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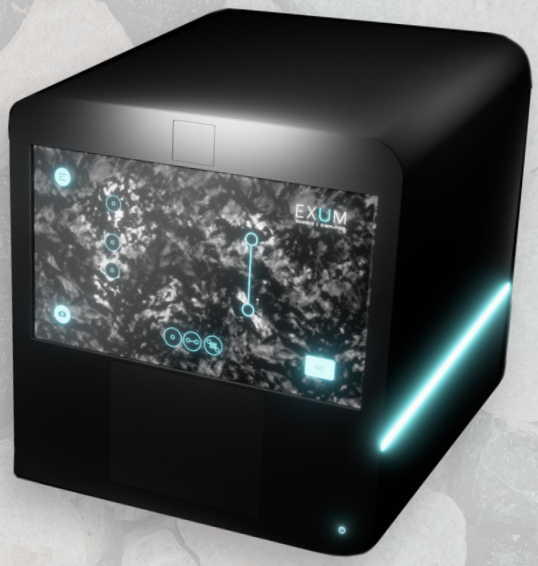
Chemical Mapping with the Massbox for Battery Applications and Beyond



The Massbox is the first commercial Laser Ablation Laser Ionization Time of Flight Mass Spectrometer (LALI-TOF-MS), which combines low detection limits with low-cost, uncomplicated operations. This work demonstrates the Massbox's imaging capabilities on materials used in batteries. We analyzed two garnet $Li_7La_3Zr_2O_{12}$ samples (LLZO) through chemical mapping, which identifies compositional changes of major and trace elements. In one analytical session, the Massbox simultaneously determined elements that span a mass range from ^{7}Li to ^{155}LaO. For these detected elements, the concentrations ranged from high weight percent to trace levels.

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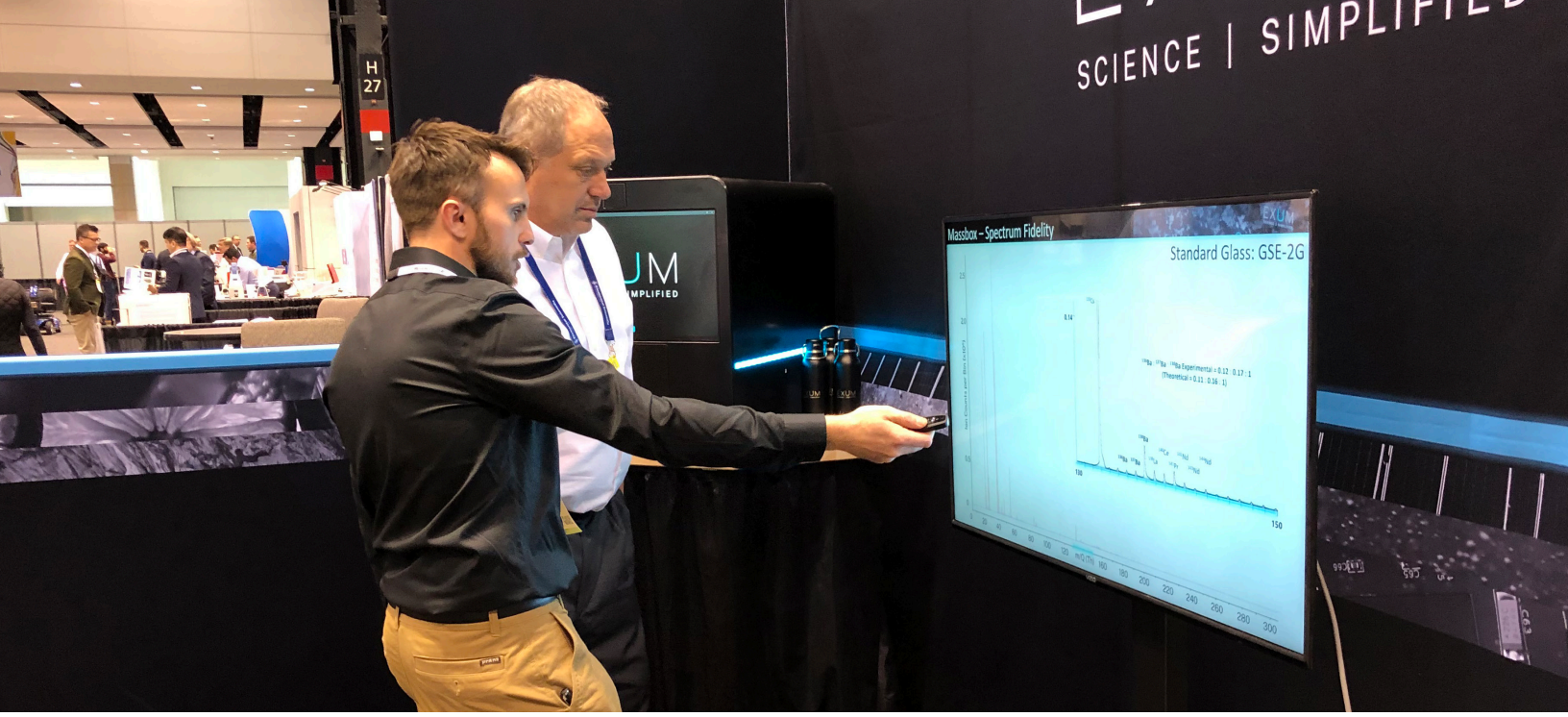
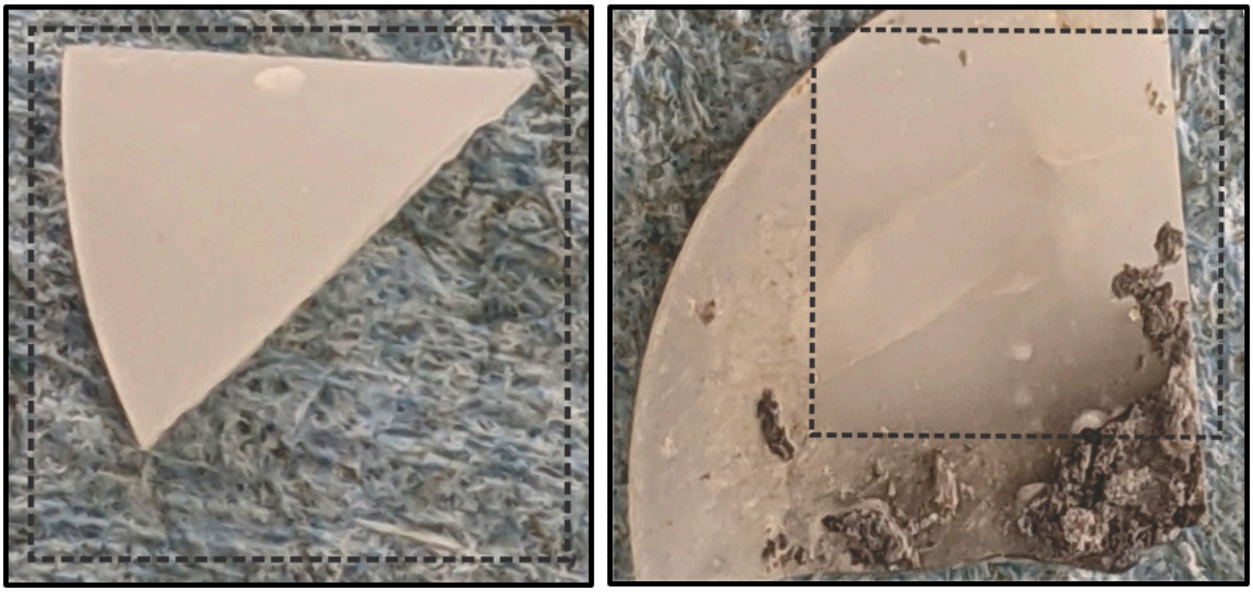


Introduction

LLZO is a material that can be used in lithium-ion batteries, and understanding its chemical composition is important to ensure its performance. By identifying any irregular dispersion of major or trace elements, researchers can classify failure mechanisms. Although this specific study focuses on battery materials, multielement chemical mapping can benefit a variety of applications, which may range from biological tissues to deposit-filled rocks.



LALI-TOF-MS

LALI incorporates two lasers to first ablate (or desorb, in the case of organics) material from the solid sample's surface and then ionize that material in a second step. By analyzing solid samples directly, LALI eliminates the intricate dissolution/digestion sample preparation procedures that complicate other methods. The initial ablation (or desorption) process creates both a temporal plasma and a neutral particle cloud, and the second laser ionizes the neutrals. Compared to other plasma-ionizing techniques, targeting neutral particles greatly reduces the matrix effects.

After ionization, the particles move through the optics system to the Time of Flight (TOF) mass analyzer, which measures the time required for ions of different masses to impact a detector. The resulting measurement creates a full mass spectrum, which facilitates multielement quantitation. Additionally, from ablation to mass analysis, the sample and its representative ions are under vacuum, which improves ion transport efficiency compared to other techniques.

METHOD AND MATERIALS

Researchers provided Exum with two LLZO samples: LLZO-1 is relatively homogenous and LLZO-2 is more heterogeneous. Because the material is air-sensitive, the two samples were sealed in an airtight pouch until they were ready for analysis. We quickly removed the two samples from the pouch and loaded them into the Massbox's sample tray. After the sample chamber closes, the system pumps down to vacuum in a few minutes. From here, we chose ~5.5-mm-by-5.5-mm raster areas across both samples and used an 11-µm laser spot size. On each sample, we analyzed the mapped area twice. The first pass determined elements found on the samples' surfaces, some of which could be surface contaminants. After polishing and removing material, the second pass showed results below the initially-ablated surface material. Each analysis took approximately six hours and generated the spatial distributions for trace and major elements between ^{7}Li to ^{155}LaO. Because the LLZO-1 results were more homogenous than those of LLZO-2, we performed two additional passes to investigate any vertical heterogeneity through depth profiling. Using a larger laser spot size, these additional maps have coarser spatial resolution and required one hour or less to perform.

Results

Figure 1 shows mapping results from LLZO-1's fourth pass. In general, we found oxide species had greater spatial heterogeneity than non-oxides. In this image, the 5-mm-by-5.5-mm mapped area covers the entire sample, including some background material. Each pixel represents one laser-ablated data point of 25 µm. The color scale indicates the measured signal intensity of a particular isotope, ^{155}LaO, with warmer colors designating higher intensities and cooler colors showing lower ones. The results demonstrate higher concentrations of LaO occur on the sample's upper edge and lowest point, which gradually fade to lower concentrations in the sample's middle section. In the figure's bottom right corner, a histogram displays the statistical distribution of these data points. The histogram's x-scale (concentration) is logarithmic, and its y-scale (frequency) is linear. This graph shows the majority of the sample falls in the low-middle (turquoise-blue) range and the distribution is slightly skewed toward the higher intensities. Because the histogram only represents heterogeneity, it does not include any background data points of zero.

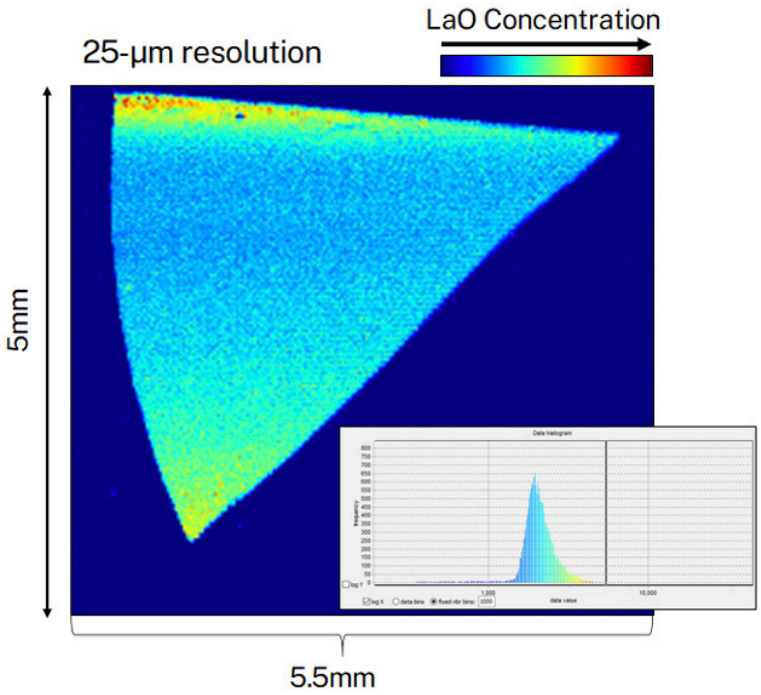


Figure 1: Mapping results from LLZO-1 fourth pass using 25-µm laser spot size. The color scale represents ^{155}LaO signal intensity, with warmer colors designating higher concentrations and cooler colors showing lower. The histogram displays the frequency of the data above background level (0).

Results (cont'd)

For the LLZO-2 heterogeneous sample, Figure 2 compares the surface map to that below the surface. In this figure, the maps show concentrations for three isotopes: ^{27}Al, ^{90}Zr, and ^{139}La. For each, the brighter colors represent higher concentrations and black indicates no concentration. Zirconium and lanthanum are both major matrix elements; however, the researchers were surprised to see such high levels of aluminum on the sample. In the repeat map below the sample's surface, the aluminum intensity was less distributed, and its boundaries were more well defined. We learned this side of the sample was previously adhered to aluminum foil during a prior experiment. This contextual information enlightened the results. The first map's ablation process removed much of the residual aluminum from the sample. As a result, the second map showed higher concentrations of the major matrix elements, zirconium and lanthanum, with the residual aluminum confined to a few discrete areas, primarily along the sample's edges.

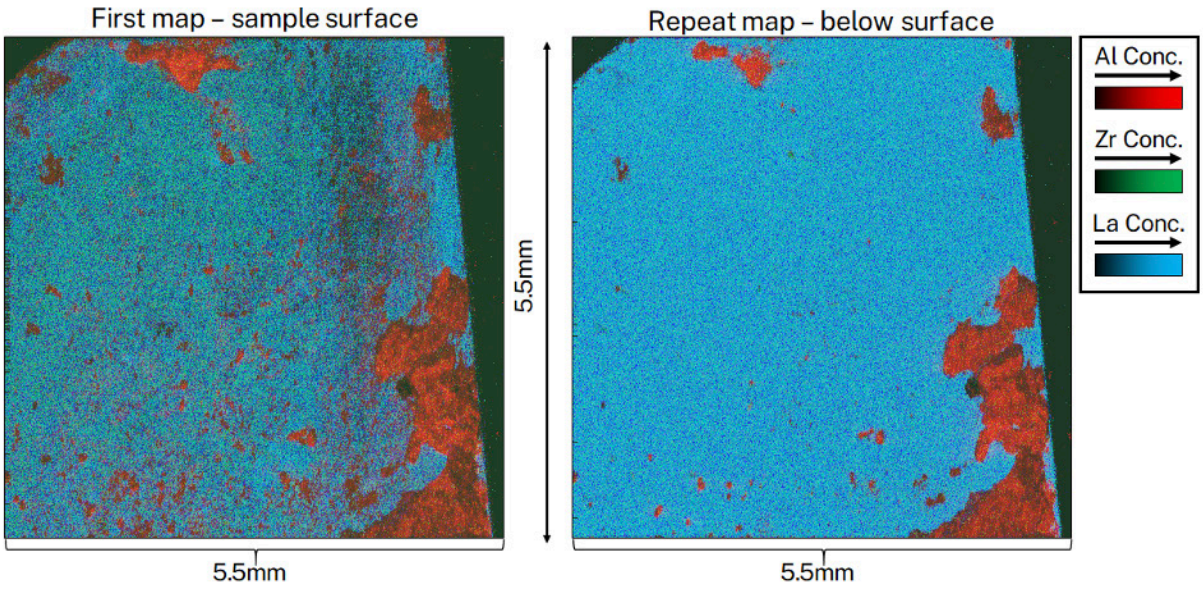
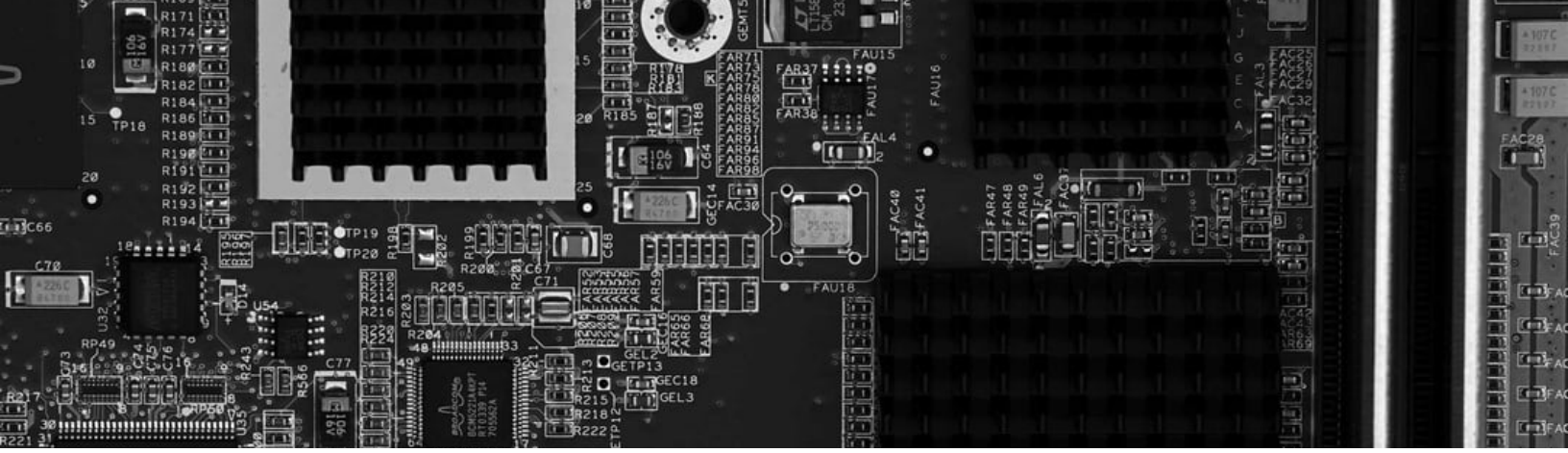


Figure 2: Mapping results from LLZO-2 first and second passes using 11-µm laser spot size. The color scales represent concentrations of three different isotopes: ^{27}Al, ^{90}Zr, and ^{139}La. The first map (left) includes results from the initial analysis on the sample's surface, and the repeat map (right) shows results below the surface.



Conclusion

With the intuitive operations of its all-in-one system, the Massbox is the ideal instrument for multielement chemical mapping applications. For trace and major elements spanning the mass range from ^{7}Li past ^{155}LaO, the Massbox generates micron-resolution maps within a single analytical session. In a few hours, these results can identify residual or contaminant material on a samples' surface and determine heterogeneity of matrix elements below the surface. In this study, the materials' compositions are important for lithium-ion battery performance; however, chemical mapping adds value to any application requiring such understanding of spatial and vertical heterogeneity.

The calibration curve shown in Figure 2 plots the average aluminum-normalized boron signal against vol% additive with the error bars representing one standard deviation. With a nearly perfect correlation coefficient of 0.997, results from the hand-mixed samples indicate a 2σ quality control limits of 2.0 +/-1.0 vol% when calculated from the boron-normalized signal and 2.00 +/-0.26 vol% when calculated from average standard deviation of the titanium-normalized signals. The standard deviation of the various sample pellets also indicates differences in homogeneity between samples. As expected, the hand-mixed samples show greater heterogeneity compared to the premixed samples provided. The hand-mixed samples had an average relative standard deviation of 6.5% for titanium-normalized signals, while the two provided samples with 2 vol% additives were much more homogeneous. The two pre-mixed samples had relative standard deviations of 2.6% and 4.3% for titanium-normalized signals, which correlates to an average 2σ quality control limit of 2.00 +/-0.06 vol%.