

The sampling and phase characterisation of black mass

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'Black mass' is the industry term used to describe a type of e-waste comprising crushed and shredded battery cells. It is an intermediate product in the recycling of spent, end-of-life, batteries. It comprises a mixture of metals including; lithium, manganese, cobalt and nickel, which are valuable recycling commodities, of increasing strategic and economic importance to meet future global demands in the 'battery revolution'. The objective of this 'phase characterisation' investigation was to provide an indicative profile of the morphological characteristics, grain size, composition and textural variability for a natural state (unprepared) and prepared (powdered) sample of black mass from Europe. It is envisaged that this is relevant to: (a) develop a pragmatic sampling strategy to ensure a non-biased, representative sample is provided for assaying; (b) determine the optimal processing route (e.g., hydrometallurgical, pyrometallurgical); (c) identify the presence of payable phases; (d) identify phases that may hinder metal recovery or penalty components; (e) develop assay procedures; and (f) assist in the identification of hazards and the mitigation of risks. The techniques used were: (1) visual examination and binocular microscopy; (2) manual scanning electron microscopy (SEM); (3) automated scanning electron microscopy with linked energy dispersive spectrometers (SEM-EDS), to characterise the phases present and particle types (using AMICS); (4) X-ray computed tomography (X-CT) to provide the 3D morphology of the particles; and (5) laser ablation inductively-coupled plasma mass spectrometry (LA-ICP-MS) to detect and quantify the phases that cannot be detected using automated SEM-EDS and X-CT. The results demonstrated that automated SEM-EDS can be used to characterise and quantify the phases present, and the phase chemistry allows the particle types to be assigned back to the primary battery components. Some phases identified are at present not linked back to the original components and further work is needed to refine the compositional groups, with the analysis of additional samples from different feeds/streams in Europe, China and USA. Interactive SEM-EDS analysis also demonstrated that there is a high-resolution chemical variability within the individual particle categories. X-CT imaging demonstrated the complex 3D textures and morphology of the particles, which is potentially significant during sample preparation and chemical analysis. Neither automated nor manual interactive analysis can determine the presence / abundance of the light elements, such as lithium. However, LA-ICP-MS was successful in detecting and quantifying lithium. Furthermore, LA-ICP-MS was able to determine contents of 67 other non-metals and metals at a 20-micron scale with ppm to ppb level detection limits.

Introduction

With the increased global demand for personal electronic devices (e.g., smart phones, computers and flat screen televisions), along with the energy transition away from conventional fossil fuels (e.g., oil, gas, coal) to electric vehicles (EV) it is predicted that there will be an enormous growth in demand for lithium-ion batteries (LIBs) (known as the 'battery revolution'), with the market value of LIBs being \$29.86 billion in 2017, but projected to increase to \$139.36 billion by 2026 (¹Chen et al., 2019). Given both; (a) the geological scarcity of battery raw materials and (b) increased requirements for sustainability and waste recycling, there is a huge potential in the recycling of LIBs (²Harper et al., 2019) with a projection that 4 million metric tons of LIB waste from EV batteries could be generated from 2015 to 2040 (³Or et al., 2019).

Existing recycling plants typically have a capacity of a few thousand tonnes, but this is expected to increase hugely (⁴Bruckner et al., 2020). During the recycling of LIBs and other e-waste such as printed circuit boards, the materials are sorted, dismantled and then processed. Following physical and thermo-mechanical processing a fine-grained powder, referred to as 'black mass' is generated (⁵Vanderbruggen et al., 2021). This black mass is the feed for subsequent hydrometallurgical or pyrometallurgical processing (e.g., ¹Chen et al., 2019; ⁴Bruckner et al., 2020; ⁶Werner et al., 2020) to recover the elements of value. Given the variable nature of the recycling feed the materials produced for processing are complex and highly variable. Significant variation in bulk chemistry, particle types and potential penalty elements may be expected.

Limited research has to date been published on the detailed characterisation of black mass (⁵Vanderbruggen et al., 2021), although there is very active research into the processing options for LIB materials (e.g., ⁷Barik et al., 2017; ⁴Bruckner et al.,

2020; ¹Chen et al., 2019; ⁸Diekmann et al., 2017; ⁹Friedrich and Schwich, 2020; ¹⁰Liu et al., 2020; ¹¹Lu et al., 2017; ¹²Pinegar and Smith, 2019; ¹³Ruismaki et al., 2020; ¹⁴Schwick et al., 2020; ¹⁵Widijatmoko et al., 2020). It is widely recognised that the variability in the composition of the black mass feed, can significantly affect the efficiency of the processing and recovery (e.g., ⁴Bruckner et al., 2020; ⁸Diekmann et al., 2017).

Objectives

The objectives of the analysis and phase characterisation of samples of black mass are to provide an initial and indicative profile of the morphology, grain size, composition and morphological characteristics of the black mass particles. This characterisation may aid in the determination of appropriate future sampling, sample preparation, assay and analysis routes.

What is Black Mass?

Black mass is the term given to processed material, such as battery cells or from the crushing and preparation of electronic scrap (e-scrap). The black mass is thought to typically consist of different ratios of mixtures of metals, including lithium, manganese, cobalt and nickel and other phases in different ratios. In general, lithium-ion batteries comprise cells with a cathode and an anode with a polymer separator (⁵Vanderbruggen et al., 2021). Black mass is the industry term for a type of electronic waste (e-waste), which essentially comprises shredded lithium-ion batteries (LIB) and is an intermediate product in the recycling of spent batteries. Black mass is used to recover metals including cobalt, lithium and nickel, to produce new LIBs. Black mass represents about 30% by weight of the original batteries and is a tradable feedstock for pyrometallurgical and hydrometallurgical processes. Relatively little is understood about the characterisation, properties, variability and behaviour of the different types of black mass. The electrodes consist of a conductive foil coated by active particles. Most commonly the anode comprises copper foils and spheroidized natural graphite, whilst the cathode is usually made up of lithium metal oxide particles on aluminium foil. These cell components are tightly packed together and adhered with an organic binder.

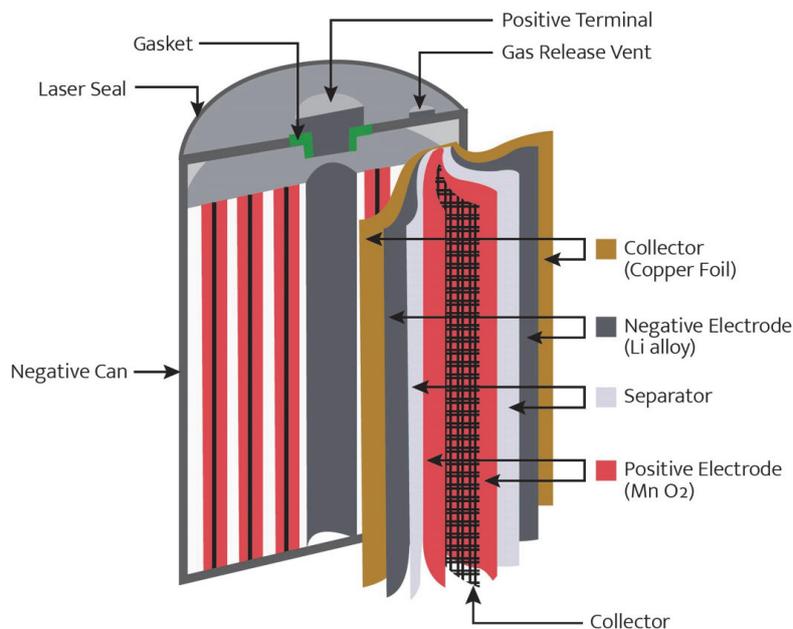


Figure 1. Typical internal structure showing the components of a lithium-ion battery (LIB).

Components of Black Mass

The typical components of a LIB are presented in Figure 1. As such, the LIB components, which may be present within a black mass powder, in terms of their functional form, comprise the following:

- The casing,
- Graphite,
- Aluminium foil,
- Copper foil,
- Lithium metal oxides.

In addition, the lithium metal oxides making up the cathodes are divided into five main cathode types, based on their chemistry as follows:

- NMC (LiNiMnCo oxides),
- LCO (LiCo oxides),
- LM(N)O (LiMn(Ni) oxides),
- LFP (LiFe phosphates),
- NCA (LiNiCoAl oxides).

Production of Black Mass

With the increased use of Li ion batteries, there is a significant body of research focussed on developing methodologies for the reprocessing and recovery of the different battery components (e.g., see the RWTH Aachen University research centre ‘Production Engineering of E-Mobility Components or PEM). At the start of the recycling process the batteries will be discharged and then after removing the housing cover, the battery will be disassembled (Figure 2).

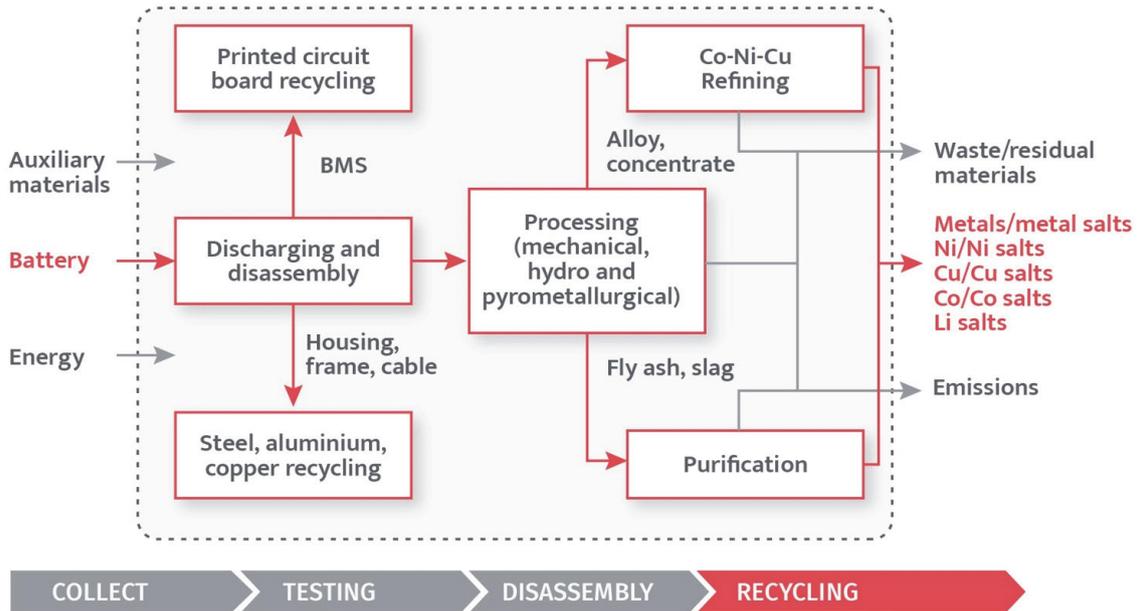


Figure 2. Initial stages in the recycling of LIBs. Note, BMS is a battery management system utilised for the safety operation of the battery pack. It basically monitors the battery to make sure it doesn’t operate outside the set safety limits.

Following disassembly, the materials go through a series of mechanical recovery stages including crushing and drying, sorting, sieving and repeated crushing. The shredded battery material is reduced in size with the formation of a mixed powder residue, known as ‘black mass’ (Figure 3). Prior to mechanical reprocessing, cell deactivation or treatment of the black mass can be carried out by pyrolysis. Black mass can be pyrolyzed at up to 700°C after separation from the shredded material to remove the electrolyte components. This stage removes the fluorine-containing components. The resultant black mass is then commonly treated in a way analogous to a mined ore concentrate, with the elements of interest recovered through either a pyrometallurgical or hydrometallurgical processing route.



Figure 3. Mechanical stages of LIBs recycling.

There is considerable current research examining different process routes for the black mass powders. For example, ⁷Barik et al. (2017) examined the leaching and separation of cobalt and manganese from shredded spent LIBs using HCl, with the step wise reprecipitation of the manganese and cobalt through the use of different reagents. ⁴Bruckner et al. (2020) reviewed the metallurgical processing routes available for industrial recycling of LIBs; they noted that one of the challenges to such operations is the inhomogeneous feed. ⁸Diekmann et al. (2017) also note that one of the challenges is the variable chemistry of the feed and noted that LFP cathodes cannot be reprocessed together with NCM cathodes. ¹⁰Liu et al. (2020) explored the recovery of LiCoO₂ and graphite through cryogenic grinding and the use of froth flotation; froth flotation was also discussed as a means to achieve cobalt recovery by ¹³Ruismaki et al. (2020). ¹²Pinegar and Smith (2019) examined the optimal shredding and milling of LIBs needed to achieve liberation of the different components.

As highlighted by several authors, the complexity and heterogeneity of the battery components and resultant black mass powders, is a significant challenge in terms of designing optimal sampling methods, sample preparation and processing routes. Consequently, previous studies (e.g., ¹⁶Zielinski et al., 2020; ¹¹Lu et al., 2017; ¹⁷Otsuki et al., 2019) have demonstrated that a multi-analytical methodology is required for the characterisation of e-waste. ¹⁶Zielinski et al. (2020) used quantitative electron microprobe elemental mapping to identify different compositional groups, whilst ⁵Vanderbruggen et al. (2021) utilised automated SEM-EDS using a Tescan TIMA system to determine the phase characteristics. A multi-analytical methodology for the characterisation of recycled batteries (e.g., ¹⁶Zielinski et al., 2020), batteries prior to recycling (¹¹Lu et al., 2017) and also printed circuit boards (¹⁷Otsuki et al., 2019) has previously been recommended. The phase characterisation of black mass and the results of preliminary research were provided by ^{18,19}Donnelly et al. (2021a, 2021b).

Potential Hazards Associated With Black Mass

The hazards associated with black mass and spent lithium-ion batteries (LIB) are relatively poorly understood. This is complex due to the variable characteristics and especially with mixed waste streams. However, anecdotal accounts supported by commissioned research conducted in Scandinavia (²⁰Nissi 2019) suggests LIB recycling and some types of black mass might be residually hazardous:

- **Toxicity and corrosive:** Fluorine-containing compounds occur in the electrolyte, separators, and electrode materials. Fluorophosphates found in electrolyte may thermally decompose if heated above 50°C and can result in the formation of hydrofluoric acid (HF), when in contact with water. Similarly, polyvinylidene fluoride (PVDF) coatings are used as both electrode binders of the active materials and as coatings on separators, and above approximately 400°C may decompose to hydrogen fluoride gas (and hydrofluoric acid if water is present). Hydrofluorine and HF have serious health risks and may be toxic and corrosive to living tissue and bone.
- **Fumes:** Over 5 ppm exposure of HF in the workspace air causes irritation of eyes, skin, mucous membranes and airways, although, the symptoms can be delayed. The associated fumes can cause respiratory corrosion, pulmonary edema and often cardiac arrhythmia. Short exposures for 50 to 250 ppm concentrations are potentially life threatening
- **Flammable and explosive:** LIB waste and black mass contains binders that may be flammable or explosive. Furthermore, there are anecdotal accounts of spontaneous combustion and ‘small’ explosions; however, this requires verification by reliable evidence. HF is not flammable itself, but when it reacts with metals and decomposes it forms flammable hydrogen gas.
- **Respiratory:** Since black mass contains fine powder, this may lead to respiratory problems.
- **Electrostatic:** The electrostatic behaviour of black mass has been observed and reported during handling and transportation.

Identification

HF is a weak acid in dilute solutions with initial signs of exposure being non-existent. As such, contact with HF can go unnoticed for long periods, enabling deeper penetration of fluorine and causing further damage to tissues and underlying bone. Exposure to concentrations of less than 20% can take up to 24 hours to generate visible symptoms. Initially, the skin swells, redness follows then white and yellow blisters are formed. HF is reactive with different materials, and its presence might be indicated by corroded glass bottles. HF can also be distinguished by its pungent smell when its concentration in air is greater than 0.04 – 0.13 ppm.

Treatment

The treatment for HF exposures is to remove contaminated clothing and rinse the contaminated area with plenty of water. Calcium gluconate gel could be used if available. If accidentally swallowed, milk, chewable calcium carbonate tablets or milk of magnesia can be given, if the patient is still conscious. In the case of inhalation, the person should be moved to an open area with plenty of fresh air. Where the patient is not breathing, artificial respiration is necessary. Oxygen can be given if it is available. Immediate medical attention is required.

Risk Mitigation, Handling, Storage and Transportation

Before the sampling, assaying or acceptance of black mass samples the corresponding material safety data sheet (MSDS) should be requested. Personal Protective Equipment (PPE) can protect from HF and associated fumes including; protective overalls, acid resistant boots, nitrile gloves, outer long sleeved gloves, gas masks or full face mask, working in a fume cupboard, with the correct rating and ventilated laboratory, if available. A personal HF detector alarm is recommended. Inspectors/chemists should be made aware of the potential for electrostatic behaviour and the level of risk hazards may be reduced by using non-electrostatic materials in the laboratory. The risk for fires and spontaneous combustion may be reduced by storing samples in isolation, in a fire proof container, regulating the atmosphere and implementing regular

inspection and thermal temperature monitoring. The development of storage, transportation and cleaning protocols are recommended including Standard Operating Procedures (SOP), Risk Assessments and Method Statements (RAMS) for each different type of black mass. Importantly, it should not be assumed that black mass from one location will behave identically to black mass samples from a different provenance or where there has been the 'blending' or mixing of different streams of LIB and black mass.

SAMPLING AND SAMPLE PREPARATION AND Standard Operating Procedure (SOP)

Description

The black mass from a European source was provided and originally described by the provider as 'cobalt nickel cake' and comprised a mixture of dark grey to black coloured fines along with fine metallic particles. It appeared in a dry and powder like condition and was described upon arrival as 'dirty and dusty' (Figure 4).



Figure 4. Unprepared sample of black mass submitted for analysis (left). The diameter of the sample dish (right) is approximately 150 mm.

Packaging and Stowage

The black mass was found packed in 'big bags' on wooden pallets and stored under a roof covering. The bags were marked with the processing plants original number in red paint spray. Various markings were found on the bags and contained a big bag producer's label. After sampling, each big bag was sealed with a plastic tie and assigned a red seal with a six digit reference number.

Weighing and Sealing

All bags were weighed by the client and a seal applied. Seals may deter casual attempts at tampering but will not prevent determined efforts to access the material.

Bulk Sampling

All the big bags were opened, and the contents were penetrated vertically, twice, from the top to bottom using a sampling spear 1.2 m long and with a 40 mm diameter, and ensuring the spear reached the bottom of the bag (²¹Holmes 2004 and ²²Dehaine 2021). One increment was drawn in the middle section of the big bag and one on the side/corner of the big bag. Due care had been given to obtain a completely filled column of black mass each time. The tubes were removed vertically, and the samples were collected in a large, clean bucket. This ensured an equal amount of sample for each spear sample increment. Afterwards, the big bags were closed and sealed.

Bulk Sample Preparation

All of the samples were combined in a single composite sample in a drum and reduced by Riffle Jones Splitter to obtain a sub-sample. The sample per container was subsequently split three times. The sub-sample was put in a bag, marked and underwent further sample preparation in the laboratory, including drying and preparation of the final analytic samples.

Drying Moisture Determination

The sample were divided into two trays. The trays and samples were weighed on an electronic precision scale, before and after drying in an electric heated and thermostatically controlled drying oven until a constant weight was achieved. A moisture content was obtained by subtracting the difference. This gave an average moisture content for five container lots as; 7.8%, 7.95%, 11.67% and 9.57%.

Comminution/Milling

The dried sample was milled/ground in a ring mill until it passed a 1 mm screen. The resulting fines were blended using

blending trays and a reduced sample was produced. This sample was further milled in a ring mill to pass a 0.112 mm screen. All oversized material was replaced into the ring mill and further milled with a nominal milling time until all the black mass passed the 112 μm sieve. The pot, ball and rings were closed with a lid and pressed pneumatically to ensure it was secured. The mill vibrated at high-speed making the rings and ball spin in an ellipse. Once the milling was finished, the pot was removed and the contents emptied. For more resistant particles of black mass, a mill containing tungsten carbide was used. Inside this pot was a tungsten carbide ball within a housing. The pot, ball and rings were enclosed with a lid and pressed pneumatically to ensure it was sealed and secured.

Blending

Following milling the black mass was blended for nominal time. The sample was collected in a plastic sample pot, closed with a screw lid. The sample pot was placed into the blender, the security cap was closed and blending sequence became initiated.

Rotary Sample Division

The prepared sample comprised 100% fines in a dried state. The powder was mixed using blending trays and the blended material was tipped into a hopper feeding a small vibrating gutter, which slowly enabled the black mass to fall into a spinning riffle, feeding eight, glass, 200 ml bottles. These bottles were attached onto a carousel head, spinning at a constant speed. Once the sample was divided, the sample bottles were detached and the contents transferred into pre-labelled, small, sample bags. The sample bags were secured and packaged into paper envelopes, which were identified and labelled with relevant information and sealed with sealing tape. A prepared and unprepared sample underwent further preparation into resin blocks for phase characterisation.

Methodology

The techniques used to analyse black mass were as follows:

- Visual examination and binocular microscopy.
- Manual scanning electron microscopy (SEM).
- Automated scanning electron microscopy with linked energy dispersive spectrometers (SEM-EDS) using advanced mineral identification and characterization system (AMICS).
- X-ray computed tomography (X-CT)
- Laser ablation inductively-coupled plasma mass spectrometry (LA-ICP-MS).

Stage 1: Visual analysis

A preliminary inspection of the black mass sample was undertaken.

Stage 2: Manual scanning electron microscopy (SEM).

Manual scanning electron microscopy (SEM) with linked energy dispersive spectrometers (EDS) provides information regarding the surface topography (shape, features, structures and textures) and composition of a sample by scanning its surface with a beam of electrons. As the electrons interact with atoms in the sample, electrons and X-rays are emitted, which are detected and processed by the instrument to produce an image and, with the addition of EDS, elemental composition information. Preliminary SEM images were collected using a TESCAN TIMA-X GMU field emission gun scanning electron microscope and a JEOL JSM-7100F field emission scanning electron microscope.

Stage 3: Automated scanning electron microscopy with linked energy dispersive spectrometers (SEM-EDS) using advanced mineral identification and characterization system (AMICS).

Automated scanning electron microscopy with linked energy dispersive spectrometers (SEM-EDS) was carried out. The analysis provides rapid determination and quantification of the mineralogy/phase chemistry, particle size and shape of a variety of sample types. The technology was initially developed for use in the mining industry for the characterisation of mineral processing products such as feeds, concentrates and tailings and has been used in the analysis of a wide range of ore types (e.g., ²³Garg et al., 2017, ²⁴Jordens et al., 2016 and ²⁵Mackay et al., 2016). Data collection is operator independent, with the acquisition of very large data sets, hence the results are statistically reliable and provide highly reproducible analyses (e.g., ²⁶Pirrie et al., 2009). There are several main automated SEM-EDS analytical systems on the market, including QEMSCAN (Thermo-Fischer), Mineralogic (Zeiss), TIMA (Tescan) and AMICS (Bruker). Automated mineralogy methods typically involve imaging of samples with a scanning electron microscope (SEM) using the backscatter electron (BSE) signal (where the image brightness is proportional to the composition of the material) to guide the rapid acquisition of spot energy dispersive X-ray (EDS) spectra. These spectra, combined with the BSE image, are used to make a phase determination and this results in a detailed compositional image of each sample. The method is optimised for speed so that very large numbers of particles are measured during analysis. The resulting images provide data not only on the particle types and their modal proportions, but also a diverse range of textural attributes such as particle size and phase association.

Analysis was undertaken with a Hitachi SU3900 scanning electron microscope fitted with a single large area (60 mm²) Bruker silicon drift detector (SDD) energy dispersive spectrometer and running the AMICS automated mineralogy package. Beam conditions are optimised for analysis and therefore an accelerating voltage of 20 kV coupled with a beam current of approximately 15 nA were used.

The samples were measured using the same analytical parameters and with a segmented field image mode of analysis. This analytical mode subdivides the BSE image into the domains (segments) of similar brightness, which represent different mineral grains and then acquires a representative EDS X-ray spectrum from a point within the segment; the mineral identified

is then assigned to the entire segment. Measurements are optimised to highlight both textural and modal mineralogical information and so an effective image resolution of microns of 1.6 μm was used. The EDS spectra acquired during the measurement are compared with a library of measured and synthetic standards and a phase identification is made on a closest match basis. Phases which are not represented in the standards list at the time of measurement are added either by acquiring reference spectra directly from the sample, or by creating a reference spectrum from the measurement itself. As the standards list can comprise hundreds of reference spectra, the data are grouped into a final, more manageable, reported list of phases. During AMICS analysis a full SEM-BSE map of the area imaged was also collected.

Stage 4: X-ray computed tomography (X-CT)

X-CT uses X-rays to obtain a series of two-dimensional (2D) radiographs of the object viewed from many different directions. This process is sometimes called a CT or X-CT scan. A computed reconstruction algorithm is then used to create a stack of cross-sectional slices from these 2D projections (radiographs) of the object. This provides a digital 3D greyscale representation (often referred to as a tomogram) of the internal structure of the object. This can be quantitatively analysed and virtually sliced in any direction or specific constituents can be digitally colour-coded, or rendered transparent, to visualize the 3D morphology (27Withers et al. 2021). A GE phoenix v|tome|x s X-ray micro computed tomography (micro-X-CT) device was used to image prepared and unprepared samples in resin blocks. They were imaged using an accelerating voltage of 100kV and a tube current of 50 mA, for a tube power of 5 W. Voxel resolution was 5 μm .

Stage 5: Laser ablation inductively coupled mass spectrometry (LA-ICP-MS)

LA-ICP-MS analyses of the same black mass sample was carried out using a Nu AttoM SC-ICPMS (Nu Instruments Ltd., Wrexham, UK). The measurements were performed on 75 isotopes covering 68 elements at low resolution using the fast scanning mode. Data reduction was handled using excel spreadsheet, which allows the baseline subtraction, outliers removal, the integration of the signal over a selected time resolve area and the quantification using known concentrations of the NIST 612 standard.

Results

Visible analysis and manual SEM

The unprepared sample of black mass comprised a heterogeneous mixture of dark grey to black coloured fines with fine metallic particles (Figure 5). The bulk powdered sample was imaged using manual SEM and showed that the powders are composed of a wide range of particle sizes and shapes. Larger particles are commonly coated with finer particles, and the larger particles are commonly composite in nature (Figure 6).

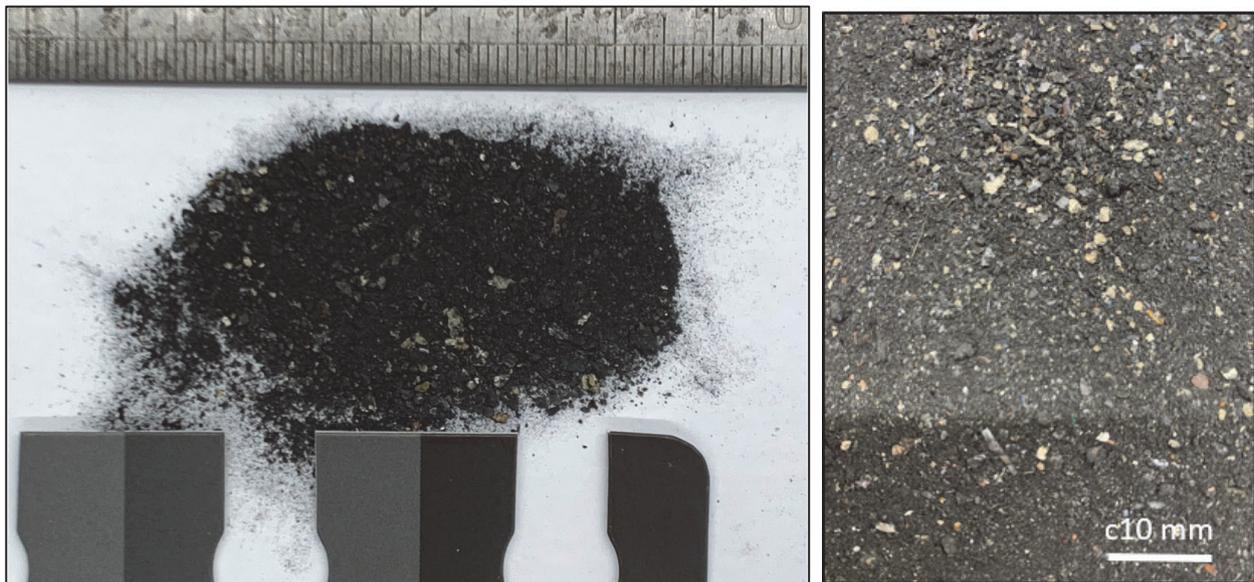


Figure 5. Unprepared sample of black mass submitted for analysis (left), note the complex heterogeneous texture of the black mass (right).

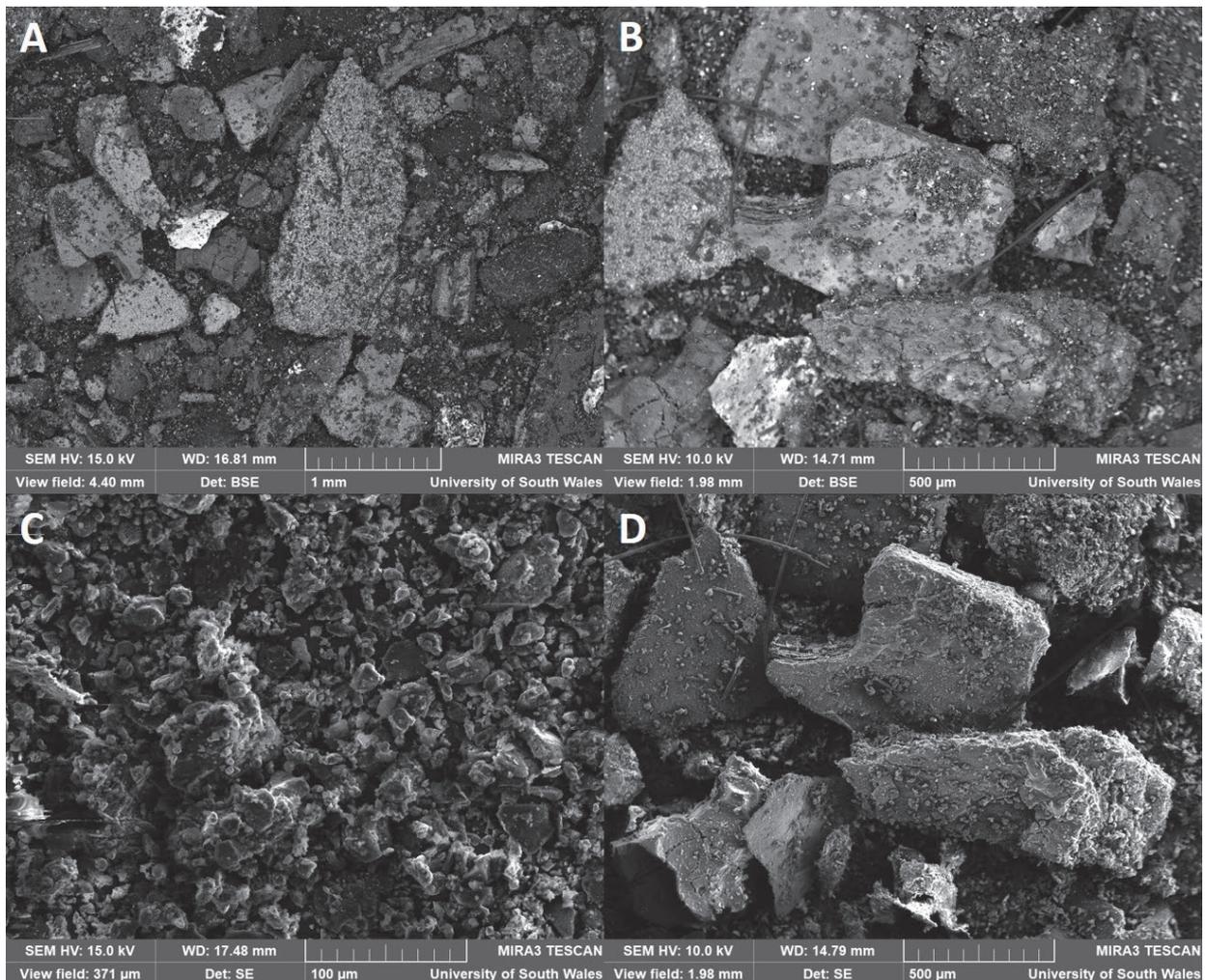


Figure 6. Scanning electron microscope images of the black mass unprepared sample. (A, B) BSE imaging, (C, D) SE imaging. Note individual scale bars.

Automated SEM-EDS

Both a prepared (powdered) and unprepared sample were measured three times using automated SEM-EDS analysis. The particles were assigned to 35 compositional groups based on the elemental composition. These compositional groups can be reclassified in terms of the likely attribution of the particles to the original battery components including: (a) graphite, (b) aluminium foil, (c) copper foil, and (d) lithium metal oxides. The lithium metal oxide category can be further divided into the five main cathode types, based on their phase chemistry: (i) NMC (LiNiMnCo oxides), (ii) LCO (LiCo oxides), (iii) LM(N)O (LiMn(Ni) oxides), (iv) LFP (LiFe phosphates) and (v) NCA (LiNiCoAl oxides). Within the data there are also; (1) particles currently assigned to mineralogical categories; these may be derived from the batteries or are cross contamination with environmental materials, and (2) metal phases, the attribution of which is currently unclear, although they may relate to parts of the battery casing or cross-contamination from other sources in the waste processing stream. Note that SEM-EDS analysis cannot determine the presence of Li, but the overall particle chemistry allows the particle types to be assigned.

The automated mineralogy images allow the particle types, as seen in the 2D measured sections to be visualised. The majority of the larger particles are complex mixed phases, often with the Al foils coated with the different Li metal oxide compounds. The Cu foil is predominantly as a separate phase, with an appearance in the 2D faces as similar to a Cu wire (Figure 7). In reality as shown by the 3D X-CT imaging these are in fact thin and complexly folded Cu sheets (Figure 8). Texturally the particles are complex, but the imaging allows them to be distinguished. In the Al foils with Li metal oxide coatings, the organic binding agents appear dark grey in the BSE images and are not characterised in the automated SEM-EDS analysis.

Micro X-CT

On completion of the interactive SEM-EDS analysis the same unprepared and prepared sample blocks were imaged using micro X-CT scanning. The aim of the micro X-CT was to image the 3D form of the particles; the automated SEM-EDS and interactive SEM-EDS data are all derived from the analysis of the 2D polished face of the analysed sample. Micro X-CT analysis allows the visualisation of the 3D particle form and can be cross-correlated with the automated SEM-EDS phase attribution carried out on a 2D surface (Figure 8).

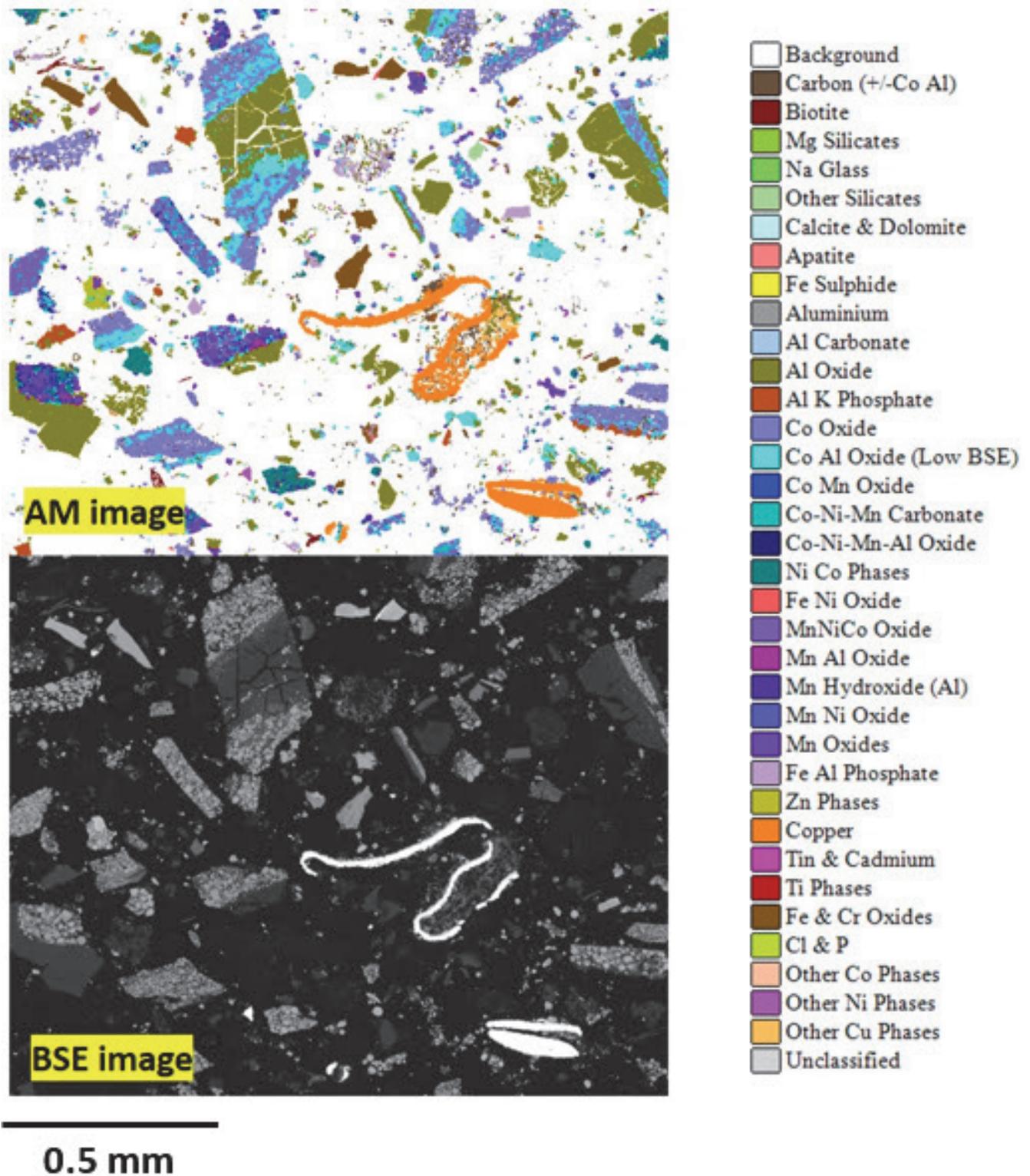


Figure 7. Automated mineralogy (AM) and SEM-BSE images for a sample of black mass. The bright phase in the SEM-BSE image is Cu foil, which in 2D sections looks like folded wire.

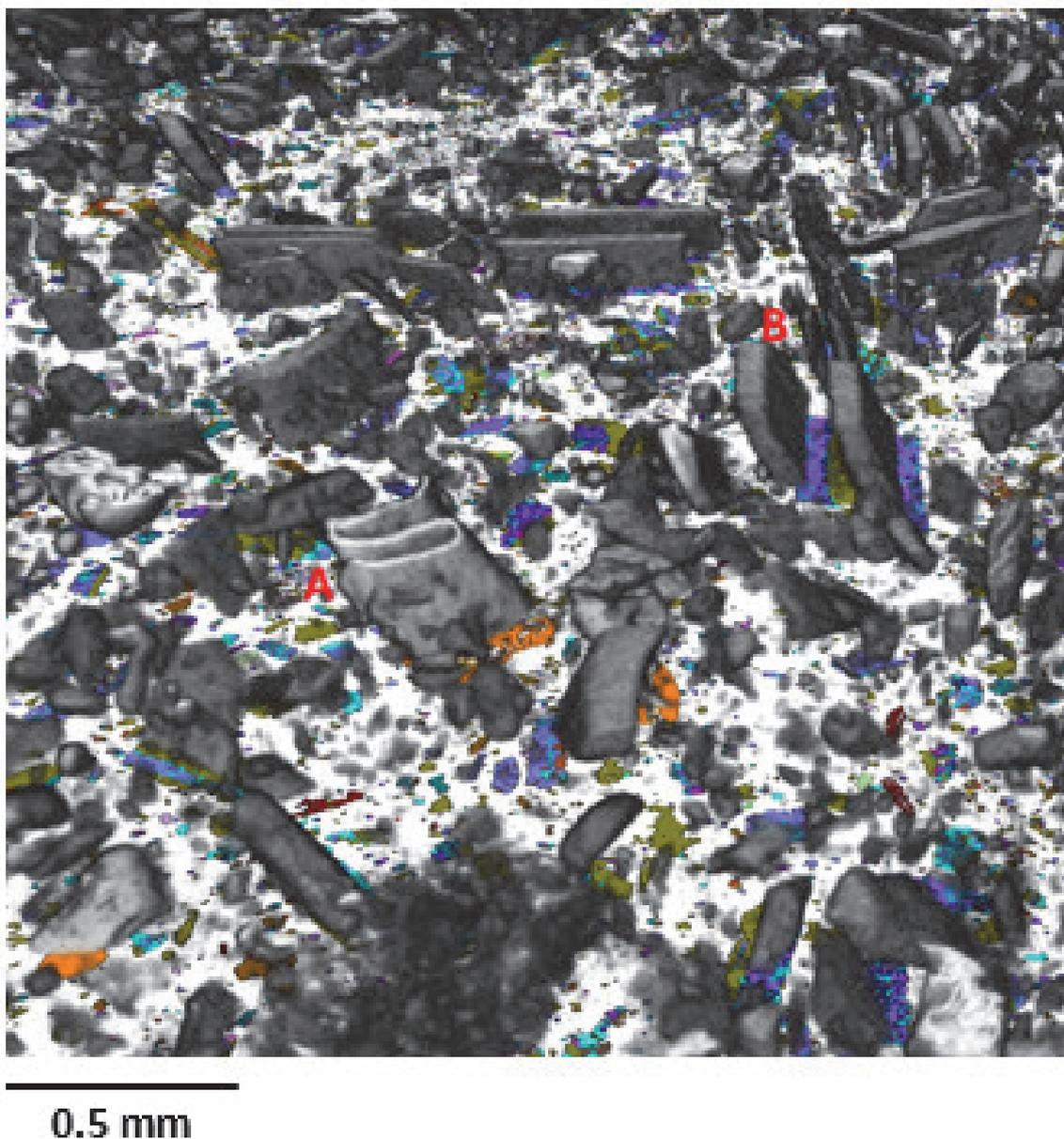


Figure 8. Enlarged micro X-CT image, from a video, showing form of (A) the Cu foil particles in 3D and (B) the form of the cathode/Al foil components.

LA-ICP-MS

On completion of the interactive micro X-CT, selected phases were analysed for minor and trace elements using laser ablation inductively-coupled mass spectrometry (LA-ICP-MS). Sixty-eight elements including Li were measured (Figure 9). The LA-ICP-MS analysis determined the Li content within the characterised particle. LA-ICP-MS analyses of the 7 spots indicated on Figure 9 are shown in Table 1 for Li, Mn, Ni and Cu. The analysis demonstrates that the methodology can detect and quantify the Li abundance confirming the automated SEM-EDS phase characterisation.

Table 1. LA-ICP-MS spot analysis of the cathode particle, units in ppm in Figure 9.

	Spot 2.1	Spot 2.2	Spot 2.3	Spot 2.4	Spot 2.5	Spot 2.6	Spot 2.7
Number of analysis	4	5	6	7	8	9	10
Li	137273	146949	117094	144534	130095	136261	132580
Mn	190843	190577	187836	194614	178263	198542	204555
Ni	189918	198121	214525	216398	206958	206486	191140
Cu	11478	23029	12929	15113	11103	25873	4507

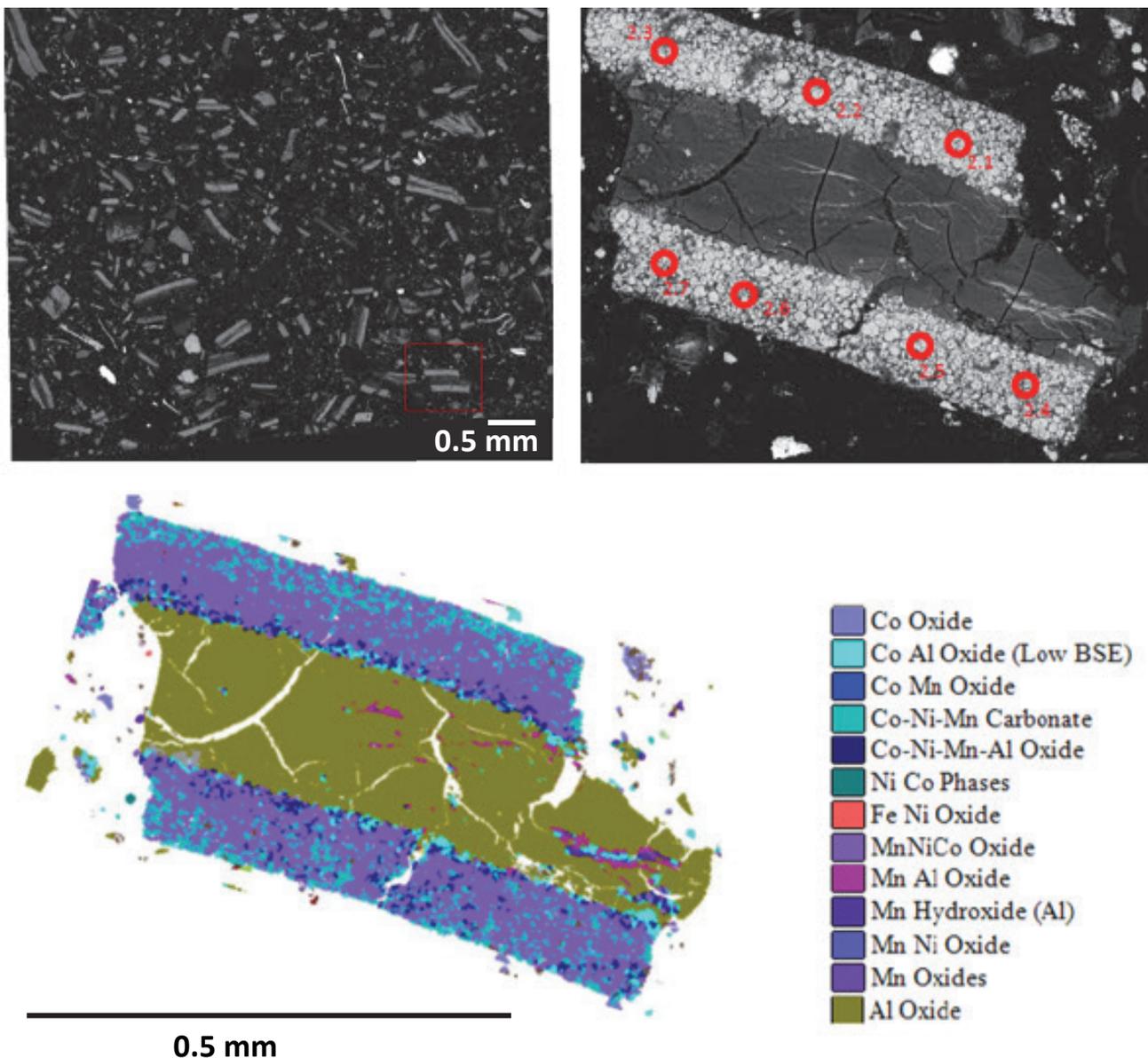


Figure 9. SEM-BSE image of the analysed sample; note the particle highlighted in the red box. Same particle, attributed to a cathode LMO, shown under SEM-BSE with the location of the laser ablation analysis (red circles) indicated and also the AMICS automated SEM-EDS particle mapping.

Conclusions

The results of this investigation to characterise a sample of black mass are as follows:

- Automated SEM-EDS can not only characterise and quantify the phases present, but also the phase chemistry allows the particle types to be assigned back to the primary battery components. However, some phases identified are at present not attributed back to the original components and further work is needed to refine the compositional groups, with the analysis of additional samples.
- Interactive SEM-EDS analysis also demonstrated that there is more detailed higher resolution chemical variability within the individual particle categories.
- Micro X-CT imaging has demonstrated the 3D form of the particles within the analysed sample volume. The 3D particle shape is potentially significant in terms of how the material will behave during subsequent grinding and chemical analysis.
- Neither automated nor manual interactive analysis can determine the presence/abundance of the light element, Li.
- LA-ICP-MS was successful in detecting and quantifying the presence of potentially strategically and economically important metals such as Li.
- Phase characterisation prior to processing is of value to potentially; (a) assist development of a suitable sampling strategy, (b) assist in determining the optimal processing route, (c) determine the presence of payable phases, (d) identify phases which may hinder metal recovery or may be regarded as penalty components, (e) aid in the development of laboratory assay procedures, and (f) assist in the identification, management and mitigation of hazards and their associated levels of risk.

- Given the different feeds within a recycling plant leading to the formation of the black mass powder for subsequent processing, such powders are likely to be variable in terms of their composition and particle characteristics.

References

- Chen, M., Zheng, Z., Wang, Q., Zhang, Y., Ma, X., Chen, C., Xu, D., Liu, J., Gionet, P., O'Connor, I., Pinnell, L., Wang, J., Gratz, E., Arsenault, R. and Wang, Y. 2019. Closed loop recycling of electric vehicle batteries to enable ultrahigh quality cathode powder. *Scientific Reports*, **9**, 1654, <https://doi.org/10.1038/S41598-018-38238-3>.
- Harper, G., Sommerville, R., Kendrick, E., Driscoll, L., Slater, P., Stolkin, R., Walton, A., Christensen, P., Heidrich, O., Lambert, S., Abbott, A., Ryder, K., Gaines, L. & Anderson, P. 2019. Recycling lithium-ion batteries from electric vehicles. *Nature*, **575**, 75-86.
- Or, T., Gourley, S.W.D., Kaliyappan, K., Yu, A. and Chen, Z. 2019. Recycling of mixed cathode lithium-ion batteries for electric vehicles: current status and future outlook. *Carbon Energy*, **2**, 6-43.
- Brückner, L., Frank, J. and Elwert, T. 2020. Industrial Recycling of Lithium-Ion Batteries. A Critical Review of Metallurgical Process Routes. *Metals*, **10**, 1107. <https://doi:10.3390/met10081107>.
- Vanderbruggen, A., Gugala, E., Blannin, R., Backmann, K., Serna-Guerrero, R. and Rudolph, M. 2021. Automated mineralogy as a novel approach for the compositional and textural characterization of spent lithium-ion batteries. *Minerals Engineering*, **169**, 106924.
- Werner, D., Peuker, U.A. & Mütze, T. 2020. Recycling chain for spent lithium-ion batteries. *Metals*, **10**, 316, <https://doi.org/10.3390/met10030316>.
- Barik, S.P., Prabakaran, G. & Kumar, L. 2017. Leaching and separation of Co and Mn from electrode materials of spent lithium-ion batteries using hydrochloric acid: Laboratory and pilot scale study. *Journal of Cleaner Production*, **147**, 37-43.
- Diekmann, J., Hanisch, C., Frobose, L., Schaliche, G., Loellhoeffel, T., Folster, A.-S. and Kwade, A. 2017. Ecological recycling of lithium-ion batteries from electric vehicles with focus on mechanical processes. *Journal of the Electrochemical Society*, **164**, A6184-A6191.
- Friedrich, B. & Schwich, L. 2020. New science-based concepts for increased efficiency in battery recycling. *Metals*, **11**, 533, <https://doi.org/10.3390/met11040533>.
- Liu, J., Wang, H., Hu, T., Bai, X., Wang, S., Xie, W., Hao, J. and He, Y. 2020. Recovery of LiCoO₂ and graphite from spent lithium-ion batteries by cryogenic grinding and froth flotation. *Minerals Engineering*, **148**, 106223.
- Lu, J., Wu, T. & Amine, and 2017. Start-of-the-art characterization techniques for advanced lithium-ion batteries. *Nature Energy*, **2**, 17011, <https://doi.org/10.1038/nenergy2017.11>.
- Pinegar, H. and Smith, Y.R. 2019. End-of-life lithium-ion battery component mechanical liberation and separation. *JOM*, **71(12)**, 4447-4456.
- Ruismaki, R., Rinne, T., Dańczak, A., Taskinen, P., Serna-Guerreo, R. and Jokilaakso, A. 2020. Integrating flotation and pyrometallurgy for recovering graphite and valuable metals from battery scrap. *Metals*, **10**, 680, <https://doi.org/10.3390/met10050680>.
- Schwich, L., Schubert, T. and Friedrich, B. 2021. Early-stage recovery of lithium from tailored thermal conditioned black mass part 1: Mobilizing lithium via supercritical CO₂-carbonation. *Metals*, **11**, 177, <https://doi.org/10.3390/met11020177>.
- Widijatmoko, S.D., Gu, F., Wang, Z. and Hall, P. 2020. Selective liberation in dry milled spent lithium-ion batteries. *Sustainable Materials and Technologies*, **23**, e00134.
- Zielinski, M., Cassayre, L., Floquet, P., Macouin, M., Destrac, P., Coppey, N., Foulet, C. and Biscans, B. 2020. A multi-analytical methodology for the characterisation of industrial samples of spent Ni-MH battery powders. *Waste Management*, **118**, 677-687.
- Otsuki, A., Mensbrugge, L. De La, King, A., Serranti, S., Fiore, L. and Bonifazi, G. 2020. Non-destructive characterization of mechanically processed waste printed circuit boards – particle liberation analysis. *Waste Management*, **102**, 510-519.
- Donnelly, L.J., Pirrie, D., Power, M., Corfe, I. Kuva, J., Lukkari, S., Lahaye, and Butcher. A. 2021a. The Phase Characteristics and Textural Variability of Black Mass. *Abstract for 26th International Congress for Battery Recycling, ICBR 2021*, Onsite and Virtual, 22-24 September 2021m Geneva, Switzerland.
- Donnelly, L.J., Pirrie, D., Corfe, I., Michaux, S. P., and Butcher A. 2021b. The Phase Characterization of Black Mass and its Commercial Implications in the Circular Economy. *20th International Automobile Recycling Congress IARC 2021*, 23-25 June 2021 Geneva, Switzerland.
- Nissi, J. 2019. 2019. *Development of Safety Protocols in Aalto University LIB Recycling Laboratory. Master's Programme in Chemical, Biochemical and Materials Engineering, Major in Sustainable Metals Processing*. Aalto University, School of Chemical Engineering, Finland.
- R.J. Holmes, "Correct sampling and measurement—the foundation of accurate metallurgical accounting", *Chemometrics and Intelligent Laboratory Systems* **74(1)**, 71 2004. doi: <http://dx.doi.org/10.1016/j.chemolab.2004.03.019>
- Dehaine, Q. 2021. Loosen the TOS stipulations and face the economic consequences. *Spectroscopy Europe*, **33(7)**, 32. doi: <http://dx.doi.org/10.1255/sew.2021.a37>
- Garg, S., Papangelakis, V., Edwards, E. and Mahadevan, R. 2017. Application of a selective dissolution protocol to quantify the terminal dissolution extents of pyrrhotite and pentlandite from pyrrhotite tailings. *International Journal of Mineral Processing*, **158**, 27-34.
- Jordens, A., Marion, C., Grammatikopoulos, T. and Waters, K.E. 2016. Understanding the effect of mineralogy on

- muscovite flotation using QEMSCAN. *International Journal of Mineral Processing*, **155**, 6-12.
25. Mackay, D.A.R., Simnadl, G.J., Ma, W., Redfearn, M. and Gravel, J. 2016. Indicator mineral-based exploration for carbonatites and related specialty metal deposits – A QEMSCAN orientation survey, British Columbia, Canada. *Journal of Geochemical Exploration*, **165**, 159-173.
 26. Pirrie, D., Power, M.R., Rollinson, G.K., Wiltshire, P.E.J., Newberry, J. and Campbell, H.E. 2009. Automated SEM-EDS (QEMSCAN) mineral analysis in forensic soil investigations; testing instrumental variability. In: Ritz, K., Dawson, L. & Miller, D. (eds) *Criminal and Environmental Soil Forensics*. Springer, 411-430.
 27. Withers, P.J., Bouman, C., Carmignato, S., Cnudde, V., Grimaldi, D., Hagen, C.K., Maire, E., Manley, M., Du Plessis, A. and Stock, S.R. 2021. X-Ray Computed Tomography. *Nature Reviews Methods Primer*, <https://doi.org/10.1038/s43586-021-00015-4>.