Application note | AN1556

Lithium mapping and depth profiling in battery electrodes

Commercializing next-generation batteries

In the battery industry, the pursuit of enhanced energy efficiency, improved safety, and cost reductions drives the exploration of advanced chemistries and innovative cell geometries. Elemental characterization plays a pivotal role across the battery life cycle. This includes stages from raw material quality control to post-cycling failure analysis. Common techniques for elemental analyses include spectroscopy or mass spectrometry for trace element detection in raw materials and x-ray-based methods for nondestructively characterizing the electrode. Although effective for a variety of use cases, these techniques fail to quantitatively measure how lithium is distributed in a battery electrode, both spatially and in depth.

Characterizing lithium distribution in electrodes is critical for improving the battery's performance, capacity, and lifespan. Understanding lithiation empowers both scientists developing advanced battery chemistries and engineers optimizing electrode geometries. First, it is important to investigate where recoverable lithium is distributed in the electrode and how much of it is nonrecoverable. Then, it is essential to determine if nonrecoverable lithium has developed into the solid electrolyte interface (SEI) layer or may have accumulated into detrimental lithium plating. Approaching the answers to these questions requires a three-dimensional understanding of lithium, other important elements, and lithium species. Until now, no instrument could reliably create elemental maps and depth profiles of lithium in air-sensitive battery electrodes.

Motive

Battery scientists and engineers need to analyze air-sensitive battery electrodes to get a three- dimensional understanding of lithium distribution. Such information informs new battery chemistries, optimized cell geometries, and enhanced failure analysis.

Result

A new technique combining Laser Ablation Laser Ionization (LALI) with Time-of-Flight Mass Spectrometry (TOF-MS) quantitatively measures lithium and other important elements spatially and in depth in a vacuum chamber that accommodates air-sensitive samples.

MASSBOX LALI-TOF-MS

Using Laser Ablation Laser Ionization Time of Flight Mass Spectrometry (LALI-TOF-MS), the EXUM™ MASSBOX™ LALI-TOF Mass Spectrometer overcomes many limitations of raditional spectroscopy and x-ray techniques. Operating under vacuum, it directly analyzes air- and moisture- sensitive solid materials. This compact, desktop solution provides spatial mapping and depth profiling alongside bulk elementa B characterization. Furthermore, its detection abilities include important low-mass elements like lithium, carbon, oxygen, and fluorine that are difficult for traditional instruments to reliably detect at trace levels.

The Massbox uses two lasers to first ablate, or release material from a solid sample's surface and then ionize neutral particles. The ablation laser enables direct analysis of solid materials without the need for complex sample preparation. By targeting neutral particles, the ionization laser ensures more representative results and reduces sample matrix effects, enhancing elemental verification. The TOF C mass analyzer generates a comprehensive mass spectrum, allowing users to investigate every detected element at each laser spot. The software verifies each element based on naturally occurring isotope patterns. The MASSBOX's user-friendly software further facilitates interpretation, ensuring that the benefits of this advanced analytical technique are accessible to a wide range of users, regardless of their chemistry background.

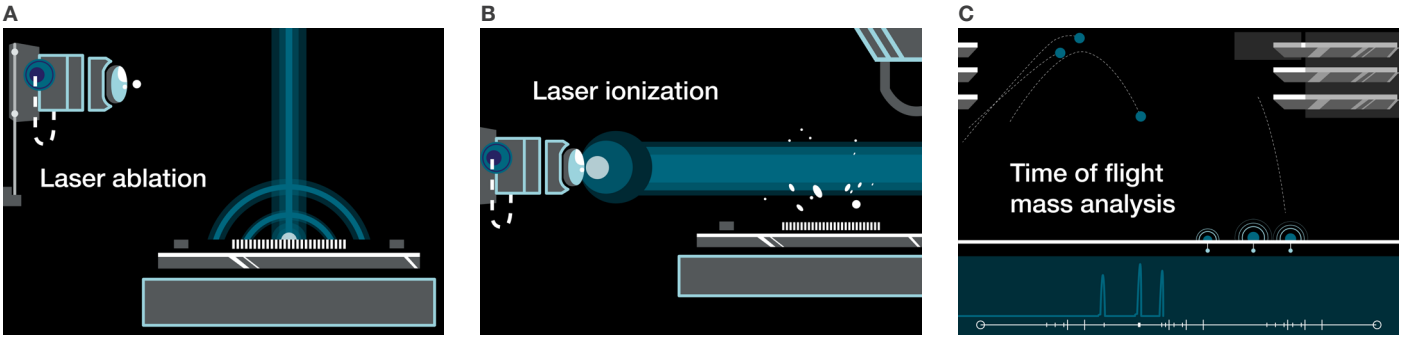

Figure 1. A) Ablation laser fires perpendicular to the sample's surface. The laser spot size is adjustable from 5-200 micron.
B) Secondary laser performs multiphoton ionization of neutral particles created by ablation process.
C) Ions are separated by Time-of-Flight mass spectrometry and detected with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

Testing pristine and cycled silicon anodes

This study involved analyzing a set of pristine and cycled silicon anodes to characterize lithium distribution and identify any other chemical differences between the samples. Figure 2 shows the three samples. The pristine anode had never been assembled into a cell and the two cycled anodes were assembled as half-cells, charged and discharged once, and torn down for this analysis. The two cycled anodes were charged and discharged at different rates.

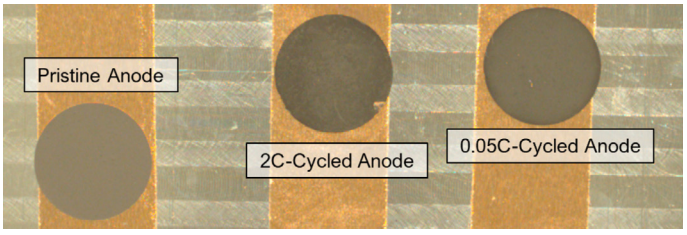

Figure 2. Image of the three study samples taken by the MASSBOX's macro camera.

Pristine anode — This freshly manufactured silicon anode had never been assembled into a cell.

2C-Cycled anode — This silicon anode was charged and discharged at a 2C (fast) rate.

0.05C-Cycled anode — This silicon anode was charged and discharged at a 0.05C (slow) rate.

Elemental mapping results

The MASSBOX LALI-TOF-MS offers detailed areal characterization through elemental mapping. With the ability to analyze areas up to 83 mm by 83 mm and an adjustable spatial resolution ranging from 5-150 microns, the MASSBOX LALI-TOF-MS provides a comprehensive view of elemental distributions. Each laser spot includes a full mass spectrum, allowing users to create maps for any element of interest. The following lithium maps (Figure 3) were acquired on the silicon anode set. On each sample, the MASSBOX LALI-TOF-MS analyzed a relatively large area (4.95 mm by 3.9 mm) with a 50-micron laser spot size. These maps show the distribution of lithium with brighter colors indicating relatively high concentrations.

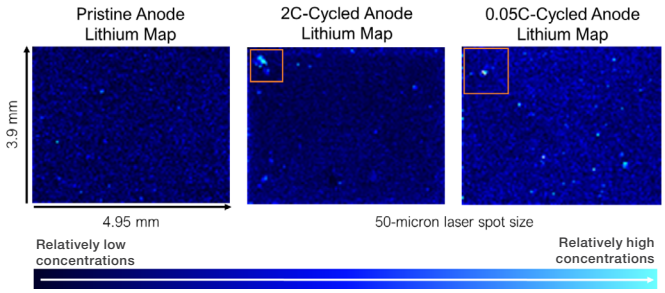

Figure 3. Lithium maps acquired on a set of silicon anodes. Bright blues indicate areas of relatively high lithium concentrations on the cycled anodes. Ideally, cycled anodes will lithiate evenly, and it is important to investigate areas of lithium accumulation as potential failure sites.

To further characterize areas of high lithium concentrations on the cycled anodes, we performed higher resolution maps with a 30-micron ablation laser spot size. Compared to the slower-cycled anode, the 2C-Cycled Anode had larger areas of high lithium accumulation which correspond with much lower relative concentrations of silicon.

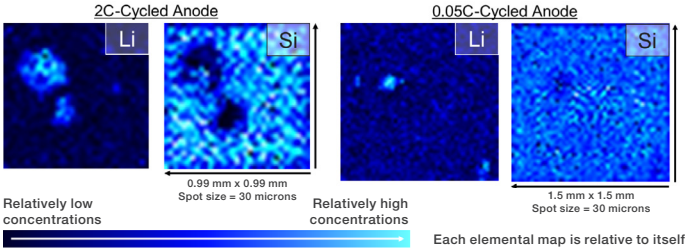

Figure 4. The left set of maps were acquired on a 0.99-mm-by-0.99-mm area on the 2C-Cycled Anode. The right set of maps were from a 1.5-mm-by-1.5-mm area on the 0.05C-Cycled Anode.

Investigating lithium distribution

As anticipated, the lithium map on the Pristine Anode shown in Figure 3 is homogeneous without large accumulations of lithium. In contrast, the large lithium maps on the cycled anodes contain bright blue “hot spots” indicating areas of high lithium concentration.

Further investigation of the bright blue areas shown in Figure 4 revealed distinct differences between the two charge rates. On the 0.05C-Cycled Anode, areas of high lithium accumulation of ~100 microns correspond to slightly lower silicon concentrations. On the 2C-Cycled Anode, the areas of high lithium are greater than 200 microns in size. It is important to characterize areas of heterogeneous lithiation as they may lead to metallic lithium plating or other failure mechanisms.

Measuring the distribution of lithium within electrodes is also important for understanding lithium ion behavior during charge and discharge cycles and characterizing the solid electrolyte interphase (SEI) layers. Ultimately, understanding lithium distribution is critical for optimizing battery performance, capacity, and lifespan.

Depth profiling lithium and lithium species

To characterize elemental distributions with depth, the MASSBOX LALI-TOF-MS creates depth profiles with single laser spots or 3D elemental maps. Figure 5 includes single-spot depth profiles from the three silicon anodes. The profile was acquired using a 75-micron laser spot. The amount of material removed per second depends on the material type and the user-defined laser power. Figure 6 shows the depth profile of copper on the Pristine Anode. Copper’s signal increased significantly ~49 seconds into the dwell, which indicates the laser fully penetrated the silicon anode and struck the copper current collector.

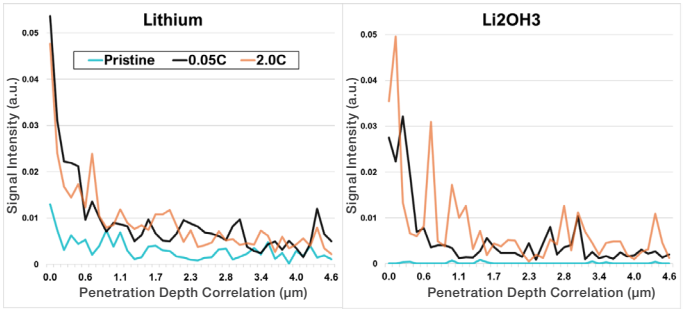

Figure 5. Depth profiles of lithium and a lithium species created using a 75-micron laser spot dwell on the three silicon anodes. Data points are the average of five laser spots, showing the signal intensity per second of dwelling and removing material. The amount of material removed per second was calibrated by measuring the laser spot’s penetration depth with a microscope.

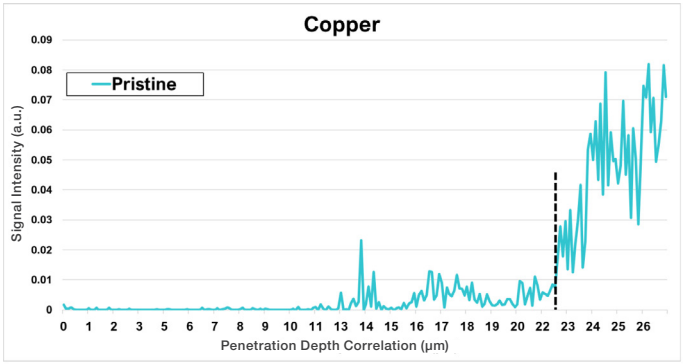

Figure 6. Depth profile of copper created using a 75-micron laser spot dwell on the Pristine Anode. Data points are the average of five laser spots, showing the signal intensity per second of dwelling and removing material. The amount of material removed per second was calibrated by measuring the laser spot’s penetration depth with a microscope. The dotted horizontal line indicates where the laser penetrated the silicon anode and struck the copper current collector.

A microscope measurement of the spot dwell crater showed the laser removed ~0.455 microns per second, allowing for a depth correlation. Figure 6 shows the sharp increase in copper (associated with the anode’s current collector) occurred at a depth of ~22 microns. Because the anticipated anode thickness is ~20 microns, this validated the depth correlation.

For both cycled anodes, the mass spectra revealed relatively high concentrations of both elemental lithium and lithium species that are likely a function of electrolyte decomposition (e.g., Li2OH3). The MASSBOX’s LALI technique is designed to break materials down to their elemental constituents. In complex matrices like cycled battery electrodes, the resulting mass spectra often contain high signals of lithium species Investigating both the elemental lithium and the lithium species is valuable for determining the source of lithium.

As shown in Figure 5, both lithium and the lithium species are highest on the cycled anodes’ surfaces, then decrease to less than 20% of their peaks within one micron below the surface.

Comparing the amount of lithium in the cycled anodes to that of the pristine anode helps determine the amount of nonrecoverable lithium after a charge and discharge cycle.

MASSBOX LALI-TOF-MS SUMMARY

Traditionally, lithium 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, depth profiling, and quantifying lithium in battery materials. The MASSBOX LALI-TOF-MS's innovative LALI technique allows detection of lithium in trace (i.e., 100s of parts-per-billion) levels. By mapping lithium and other elements of the periodic table simultaneously, users can determine whether high lithium accumulations are associated with metallic lithium (i.e., plating), electrolyte decomposition, or the SEI layer. In this study, the MASSBOX LALI-TOF-MS pinpointed areas of high lithium accumulation on cycled anodes' surface layers. Then, depth profiles showed vertical distributions of lithium and lithium species likely associated with electrolyte decomposition. Such information is critical for optimizing the performance of new electrode materials, like silicon, and characterizing failure mechanisms.

The MASSBOX LALI-TOF-MS advances users' understanding of lithium behavior within battery electrodes to set the stage for transformative improvements in battery design and lifecycle management. Its compact package, streamlined operations, and user-friendly software enhance accessibility. The MASSBOX LALI-TOF-MS operates under vacuum and features an advanced air-free transfer system, ensuring that lithium and other reactive materials can be analyzed without exposure to the atmosphere. This capability is crucial for preventing atmospheric reactions, preserving the integrity of the sample for accurate elemental analysis. Decreasing the time required for battery researchers and developers to characterize lithium behavior in electrodes accelerates research and product development cycles. In addition to the capabilities presented here, the MASSBOX LALI-TOF-MS provides quantitative analysis and rapid screening for quality control and quality assurance.

Elemental mapping

Depth profiling

Rapid screening

Quantitative analysis

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