



2014 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>	58%

## Budget

<b>Total Project Funding</b>	\$1,149,879
<b>Funding Received</b>	\$149,948 (Phase I) (6/2012 – 6/2013) \$374,974 (Phase II to date) (8/2013 – 4/2014)
<b>Funding Expected</b>	\$624,956 (thru 8/2015)

## Barriers/Targets

- Rapid QC/QA of Li ion battery raw materials and fabricated components
- Cost effective R&D tool for next generation Li ion battery chemistry
- Manufacturing technology to improve Li ion battery device yield and performance

## Partners

- Dr. Vasillia Zorba, Lawrence Berkeley National Laboratory

# Relevance/Objective

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



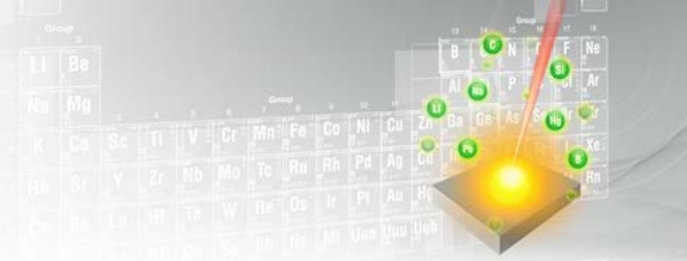
## Objectives

- ❑ Assess **LIBS (Laser Induced Breakdown Spectroscopy)** for chemical composition characterization of Li ion battery materials and components.
- ❑ Develop **LIBS** calibration algorithm for quantifying elemental composition of raw materials used in battery electrodes & electrolytes.
- ❑ Develop **LIBS** for chemical composition imaging (2D & 3D) geared towards in-line process monitoring of Li ion battery components and cells.
- ❑ Design beta LIBS instrument that is rapid and cost effective for Li-ion battery R&D and manufacturing QC.

## 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

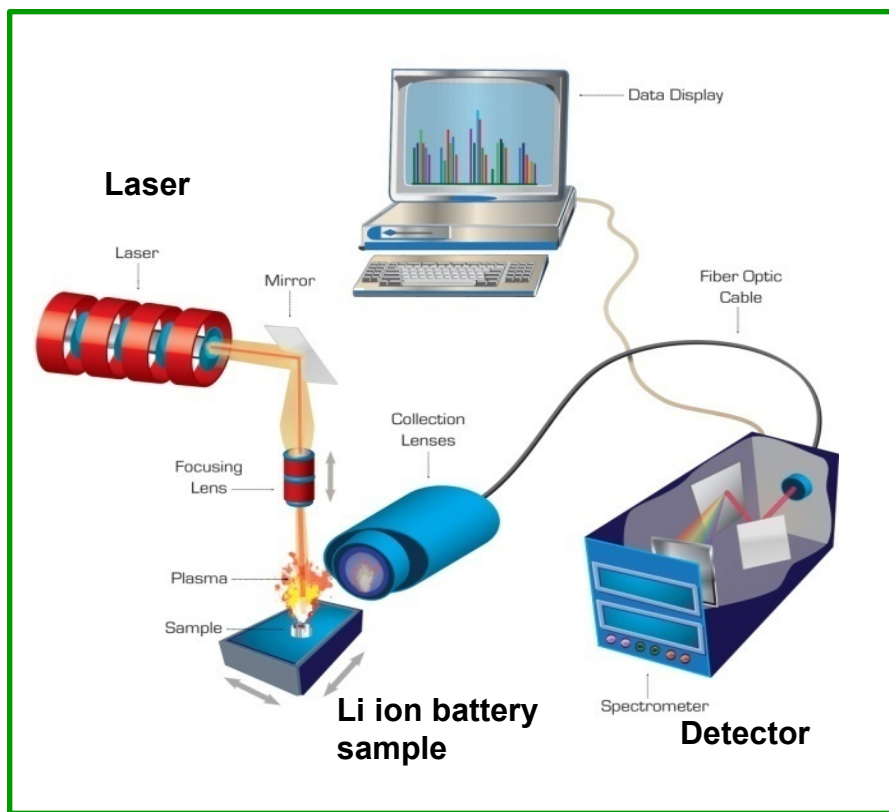


Month/Year	Milestone or Go or No-Go Decision
<b>Sep-2012</b>	Experimental LIBS setup comprised on different lasers and detector options - Investigate the feasibility of Li ion battery material applications <b>(Completed)</b>
<b>Nov-2012</b>	Evaluation of optimum LIBS detectors for best quantum efficiency 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 laser beam control and sample imaging system for auto-sampling method <b>(Initial design completed)</b>
<b>Apr-2014</b>	Optical design optimization - plasma light collection for required sampling method and light loss minimization <b>(Initial design completed)</b>
<b>Jun-2014</b>	Test and develop methods/protocols for the ex-situ LIBS analysis of thin films and interfacial layers on Si electrodes (On-going)

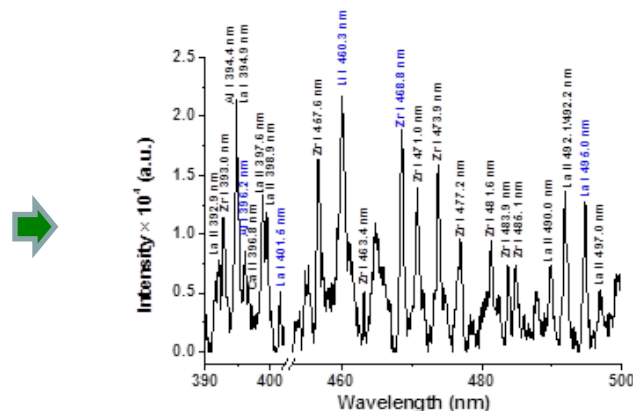
# Approach

## *LIBS System Development*

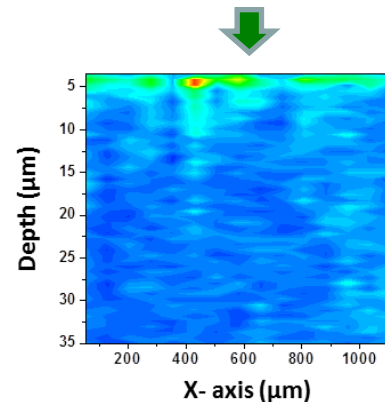
**Technical Concept:** Use focused laser beam to ionize Li ion battery materials and analyze generated laser plume for direct and rapid chemical composition in any environment (e.g. air)



*Schematic of LIBS system*



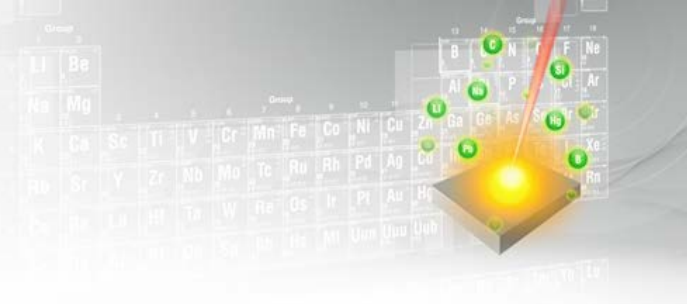
*LIBS spectral emission*



*Elemental imaging*

# Approach

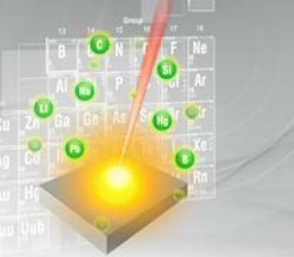
## *LIBS System Development and Implementation*



- 1. Evaluate optimum lasers & detectors for analyzing key elements in Li ion battery components.**
- 2. Develop synchronized sample movement control with respect to laser pulsing for different analysis mode:**
  - Bulk material analysis
  - Micro-analysis
  - Spatially-resolved analysis:
    - ☐ Elemental mapping
    - ☐ Depth profiling
- 3. Demonstrate different analysis modes in:**
  - raw materials
  - fabricated components and
  - cycled cell modules
- 4. Develop data processing algorithm for quantitative analysis of elements.**
- 5. Design and advance beta-LIBS instrument based on optimized hardware parameters.**

# Technical Accomplishment –

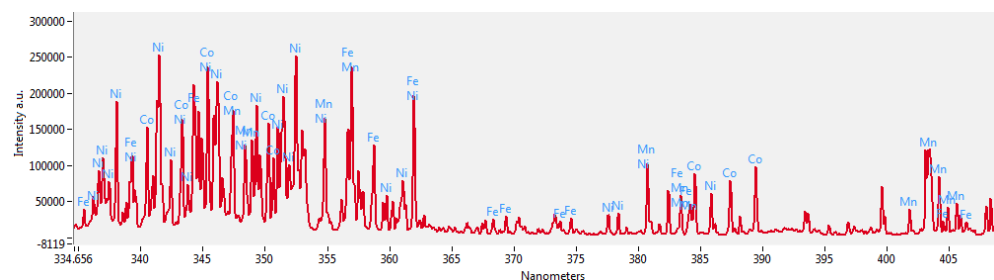
## *Bulk elemental analysis of raw electrode materials*



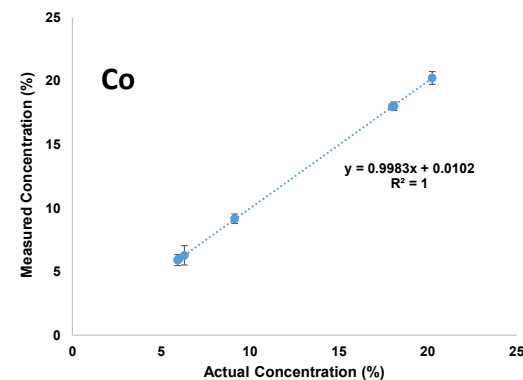
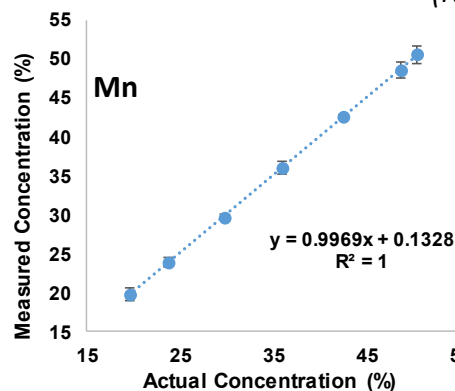
- LIBS was demonstrated to be effective in **directly and rapidly** analyzing primary elements that determine the chemistry of Li ion battery cathodes and anodes.
- An advanced calibration algorithm was developed to provide accurate and precise **quantitative** analysis of important elements.
- Powder samples can be formed into solid pellets and directly analyzed for composition without time consuming acid digestion (e.g. ICP-OES, ICP-MS, etc.)



*Raw cathode powders into pellets*



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



*Mn & Co concentration calculation with advanced calibration algorithm*

LIBS shows promise as an effective in-line instrument for performing QC of Li ion battery raw electrode materials.

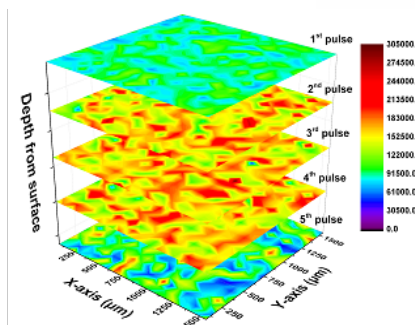
# Technical Accomplishment –

## Anodes: PVDF Binder Distribution

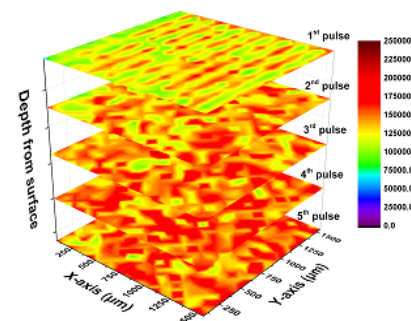
- LIBS was used to study the effect of mixing conditions on the distribution of PVDF in graphite anodes.

- Four graphite anodes with:
  - Identical average PVDF concentration
  - Different mixing conditions

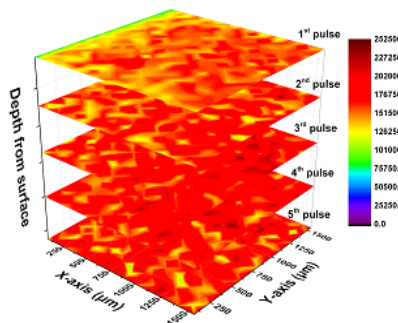
Anode 1



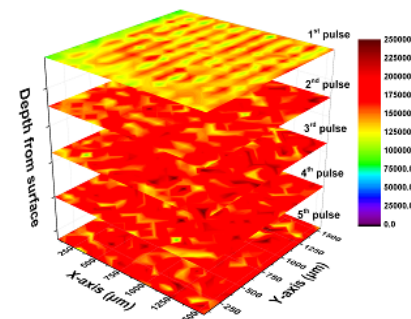
Anode 2



Anode 3



Anode 4



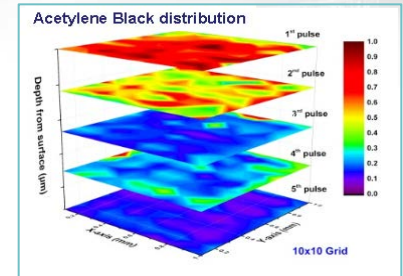
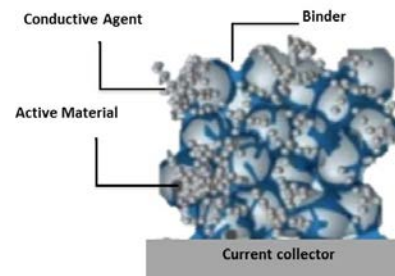
PVDF binder distribution in four graphite anodes for the first 5 laser pulses (20 μm from the surface). Maps were produced by probing atomic fluorine emission across an 1.6 x 1.6 mm<sup>2</sup> area.

Spatially-resolved chemical imaging with LIBS is used to study elemental distribution in cell components that affects the electrochemical behavior of Li-ion cells.

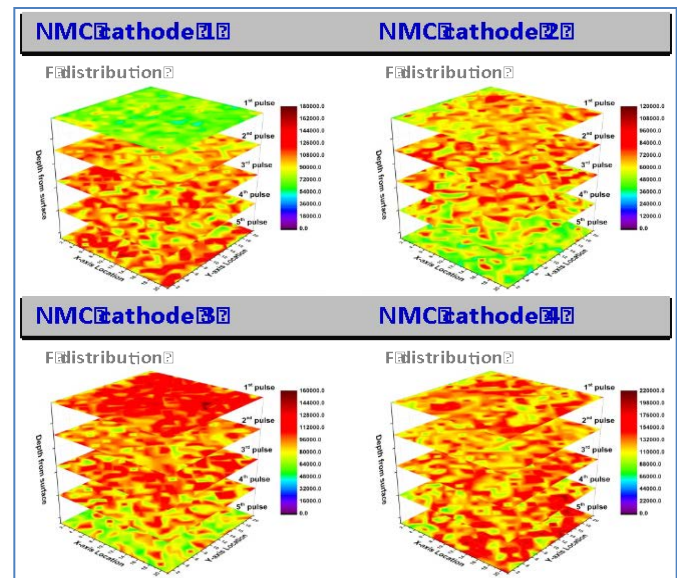
# Technical Accomplishment –

## *Cathodes: Binder & Conductive Agent Distribution*

- LIBS 3D chemical element imaging capability was developed for the Li ion battery electrodes.
  - ❑ *Optimized laser and detection parameters*
  - ❑ *Investigated the ideal emission line for different elements*
- LIBS chemical imaging enabled visualization of binder distribution and conductive agent, both critical to the battery performance.
- Software capability is being developed to output 3D chemical data to allow fast diagnostics of fabricated electrodes



3D imaging of Acetylene Black (conductive agent) in NMC cathodes

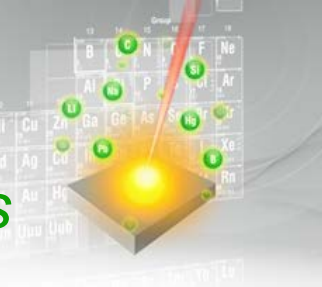


Distribution of binder (PVDF) for 4 NMC cathodes with different synthesis and mixing parameters

Rapid chemical imaging by LIBS enables monitoring on chemistry consistency of Li ion battery components.

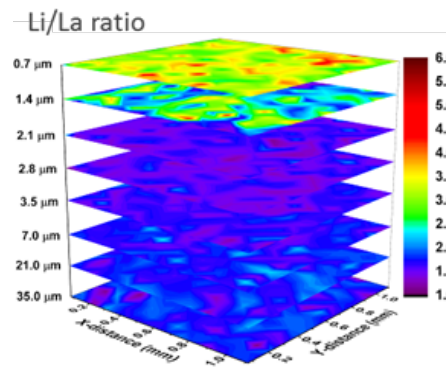
# Technical Accomplishment –

## *Elemental Ratio Mapping in Solid State Electrolytes*

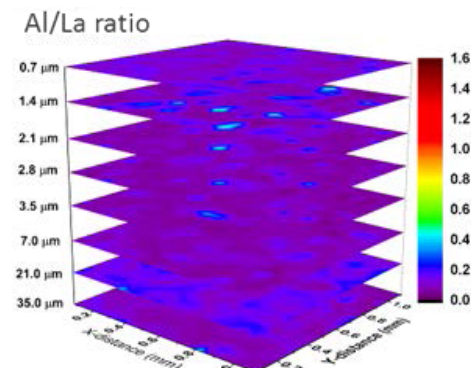


Electrochemical behavior		
Sample	Interfacial resistance	Conductivity
1	540 Ohm·cm <sup>2</sup>	2.3×10 <sup>-4</sup> S/cm
2	2000 Ohm·cm <sup>2</sup>	1.1×10 <sup>-4</sup> S/cm

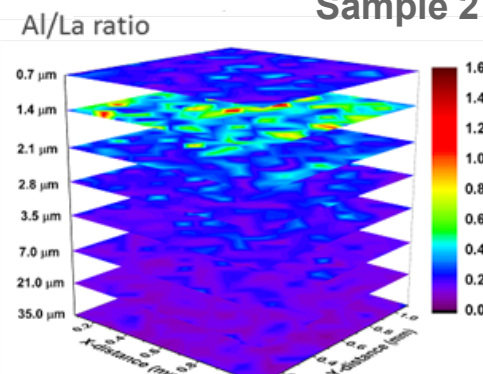
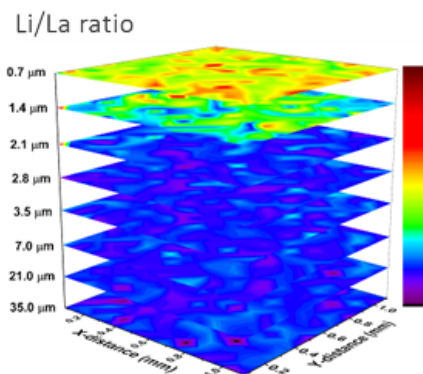
Li/La



Al/La Sample 1



Sample 2



Sample 1: pellet made in fresh powder

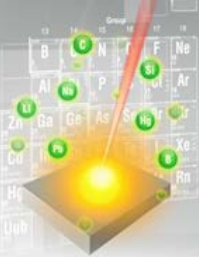
Sample 2: pellet made in powder annealed for 6h

- LIBS was successfully utilized to map elemental ratios of key elements in Li<sub>7</sub>La<sub>3</sub>Zr<sub>2</sub>O<sub>12</sub> (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.

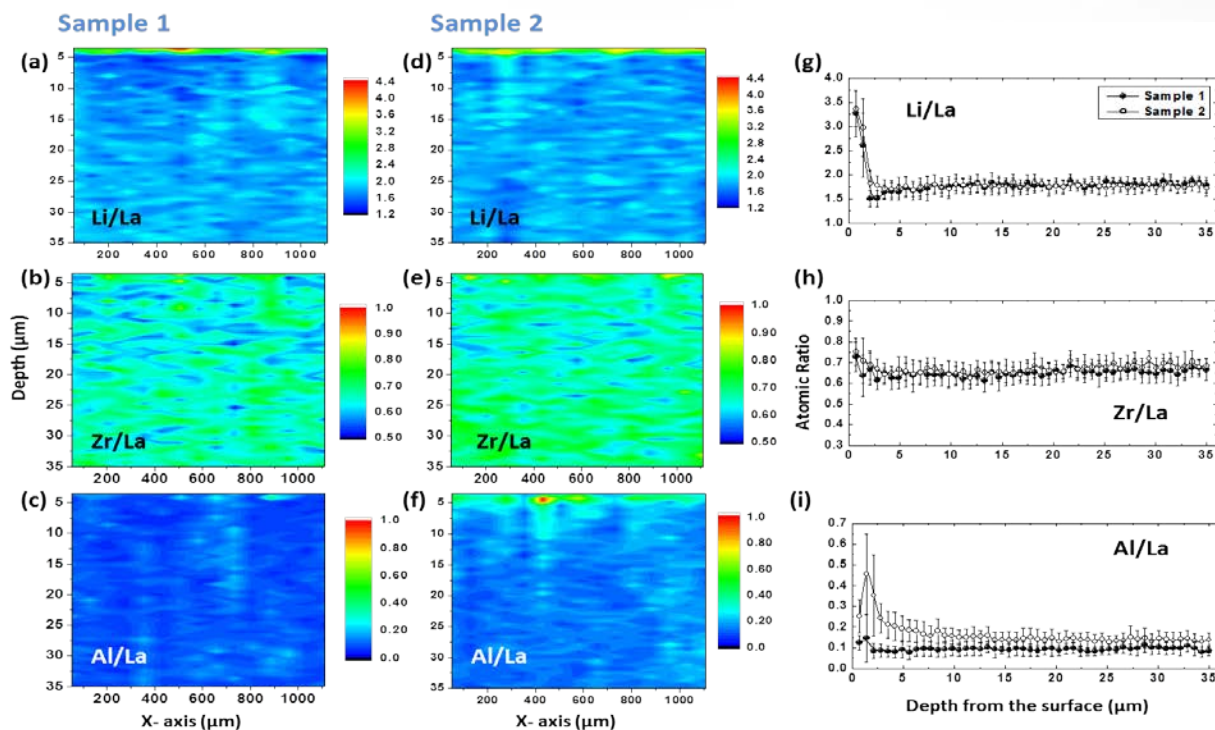
In Li ion battery material R&D, LIBS may help link chemistry variation produced by different manufacturing process to specific battery performance trend.

# Technical Accomplishment –

## Cross-sectional Imaging and Depth Profiling



- LIBS was successfully used to provide cross-sectional chemical maps of atomic ratios in Al-substituted LLZO solid electrolyte.
- Depth profiling provides precise quantification of the variation of chemical composition with depth and the inhomogeneity of the distribution across each lateral plane.

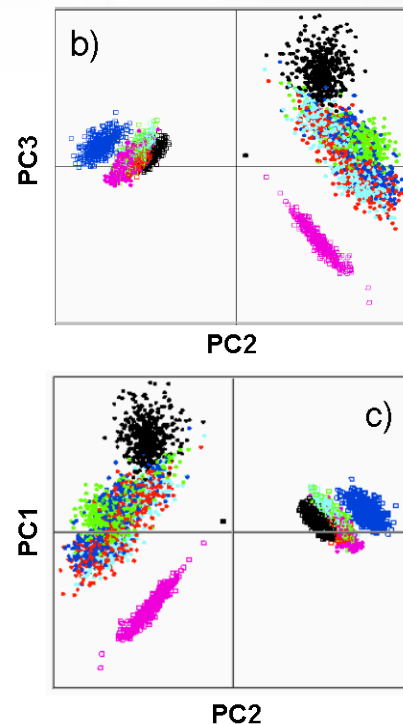
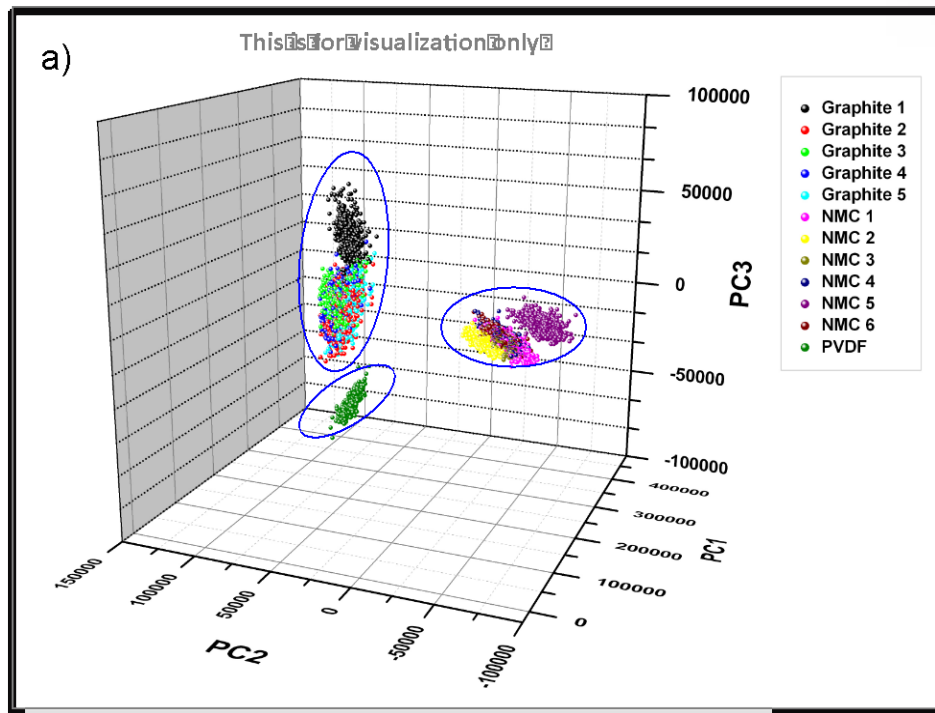
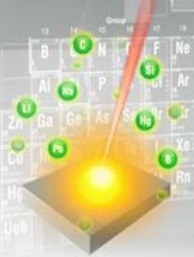


Atomic ratio (Li/La, Zr/La, Al/La) maps as a function of depth across a section of the two LLZO samples (a-f), and average atomic ratio as a function of depth (g-i). The error bars represent the standard deviation in the atomic ratios across each lateral map.

L. Cheng et al. *J. Mater. Chem. A* **2**, 172 (2014).

# Technical Accomplishment –

## *Development of Material Discrimination Chemometric Algorithm*

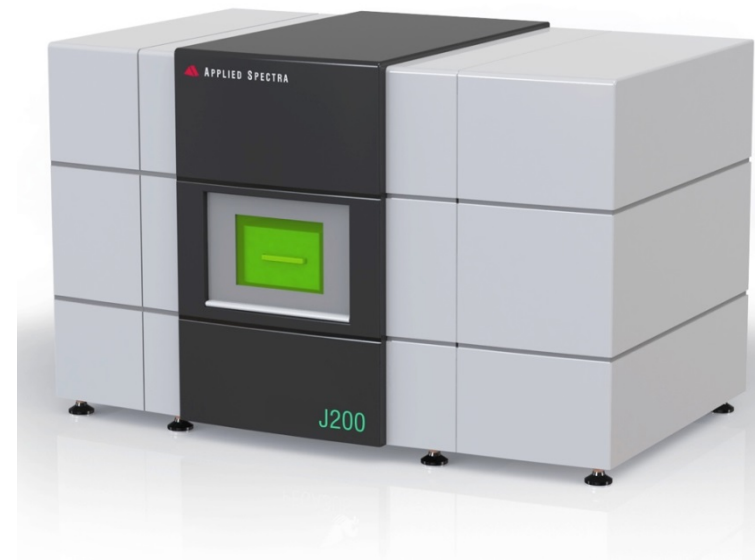


- Chemometric algorithm was developed to classify Li ion battery materials based on major and minor chemical content.
- The developed algorithm will be used to screen raw materials or battery components that do not meet the composition requirements due to inclusion of unwanted impurities or composition values outside of allowed limits.

# Technical Accomplishment –

## *Design of LIBS Instrument for Li ion Battery Material Analysis*

- Laser and detector specification set and driven by analytical requirements for initial applications investigated.
- User GUI for hardware control and data output display designed.
- Developed calibration algorithm for quantitative analysis and material classification being integrated into software features.
- Instrument platform and optics design to be further refined to improve detection sensitivity and to allow flexible sampling protocols required by different applications.



# 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



**APPLIED SPECTRA**

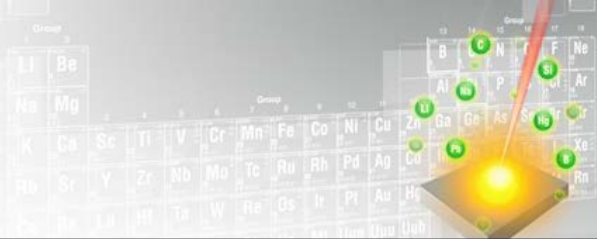
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# Remaining Challenges and Barriers



- High detection sensitivity required for analysis of impurities in Li ion battery materials
- High measurement precision desired for analyzing small compositional variation over the analyzed area or depth
- High analysis throughput essential for LIBS to be effective as in-line QC technique for Li ion battery manufacturing
- Special sample handling protocol for Li ion battery materials that cannot be exposed to air
- Construction of special Li ion battery cell to allow optical access to cathode, anode, and electrolytes for *in situ* monitoring measurement at different battery cycling
- Long incubation time for industry to adopt new technology

# Future Works



Time	Tasks
<p><b>Remainder of 1<sup>st</sup> year Phase II program (thru 8/2014)</b></p>	<ul style="list-style-type: none"> <li>• <b><i>LIBS instrument design enhancement to improve sampling capabilities and detection sensitivity</i></b> <ul style="list-style-type: none"> <li><input type="checkbox"/> Optical engineering to improve laser beam characteristics to improve depth profiling resolution</li> <li><input type="checkbox"/> Upgrade of optical components to improve light collection efficiency</li> <li><input type="checkbox"/> Evaluation of more sensitive detector camera</li> </ul> </li> <li>• <b><i>LIBS application demonstration for ex-situ SEI layer</i></b> <ul style="list-style-type: none"> <li><input type="checkbox"/> Development of special air tight chamber to prevent sample exposure to air to compromise the integrity of SEI film</li> <li><input type="checkbox"/> Study on formation and chemical composition of SEI layer with different electrolyte additives</li> </ul> </li> </ul>
<p><b>2<sup>nd</sup> year Phase II program (8/2014 to 8/2015)</b></p>	<ul style="list-style-type: none"> <li>• <b><i>Design of user friendly data acquisition and processing software GUI</i></b> <ul style="list-style-type: none"> <li><input type="checkbox"/> Software GUI that allows quick deployment of sampling protocols (bulk analysis, micro-analysis &amp; spatially resolved analysis)</li> <li><input type="checkbox"/> Integrated data analysis module for qualitative elemental screening, full quantitative analysis, and classification of Li ion battery materials</li> <li><input type="checkbox"/> Display of chemical imaging result</li> </ul> </li> </ul>

# Future Works



Time	Tasks
<p><b>2<sup>nd</sup> year Phase II program (8/2014 to 8/2015)</b></p> <p><b>(Continued)</b></p>	<ul style="list-style-type: none"> <li>• <b><i>Assess LIBS capabilities for in-situ analysis of interfacial layer</i></b> <ul style="list-style-type: none"> <li>❑ Design of special Li ion battery cell to allow optical access to SEI layer grown on different model electrode systems</li> <li>❑ Investigate SEI layer formation and compositional variation during cycling</li> </ul> </li> <li>• <b><i>Reduction of sampling and data analysis time to improve analysis throughput</i></b> <ul style="list-style-type: none"> <li>❑ Optimize sampling method for key applications to reduce measurement time without compromising accuracy and precision performance</li> <li>❑ Improve the efficiency of the data processing algorithm for chemical imaging and quantitative analysis</li> </ul> </li> <li>• <b><i>Build beta-LIBS instrument for Li ion battery applications</i></b> <ul style="list-style-type: none"> <li>❑ Installation at key R&amp;D and commercial customers based on initially developed applications</li> </ul> </li> </ul>

# Summary

## Objectives

- Develop LIBS for rapid chemical characterization instrument to accelerate Li ion battery R&D and to enable in-line QC for raw materials and fabricated components.

## Approach

- Demonstrate LIBS for practical applications and define instrumentation specification based on proven applications.
- Develop intuitive software GUI with full quantitative analysis & chemical imaging capability.

## Technical Accomplishment

- Quantitative & material classification analysis by LIBS demonstrated for raw electrode materials
- 2D & 3D compositional imaging demonstrated for cathode, anode, and solid state electrolytes
- Initial LIBS instrument hardware specification defined and platform design completed

## Future Works

- Demonstration of LIBS for ex-situ & in-situ analysis of interfacial layer of the electrode
- Instrument design and software improvement to enhance detection sensitivity and analysis throughput
- Build of the beta-LIBS instrument

