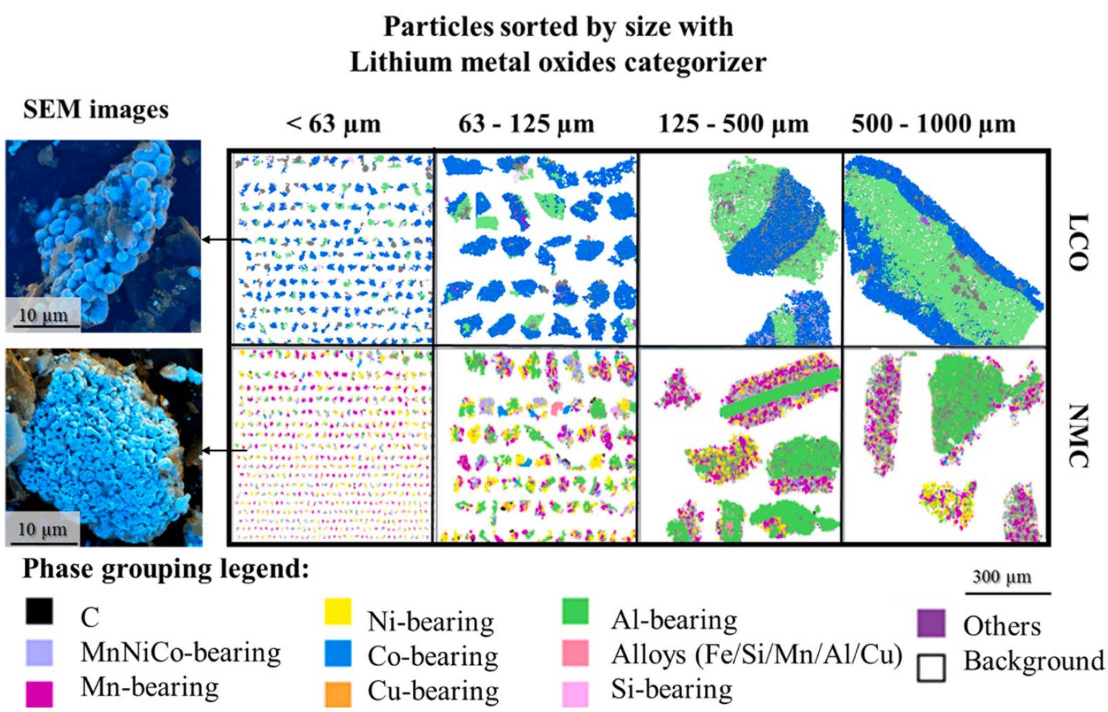
Automated mineralogy as a novel method for black mass characterization

This application note is focused on the black mass characterization methods that are the subject of the article *Automated mineralogy as a novel approach for the compositional and textural characterization of spent lithium-ion batteries* authored by Dr. Anna Vanderbruggen et al. (2021). The full article can be found here.

Introduction

Lithium-ion batteries (LIBs) have become indispensable energy storage solutions, powering a wide range of products from portable electronics to electric vehicles. However, this increasing consumption of LIBs also leads to a surge in spent battery waste, raising environmental concerns and accelerating the need for effective recycling processes. One such secondary material generated during LIB recycling is black mass, which is obtained through pyrolysis, crushing, and sieving of spent LIBs. Effective extraction of valuable materials from the black mass requires thorough understanding of its textural and compositional features. The black mass is heterogeneous in terms of shape and density, making its comprehensive characterization a challenging task.

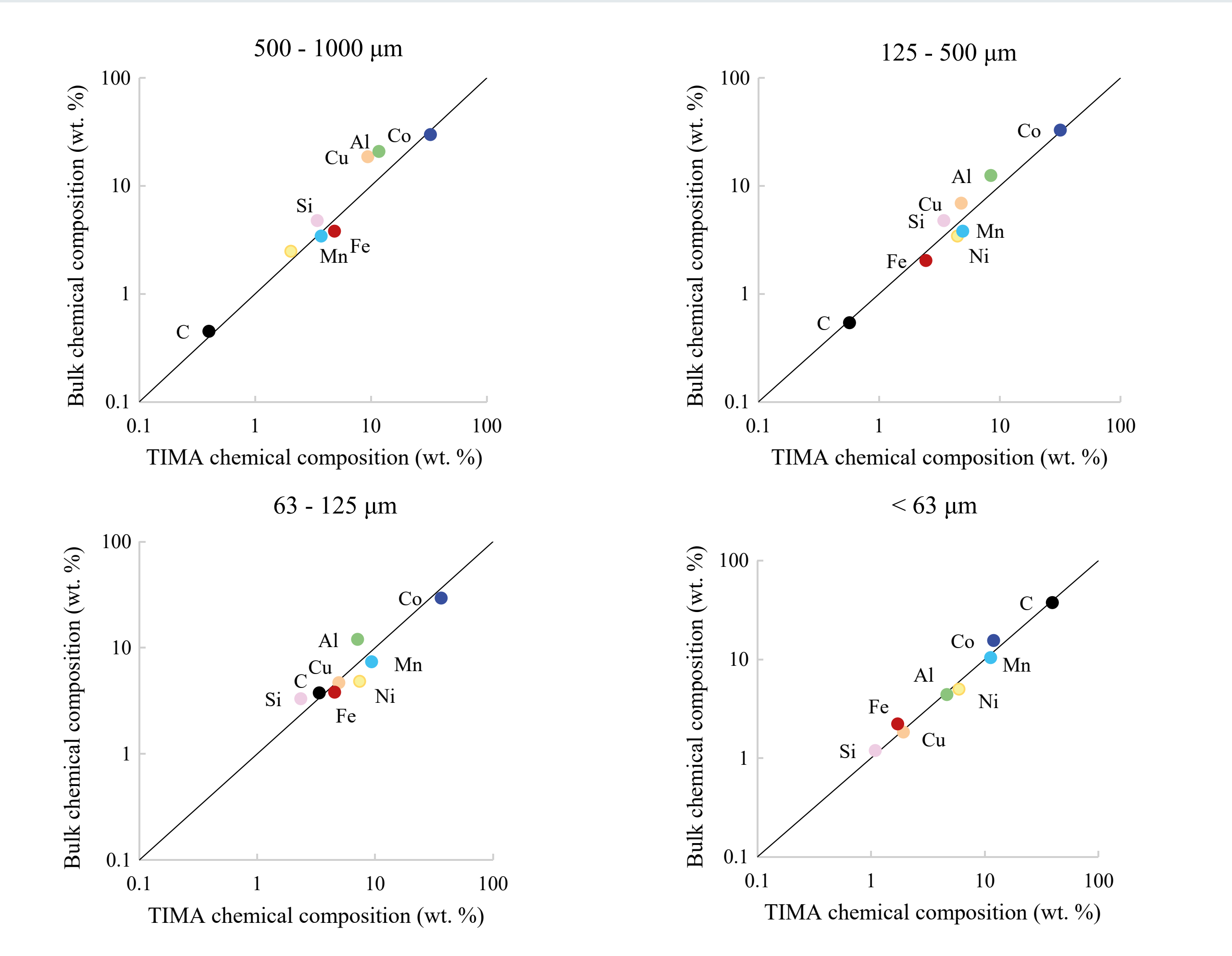


▲ **Fig. 1:** Catagorizer scripts developed and executed in TESCAN TIMA offline software are used for particle sorting and phase grouping (Vanderbruggen et al. 2021).

Automated mineralogy is a powerful tool for analyzing the black mass at the particle level and provides valuable insights into its composition and properties. Automated mineralogy identifies each individual particle type in the sample, which is the first step to quantifying recovery efficiency and improving recycling processes.

Materials and Methods

In the study of Vanderbruggen et al. (2021), a black mass sample from Accurec Recycling GmbH was characterized specifically to validate the homogeneity and representativeness of the sample. Homogenization and splitting into size fractions (< 63, 63–125, 125–500 and 500–1000 µm) were conducted to facilitate accurate analysis. Individual fractions were further split into replicates for automated mineralogy, X-ray fluorescence (XRF), and elemental assays. The replicates for automated mineralogy analysis were mounted into iodine-doped epoxy to allow quantification of the carbon-based materials. To differentiate among the various LIB components in the black mass, categorizer scripts were developed in the TIMA offline software. These scripts distinguish the Al foils, Cu foils, graphite, lithium metal oxides, and other metal alloy particles present in the sample. The different categories were defined by the quantity of the phases present, allowing lithium metal oxides to be further subdivided (see Figure 1). Additionally, the degree of liberation of components during the recycling process was calculated.



▲ **Fig. 2:** Composition obtained by bulk chemical assays (XRF) plotted against chemical composition data calculated by TIMA for each analyzed fraction (Vanderbruggen et al. 2021).

Results and Discussion

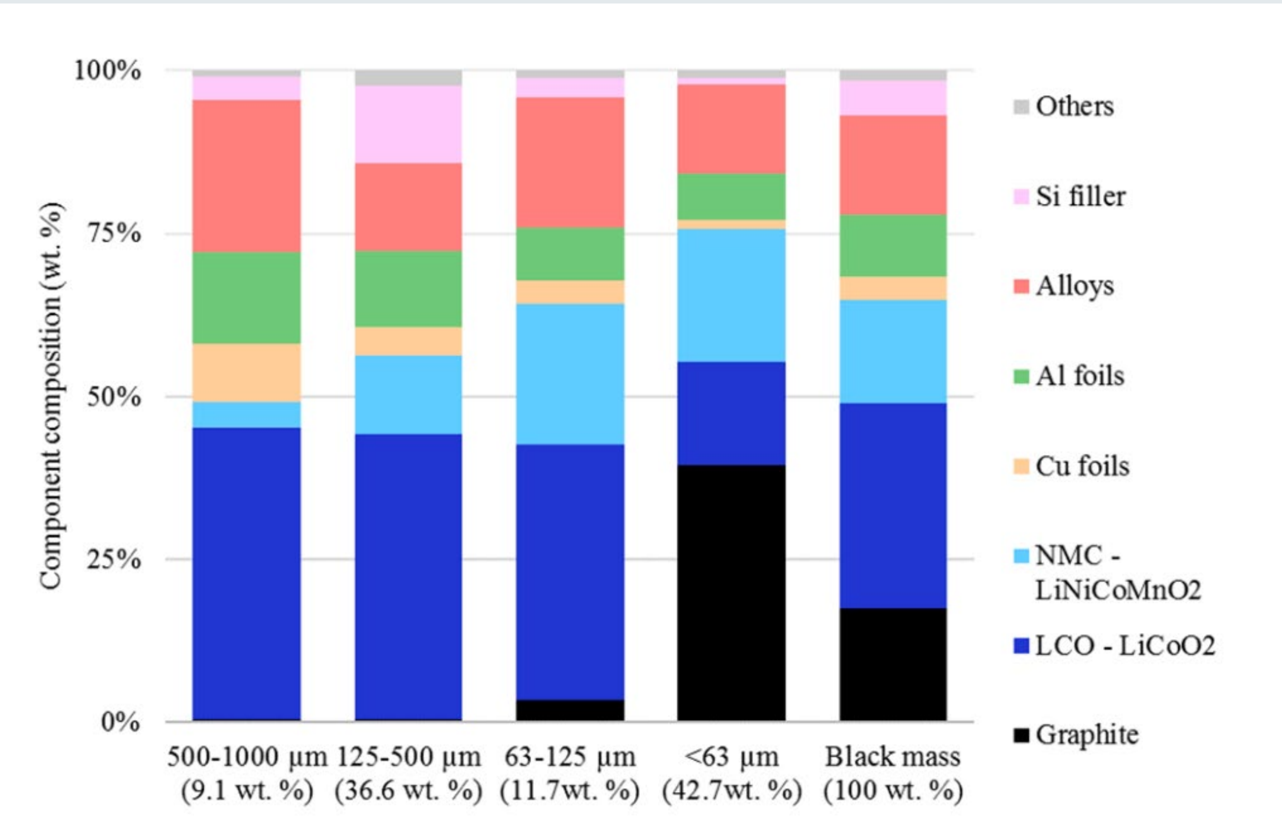
Automated Mineralogy data were validated against compositional data obtained by the XRF method. Composition calculated by TIMA correlated well with the assay data for fine fractions, with accuracy decline for only the coarse fraction (see figure 2). To improve the correlation for the coarse fractions, analysis of additional replicate would be necessary.

Analysis of the black mass revealed the presence of multiple LIB components, such as lithium metal oxides, graphite, Al/Cu currrent collector foils with different levels of oxidation, fragments of battery casing containing quartz filler (reported as Si filler), and other alloys (see Figure 3).

Typically, aluminum current collector foils are partially oxidized. This may be the result of the pyrolysis process, but electrochemical processes during the battery operation may also contribute. The degree of the oxidation is therefore dependent on the selected recycling process as well as on the operational history of individual batteries. Aluminum current collector foils are concentrated in the fine fraction since they become more brittle during the thermomechanical processing. Copper current collectors, which are more stable both mechanically and thermally, are concentrated in the coarse fraction.

Automated Mineralogy was able to identify the weight ratio at 2:1 for the cathode particles of two different chemistries, namely the lithium cobalt oxide (LCO) and nickel manganese oxides (MNC). Other chemistries such as nickel cobalt aluminum oxides (NCA), or lithium iron phosphates (LFP), also could be identified by this technique. For the purposes of this study, all carbon particles were treated as graphite.

Combining thermomechanical treatment with sieving concentrates the copper in the coarse fraction. The graphite, on the other hand, tends to concentrate in the fine fraction below 63 µm. Other components such as lithium metal oxides and aluminum foils were distributed more evenly.



▲ **Fig. 3:** Content of the lithium battery components fraction by fraction (Vanderbruggen et al. 2021).

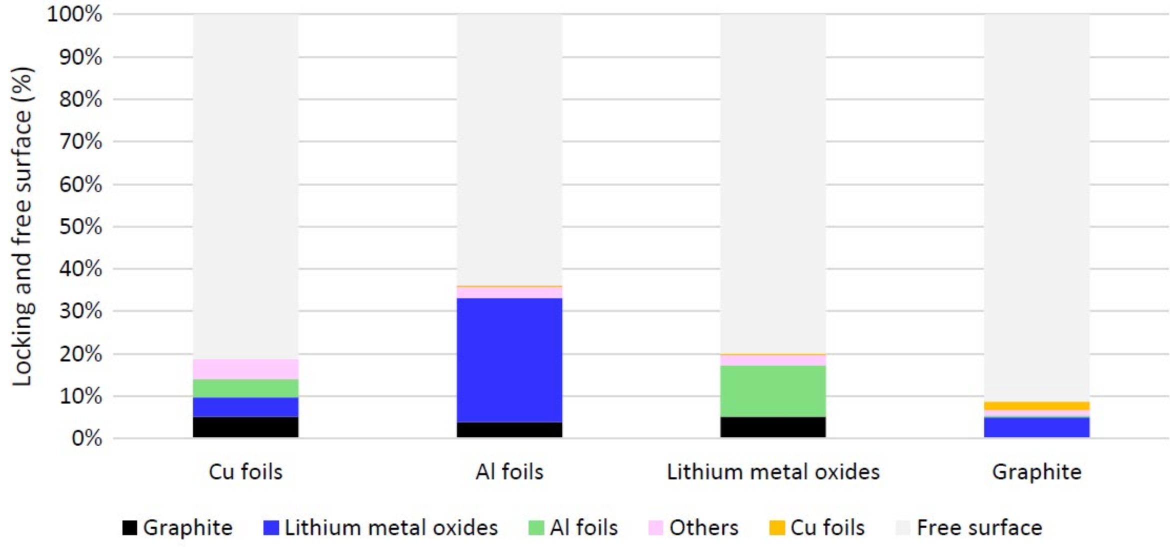


Fig. 4: Locking and free surface of LIB components (Vanderbruggen et al. 2021).

Copper current collector foils are liberated more efficiently from the graphite compared to the aluminum foils from the lithium metal oxides (see Figure 4). This is probably because the binder adheres preferentially to the oxide cathode components rather than to the graphite, as reported by Widijatmoko et al. (2020).

Copper foils are a soft and pliable material that often entrap fragments of other unrelated components such as lithium metal oxides or even the aluminum foils. This secondary type of association forms during the shredding process. Graphite particles were well liberated and fit within the 20–30 µm size range of individual spheroidized graphite particles.

Conclusion and Outlook

Automated Mineralogy demonstrated its efficiency for characterizing the black mass obtained from spent LIBs. The detailed information on individual particle composition and properties enhances our understanding of the factors associated with the behavior of black mass particles throughout the recycling process. The categorizer scripts developed for this study can be applied to other black mass samples, thereby facilitating the optimization of recycling processes. Texture-based particle characterization proves to be more efficient when compared to approaches that are based solely on bulk chemistry, because many elements may be present in more than one component.

Automated Mineralogy allowed us to identify the effects of the thermomechanical black mass treatment, such as selective liberation of copper foils in contrast to aluminum foils, susceptibility of aluminum foils to oxidation resulting in greater brittleness and breakdown, efficient graphite liberation, and identification of unexpected metallic alloys. A deeper comprehension of the different components' behaviors during recycling processes will be instrumental in designing more efficient and sustainable recycling strategies for LIBs. Industrially-produced black mass is expected to contain compounds from multiple battery technologies, making particle by particle characterization by means of automated mineralogy even more important.

As the demand for LIBs continues to grow, recycling and resource recovery will be increasingly critical for the circular economy. By improving recycling techniques, we can reduce the environmental impact and unlock the full potential of the valuable resources that can be recovered from within spent LIBs.

Acknowledgment:

We would like to thank Dr. Anna Vanderbruggen from Helmholtz Institute Freiberg for providing permission to use her study to create this application note.

Literature:

Vanderbruggen, A., Gugala, L., Blanin, R., Bachman, K., Serna-Guerrero, R., Rudolph, M. (2021): Automated mineralogy as a novel approach for the compositional and textural characterization of spent lithium-ion batteries. Minerals Engineering 169, 106924.

Widijatmoko, S.D., Gu, F., Wang, Z., Hall, P., 2020. Selective liberation in dry milled spent lithium-ion batteries. Sustain. Mater. Technol. 23.

TESCAN GROUP, a.s.
Libušina tř. 21, 623 00 Brno - Kohoutovice / Czech Republic
(phone) +420 530 353 411 / (email) sales@tescan.com / marketing@tescan.com