Depth Profiling Analysis of Li-Ion Batteries by Laser Induced Breakdown Spectroscopy (LIBS) and Laser Ablation-Inductively Coupled Plasma-Mass Spectrometry (LA-ICP-MS)

Lawrence Berkeley National Laboratory

C. Derrick Quarles Jr.*, Jhanis J. Gonzalez*$, and Richard E. Russo*$

* Applied Spectra, Inc. Fremont, CA

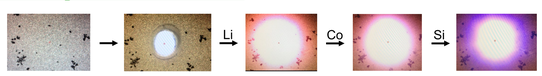
$ Lawrence Berkeley National Laboratory, Berkeley, CA

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 be analyzed 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 Analytik Jena PlasmaQuant® MS 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 and LA-ICP-MS to perform depth-profiling measurements on solid state batteries, display chemical maps that represent chemical distribution by depth, and ability to acquire quantitative data is 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.

LIBS – Depth Profile:



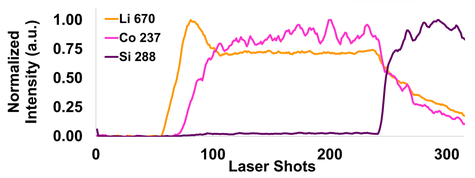


Figure 1. Example of a LIBS spectrum from a solid state Li-ion battery analysis.

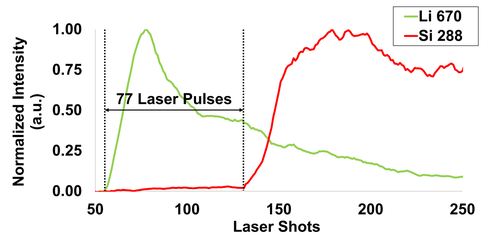


Figure 2. Illustration of how a layer in a sample is measured using the LIBS response. Li signal starts the layer and the Si signal represents the end of that layer.

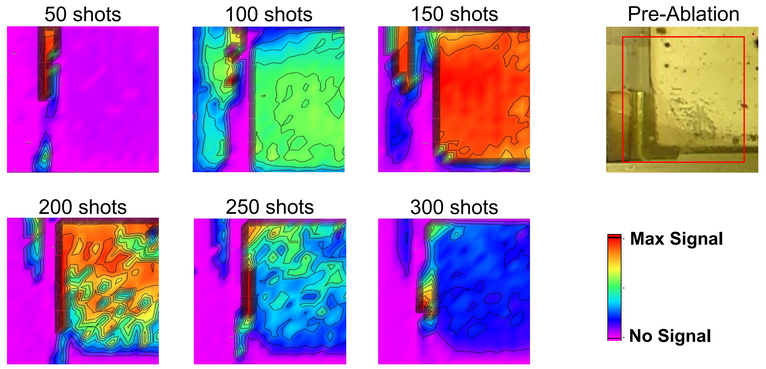
Table 1. Depth measurements for solid state Li-ion batteries.

Layer	Sample 1		Sample 2		Sample 3	
	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).

LIBS – Depth Profile Surface Maps:

Figure 3. 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 response at 50, 100, 150, 200, 250, and 300 laser pulses.



Tandem LA-ICP-MS and LIBS – Depth Profile:

Figure 4. LIBS depth profile response **(Left)** for Li, Co, Cu and Si. Generic solid state Li-ion battery structure **(Right)**. Method Conditions: 266 nm laser at 10 Hz and 6.0 mJ, 250 laser pulses (spectrum from each laser pulse collected), and a 250 µm spot size.

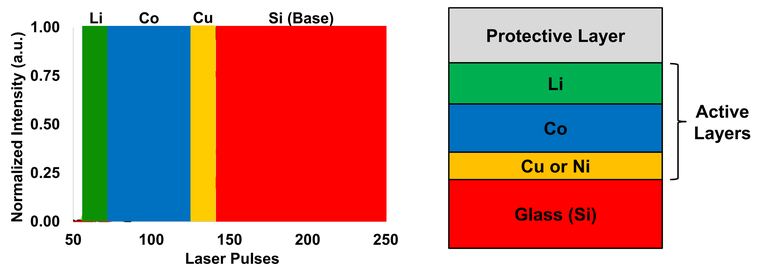
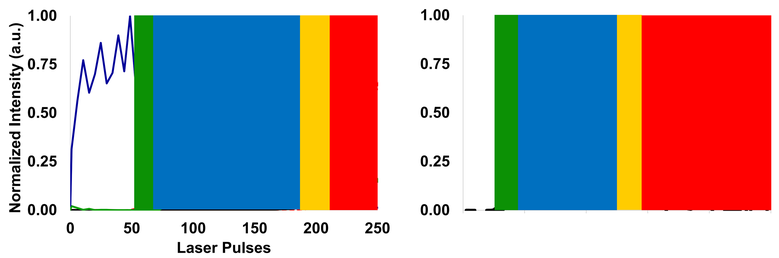


Figure 5. **(Left)** LA-ICP-MS depth response for Al, Ni, Zr, and Sb. **(Right)** LIBS depth response for O and H.



LA-ICP-MS:

Table 2. Semi-quantitative analysis using ASI J200 Tandem LA – LIBS instrument in combination with Analytik Jena PlasmaQuant® Elite MS ICP-MS. Since no Li-ion battery standard was available, NIST SRMs 610 – 614 (trace metals in glass) were used to create the calibration curve for the subsequent semi-quantitative analysis. Samples A, B, and C were analyzed for Al, Ca, Cr, Fe, Zn, Ga, Sr, Zr, Nb, and Sb.

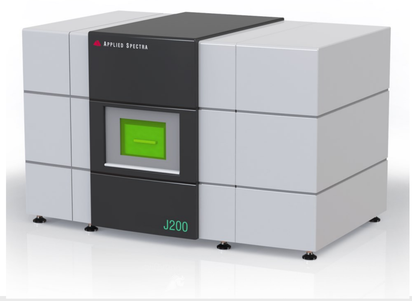
		Concentration Detected (ppm)								
Layers	Sample	^{27}Al	^{44}Ca	^{52}Cr	^{57}Fe	^{66}Zn	^{71}Ga	^{88}Sr	^{90}Zr	^{121}Sb
Protective	A		7642	162		706				549
	B		8576	176		148				545
	C		8141	168		180				515
Li	A	25458	13636	374			8.6	17		
	B	25421	13168	417			2.4	15		
	C	24049	13216	364			9.3	17		
Co	A			665				19	42	
	B			368				16	233	
	C			401				16	30	
Cu	A			1566	291					
	B			330	0.33					
	C			686	0.13					

Conclusions:

- The ASI tandem J200 LA – LIBS system provides the ability to perform simultaneous LA-ICP-MS and LIBS measurements.
- LIBS allows for fast data collection and processing (seconds – minutes).
- LIBS provides a fast depth profiling tool and provides detection for elements that are more difficult such as F, H, N, and O.
- LA-ICP-MS provides the ability to detect contaminants or additives that may be in low concentrations.
- Depth resolution 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.

Analytik Jena PlasmaQuant® MS Elite ICP-MS

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



All data wascollected using the J200 Tandem LA – LIBS Instrument with Axiom Software from Applied Spectra, Inc. in combination with Analytik Jena PlasmaQuant® MS Elite ICP-MS.

Acknowledgements:

Thank you to Analytik Jena for supplying the PlasmaQuant® MS Elite ICP-MS instrument that is being used at the ASI facility.

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