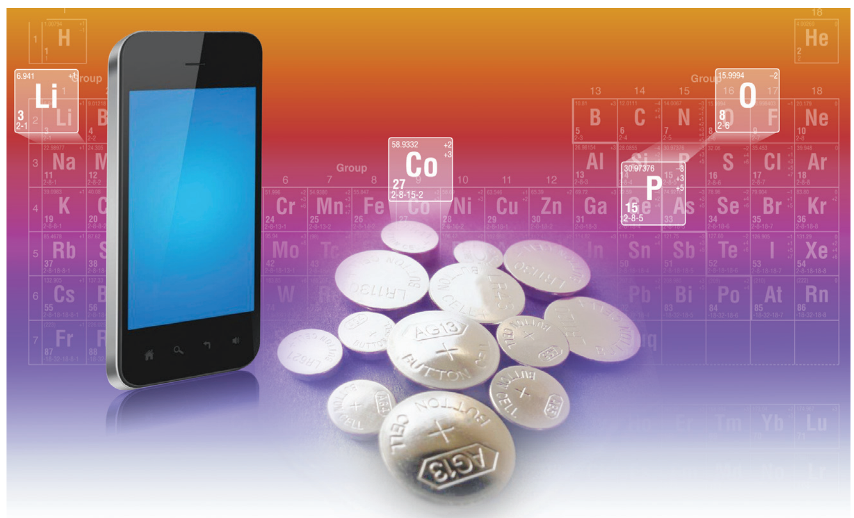
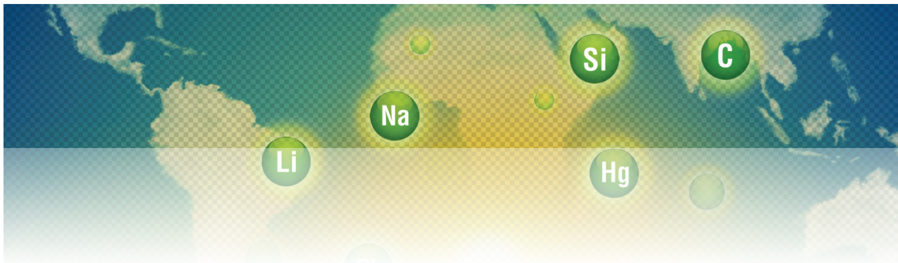
Depth Profile Analysis of Solid State Li-Ion Battery Device by Laser Induced Breakdown Spectroscopy (LIBS)

Introduction

In today's society, electronic devices such as smart phones and tablets are becoming a vital part of daily human activities. These electronics are constantly evolving to deliver a more compact form factor and lighter weight, yet, the power output and battery life requirements have become increasingly demanding. In order to meet these technical challenges, Li-ion battery technology has also advanced to generate higher energy output and provide enhanced cycling performance all while remaining compact and light.



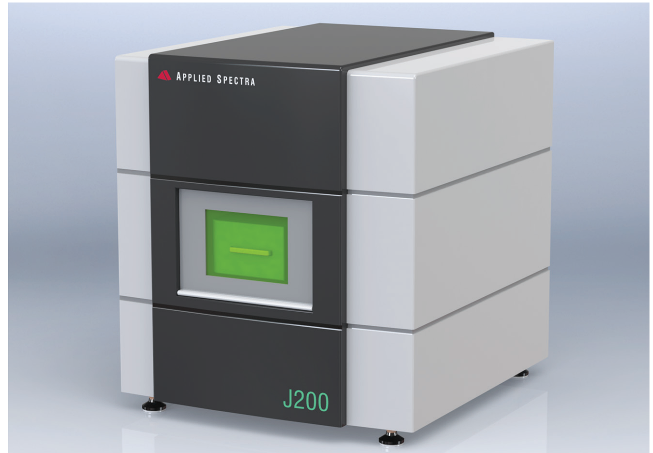
This technical note highlights the ability of Laser Induced Breakdown Spectroscopy (LIBS) to perform depth-profiling analysis of key elements that represent the chemical makeup of important Li-ion battery components. These components include the cathode, anode, and solid-state electrolytes. Typical solution-based elemental analysis techniques, such as ICP-OES and ICP-MS, cannot reveal structural information of these components. XRF, another popular elemental analysis technique, cannot provide elemental coverage for important elements of Li-ion battery electrodes, such as Li, B, C, O, F, and N. Other surface and depth profiling analysis techniques, like SIMS, GD-MS, AES, and XPS, require complex vacuum instrumentation, suffer from low measurement throughput, or are expensive. LIBS offers depth profiling capability for Li-ion battery components in a lab or on a factory floor with excellent throughput. LIBS also has elemental coverage from H – Pu with a large dynamic range (ppm to wt. %)



Operating Parameters

Applied Spectra Inc.'s J200 LIBS Instrument

- 266 nm Nd:YAG laser (ns) and a broadband detector
- Sample chamber with helium or argon gas flow
- ASI Axiom software for instrument operation
- LIBS data analyzed with Applied Spectra Data Analysis Software package



Applied Spectra Inc.'s J200 LIBS System

Sample Analysis

Figure 1 displays the typical device structure of a solid state Li-ion battery. The critical components include the anode, cathode, and solid-state electrolyte. These components are placed in between current collector layers typically made out of metallic film. In addition, the encapsulation layer protects the entire fabricated structure.

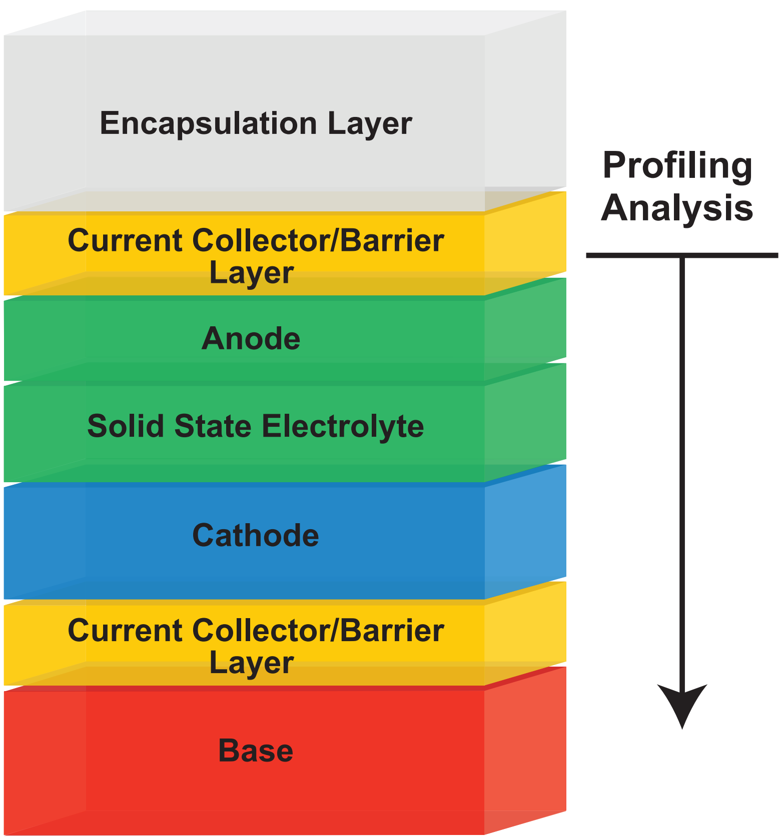


Figure 1. Typical solid-state Li-ion battery device structure.

The lithium ions flow back and forth between the cathode and anode during the charging and discharging cycles, creating electrical power. The solid-state electrolyte facilitates the lithium ion transfer between the cathode and the anode while preventing the cell from short-circuiting. To achieve higher power density and longer lifetime between each charging cycle, different battery component chemistries have been evaluated and developed. The different cathode chemistries includes Lithium Cobalt Oxide ($LiCoO_2$), Lithium Manganese Oxide ($LiMn_2O_4$), and Lithium Iron Phosphate ($LiFePO_4$). Finally, some of the popular chemistries for the solid-state electrolytes include LIPON, Lithium Phosphate (Li_3PO_4), and Lithium Lanthanum Titanium Oxide (LLTO).

For our study, a sample device with the component chemistry of Li metal (anode), LIPON (solid-state electrolyte), and $LiCoO_2$

(cathode) was obtained. Before analysis, the J200 LIBS instrument (in non-detection mode) was used to remove the current collector layer of the component structure shown in Figure 1. The current collector was made out of Ti film and the entire battery device was fabricated on Si base material.

The analyses were carried out using the J200 LIBS instrument with a 266 nm laser. The data was analyzed using ASI's Data Analysis Software. The Li-ion battery sample was analyzed under a helium purged chamber to remove O emission line interference from the atmosphere and to improve the accuracy of the O measurements. The atomic line for each element of interest was monitored for each laser pulse and then plotted. The tracked elements include Li, P, O, Co, Ti, and Si. These elements are primary elements that represent the chemistry of the anode, solid-state electrolytes, cathode, current conductor, and substrate.

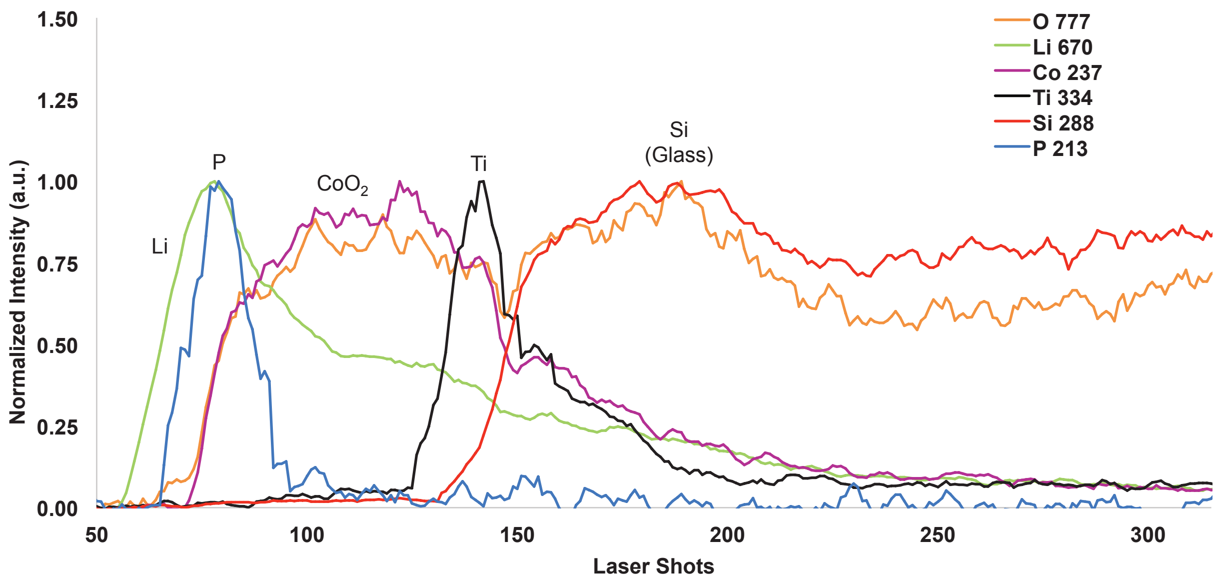


Figure 2. Elemental depth profiling of a Li-ion battery device structure (Li metal anode, LiPON solid-state electrolyte, LiCoO2 cathode, and Ti current collector on top of a glass substrate.)

In Figure 2, it is easy to see when the user has started to ablate the different layers of the battery device by the initial detection of atomic emission lines associated with the characteristic elements of different components. For example, the laser ablation of Li metal anodes will be accompanied by strong Li emission signal. As the ablation proceeds into the LiPON solid-state electrolyte layer, the P emission signal is detected. Similarly, Co and O emission lines can be used to track the ablation of the $LiCoO_2$ cathode layer and to evaluate the relative compositional variation within the cathode layer.

The depth profiling resolution for different Li-ion battery components can be determined by measuring the ablated depth at the beginning of each new layer, and by then counting the number of laser pulses it takes to reach the next layer. The depth profiling resolution in this study ranged from 0.2 to 0.42 mm for the differing component layers.

Table 1. Displays the depth resolution per layer for the Li-Ion battey tested.

Layer	Depth (μm)	Depth per Laser Pulse (μm)
Li metal	2	0.242
LiPON	3	0.429
$LiCoO_2$	20	0.370
Ti	1	0.200
Glass	Core	-

Conclusion

LIBS provides a rapid and cost effective way to understand primary chemistry variation that may exist within different Li-ion battery components due to chemistry change after many charge cycles or drifts in the manufacturing processes. This technology is a fit for high volume QC measurements due to the rapid analysis time. With LIBS it is now possible for Li-ion battery industries to monitor the impact of process variables on key component chemistry all while improving product consistency and yield.