Application note | AN1555

New technology for rapid elemental analysis, mapping, and depth profiling battery materials

The challenge

As today's battery industry strives to improve energy efficiency and reduce costs, innovative new materials are being tested, developed, and brought to market. From raw material quality control to post- cycling failure analysis, elemental characterization is a critical piece of the battery life cycle. Despite its importance, performing elemental characterization is difficult and time-consuming, requiring multiple analytical instruments, complicated operational and calibration procedures, and trained chemists. Traditional mass spectrometry and spectroscopy techniques involve digesting solid material with acid for the most accurate elemental analyses. This results in a bulk composition of the material only and fails to identify how elements change spatially or in depth. Investigating elements' spatial distributions is especially critical for diagnosing failures in the manufacturing process, after cycling, and post-mortem.

The solution

A new mass spectrometry technique offers trace-level quantification of nearly the entire periodic table, elemental mapping, and depth profiling in a compact, desktop package. Further, the analytical process is performed under vacuum, enabling analysis of air- and moisture-sensitive materials. Because it directly analyzes solid materials, it minimizes the sample preparation procedures and accelerates the ability to gather impactful information outside of a traditional laboratory environment.

Motive

A single desktop instrument that provides compositional analysis, elemental mapping, and depth profiling of battery materials that empowers the industry to develop and manufacture innovative materials.

Result

Instead of using a full laboratory's worth of multiple analytical instruments, or spending thousands on third party lab analysis, the EXUM™ MASSBOX™ reduces the time required for quality control of raw and recycled materials, accelerates compositional analysis of electrodes, enhances understanding of solid electrolyte interface (SEI) formation, and increases failure analysis capabilities.

MASSBOX LALI-TOF-MS

The EXUM™ MASSBOX™ Laser Ablation Laser Ionization Time of Flight Mass Spectrometer (LALI-TOF-MS) addresses many challenges associated with other analytical techniques to offer rapid, high-sensitivity quantification of nearly the entire periodic table. The ionization source, LALI, uses two lasers to first ablate, or release, material from a solid sample's surface and then ionize neutrals present in the ablated B material. The laser ablation process allows direct analysis of solid materials, like pelletized powders or torn-down cell components, without the complicated procedures of other techniques that require liquid samples. Figure 1 summarizes the LALI-TOF-MS process.

The ionization laser targets the neutral particles created by ablation, which are more representative of the sample's constituents than plasma-generated ions. Overall, LALI results in more reliable elemental verification and reduces sample matrix effects. After ionization, the TOF mass analyzer creates a full mass spectrum at each laser spot, as shown below. Figure 2 displays an example mass spectrum from analyzing a solid-state electrolyte material, LLZO. Based on the naturally occurring isotope patterns, the software verifies each detected element. The text boxes denote major elements ranging from low-mass elements like lithium (Li) to high-mass elements like lanthanum (La) and tantalum (Ta). Few analytical instruments are able to reliably detect low-mass and high-mass elements in the same analytical session. After isotopically verifying each element, the MASSBOX's software labels the peaks so the user does not need to have chemistry expertise in order to interpret the mass spectrum.

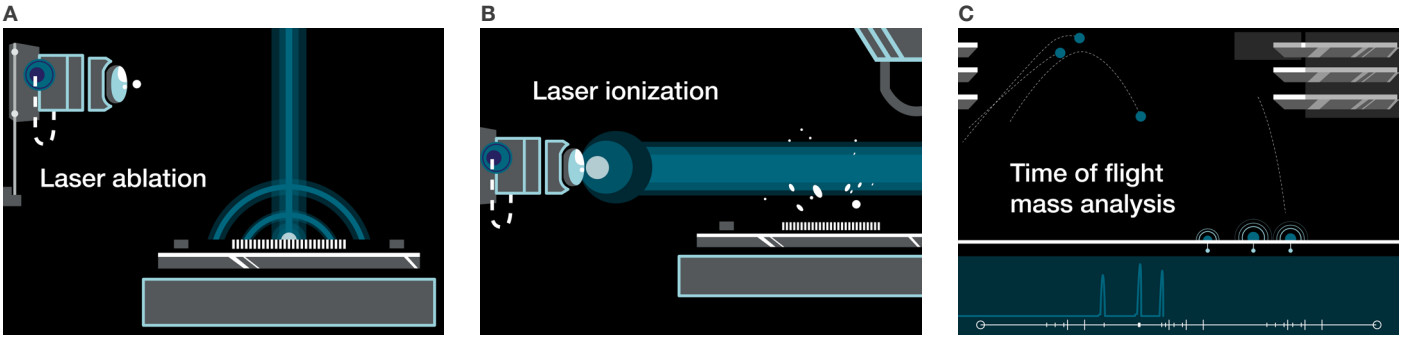

Figure 1. A) Ablation laser fires perpendicular to the sample's surface. The laser spot size is adjustable from 5-200 micron.
B) Secondary laser performs multiphoton ionization of neutral particles created by ablation process.
C) Ions are separated by Time-of-Flight mass spectrometry and detected with a multichannel plate (MCP).

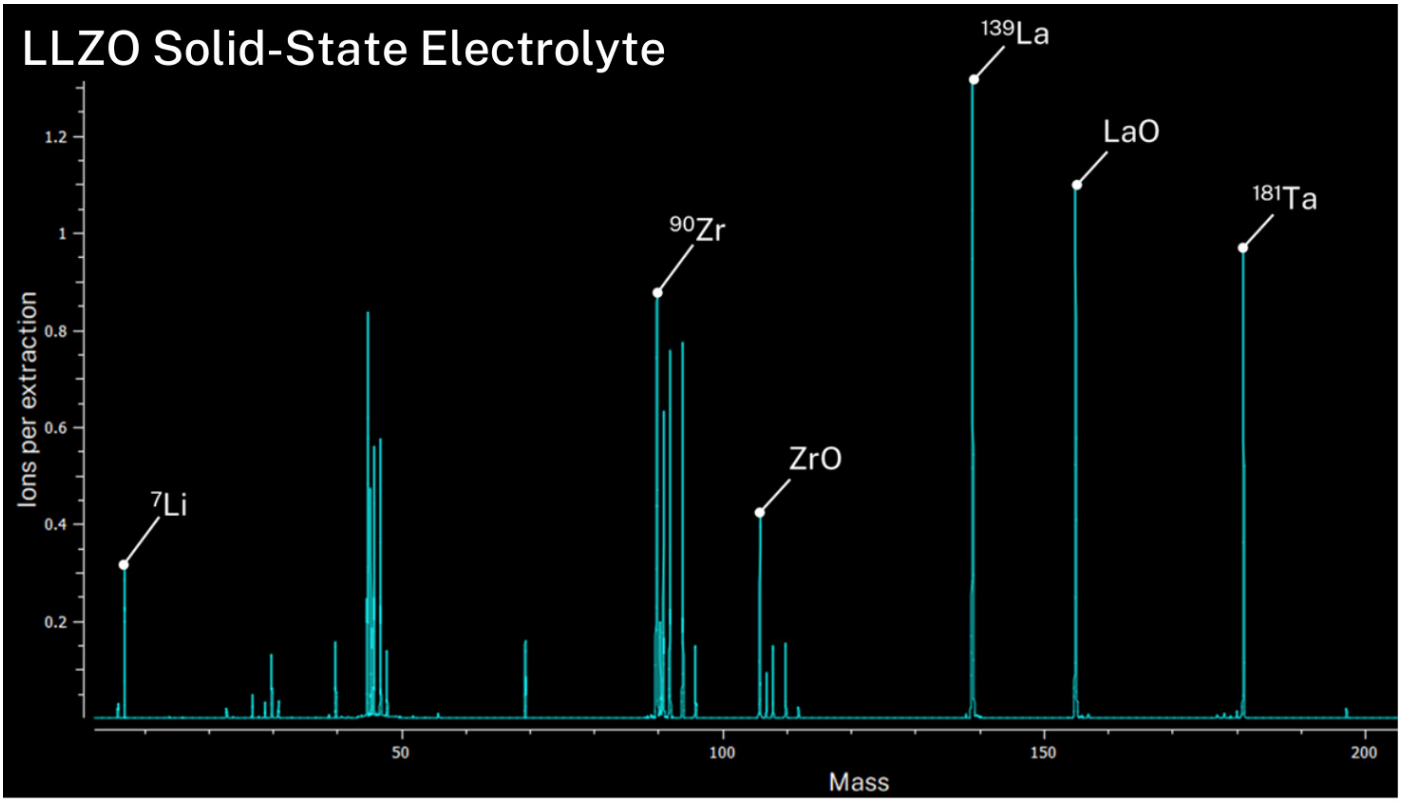

Figure 2. Mass spectrum from a LLZO solid- state electrolyte sample, analyzed by the Massbox. The text boxes indicate the major elements that were isotopically verified by the software. The software labels the peaks, so the user does not need chemistry expertise to interpret the data.

Elemental mapping

In addition to bulk elemental characterization, the MASSBOX LALI-TOF-MS performs elemental mapping. In each analytical session, it can analyze an area up to 83 mm by 83 mm. The resulting map's spatial resolution is determined by the ablation laser's spot size, which is adjustable from 5-150 microns. Each laser spot contains a full mass spectrum of data, and the resulting map reveals the variation of any element of interest. Figure 3 shows an example set of maps from analyzing a LLZO solid- state electrolyte sample. On the map, each pixel is a 50-micron laser spot, and the color scale indicates the relative concentration of the elements. Brighter blues are higher concentrations and darker blues are lower. Figure 3 shows the maps of two major matrix elements, zirconium (Zr) and La. Within the wedge shape of the sample, these elements have generally high concentrations, with the exception of several defects with lower concentrations.

Chemically diagnosing defects

To investigate a defect's composition, the user creates a second, smaller analysis over the area of interest. Figure 4 shows a set of maps resulting from a 3.5 mm by 4.5 mm scan over the top part of the sample. The yellow arrow indicates the defect with very low concentrations of the matrix elements, Zr and La. The smaller maps reveal high concentrations of lithium oxide (LiO) and several metallic contaminant elements such as chromium (Cr), copper (Cu), and iron (Fe).

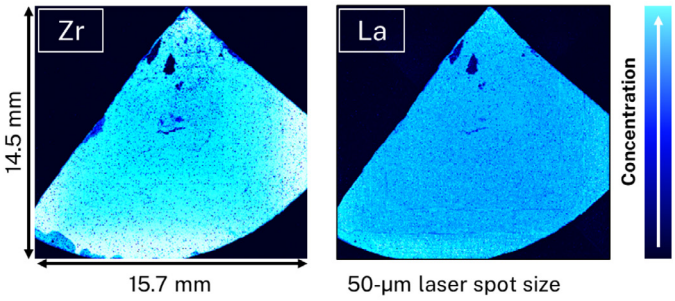

Figure 3. Mapping results acquired by the MASSBOX LALI-TOF-MS on a LLZO solid-state electrolyte sample. The analysis area is 15.7 mm by 14.5 mm with a 50-micron laser spot size. The color scale shows relative concentration of each element with brighter colors indicating higher concentrations. The darkest blue indicates the area outside the sample's boundaries. Dark blue areas within the sample boundaries identify defects with very low concentrations of matrix elements, Zr and La.

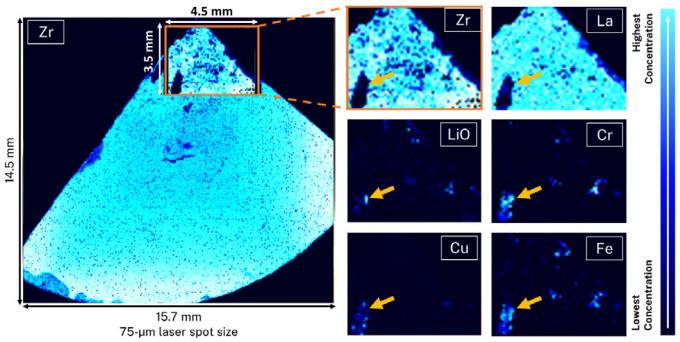

Figure 4. Mapping results acquired with a second scan over the sample's top portion to investigate the defect's composition. The smaller analytical area is 4.5 mm by 3.5 mm with a 75-micron laser spot size. The arrow indicates the defect with low concentrations of matrix elements, Zr and La, and high concentrations of LiO, Cr, Cu, and Fe.

3D elemental mapping

To understand the failure of battery materials after cycling, it is important to determine how deep the failure or contamination penetrates. Figure 5 shows an example of repeat analyses over the same sample. This LLZO solid-state electrolyte sample was analyzed with a 14.5 mm by 13.3 mm raster area with a 50-micron laser spot size. The analysis was repeated three times and Figure 5 shows the resulting map of lithium (Li) concentrations. The researchers expected to see Li on the sample's surface, and this was confirmed with many bright blue areas on the surface map. The researchers also anticipated Li dendrites had formed within the electrolyte below the surface. The second pass demonstrates a decrease in Li concentration compared to the surface map because the sample is a much darker blue. The third pass again shows bright blue spots of high Li concentration, which may be indicative of dendritic growth within the electrolyte as a result of cycling.

Single-spot depth profiles

In addition to repeat elemental mapping, the MASSBOX LALI-TOF-MS also creates depth profiles with single laser spots. Figure 6 shows an example 60-sec laser spot dwell on the same sample in Figure 5.

For reference, the top right corner shows a Zr map from this LLZO sample. The red circle indicates the laser spot. Here, the concentration of the major matrix element, Zr, is relatively low, indicating a potential failure area. Figure 6 shows the signal intensity of Li versus dwell time, which represents the concentration of Li in depth.

Similar to Figure 5, this graph shows relatively high concentrations of Li at the sample's surface (time 0) which initially decrease with depth. At ~25 seconds into the dwell, the spike indicates an abnormally high concentration of Li, which could be a lithium dendrite or plating. Because each laser spot includes a full mass spectrum of data, a spot dwell can reveal how any element of interest changes in depth.

The amount of material removed is dependent on the user-defined laser power and material type. For this sample, a microscope measurement showed the laser removed ~1.8 micron per second, allowing a correlation of the Li spike's occurrence with the depth below the sample's surface.

MASSBOX LALI-TOF-MS summary

This study highlights the MASSBOX LALI-TOF-MS as a versatile technique for elemental analysis throughout the battery lifecycle. It can accelerate new battery chemistry development, process control during electrode manufacturing, and failure analysis during cell testing. It can also verify the quality of material and identify trace impurity elements during mining, processing, and recycling.

MASSBOX LALI-TOF-MS addresses critical needs in materials characterization across the lithium-ion battery value chain through:

- Quantification from lithium to uranium
  - Full quantification of battery and raw materials, from trace to bulk concentrations, determines the origin of contaminants, diagnoses failures, verifies the quality of black mass, and more.
- Elemental mapping
  - Large-scale elemental maps with micron-level resolution provide a comprehensive visualization and spatial distribution of elements within battery and raw material samples.
- Depth profiling
  - 3D elemental maps characterize complex battery materials, locate lithium, and diagnose failures.
- Air-free characterization
  - Analysis performed under vacuum allows accurate characterization of air- and moisture-sensitive materials.

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**