APPLICATION NOTE - 37

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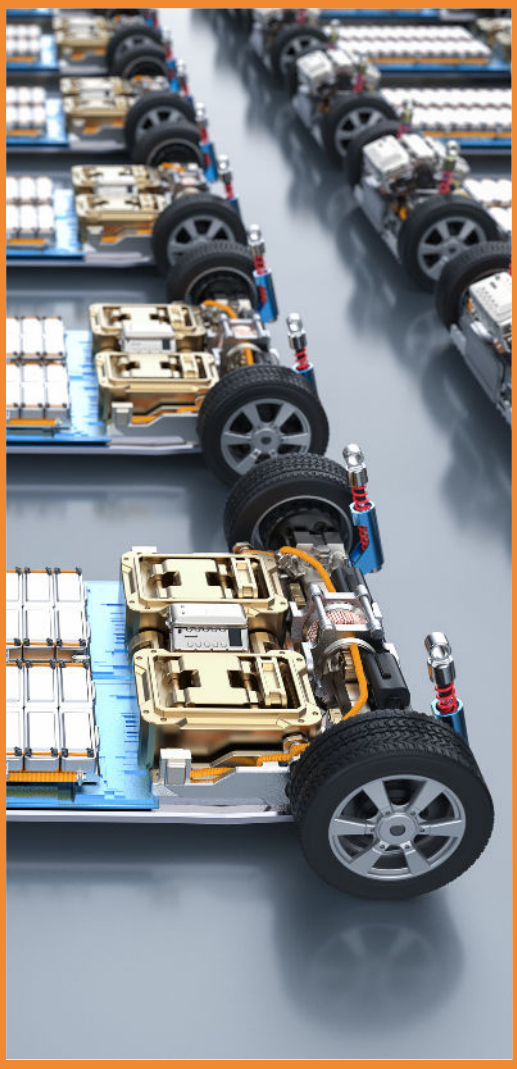
X-MET8000



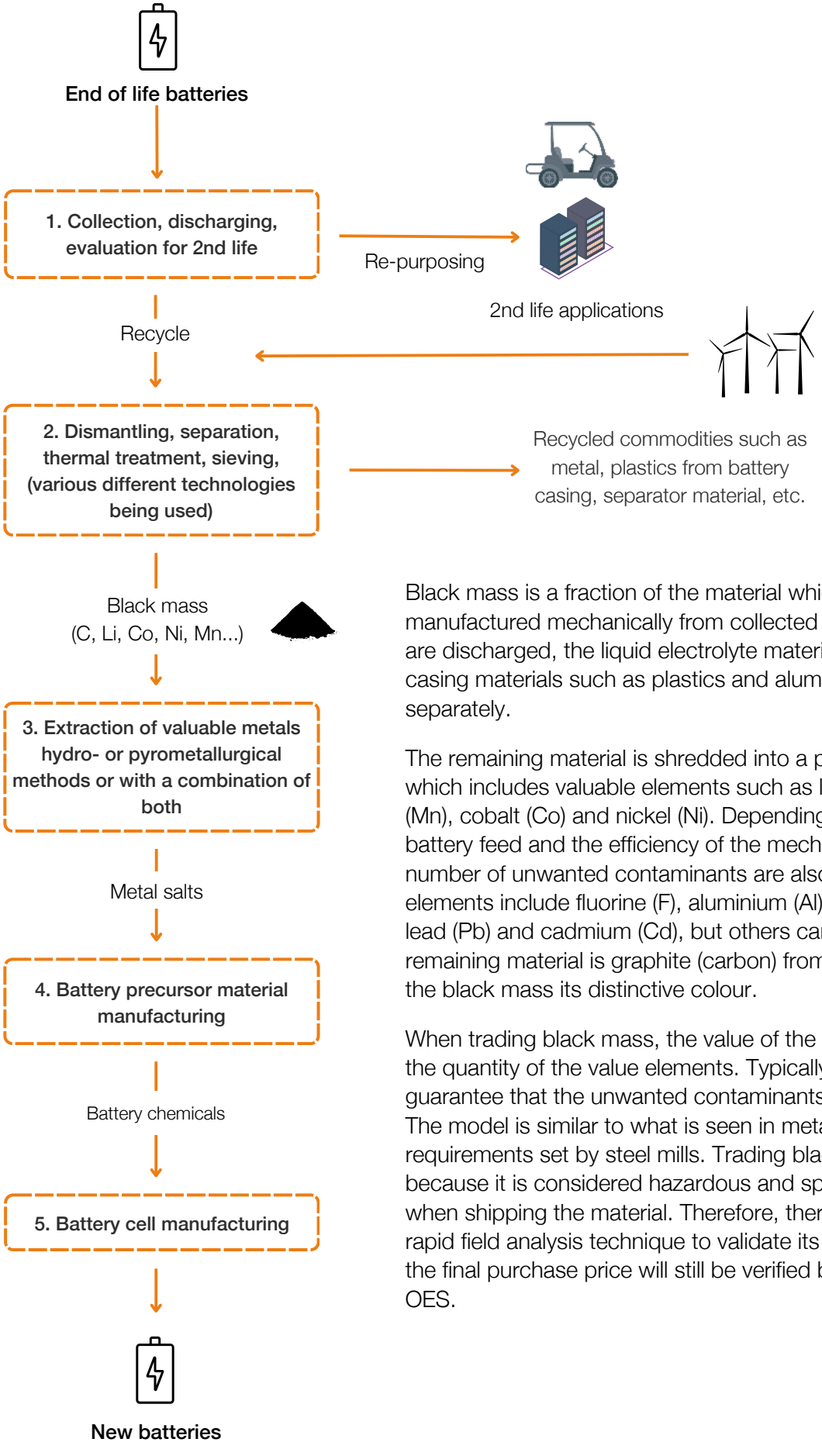
X-MET8000 EXPERT GEO FOR THE RAPID SCREENING OF VALUE ELEMENTS IN RECYCLED Li-ION BATTERIES

BACKGROUND

The transition to electric vehicles is heavily dependent on a steady supply of Li-ion batteries. The demand for batteries is skyrocketing, and this trend will continue in the future. As Li-ion batteries are manufactured from scarce elements, such as Lithium (Li), Cobalt (Co) and Nickel (Ni), recycling will be essential to ensure sufficient supply of raw materials now and in the future.

WHAT IS BLACK MASS?

The recycling of Li-ion batteries includes many steps and technologies. It is far more complex than, for example, metals recycling, and several competitive technologies are being introduced for collecting the batteries, processing them to black mass and further refining the material to be used again as a raw material for new batteries.



Black mass is a fraction of the material which is typically manufactured mechanically from collected batteries. The batteries are discharged, the liquid electrolyte materials are collected, and casing materials such as plastics and aluminium are recovered separately.

The remaining material is shredded into a powder called black mass, which includes valuable elements such as lithium (Li), manganese (Mn), cobalt (Co) and nickel (Ni). Depending on the purity of the battery feed and the efficiency of the mechanical process, a small number of unwanted contaminants are also often present. These elements include fluorine (F), aluminium (Al), phosphorus (P), iron (Fe), lead (Pb) and cadmium (Cd), but others can also be present. The remaining material is graphite (carbon) from the anode, which gives the black mass its distinctive colour.

When trading black mass, the value of the material is determined by the quantity of the value elements. Typically, the supplier will also guarantee that the unwanted contaminants are below certain levels. The model is similar to what is seen in metals recycling and the requirements set by steel mills. Trading black mass is complicated because it is considered hazardous and special conditions apply when shipping the material. Therefore, there is a clear need for a rapid field analysis technique to validate its composition, even though the final purchase price will still be verified by the buyer with ICP-OES.

INSTRUMENTATION

Handheld X-ray fluorescence (HHXRF) is a well-known and widely used method for on-site screening and analysis of a broad variety of sample types. Results are available in seconds (no need to wait for time-consuming and costly laboratory analysis results), enabling users to make decisions on the spot (e.g. check that the material meets specifications).

Hitachi High-Tech's X-MET8000 Expert Geo is an HHXRF analyzer that offers versatility and can be used for the rapid screening of the value elements in black mass to make a preliminary valuation of the material before it is shipped.

It is easy to use, and helps dramatically reduce the need for laboratory analysis and the associated cost.

Its large-area silicon-drift detector (SDD) and revolutionary BOOST™ technology provide up to 10 times the sensitivity of other HHXRF models, delivering excellent precision for results you can trust, day after day. There is no need for restandardization or detector cooldown periods between analyses, even in hot weather.

IP54 rated and tested to MIL-STD 810G for vibration, shock and drop (Method 514.6, Procedure I, Category 4; Method 516.6, Procedures I and IV), the X-MET8000 Expert Geo is rugged and won't let you down. The collected data is automatically saved on the device, and can be shared instantly via WiFi connection by using the Hitachi High-Tech ExTOPE Connect app and cloud service.

SAMPLING AND SAMPLE PREPARATION

Black mass is a challenging sample type due to its composition and varying degrees of homogeneity. The chemical composition can vary significantly depending on the source and type of Li-ion batteries, and the first mechanical process steps will impact homogeneity and particle size distribution. Lithium, manganese, cobalt and nickel are present in the sample as compounds, while aluminum and copper are in pure metallic form. Therefore, correct sampling and sample preparation techniques are critically important for successful analysis.

Samples are often traded in large bags, weighing around 1000kg each. When taking a sample for X-MET analysis, the sample will need to represent the whole batch. A sampling spear is an effective tool to take a representative sample from a bag. Sampling spears are readily available from several online stores selling sample preparation tools.

The spear is pushed through the material, all the way to the bottom, and then pulled out. The slots in the spear collect some sample from various depths in the bag which helps to mitigate the segregation effect. The collected sample fractions are then combined and mixed carefully.

The sample is placed in a sample cup prepared with 3.5µm Mylar® film. Black mass is a low-density sample which scatters X-rays. Therefore, suitable radiation safety accessories, such as the light stand and safety shield or the benchtop stand must be used for the analysis. It is good practice to check the analyzer's protective window for contamination, and change it if contamination is suspected.

When measuring the sample, it is recommended to use the X-MET's averaging function and take a minimum three repeats in order to get a representative result for the bulk sample. It is also a good practice to shake the sample cup lightly and tap it gently on a clean surface between each measurement.

CALIBRATION

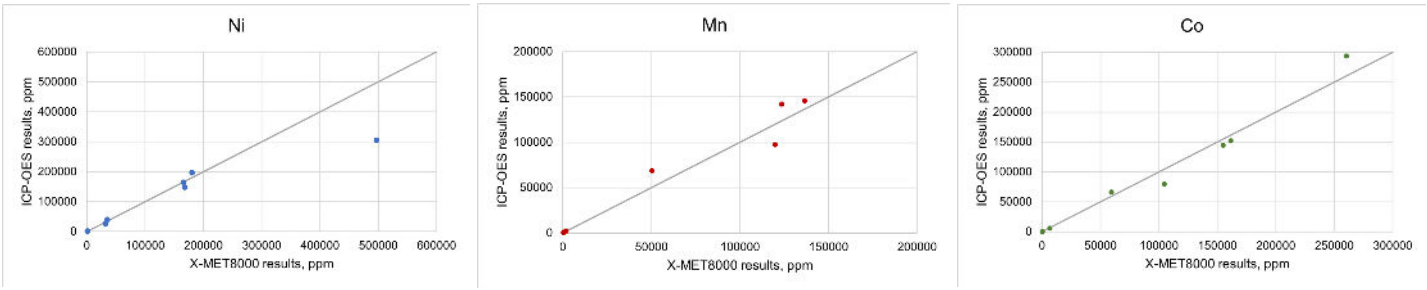
Black mass samples are measured using the X-MET's pre-loaded Black Mass FP calibration. This calibration can be used as is for screening purposes. For more accurate measurements, it is recommended to use either the "type standard" or the "matrix correction" function to further improve the accuracy for specific battery types. Customer samples with reliable analysis data are required to make adjustments to the calibration.

For quick screening purposes and the determination of Mn, Ni and Co in percent levels, a 10-15 second measurement time should be sufficient. When screening for contaminants in parts per million (ppm) levels, measuring light elements (Mg, Al, Si, P, S) or when higher accuracy is needed, the measurement time should be increased to 30-60 seconds or longer.

Note: Due to the limitations of XRF technology, lithium and fluorine analysis cannot be performed with the X-MET8000.

ANALYTICAL PERFORMANCE

The results below are example data from a real customer case. The samples were measured with Black Mass FP with a type standard correction, and used 60-second measurement time. Concentration values were provided by the customer and were obtained with ICP-OES analysis.



The graphs show good correlation between the X-MET results and the ICP values. The accuracy is sufficient to give an indication of the black mass value as well as to verify the battery type such as NMC811, NMC622 or LFP to name a few. When trading the material and determining its accurate composition, it is important to make parallel measurements with ICP-OES. Other elements such as Al, P, Fe and Cu can also be determined as they give an indication of the presence of contaminants from battery casing, electronics, etc.

Note that differences in Cu readings between XRF and ICP may sometimes be significant since these elements are present in pure metallic form. These create "hotspots" that can skew the analysis results when high numbers of particles are present in the sample volume being measured.

SUMMARY

The X-MET8000 Expert Geo with Black Mass FP calibration is an efficient tool for quick determination of black mass composition in field conditions. The results obtained with the X-MET will help black mass refiners to source the right materials and reduce the risk of incorrect valuation before any pre-shipment payments are made to their suppliers.

ORDERING INFORMATION

X-MET8000 Expert Geo Battery Recycling package. This includes the analyzer, light stand and safety shield, sample cups and film.

Optional accessory:

| Benchtop stand for a laboratory-like operation

Visit www.hitachi-hightech.com/hha for more information.

Hitachi High-Tech Analytical Science