Application note | AN1627

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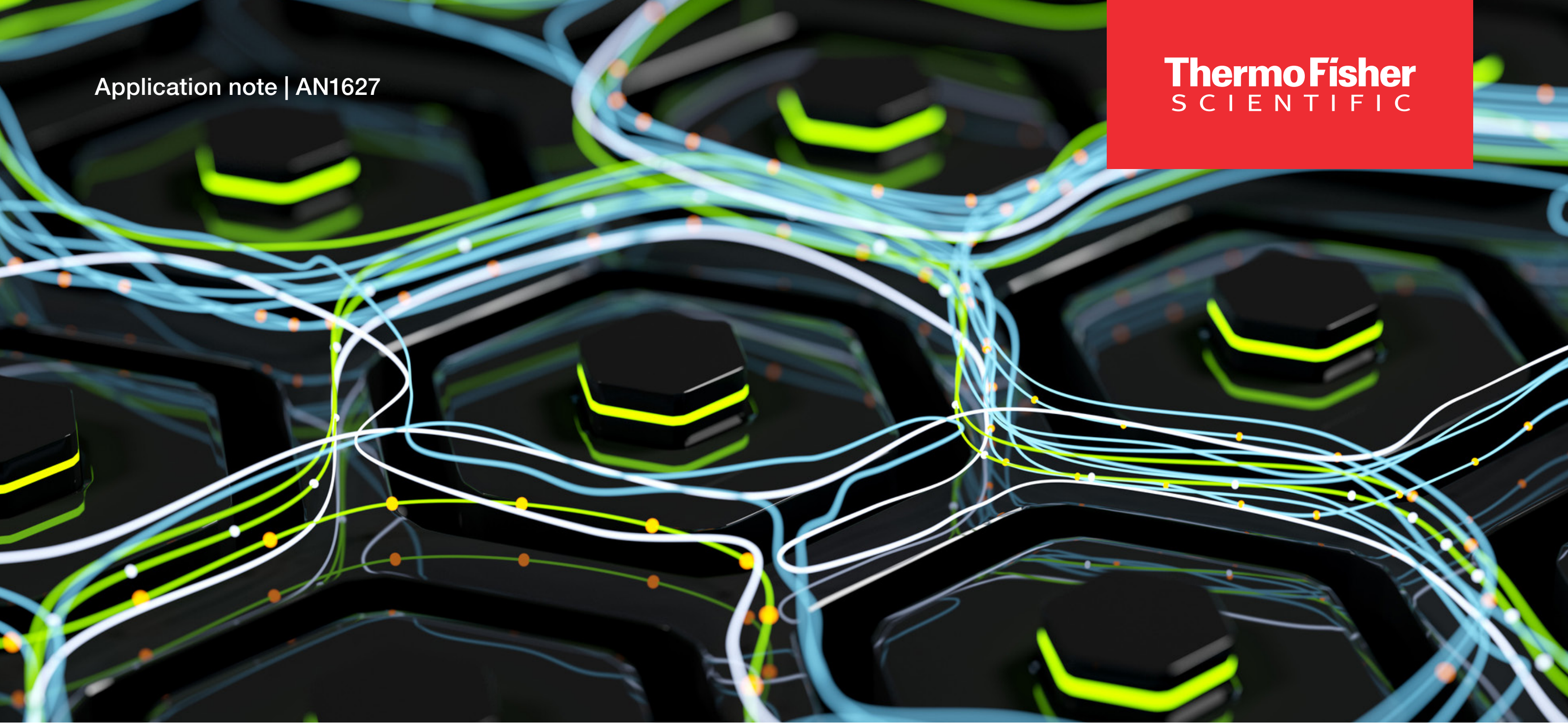

Identifying contamination in battery electrodes

The challenge

As the global demand for energy storage intensifies, the battery industry faces pressure to expedite the development of advanced battery technologies. Establishing manufacturing lines—a process that can extend over a year—requires sophisticated analytical tools to provide immediate feedback and sustain rapid development cycles. The industry recognizes that cell manufacturing scrap rates, which range from 5 to 30%, are especially high during the ramp-up phase or when introducing new processes. Electrode manufacturing is a critical and costly step, affecting all subsequent processes. Elemental characterization is integral to this process, ensuring homogeneously distributed active elements and the absence of contaminants in the coated electrodes. Contaminants and surface impurities on the electrodes can lead to short circuits when assembled into a full cell. Thus, it is critical to quickly identify such contaminants, diagnose their source(s), and implement changes to the manufacturing line.

Traditional offline analytical methods, which require extensive resources and specialized operators, are costly and time-consuming, making them less than ideal for the fast-paced environment of battery production. Some deliver bulk compositional data only, lacking the capacity to provide detailed insights into the arial and depth distribution of elements. Cell manufacturers typically rely on a lab's worth of spectroscopy and microscopy tools to characterize common defects like particle contamination and inhomogeneities in electrode composition, delaying the feedback loop to efficiently scale up new manufacturing processes.

The motive

As advanced battery cell manufacturing ramps up to meet increasing demand, a focus on quality assurance is needed to ensure efficient production of high performing, safe products. This requires analytical instruments capable of quickly identifying and diagnosing the common defects encountered during manufacturing.

The result

Instead of requiring a full laboratory's worth of multiple analytical instruments, or costly third-party lab analysis, the EXUM™ MASSBOX™ LALI-TOF Mass Spectrometer demonstrates its abilities to rapidly verify homogeneously distributed active elements in a cathode sample and identify and diagnose contaminants on the anode sample.

The solution

Laser Ablation Laser Ionization Time of Flight Mass Spectrometry (LALI-TOF-MS), used by the MASSBOX LALI-TOF-MS, emerges as a transformative battery material characterization solution. Offering trace-level quantification, elemental mapping, and depth profiling, the MASSBOX LALI-TOF-MS overcomes traditional challenges. Furthermore, its detection abilities include important low-mass elements like lithium, carbon, and oxygen, that are traditionally difficult to reliably quantify using other analytical techniques. Operating under vacuum, it directly analyzes air- and moisture-sensitive materials. This compact, desktop solution minimizes sample preparation procedures and expedites insights near the manufacturing line.

LALI-TOF-MS

The MASSBOX LALI-TOF-MS employs a dual-laser LALI technique, where the first laser ablates material from the sample's surface, and the second laser ionizes the released particles. The ablation laser directly analyzes solid materials like the electrode samples shown in Figure 2. The ionization laser then targets neutral particles created by the ablation process, ensuring a more accurate representation of the sample's constituents compared to the plasma-generated ions in traditional mass spectrometry techniques. This approach improves elemental verification and minimizes sample matrix effects. After ionization, the TOF mass analyzer generates a full mass spectrum at each laser spot, ranging from low-mass elements like lithium and carbon to high-mass metallic elements. This facilitates multielement quantification and broad-scale elemental mapping.

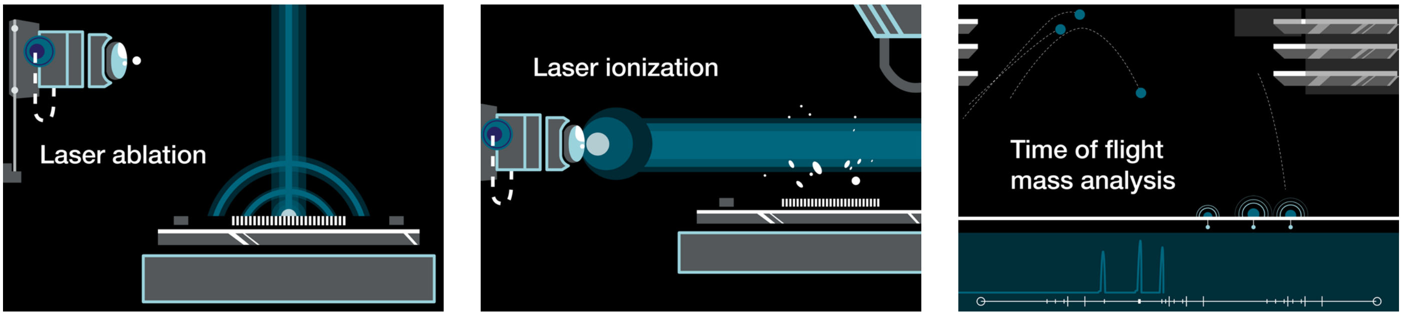

Figure 1. A) Ablation laser fires perpendicular to the sample's surface. The laser spot size is adjustable from 5-150 microns.
B) Secondary laser performs multiphoton ionization of neutral particles created by ablation process.
C) Ions are separated by Time-of-Flight mass spectrometry and detected with a multichannel plate (MCP).

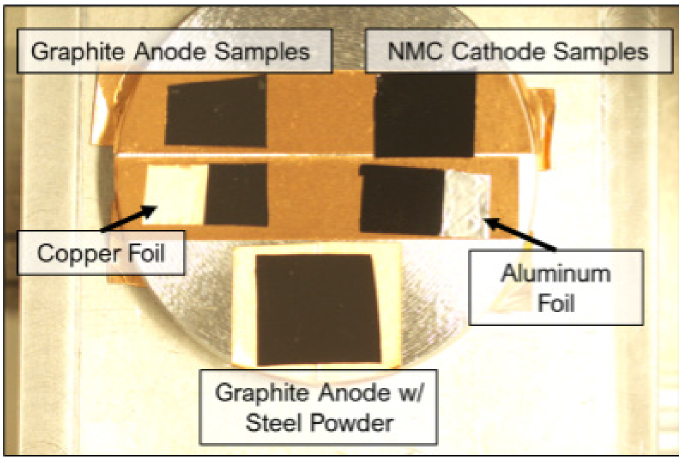

Figure 2. Image from the instrument's macrocamera showing a set of coated electrode samples within the MASSBOX LALI-TOF-MS's 83-mm by 83-mm analysis area. Displayed are three graphite-coated copper foil anodes and two nickel-manganese-cobalt-coated aluminum foil cathodes, all secured with copper tape. This image highlights the MASSBOX LALI-TOF-MS's capacity for direct analysis of diverse electrode materials, streamlining elemental assessment in battery production.

Elemental mapping of electrodes

Figure 2 demonstrates the MASSBOX LALI-TOF-MS's ability to analyze diverse electrode samples that fit into the 83-mm by 83-mm analysis area. For this study, the analyst adhered sets of electrodes—three from graphitecoated copper foils (anodes) and two from lithium-nickel-manganesecobalt-coated aluminum foils (NMC cathodes)—directly onto the sample holder using copper tape.

To identify contaminants or local variations in the electrodes' active materials, the MASSBOX LALI-TOF-MS offers detailed spatial insights through elemental mapping.

The LALI technique, with an adjustable laser spot size of 5-150 microns, captures comprehensive elemental distributions across a range of sample types. As an example of the MASSBOX LALI-TOF-MS's results, Figure 3 features an elemental map across the edge of a cathode sample, combining both the aluminum foil and the lithium-NMC coating.

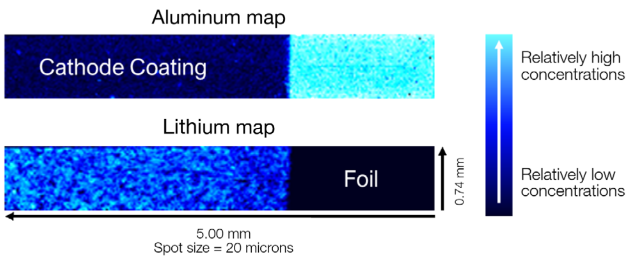

Figure 3. Elemental mapping across the cathode sample's edge, analyzed over a 5 mm by 0.74 mm area with a 20-micron laser spot size. The color scale illustrates relative concentrations: brighter colors denote higher levels. The right third of both maps reveals the aluminum foil, and the left two-thirds covers the NMC cathode coating, which has high concentrations of lithium.

This section of the cathode was analyzed over an area of 5 mm by 0.74 mm using a 20-micron laser spot size. The mapping reveals the elemental concentration visually: brighter colors indicate higher concentrations, and each map is relative to itself. The left two-thirds of the map covers the NMC coating, and the right one-third includes the aluminum foil, as evidenced by the high concentration of aluminum shown in the top map. The bottom map displays lithium, which is absent on the right part of the map (the foil) and homogenously distributed in the NMC coating. Identifying any inhomogeneities in lithium and other active elements is an important part of electrode manufacturing quality control. To achieve fast charging and long lifetimes, battery cells should be composed of electrodes with homogeneously distributed active materials.

Investigating lithium distribution

Figure 3 shows a homogeneous lithium (Li) map on a pristine, newly manufactured cathode. Measuring the distribution of Li within electrodes is also important for understanding Li ion behavior during charge and discharge cycles, characterizing the solid electrolyte interphase (SEI) layers, and identifying areas of accumulation that may lead to plating or other failure mechanisms. Ultimately, understanding Li distribution is critical for optimizing battery performance, capacity, and lifespan.

Traditionally, Li is a challenging element to reliably measure and quantify with conventional techniques. Addressing these limitations, the MASSBOX LALI-TOF-MS emerges as a valuable solution for mapping and quantifying Li in electrodes. MASSBOX MS's innovative LALI technique allows detection of Li in trace (i.e., 100s of parts-per-billion) levels. By mapping Li and other elements of the periodic table simultaneously, users can determine whether the accumulation is associated with metallic Li (i.e., plating) or the solid electrolyte interface (SEI) layer. For SEI characterization, the MASSBOX LALI-TOF-MS identifies areas of high Li concentrations with correspondingly high carbon, oxygen, and fluorine.

Identifying and diagnosing contamination

This study tested the MASSBOX LALI-TOF-MS 's ability to swiftly detect contamination by intentionally sprinkling 316L stainless steel powder on an anode sample. The steel powder's composition is 63.3% iron (Fe), 17.9% chromium (Cr), and 13.9% nickel (Ni) and its average particle size is 38 microns.

The initial analysis covered a 1-mm-by-1-mm area using a 20-micron spot size, revealing multiple hot spots of Cr, as depicted in the images in the left of Figure 4. Subsequent analysis with a finer resolution (510 microns by 525 microns and a 15-micron spot size) confirmed the presence of stainless-steel particles, indicated by yellow circles rich in Fe, Cr, and Ni. Additionally, red circles highlight another contaminant with high concentrations of Ni, Li, Mn, and Co. This is likely from the lithium-NMC cathode, suggesting cross- contamination between electrodes.

Such findings underscore the risk of cross-contamination in manufacturing facilities, especially when anode and cathode production lines are close. The MASSBOX LALI-TOF-MS efficiently pinpoints and chemically diagnoses these contaminants, offering critical insights within about 30 minutes—significantly faster than conventional methods that require extensive sample preparation.

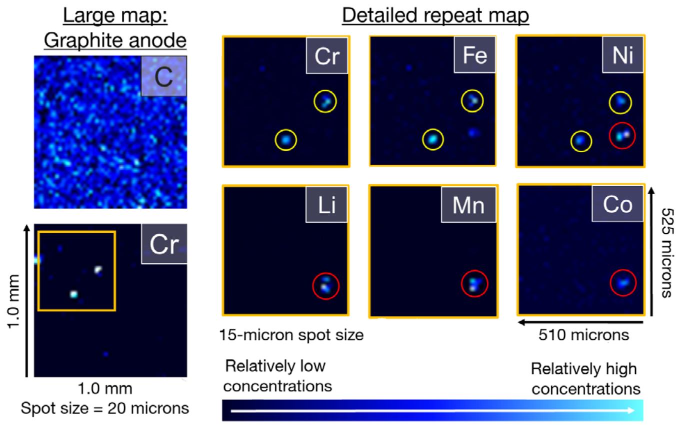

Figure 4. Detailed mapping of contamination on a graphite anode sample. An initial 1-mm-by-1-mm area scan identified stainless steel particles, as evidenced by chromium (Cr) hot spots. Subsequent higher-resolution mapping revealed distinct particles of stainless steel and an unexpected contaminant from lithium-NMC cathode material.

Depth profiling

In Figure 4, the large map on the left is from the sample's surface while the repeat map on the right is one layer below the surface. The MASSBOX LALI-TOF-MS typically removes ~100s of nanometers of material per raster area (this depends on the material type, the user-defined laser power, and the user-defined laser spot overlap). Analyzing an electrode with multiple rasters repeated on the same area creates a 3D reconstruction with valuable insights into the distribution of active elements, contaminants, and degradation mechanisms. Although generating a millimeter-scale 3D analysis with micron-scale lateral resolution and nanoscale depth resolution requires multiple hours, the MASSBOX LALI-TOF-MS's software allows users to set up long analyses to run without intervention (i.e., overnight).

In addition to 3D elemental mapping, the MASSBOX LALI-TOF-MS also creates quick depth profiles with single laser spots. This process typically removes ~10s of nanometers per laser shot, resulting in ~100s of nanometers of material removed per second. For a given material, the user correlates the amount of material removed per second by measuring the depth of the laser spot dwell with a microscope.

MASSBOX LALI-TOF-MS summary

The MASSBOX LALI-TOF-MS stands out as a vital asset for advanced battery manufacturing, offering rapid feedback that accelerates the development of manufacturing lines. Its compact design, streamlined operations, and userfriendly interface allow for high-performance materials testing near the manufacturing line.

This study highlights the MASSBOX LALI-TOF-MS's proficiency in scanning millimeter-scale areas of coated electrodes, pinpointing contaminant particles down to the micron scale, and effectively diagnosing their origins—all within less than 30 minutes. Although the steel particles were intentionally introduced during laboratory tests, the MASSBOX LALI-TOF-MS also uncovered unexpected contamination from the lithium-NMC cathode. This demonstrates the MASSBOX LALI-TOF-MS's competence for identifying particle contamination in a manufacturing environment. The industry recognizes that contaminants can originate from a variety of sources, including the raw materials, the manufacturing equipment, the environment, and human handling.

A significant benefit of the MASSBOX LALI-TOF-MS is its ability to detect all elements present without requiring the user to specify which elements to seek. This provides critical insights that go beyond standard expectations and ensures thorough quality control in electrode manufacturing. By facilitating quicker, higher-sensitivity assessments of material compositions and contamination, the MASSBOX LALI-TOF-MS is pivotal in advancing the reliability and safety of batteries, pushing the industry towards more energy-efficient solutions. In addition to the capabilities demonstrated in this study, the MASSBOX LALI-TOF-MS's elemental mapping and depth profiling can accelerate product development cycles and post-mortem failure analyses. Because the analytical process occurs under vacuum, it is suitable for air- and moisture-sensitive battery materials. Furthermore, its quantitative analysis empowers quality engineers to rapidly verifying raw materials meet specifications.

Elemental mapping

Depth profiling

Rapid screening

Quantitative analysis

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Thermo Fisher Scientific is an authorized distributor of the EXUM MASSBOX LALI-TOF mass spectrometer in Europe, United Kingdom, and China. For all other regions, please contact us at marketing.ppa@thermofisher.com.

Learn more at **thermofisher.com/massbox**

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