



2015 DOE Vehicle Technologies Annual Merit Review

# ***Real-time Metrology for Li-ion Battery R&D and Manufacturing***

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**Applied Spectra, Inc**

**Project ID: ES206**



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# Overview

## Timeline

<b>Project Start</b>	06/28/2012 (Phase I) 08/14/2013 (Phase II)
<b>Project End</b>	08/14/2015
<b>Percent Complete</b>	87%

## Budget

<b>Total Project Funding</b>	\$1,149,879
<b>Funding Received</b>	\$149,948 (Phase I) (6/2012 – 6/2013) \$832,500 (Phase II to date) (8/2013 – 4/2015)
<b>Funding Expected</b>	\$167,500 (thru 8/2015)

## Barriers/Targets

- **Cost efficiency:** The developed LIBS instrument needs to be cost-effective for routine Li-ion battery material analysis.
- **Applications:** The developed LIBS instrument must address a wide range of Li ion battery chemistry and new materials.

## Partners

- Dr. Vasillia Zorba, Lawrence Berkeley National Laboratory

# Relevance/Objective

## *Real-time Metrology for Li-ion Battery R&D and Manufacturing*



## Objectives

- ❑ Develop **LIBS (Laser Induced Breakdown Spectroscopy)** for chemical composition characterization of Li ion battery materials and components
- ❑ Design *cost effective LIBS* instrument to perform rapid chemical QC for battery manufacturing processes.
- ❑ Enable a wide range of Li ion battery component analysis applications to help the industry to accelerate new material development and to improve manufacturing process.

## Addressed Targets

- ❑ Use of innovative spectroscopic technique to understand the effect of battery material composition on battery performance and failure.
- ❑ Li ion battery material QC to improve manufacturing yield and consistency.

# Project Milestones



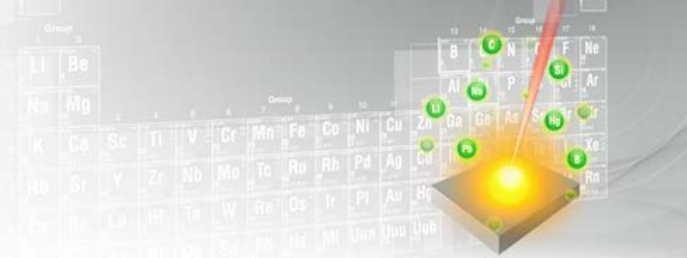
Month/Year	Milestone or Go or No-Go Decision
<b>Sep-2012</b>	Experimental LIBS setup comprised on different lasers and detector options - Investigate the feasibility of Li ion battery material applications <b>(Completed)</b>
<b>Nov-2012</b>	Evaluation of optimum LIBS detectors for best quantum efficiency and dispersion characteristics <b>(Completed)</b>
<b>Dec-2012</b>	Development of LIBS data processing software and prototype GUI for data display <b>(Completed)</b>
<b>Mar-2013</b>	Proof-of-concept analysis for Li ion battery cathodes, anodes, electrolytes for primary elemental composition, impurities, and elemental imaging <b>(Completed)</b>
<b>Jun-2013</b>	Phase II Go or No-Go Decision <b>(Passed and Phase II awarded)</b>
<b>Dec-2013</b>	Development of beta-LIBS instrument hardware design for laser sampling control <b>(Initial design completed)</b>
<b>Apr-2014</b>	Optical design optimization - plasma light collection for required sampling method <b>(Initial design completed)</b>



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# Project Milestones

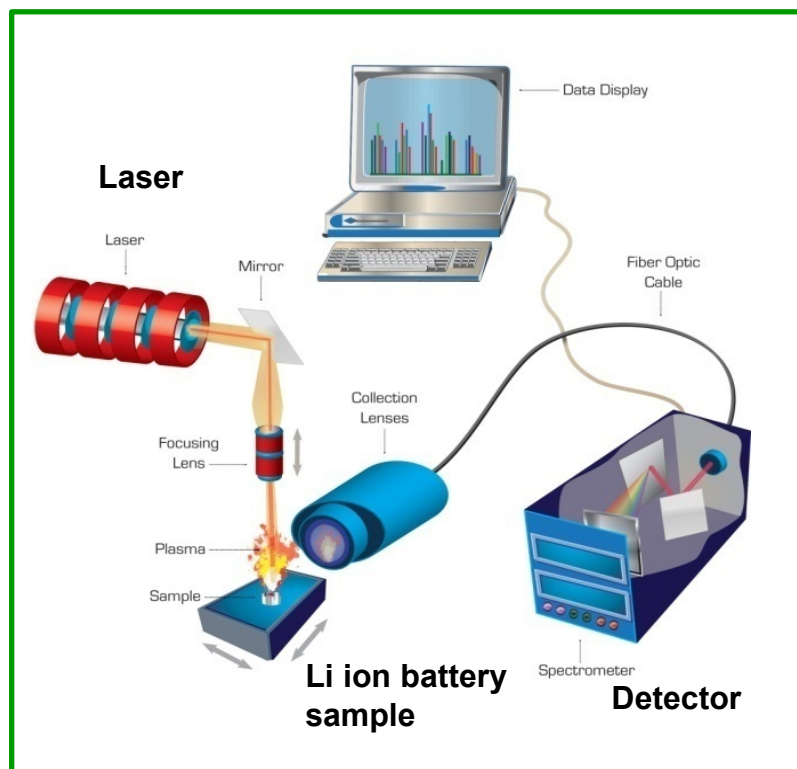


Month/Year	Milestone or Go or No-Go Decision
Sep-2014	Instrument software GUI and data analysis program development – optimized for simple user experience & speed of the analysis (Completed)
Nov-2014	First beta-LIBS instrument for Li ion battery material and component analysis released (Completed)
Jan-2015	LIBS instrument cost reduction program initiated for industry wide adoption (On-going to date)
Mar-2015	Analysis demonstration on the cost-effective instrument platform - electrode raw materials and battery components for primary elemental composition, impurities, and elemental imaging (Completed)
April-2014	<b><i>LIBS instrument installation for initial R&amp;D and industry customers</i></b>
Jun-2014	Development of additional analytical applications to understand electrode and electrolyte chemistry change during battery cycling (On-going till the end of the program)

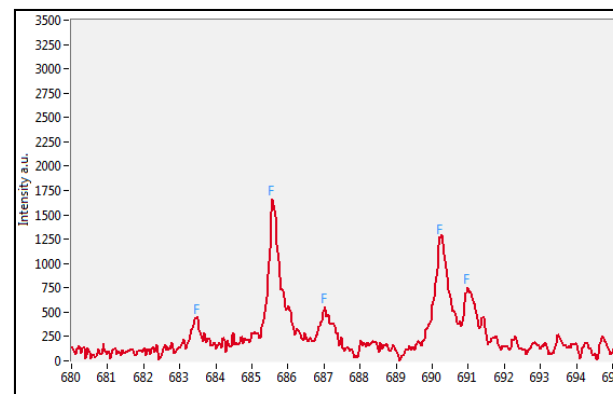
# Approach

## *LIBS Instrument Development for Li-ion battery R&D and Industry*

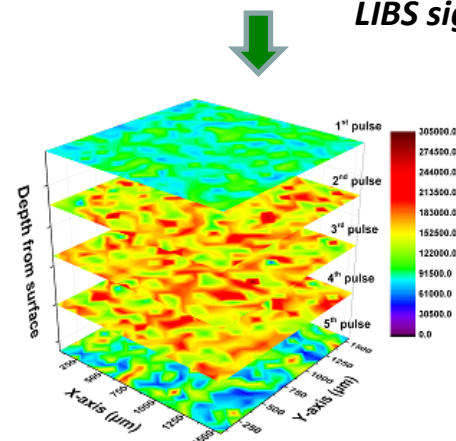
Use light emission generated by laser ablation applied on Li-ion battery materials and components for direct and rapid chemical composition in any environment (e.g. air)



*Technical Concept of LIBS Analysis*



*LIBS signal from PVDF binder*



*Binder distribution imaging in the anode*

# Approach

## *LIBS Instrument Development*



### **LIBS Sampling Flexibility**

- Bulk material analysis
- Micro-analysis
- Spatially resolved analysis
  - Depth profiling
  - Elemental mapping



### **Development of Analytical Applications**

- Raw material analysis
- Fabricated cell components
- Cycled cell modules



### **LIBS Instrument design**

- Optimized detector for required sensitivity
- Practical software GUI
- Speed of data analysis
- Cost efficiency



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# Technical Accomplishment –

*LIBS instrument designed and available for Li-ion battery material analysis*



- **LIBS instrument configuration optimized for Li ion battery raw material and cell component analysis**
  - ☐ Detection sensitivity
  - ☐ Laser beam delivery
- **Development of software GUI for technician level operation**
- **Improvement in data acquisition and analysis speed**
- **Instrument cost reduction achieved**
  - ☐ Significantly lower cost with respect to GD-MS, GD-OES, SIMS, Auger
  - ☐ Lower operating cost with respect to ICP-OES & ICP-MS



J200 LIBS Instrument  
for Li-ion battery material  
analysis



# Technical Accomplishment –

## *Initial Customer Adoption & Growing Applications*

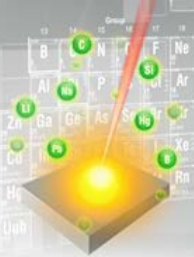


- ***Customer adoption of LIBS instrument***
  - ☐ Next generation Li-ion battery chemistry R&D
  - ☐ Raw material composition analysis for battery electrodes
  - ☐ Solid state electrolyte analysis in the Li-ion battery cell
- Other applications evaluated and demonstrated:
  - ☐ Binder distribution in the battery electrode
  - ☐ Conductive distribution analysis
  - ☐ Elemental depth profiling QC for the Li-ion battery cell
  - ☐ Cell component thickness QC
  - ☐ Solid electrolyte composition analysis
  - ☐ Metal contamination on the electrode surface

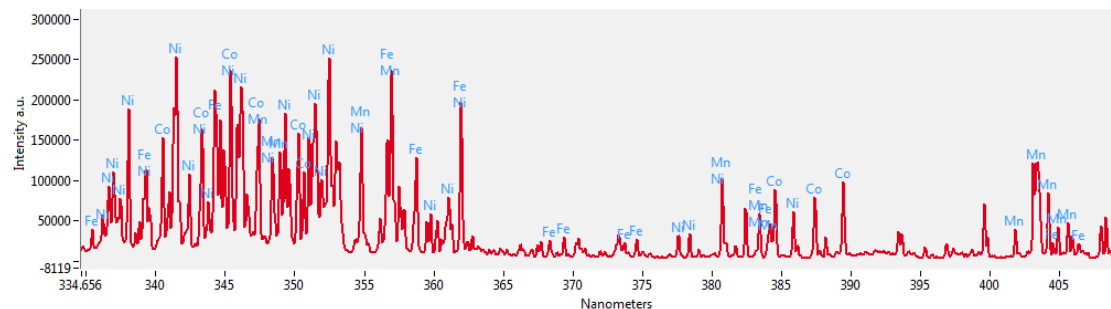


# Technical Accomplishment –

## *Rapid QC of incoming raw electrode materials*



*Raw NMC cathode powders into pellets*



*LIBS spectra with emission lines of key elements in raw cathode (NMC) materials*

Sample #	Li		Ni		Co		Mn	
	LIBS conc (wt %)	% Bias	LIBS conc (wt %)	% Bias	LIBS conc (wt %)	% Bias	LIBS conc (wt %)	% Bias
Sample #1	7.51 ± 0.02	7.9	23.91 ± 0.52	0.5	17.86 ± 0.41	-1.3	17.45 ± 0.32	-1.1
Sample #2	7.54 ± 0.04	2.9	42.10 ± 0.19	-0.9	6.07 ± 0.12	1.3	11.08 ± 0.17	2.6

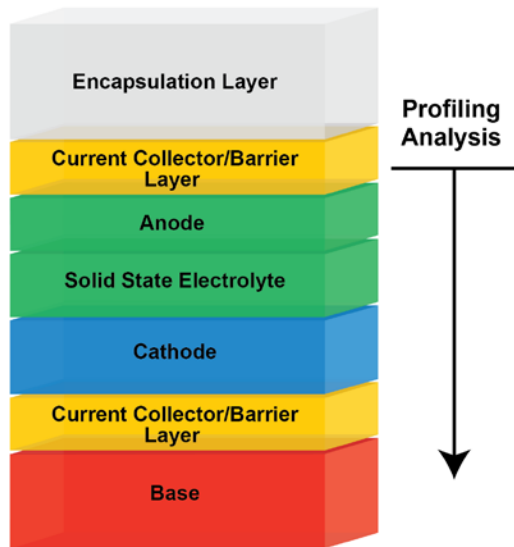
*Excellent correlation of LIBS composition with ICP-OES result for raw NMC cathode materials*



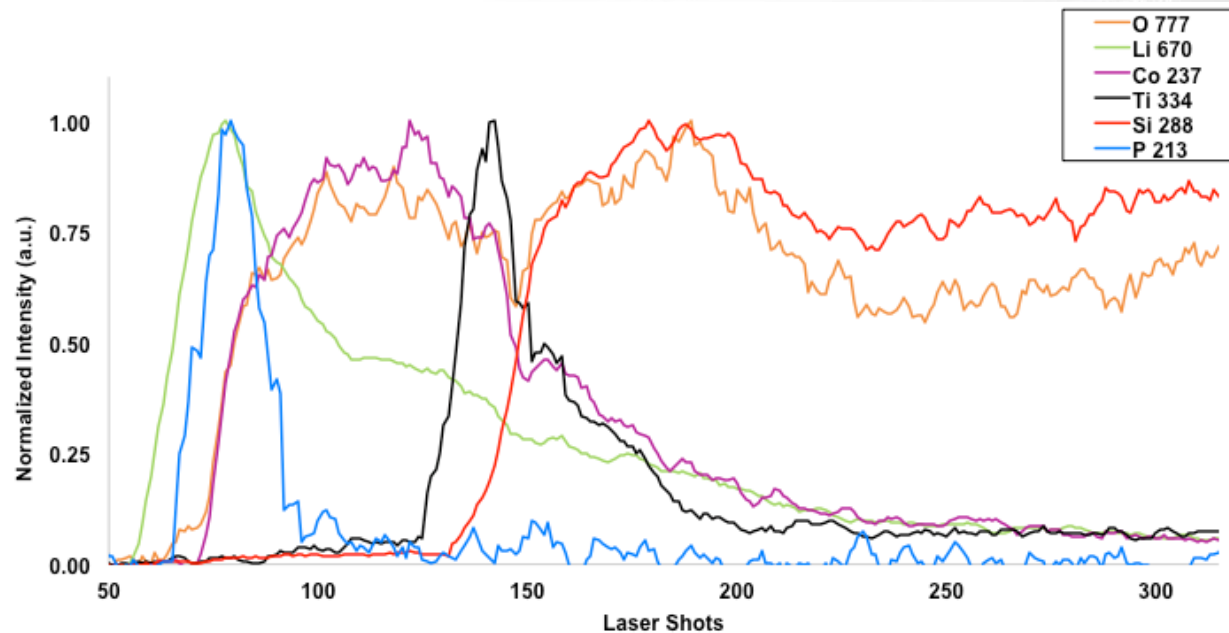
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# Technical Accomplishment –

## *Li-ion battery cell depth profiling*



Typical solid state Li-ion battery structure

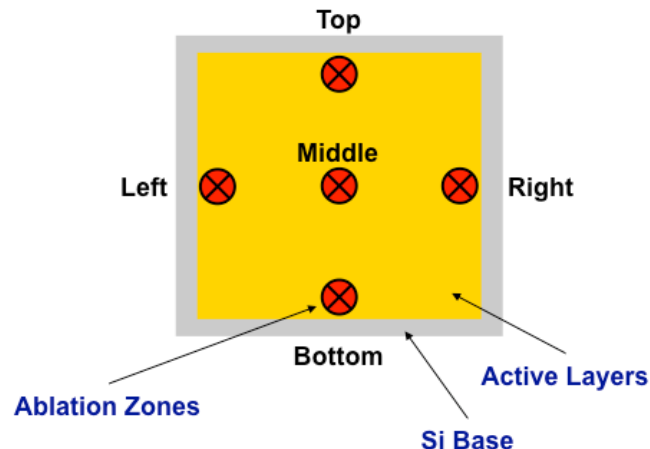
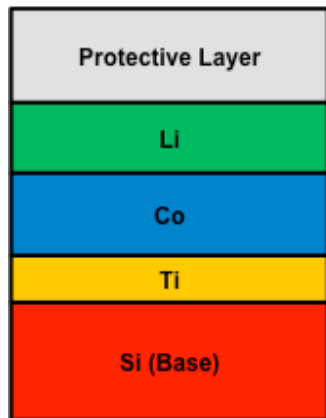


*Elemental Depth profiling of solid state Li-ion battery device structure. Li metal anode, LiPON solid state electrolyte, Ti current collector on top of glass substrate*

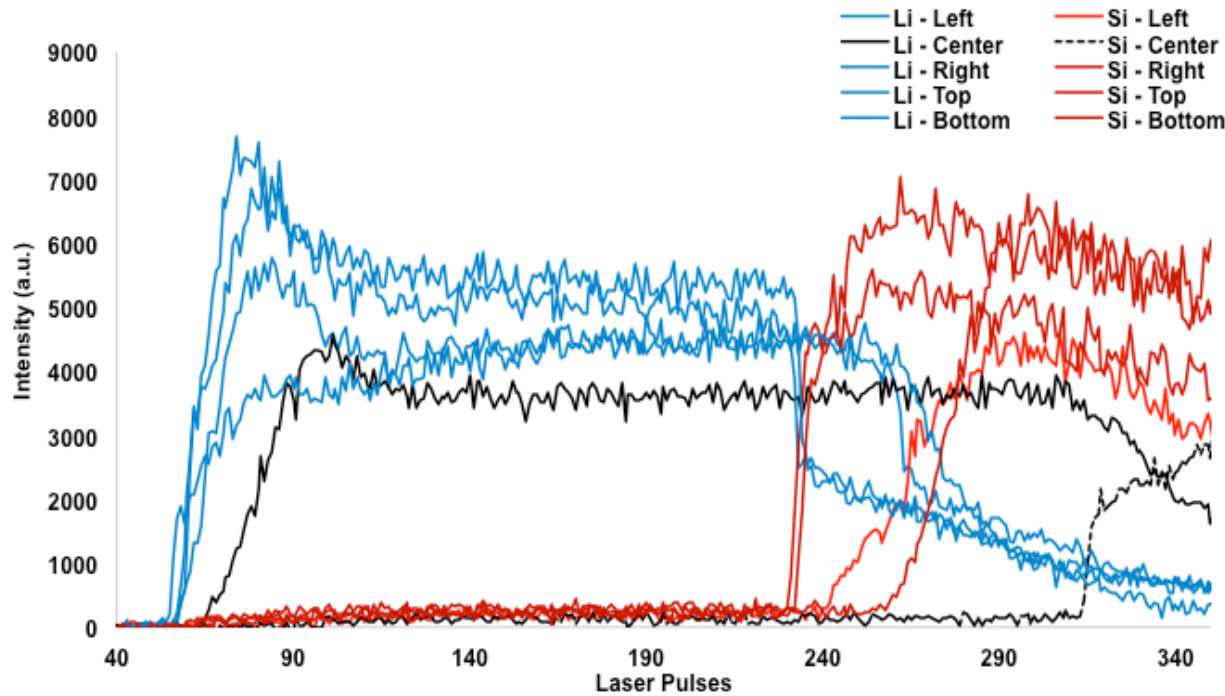
- Monitor key elements in cathode, anode, and solid state electrolytes
- Difficult elements such as Li, C, O, N, and F etc. by conventional techniques such as XRF are monitored quickly by the LIBS instrument.

# Technical Accomplishment –

## *Thickness QC of battery structure*



- Tracking LIBS signal associated with key elements allows determination of thickness consistency for single fabricated cell component or across different battery structures.



- Thickness computing algorithm has been developed based on LIBS depth profiling spectra.
- The estimated thickness measurement correlates well with respect to white-light interferometric microscope data.



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# Technical Accomplishment –

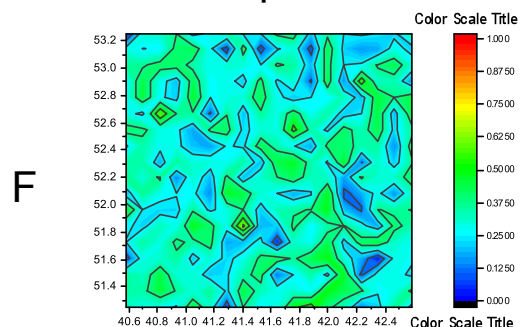
## Anodes: PVDF Binder & Carbon Distribution



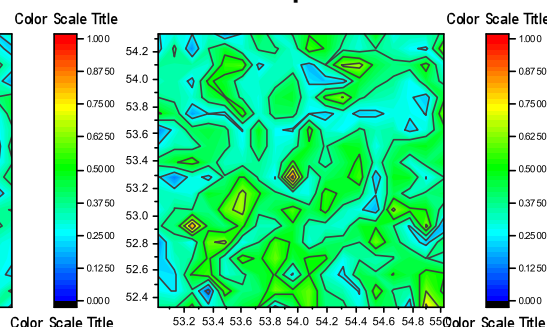
Sample	Graphite conc (%)	AB conc (%)	PVDF conc (%)	1st mixing time (min)	2nd mixing time (min)	Thickness
1	88.78	3.07	8.2	8	4	33
2	88.78	3.07	8.2	8	20	41
3	88.78	3.07	8.2	8	52	40
4	88.78	3.07	8.2	8	120	31

- Same average binder concentration
- Different mixing time
- 2D of binder and carbon for first 30 micron of anode

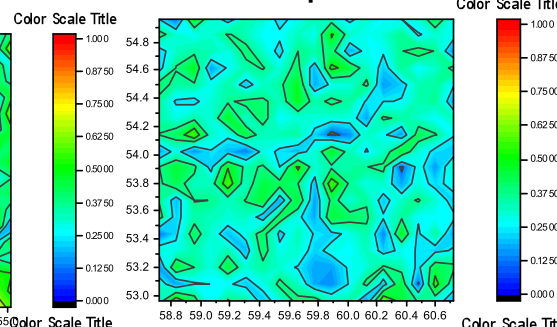
Sample #1



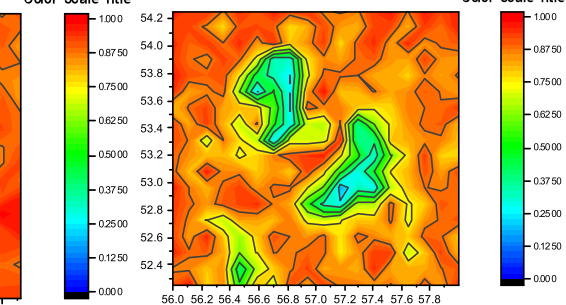
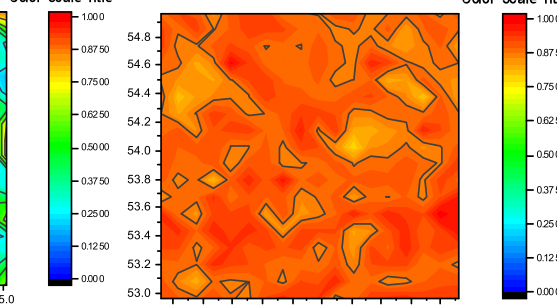
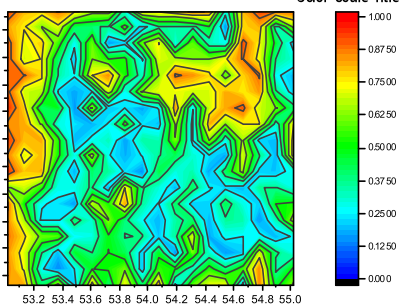
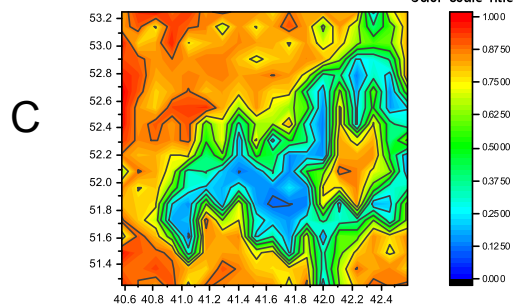
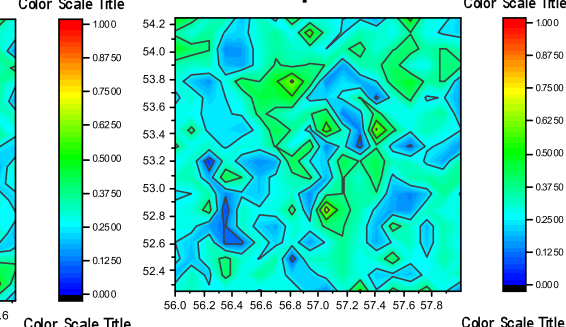
Sample #2



Sample #3



Sample #4



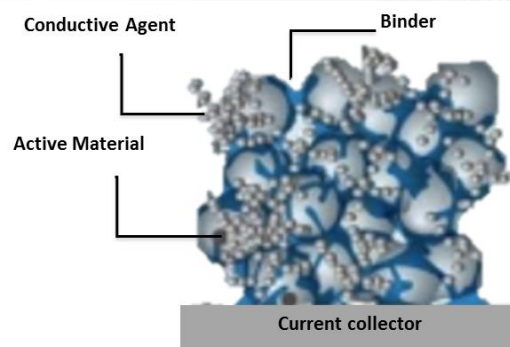
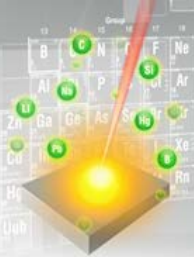
18 X 18 sampling, 40 micron, 2 mm x 2 mm area

LIBS help identify influence of different process condition (i.e. mixing time) the binder and carbon distribution.



# Technical Accomplishment –

## *Cathodes: Binder & Conductive Agent Distribution*



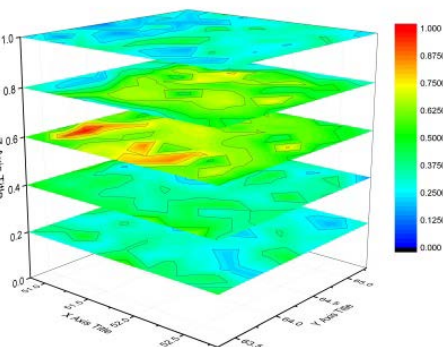
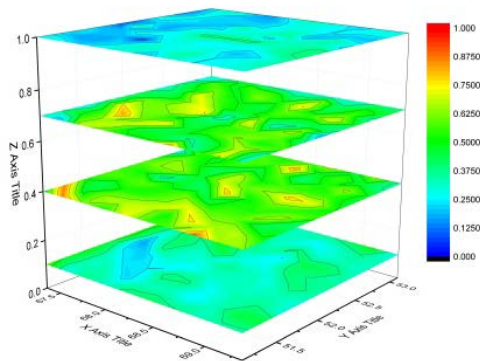
- Same average binder concentration
- Different mixing time
- 2.5 rpm mixing speed
- 3D of binder and conductive agent distribution imaging in the tested two cathodes

Sample	AB conc (%)	PVDF conc (%)	NMC conc (%)	1st mixing time (min)	2nd mixing time (min)	Thickness
Sample #1	3.2	4	92.8	8	27	43
Sample #2	3.2	4	92.8	8	120	59

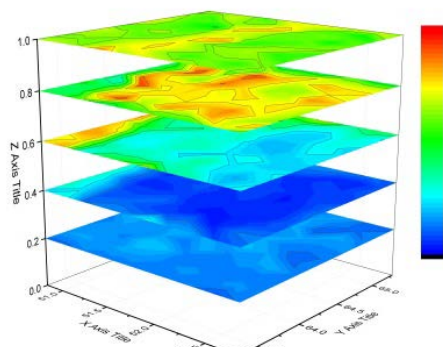
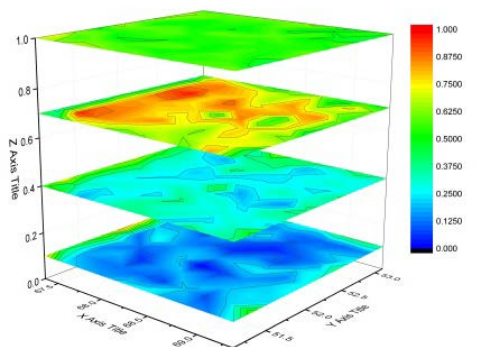
Sample #1

Sample #2

PVDF (F)



Conductive Agent (AB)



10 X 10 sampling, 250 micron laser spot, 2 mm x 2 mm area

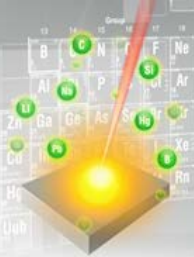
The LIBS instrument software rapidly processes emission signal into binder and conductive agent map in the battery electrodes.



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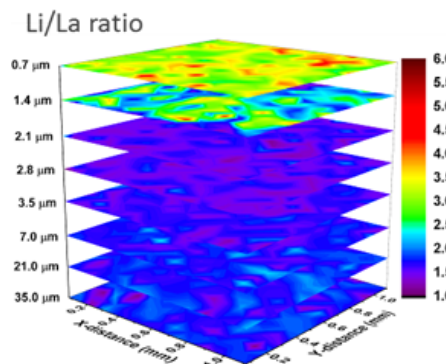
# Technical Accomplishment –

## *Elemental ratio mapping in solid state electrolytes*



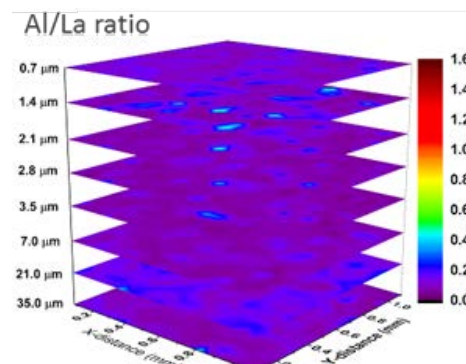
Electrochemical behavior		
Sample	Interfacial resistance	Conductivity
1	540 Ohm·cm <sup>2</sup>	$2.3 \times 10^{-4}$ S/cm
2	2000 Ohm·cm <sup>2</sup>	$1.1 \times 10^{-4}$ S/cm

Li/La

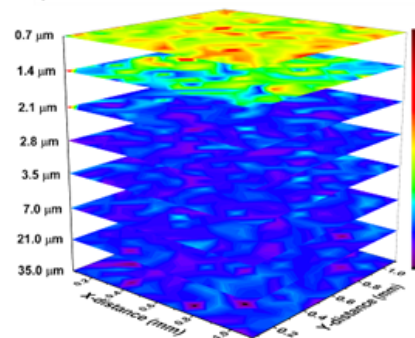


Al/La

Sample 1

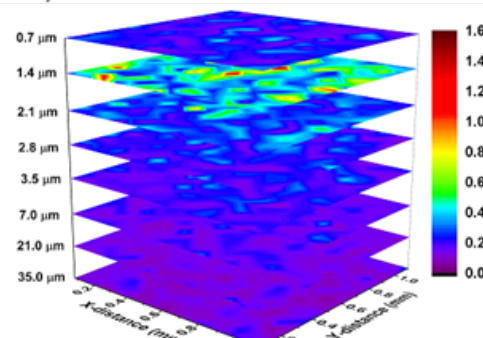


Li/La ratio



Al/La ratio

Sample 2



Sample 1: pellet made in fresh powder

Sample 2: pellet made in powder annealed for 6h

- LIBS was successfully utilized to map elemental ratios of key elements in  $\text{Li}_7\text{La}_3\text{Zr}_2\text{O}_{12}$  (LLZO) solid electrolyte.
- LIBS has identified elemental ratios (Al/La in the figure to right) whose difference lead to significantly different electrochemical behavior such as interfacial resistance & conductivity.

The developed LIBS instrument can determine the impact of chemistry variation produced by different manufacturing process on the battery performance.

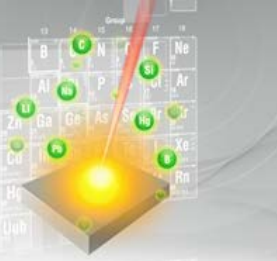


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# Responses to Previous Year Reviewers' Comments



## Comments from the 2014 Annual Merit Review

## Response

*"The reviewer remarked that it is not clear how significant an improvement to a manufacturing process would result from the inclusion of this analysis tool."*



The 2nd year Phase II work shows that slight parameter difference electrode manufacturing conditions such as mixing time can lead to difference in binder and conductive agent distribution and chemistry variance. Thus, the developed instrument can provide rapid feedback to select the optimum process condition and monitor consistency of the chemistry for fabricated components.

*"The reviewer noted that a 3D analysis of begin-of-life and end-of-life electrodes should be a part of the project."*



The 2<sup>nd</sup> year Phase II work demonstrates the depth profiling capability of LIBS for different battery cell component. The developed 3D mapping capability now can be used to determine the chemistry change for the end-of-life electrode. The investigation on this topic is being conducted with Li-ion battery research collaborator.

# Responses to Previous Year Reviewers' Comments

## Response

## Comments from the 2014 Annual Merit Review

*"The reviewer indicated that it is not clear from the investigation how this tool and the analytical data it generates complement other test methods."*



LIBS is highly complementary to other analytical techniques commonly used by Li-ion battery researchers and manufacturers such as XRF, ICP-OES, and GD based techniques. LIBS measures elements that are difficult for XRF such as Li, C, O, N, and F. Unlike ICP based technique, LIBS measures key elements directly from the battery components without acid digestion to obtain spatial composition information. LIBS provides significantly higher measurement speed and spatial resolution with respect to GD based techniques. Many complementary chemical information can be obtained quickly with LIBS when used in conjunction with other analytical techniques.

# Collaboration with Other Institutions



## Partners for Co-Technology Development and Validation

National  
Laboratory



### ***Lawrence Berkeley National Laboratory/ Dr. Vassilia Zorba***

- SBIR program sub-contractor
- Conducts LIBS experiment involving state of the art femtosecond lasers
- Provides access to the next generation Li ion battery research topics
- Advises on the direction of LIBS applications based on critical Li ion battery material research trends and needs

Industry

### ***Major US electric vehicle & Asian Li ion battery cell manufacturers***

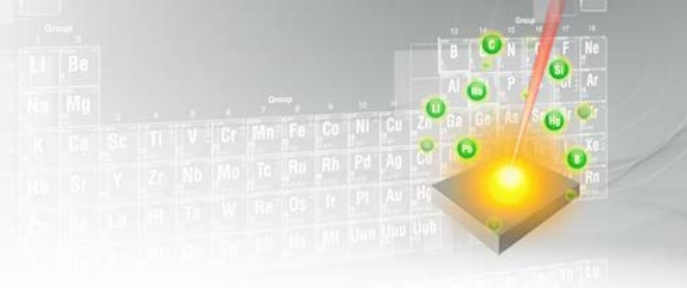
- Provides Li ion battery samples for technology validation
- Serves as beta instrument evaluation sites

# Remaining Challenges and Barriers



- The industry adoption cycle of the LIBS technology can be long - the adoption of new technology by the industry requires education and validation.
- With growing emphasis on reducing Li-ion battery manufacturing cost, the LIBS technology needs to demonstrate higher cost-efficiency to become practical for “in-line” chemical sensor.
- Some Li-ion battery materials cannot be exposed to air and special sample handling hardware and protocol need to be developed.
- The *in-situ* monitoring of battery components at various cycling stage requires challenging construction of special Li ion battery cell to allow optical access to cathode, anode, and electrolytes.

# Future Works



Time	Tasks
<p>Remainder of 2<sup>nd</sup> year Phase II program (thru 8/2015)</p>	<ul style="list-style-type: none"> <li>• <b><i>Expand LIBS application to both ex-situ and in-situ analysis of interfacial layer</i></b> <ul style="list-style-type: none"> <li>❑ Development of special air tight chamber to prevent sample exposure to air to compromise the integrity of SEI film</li> <li>❑ Study on formation and chemical composition of SEI layer with different electrolyte additives</li> <li>❑ Investigate SEI layer formation and compositional variation during cycling</li> </ul> </li> <li>• <b><i>Support the initial customers in adopting the technology and enabling target applications</i></b></li> <li>• <b><i>Industry reach-out/marketing campaign to educate and demonstrate the LIBS for developed Li-ion battery material analysis applications</i></b></li> </ul>

# Summary

## Objectives

- Develop rapid chemical characterization capability based on LIBS to accelerate Li-ion battery material R&D and to enable in-line chemical QC for battery manufacturing

## Approach

- Demonstrate LIBS for practical Li-ion battery material and component analysis applications
- Define instrumentation specification based on the proven applications.
- Develop intuitive software GUI, quantitative analysis algorithm & chemical imaging capability.

## Technical Accomplishment

- LIBS instrument developed and released for commercial adoption
- Application demonstrated for ***raw electrode material analysis, electrode depth profiling, binder and conductive distribution mapping, solid electrolyte element analysis, and component layer thickness QC***
- LIBS instrument installations for Li-ion battery material R&D institutes and commercial companies

## Future Works

- Development of LIBS for interfacial layer analysis (SEI)
- Technical support for early customers to ensure full adoption of the technology
- Industry reach-out and education on the developed LIBS instrument