Application note

Optimizing lithium-ion battery recycling operations using handheld XRF analysis

Introduction

The shift to a low-carbon economy and the adoption of electric vehicles will drive an exponential increase in the demand for lithium-ion batteries. As a corollary to this, the International Energy Agency expects the demand for some key commodities to increase significantly over the next two decades: the demand for Copper (Cu) is anticipated to increase by more than 40%; for nickel (Ni) and cobalt (Co), by 60-70% each; and for lithium (Li), by nearly 90%.[1] This will translate into increased mining activities and potentially generate larger amounts of deleterious waste.

To reduce the environmental impact and limit reliance on scarce commodities associated with economical and geopolitical implications, several countries have implemented regulations regarding producers' responsibilities.[2] These regulations contain both incentives and accountability guidelines for lithium-ion battery and electric vehicles manufacturers. Their goal is to facilitate the emergence of a circular economy in which recycling will increasingly contribute to the supply of the strategic raw materials.

Lithium-ion batteries are made of multiple components, the most valuable being the cathode that contains between 40 and 70% [3,4] of the total value of the battery, depending on its exact chemistry. As of 2023, lithium nickel cobalt manganese oxides (NCM) account for 66% of lithium-ion battery cathode active materials for electric vehicles, followed by lithium iron phosphates (LFP) which account for 24%, and lithium nickel cobalt aluminum oxide (NCA) accounts for the remaining 10%.[3]

Lithium-ion battery recycling workflow

To recycle lithium-ion batteries, several routes are available involving numerous possible combinations of thermal and mechanical treatments as well as pyrometallurgy or hydrometallurgy processes.

A common workflow incorporates a first phase where the lithium-ion batteries are discharged, and the battery pack and modules are dismantled to obtain battery cells. In the second phase, the battery cells undergo shredding, sieving, and separation by density and magnetism. In this stage, current collectors—generally aluminum and copper foils—are separated from black mass, which is a powder containing active materials from the cathode (NCM, LFP, NACA) and anode (graphite).

In a following stage, black mass can be treated in several steps using chemicals in so-called hydrometallurgical processes to recover pure salts of lithium, nickel, cobalt, and manganese. Alternatively, black mass can be directly smelted (pyrometallurgy) to recover cobalt, nickel and, in some cases copper, in the form of a metal alloy, while lithium is transferred to the slag phase. Finally, after using pyrometallurgy, the obtained alloy is refined into pure salts of base metals using simplified hydrometallurgical processes. It is important to note that not all process routes are economically viable for every type of cathode material.

The need for rapid chemical analysis throughout the recycling workflow

With the high variability of input material and the use of multiple process steps for the recovery of several valuable commodities, the recycling of lithium-ion batteries is complex. Mostly, the recovered materials need to be analyzed after each major step, either to verify purity or to ensure adequate composition of feedstock for the next step. In addition, companies upstream of the recycling workflow where black mass is recovered need to estimate the market value of the spent battery material shipped to downstream recyclers. Laboratory analysis of these materials can be time-consuming and expensive to run, with costs sometimes exceeding the value of the analyzed material itself; this creates a need for cost-effective, on-site analysis of recycled materials to enable fast, real-time decisions during the recycling process.

Handheld X-ray Fluorescence Analysis

Handheld X-ray fluorescence analysis (HHXRF) is an elemental analysis technique that has proven to be cost-effective in recycling areas such as scrap metal and automotive catalytic converters. HHXRF can measure elements from magnesium (Mg) to uranium (U) in various types of materials such as metals and alloys; non-metallic inorganic materials such as ceramics; or ores or plastics. The Thermo Scientific™ Niton™ XL2 and Thermo Scientific™ Niton™ XL5 Plus Handheld XRF Analyzers deliver accurate elemental analysis in real time, with little or no sample preparation, across multiple steps of the lithium-ion battery recycling workflow. Although handheld XRF does not detect lithium, it can measure most elements from the periodic table including nickel or cobalt which often command much higher value than the lithium in a lithium-ion battery.[4]

Handheld XRF is mostly used upstream of the recycling process:

- HHXRF can identify the type of cathode scrap films from gigafactories, which represents about 70% [4] of the feedstock in battery recycling. Identifying the type of cathode material (Figure 1) is essential to select an appropriate recycling route. While pyrometallurgy (smelting) is very efficient for recovering nickel and cobalt from NCM cathode films, it is not suitable for LFP cathode films. This is because lithium, the only commodity of high value in LFP cathode material, is transferred to the slag phase where it is very expensive to recover with further hydrometallurgical processes.
- For batteries at their end-of-life stage, HHXRF can be used at the start of the recycling process to sort battery housings obtained from dismantled spent batteries. The housings are typically made of different grades of stainless steel or aluminum alloys. HHXRF is also employed following shredding, magnetic separation, density separation, and sieving of end-of-life battery cells to analyze the resulting products. Those products range from copper and aluminum foils to black mass. Analyzing the fractions of each product using HHXRF provides information for risk assessment (e.g., verifying the absence of toxic metals), adequate material treatment, and process efficiency. Black mass, the most valuable product, can be analyzed for the amounts of nickel, cobalt, manganese, and other elements with minimal sample preparation. Analysis can be performed either directly in bags for fast, semi-quantitative measurements (Figure 2a), or using sample cups and a test stand for more precise and accurate measurements (Figure 2b). In the latter approach, elements such as phosphorous, silicon, or aluminum can be quantified in addition to nickel, cobalt, manganese, copper, and iron.

Handheld XRF can also be used to easily and accurately analyze the main product from smelting (pyrometallurgy) and measure the amount of nickel, cobalt, and copper in the alloy.

Figure 1. Sorting production scrap with HHXRF by identifying types of scrap cathode films.

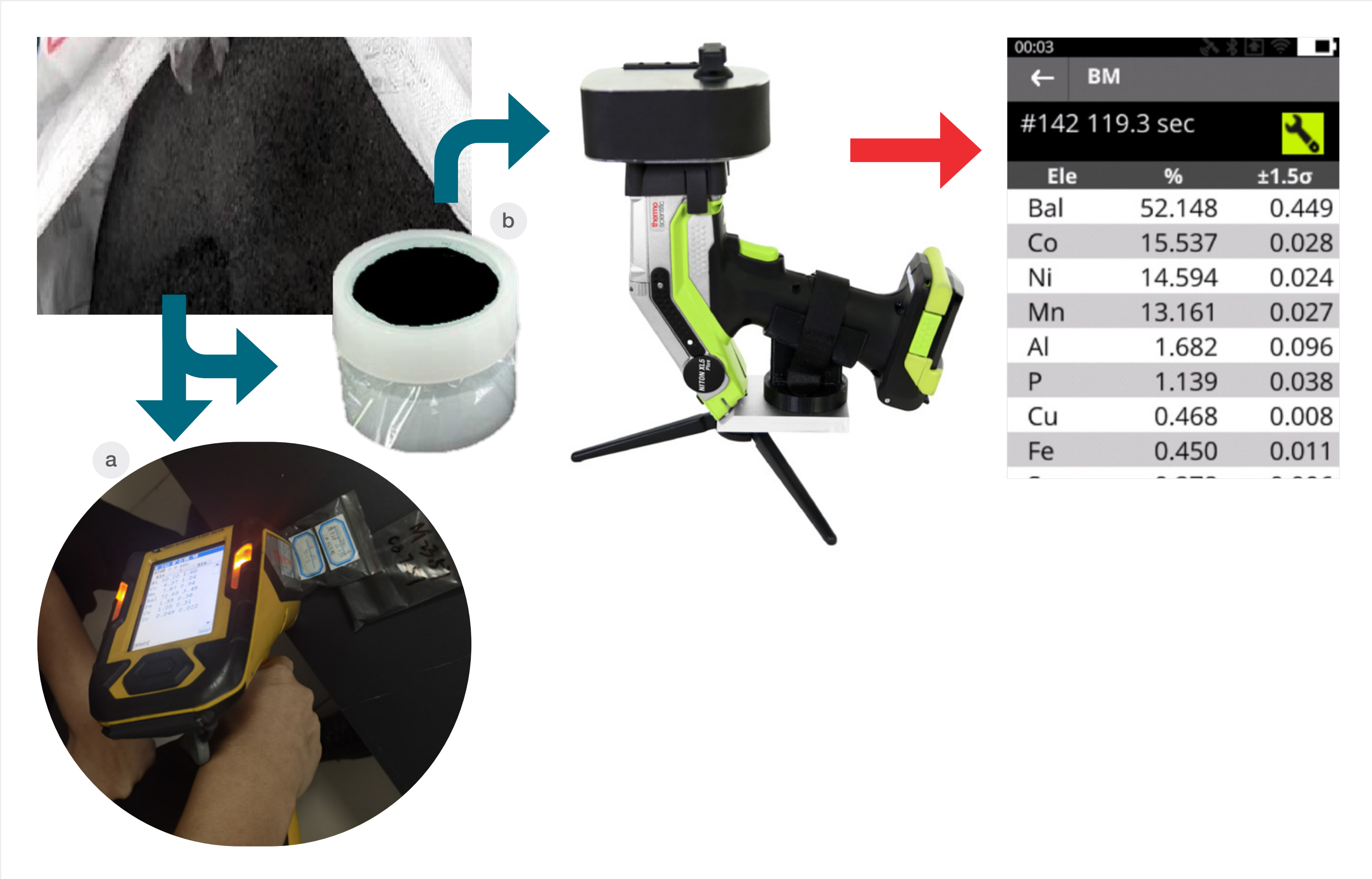

Figure 2. Workflow for rapid analysis of black mass: (a) semi-quantitative analysis of black mass in bags (base metals such as copper, nickel, cobalt, or manganese) using the Niton XL2 XRF Analyzer; (b) quantitative analysis of the full element range from Mg–U in sample cups using the Niton XL5 Plus XRF Analyzer.

Conclusion

There is no ideal process to recycle lithium-ion batteries that simultaneously incorporates low environmental impact, high metal recovery yield, and economic viability. Because of the variety of technologies and materials used, recycling lithium-ion batteries is a complex journey with multiple possible paths. HHXRF helps recyclers by generating lab-quality data in real time, allowing them to optimize their processes and make fast decisions that generate significant benefits:

- Unwanted materials containing heavy metals such as lead or cadmium can be prevented from entering subsequent steps in the recycling workflow.
- Materials can be accurately sorted and adequate processes for recovery selected depending on the material type (e.g., LFP vs. MCM).
- The economic value of incoming and outgoing material can be more accurately estimated.

References

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