



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

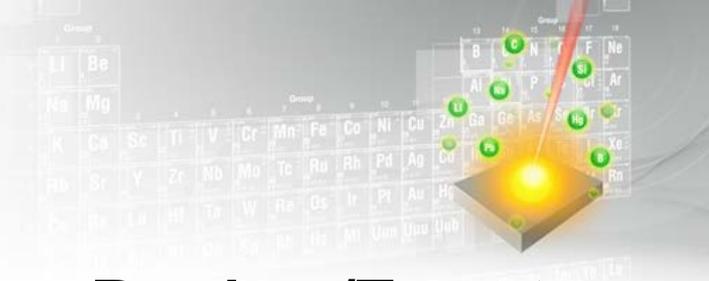


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APPLIED SPECTRA
A Laser Solutions Company

Overview



Timeline

| | |
|-------------------------|---|
| Project Start | 06/28/2012 (Phase I) 08/14/2013 (Phase II) |
| Project End | 08/14/2015 |
| Percent Complete | 58% |

Budget

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

Barriers/Targets

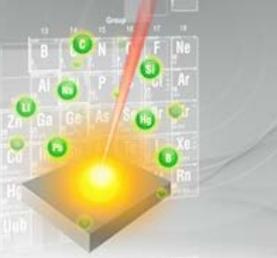
- Rapid QC/QA of Li ion battery raw materials and fabricated components
- Cost effective R&D tool for next generation Li ion battery chemistry
- Manufacturing technology to improve Li ion battery device yield and performance

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



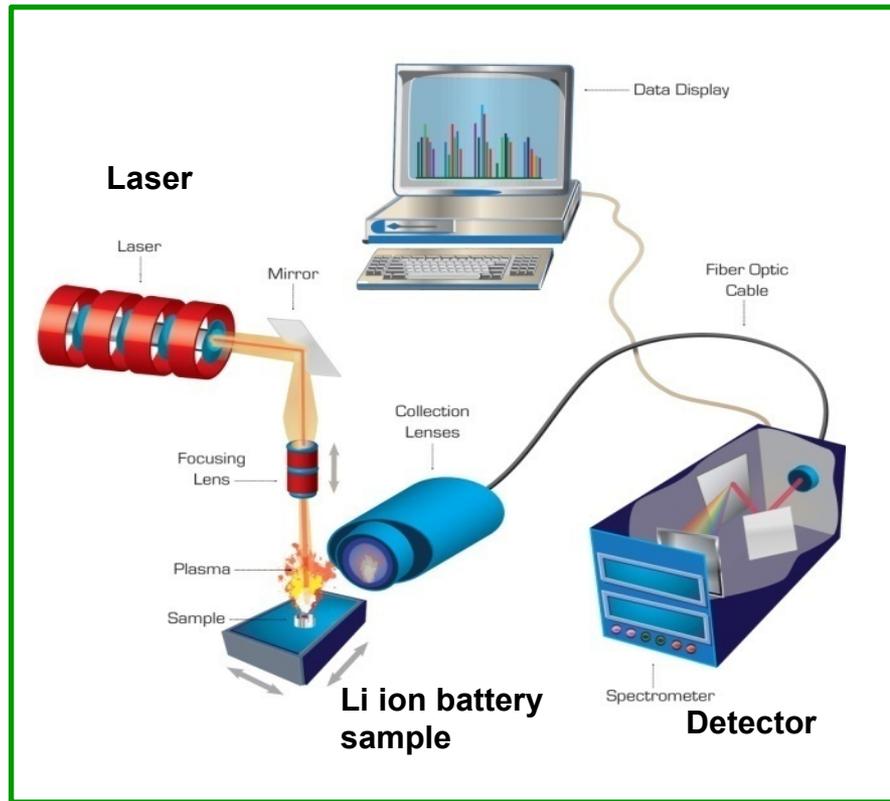
| Month/Year | Milestone or Go or No-Go Decision |
|-----------------|---|
| Sep-2012 | Experimental LIBS setup comprised on different lasers and detector options - Investigate the feasibility of Li ion battery material applications (Completed) |
| Nov-2012 | Evaluation of optimum LIBS detectors for best quantum efficiency and dispersion characteristics (Completed) |
| Dec-2012 | Development of LIBS data processing software and prototype GUI for data display (Completed) |
| Mar-2013 | Proof-of-concept analysis for Li ion battery cathodes, anodes, electrolytes for primary elemental composition, impurities, and elemental imaging (Completed) |
| Jun-2013 | Phase II Go or No-Go Decision (Passed and Phase II awarded) |
| Dec-2013 | Development of beta-LIBS instrument laser beam control and sample imaging system for auto-sampling method (Initial design completed) |
| Apr-2014 | Optical design optimization - plasma light collection for required sampling method and light loss minimization (Initial design completed) |
| Jun-2014 | Test and develop methods/protocols for the ex-situ LIBS analysis of thin films and interfacial layers on Si electrodes (On-going) |

Approach

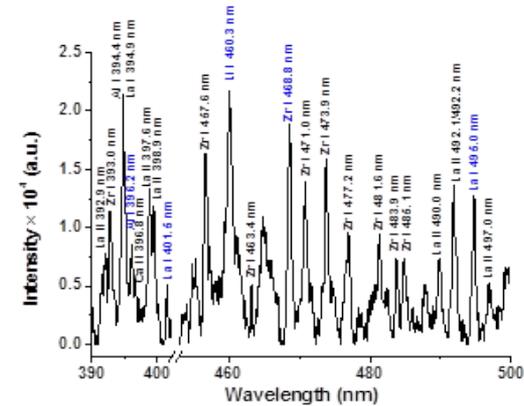
LIBS System Development



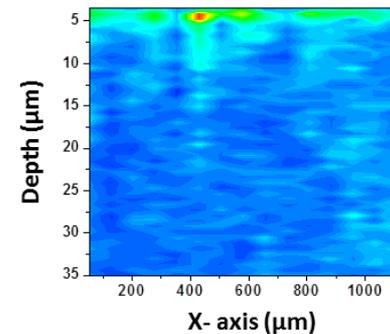
Technical Concept: Use focused laser beam to ionize Li ion battery materials and analyze generated laser plume for direct and rapid chemical composition in any environment (e.g. air)



Schematic of LIBS system



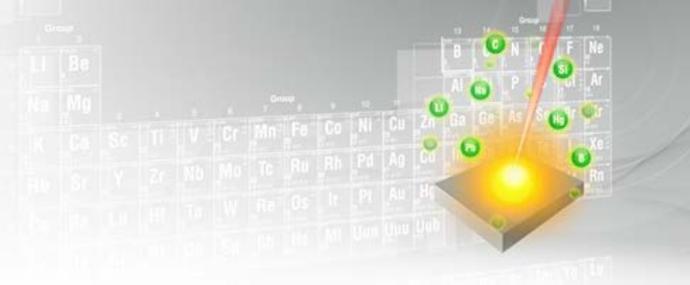
LIBS spectral emission



Elemental imaging

Approach

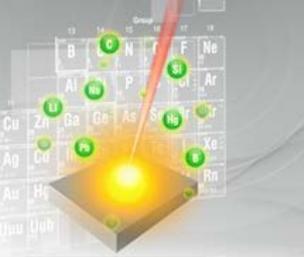
LIBS System Development and Implementation



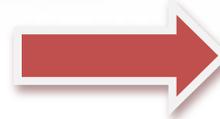
- 1. Evaluate optimum lasers & detectors for analyzing key elements in Li ion battery components.**
- 2. Develop synchronized sample movement control with respect to laser pulsing for different analysis mode:**
 - Bulk material analysis
 - Micro-analysis
 - Spatially-resolved analysis:
 - Elemental mapping
 - 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 –

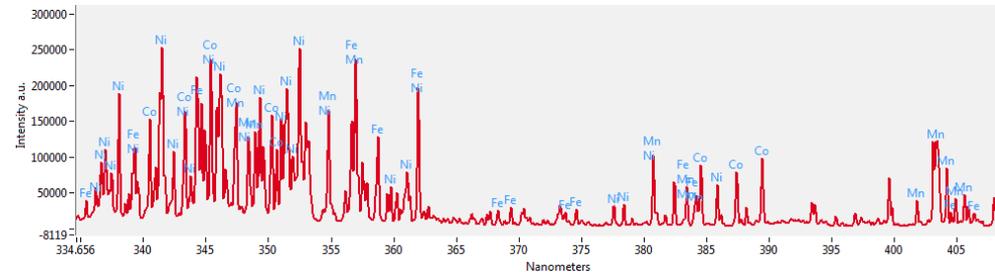
Bulk elemental analysis of raw electrode materials



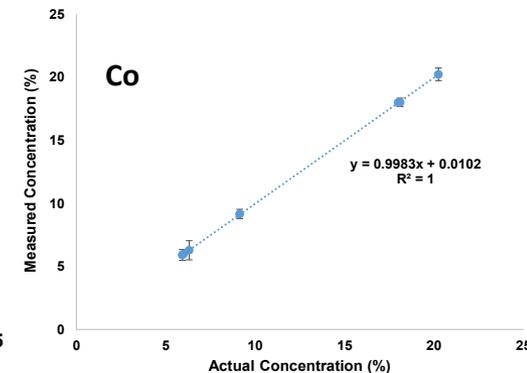
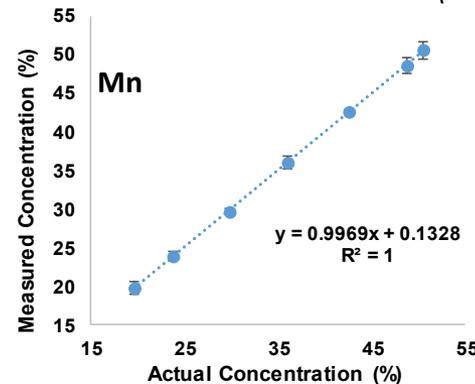
- LIBS was demonstrated to be effective in **directly and rapidly** analyzing primary elements that determine the chemistry of Li ion battery cathodes and anodes.
- An advanced calibration algorithm was developed to provide accurate and precise **quantitative** analysis of important elements.
- Powder 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

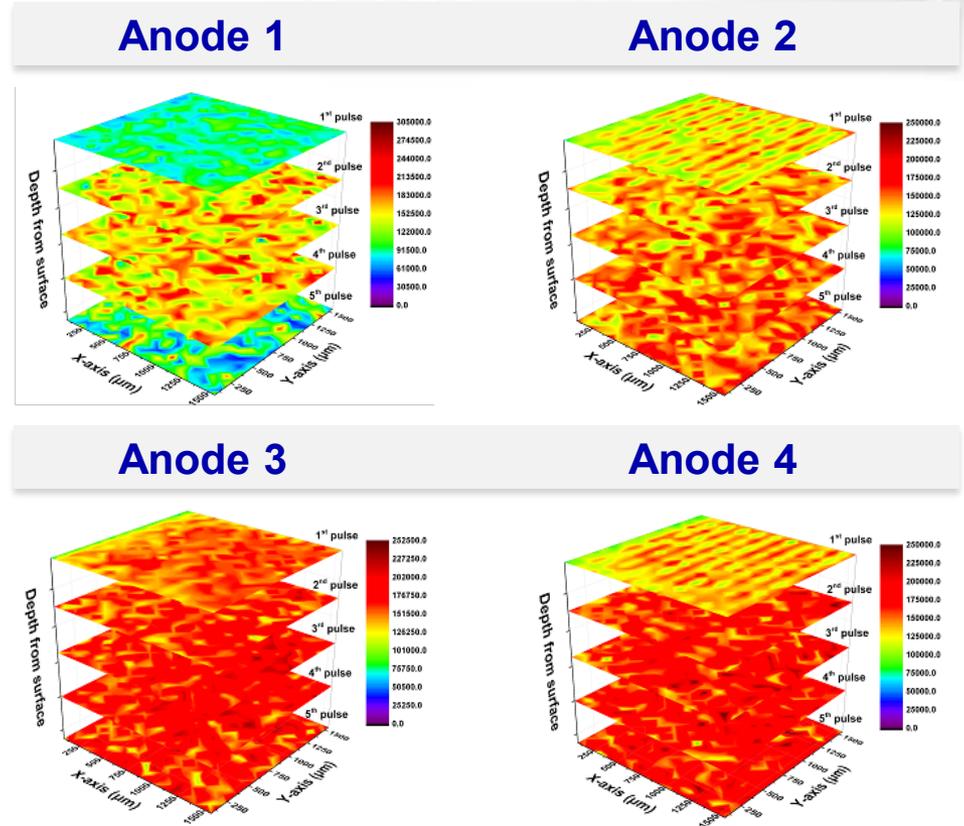
LIBS shows promise as an effective in-line instrument for performing QC of Li ion battery raw electrode materials.

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



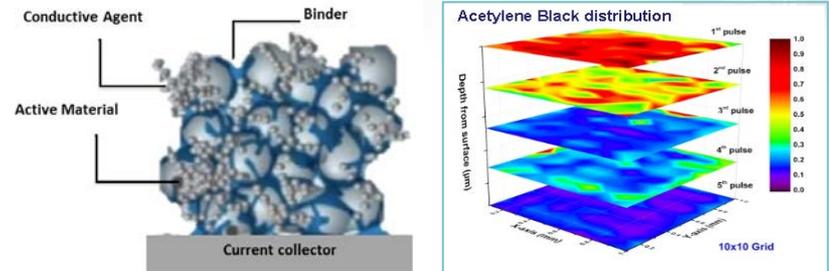
PVDF binder distribution in four graphite anodes for the first 5 laser pulses (20 μm from the surface). Maps were produced by probing atomic fluorine emission across an 1.6 x 1.6 mm² area.

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

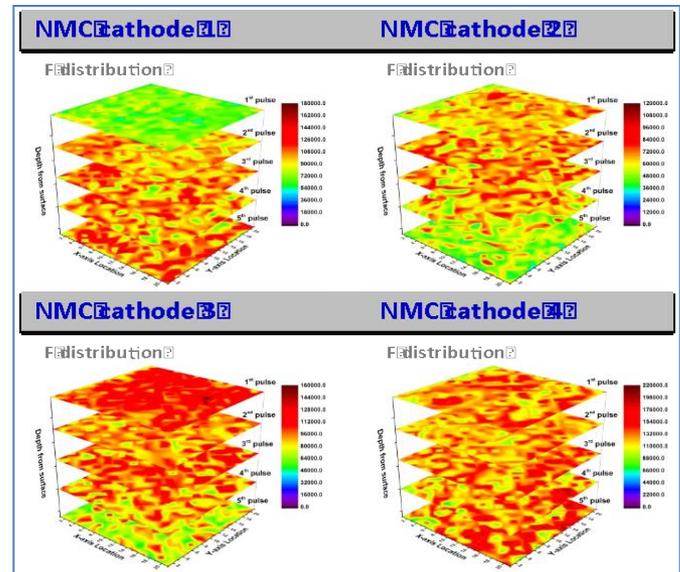
Technical Accomplishment –

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

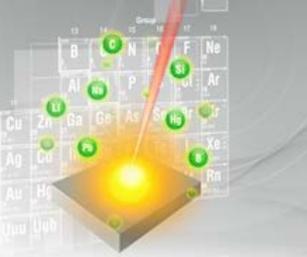


Distribution of binder (PVDF) for 4 NMC cathodes with different synthesis and mixing parameters

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

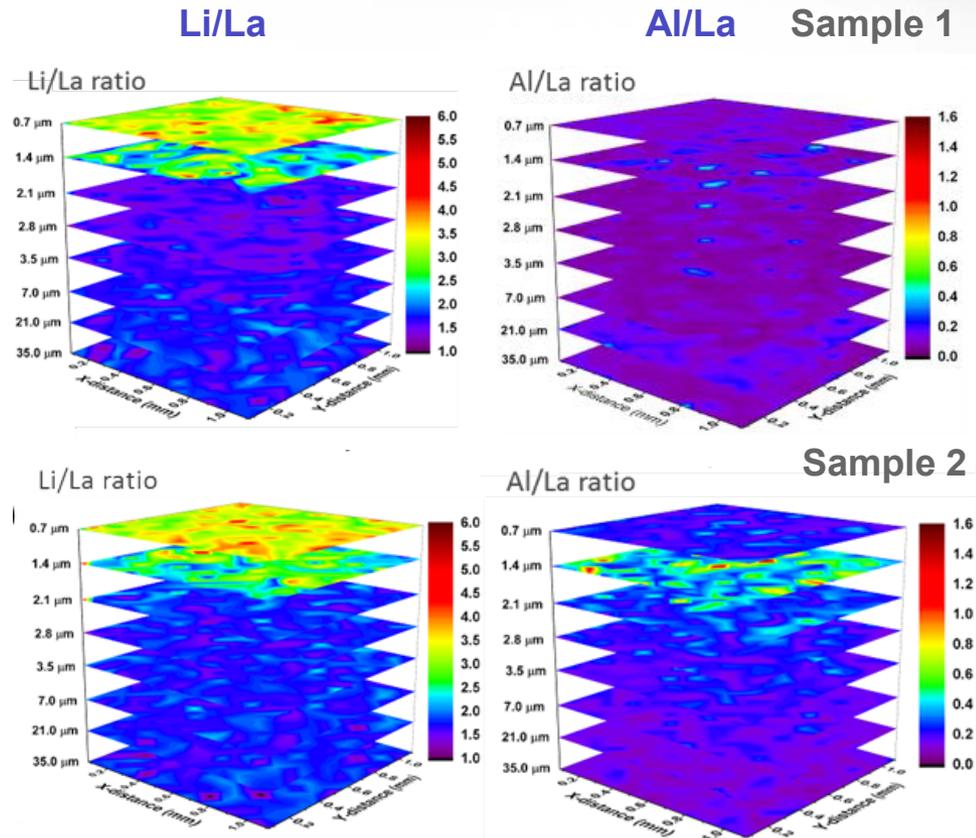
Technical Accomplishment –

Elemental Ratio Mapping in Solid State Electrolytes



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

- LIBS was successfully utilized to map elemental ratios of key elements in Li₇La₃Zr₂O₁₂ (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.



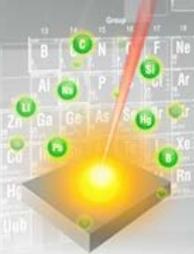
Sample 1: pellet made in fresh powder

Sample 2: pellet made in powder annealed for 6h

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

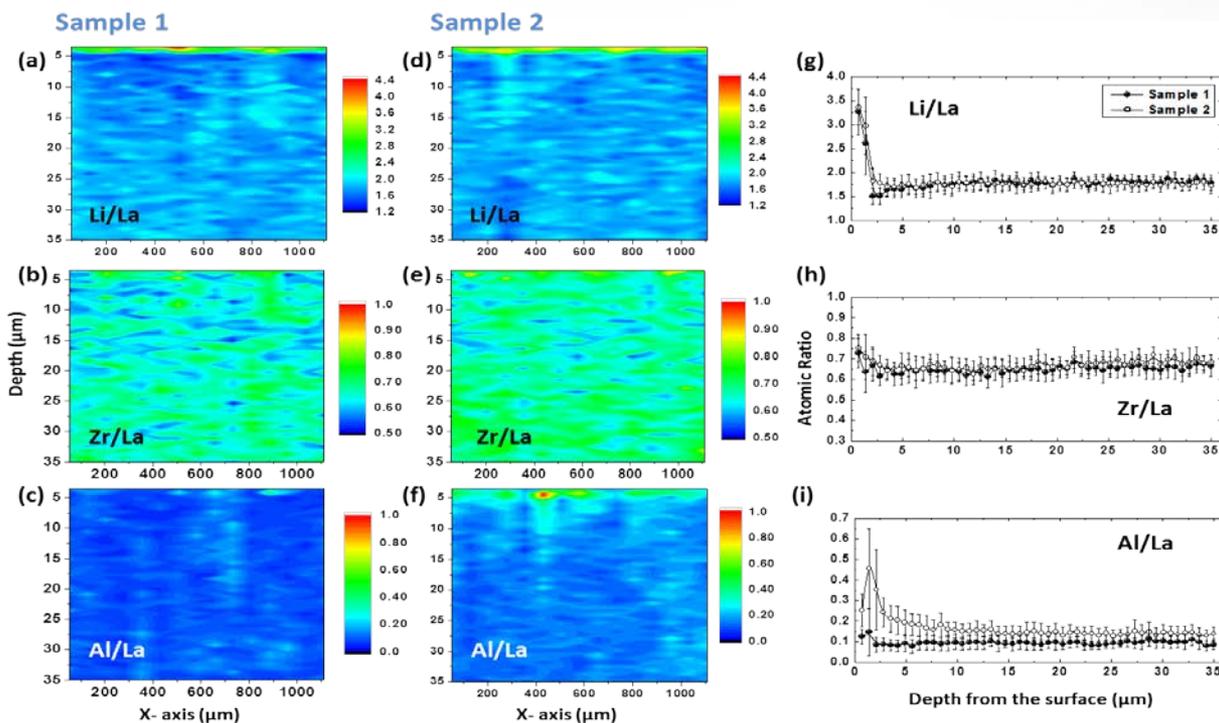
Technical Accomplishment –

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.

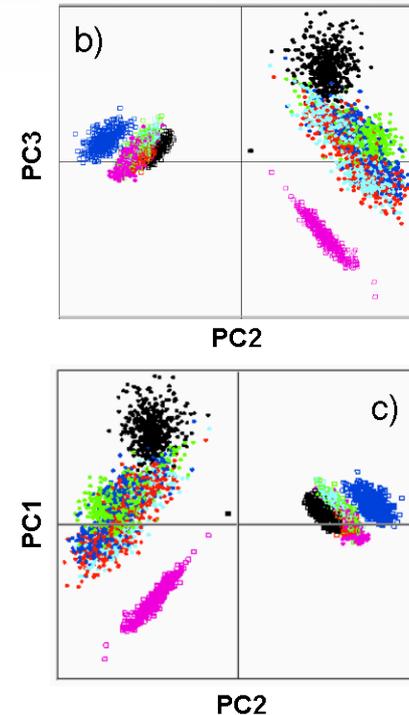
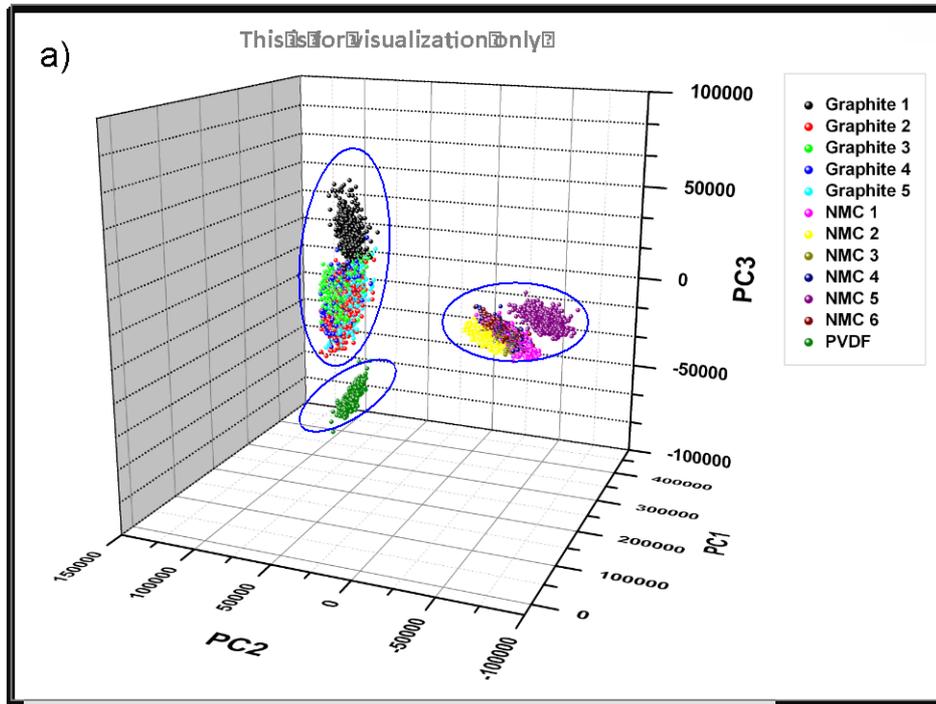
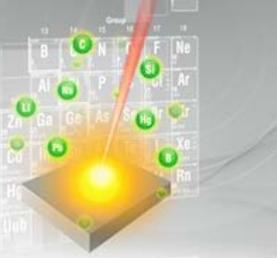


Atomic ratio (Li/La, Zr/La, Al/La) maps as a function of depth across a section of the two LLZO samples (a-f), and average atomic ratio as a function of depth (g-i). The error bars represent the standard deviation in the atomic ratios across each lateral map.

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

Technical Accomplishment –

Development of Material Discrimination Chemometric Algorithm

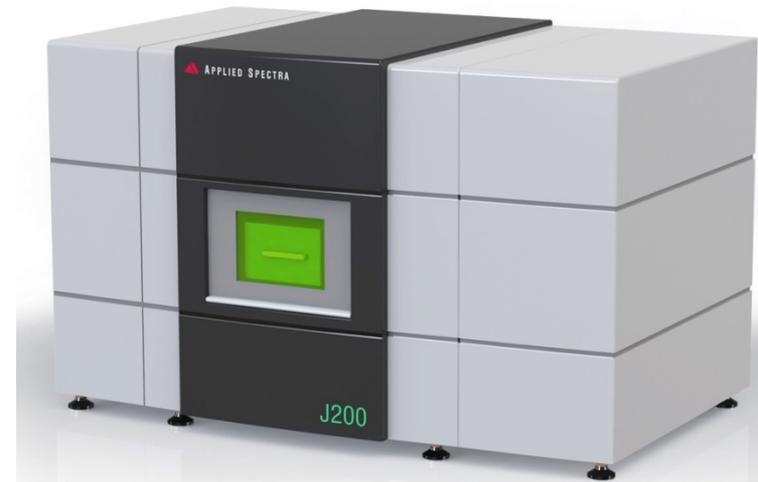


- Chemometric algorithm was developed to classify Li ion battery materials based on major and minor chemical content.
- The developed algorithm will be used to screen raw materials or battery components that do not meet the composition requirements due to inclusion of unwanted impurities or composition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

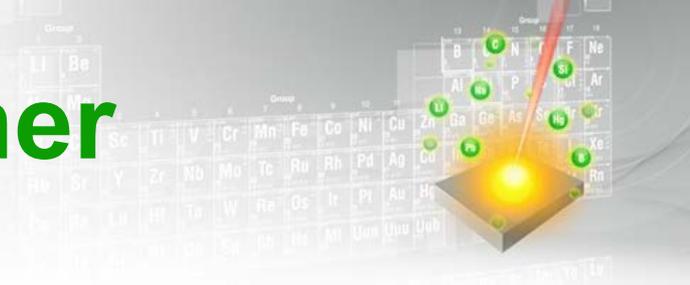
Technical Accomplishment –

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

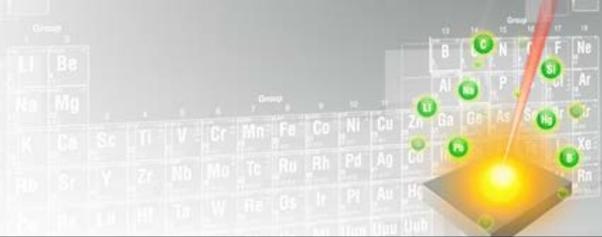
Remaining Challenges and Barriers



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

Future Works



| Time | Tasks |
|---|--|
| <p data-bbox="42 429 394 572">2nd year Phase II program (8/2014 to 8/2015)</p> <p data-bbox="98 629 336 672">(Continued)</p> | <ul data-bbox="452 429 1881 1215" style="list-style-type: none"><li data-bbox="452 429 1881 658">• <i>Assess LIBS capabilities for in-situ analysis of interfacial layer</i><ul data-bbox="610 479 1843 658" style="list-style-type: none"><li data-bbox="610 479 1843 565">❑ Design of special Li ion battery cell to allow optical access to SEI layer grown on different model electrode systems<li data-bbox="610 572 1843 658">❑ Investigate SEI layer formation and compositional variation during cycling <li data-bbox="452 694 1881 1029">• <i>Reduction of sampling and data analysis time to improve analysis throughput</i><ul data-bbox="610 793 1881 1029" style="list-style-type: none"><li data-bbox="610 793 1881 929">❑ Optimize sampling method for key applications to reduce measurement time without compromising accuracy and precision performance<li data-bbox="610 936 1881 1029">❑ Improve the efficiency of the data processing algorithm for chemical imaging and quantitative analysis <li data-bbox="452 1079 1881 1215">• <i>Build beta-LIBS instrument for Li ion battery applications</i><ul data-bbox="610 1129 1881 1215" style="list-style-type: none"><li data-bbox="610 1129 1881 1215">❑ Installation at key R&D and commercial customers based on initially developed applications |

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