Evaluation of Laser Induced Breakdown Spectroscopy (LIBS) As a Viable Tool for Analyzing Li-Ion Battery Components

C. Derrick Quarles Jr.*, Dayana Oropeza$, Jhanis J. Gonzalez*$, Vassilia Zorba$, and Richard E. Russo*$

Lawrence Berkeley National Laboratory

* Applied Spectra, Inc. Fremont, CA
$ Lawrence Berkeley National Laboratory, Berkeley, CA

Introduction:

The J200 tandem LA – LIBS instrument from Applied Spectra, Inc. provides the unique capability of combining the analytical benefits of both LIBS and LA-ICP-MS. Specifically, LIBS can be used for the analysis of H – Pu, which includes non-metals such as H, N, O, and halogens (e.g. F) that are difficult (or impossible) to analyze in conventional ICP-MS systems. Additionally, LA-ICP-MS complements the LIBS analysis by providing trace elemental and isotopic ratio compositions. This tandem instrument, in combination with a Bruker Aurora Elite ICP-MS, expands the dynamic range of analysis from sub-ppb levels with LA, to % levels with LIBS, while also increasing the elemental coverage (typical ICP-MS elements + H, Ar, He, O, and F detection with LIBS).

The evaluation of LIBS to perform quantitative measurements on battery materials, depth-profiling measurements on solid state batteries, display chemical maps that represent chemical distribution by depth, and ability to acquire quantitative data will be presented. These types of analyses can be useful for new battery design structures, quality control, and to assess potential contamination. 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.

Battery Materials – Quantitative:

Figure 1. LIBS spectrum displaying the detection of Ni, Mn, Co, Ca, and Li. LIBS spectrum was collected from 185 – 1050 nm, but only the spectral regions below were displayed for visual purposes.

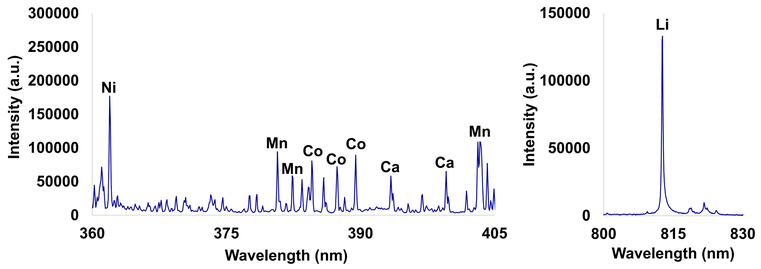


Table 1. Accuracy and precision for the Li, Ni, Co, and Mn multivariate calibration model that was developed using the entire LIBS spectrum. Cathode powders were pressed into 30 mm pellets. The ASI J200 system with a 266 nm laser was used to analyze 9 replicates (3 x 3 grid) per sample with a laser spot size of 200 µm.

	Li		Ni		Co		Mn	
Sample	Multivariate (wt %)	% Bias	Multivariate (wt %)	% Bias	Multivariate (wt %)	% Bias	Multivariate (wt %)	% Bias
2	7.51 ± 0.02	7.9	23.9 ± 0.5	0.5	17.9 ± 0.4	-1.3	17.5 ± 0.3	-1.1
5	7.54 ± 0.04	2.9	42.1 ± 0.2	-0.9	6.07 ± 0.12	1.3	11.1 ± 0.2	2.6

Solid State Batteries – Depth Profiling:

Figure 2. **(Left)** Generic solid state Li-ion Battery structure. **(Right)** LIBS depth profile response for Li, Co, and Si from sample 2. ASI J200 - 266 nm laser at 10 Hz and 4.5 mJ, 400 laser pulses (spectrum from each laser pulse collected), 250 µm spot size, and a 1.0 L/min helium purged sample chamber.

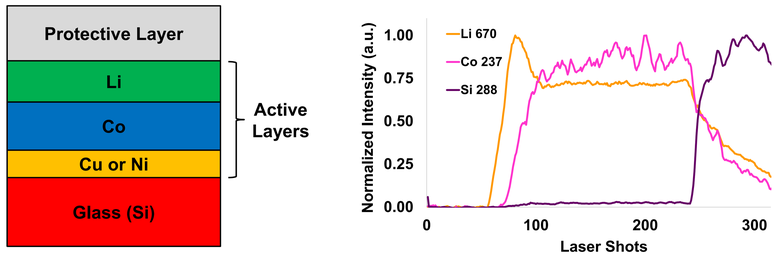


Figure 3. **(Left)** LIBS depth profile response for Li, Co, Cu and Si from sample 1. **(Right)** LIBS depth profile response for O and H. ASI J200 - 266 nm laser at 10 Hz and 4.5 mJ, 400 laser pulses (spectrum from each laser pulse collected), 250 µm spot size, and a 1.0 L/min helium purged sample chamber.

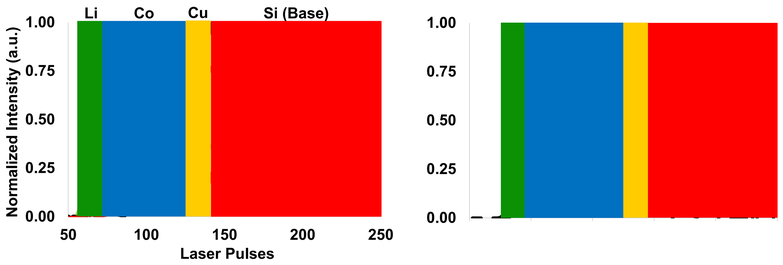


Figure 4. Chemical contour mapping using 266 nm ns laser, 6 channel CCD, 250 µm laser spot size, 400 laser pulses per location, 400 locations (20 x 20 grid), 100 mm2, 0.5 mm spacing. Maps display the Li signal at 50, 100, 150, 200, 250, and 300 laser pulses.

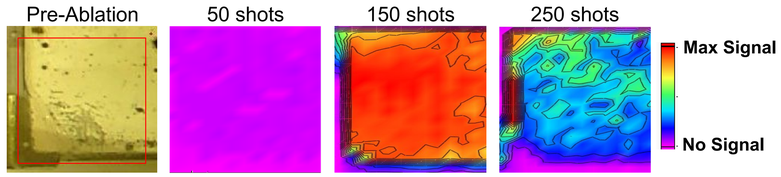


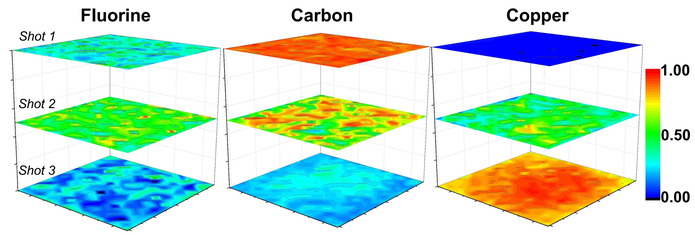
Table 2. Depth measurements for solid state Li-ion batteries.

	Sample 1		Sample 2		Sample 3	
Layer	Depth* (µm)	Depth per Laser Pulse (µm)	Depth* (µm)	Depth per Laser Pulse (µm)	Depth* (µm)	Depth per Laser Pulse (µm)
Film	60	1.09	60	1.07	60	1.07
Li	2	0.242	2	0.265	2	0.222
Li-O	3	0.429	3	0.429	4	0.444
$LiCoO_2$	20	0.370	60	0.367	50	0.391
Cu or Ni	1	0.200	2	0.200	2	0.200

* Depth measured with a Zygo Microscope (white light interferometric).

Cathode/Anode – Chemical Mapping:

Figure 5 Effect of mixing time on binder distribution from lithium battery anode samples. The fluorine (F 685.6 nm), carbon (C 247.9 nm), and copper (Cu 324.7 nm) distribution in a graphite anode were measured using ASI's J200 LIBS instrument equipped with a 266 nm laser and a multi-channel broadband detector that covers a spectral window of 185 – 1050 nm. Displayed below are the elemental maps from a sample that was mixed for 52 minutes (88.78 % graphite, 3.07 % AB, and 8.20 % PVDF). A 4 mm^2 area was sampled using a 18 x 18 grid with a 40 µm laser spot size.



Conclusions:

- The ASI J200 LIBS system provides the ability to perform quantitative measurements on raw materials in powder form or pressed pellets.
- ASI's data analysis software package allows for easy development of multivariate calibration curves based on full LIBS spectra.
- Multivariate calibration model resulted in good accuracy (-1.3 – 7.9 %) and precision (0.3 – 2.2 %) for Li, Co, Ni, and Mn.
- LIBS allows for fast data collection and processing (seconds – minutes).
- LIBS provides a fast depth profiling tool that can detect elements that are difficult by traditional techniques such as F, H, N, and O.
- Depth resolution for these solid state Li-ion batteries resulted in an ablation rate of 200 – 450 nm per laser pulse.
- Chemical maps provide information about the quality of the finished battery product.
- ASI's Data Analysis software allows fast elemental mapping of both LIBS and LA-ICP-MS data.

ASI J200 Tandem LA – LIBS System
266 nm ns laser with a 6 channel CCD

All data was collected using the J200 LIBS Instrument with Axiom Software from Applied Spectra, Inc.

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