

Characterization of Materials for Li-ion Batteries:

Success Stories from the High
Temperature Materials Laboratory
(HTML) User Program

DOE 2010 Vehicle Technologies Annual Merit Review and Peer Evaluation Meeting

Dr. Andrew Payzant

HTML User Program

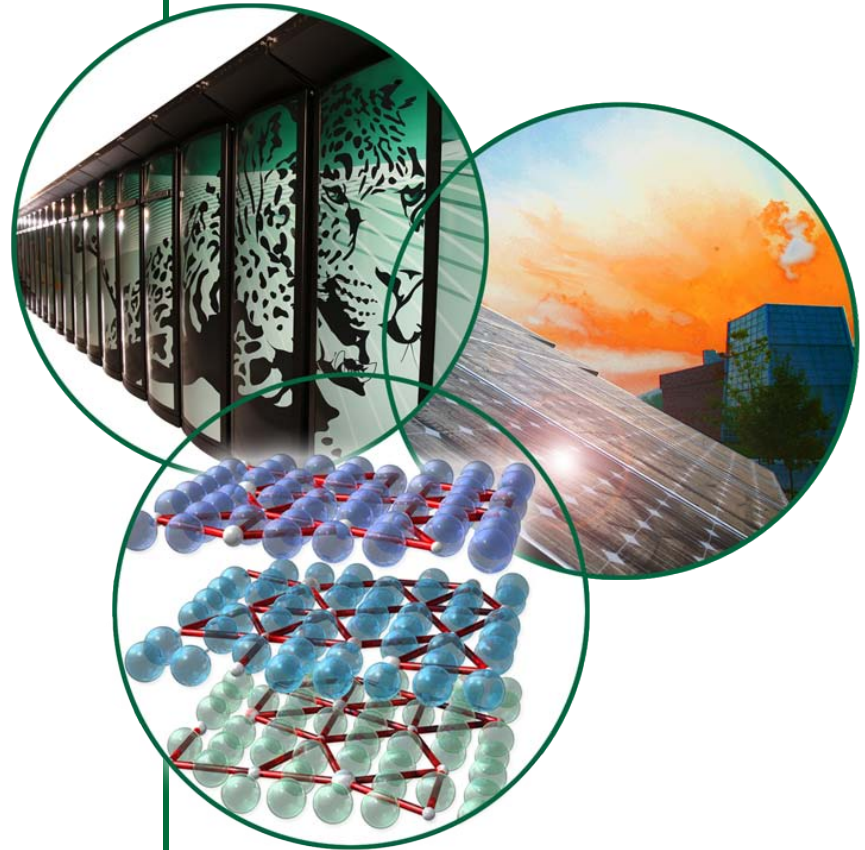
Materials Science and Technology Division
Oak Ridge National Laboratory

Washington, DC
June 9, 2010

Sponsored by
U.S. Department of Energy, Assistant Secretary for Energy Efficiency
and Renewable Energy, Office of Vehicle Technologies



This presentation does not contain any proprietary,
confidential, or otherwise restricted information.



The HTML User Program: Background

- The HTML is a National User Facility that supports the missions of DOE, EERE and the Vehicle Technologies Program in particular, by working with industry, universities, and other national laboratories to develop energy-efficient technologies that will enable the U.S. to use less petroleum. The HTML is organized into six user centers, which are clusters of highly skilled staff and sophisticated, often one-of-a-kind instruments for materials characterization.
- Access to the HTML User Program is provided through the HTML User Program proposal process. Research proposals are reviewed by a committee and approved based on scientific merit, relevance of the proposed research to the mission of DOE's Vehicle Technologies Program, and feasibility. Projects have a well-defined scope, and research is completed within 24 months and normally involves one or more user visits to the HTML.
- Both nonproprietary and proprietary research is conducted within the HTML User Program. There are generally no charges for nonproprietary research projects, and users conducting nonproprietary research must agree to submit research results for publication in the open, refereed literature. A nonproprietary project is complete when the results are published in the open literature and/or presented at a professional conference. For proprietary research, the user owns the research data, and all costs at the HTML are paid by the user based on DOE guidelines for ORNL costs.

The HTML User Program – FY2009 Activity

During FY2009, the HTML User Program collaborated with 11 companies, 14 universities, and 3 national laboratories on 41 user projects addressing critical technical barriers to achieving the goals of DOE's Vehicle Technologies Program. There were 107 researchers who visited the HTML for a total of 562 days to conduct experiments.

The HTML User Program FY2009 budget was \$5,066,946 and was allocated as follows:

- Capital equipment: \$514,025
- Operations: \$4,552,921

Users cost-share their HTML user projects through:

- 1) direct involvement with HTML staff members during the development of the user project;
- 2) funding their travel to the HTML to perform research;
- 3) cost of materials provided by the user or the research performed prior to the user project;
- 4) collaboration with HTML staff members to analyze the data and publish the results.

The HTML also supports the education and preparation of a new generation of scientists and engineers. During FY2009, students and professors from 14 universities participated in the HTML User Program. Four of those students earned their Ph.D. degree and three earned their M.S. degree based in part on research they conducted through the HTML User Program.

Relevance to the VT Program

- The Vehicle Technologies Program funds the operation of the HTML User Program to maintain world-class expertise and instrumentation capabilities for materials characterization to work with industry, universities and national laboratories toward the goals of the Vehicle Technologies Program.
- The HTML User Program capabilities also support the activities of the Vehicle Technologies Program's subprograms in Lightweight Materials, Propulsion Materials, Energy Storage, and Thermoelectric Conversion at the Oak Ridge National Laboratory.
- This poster presentation highlights **four** of the 41 user projects managed by the HTML User Program during FY2009, **and** a more recent FY2010 project. These user projects address critical barriers such as fundamentals of operation, cost, performance, and life of lithium-ion batteries.

Highlights of four HTML User Program projects utilizing advanced characterization methods for battery materials

- **Brookhaven National Laboratory**
“*In situ* XRD studies of cathode and anode materials for lithium-ion batteries”
- **University of Michigan**
“Characterization of battery active materials”
- **Massachusetts Institute of Technology**
“Structural analyses of battery materials for the electrification of vehicles”
- **Oak Ridge National Laboratory / UT Knoxville**
“Development of in-situ XRD and AE techniques for examination of fatigue behavior in lithium-ion battery electrodes”



Brookhaven National Laboratory



“In-situ XRD studies of cathode and anode materials for lithium-ion batteries”

Timeline

- Start date: 4/1/2008
- End date: 8/30/2010
- % complete: 95%

Budget

- Included in the user center allocations from the annual budget of the HTML User Program; users cost-share as noted on slide #3.

Barriers

- Cost
- Durability
- Fundamentals

Collaborators

- **BNL Users:** Kyung-Wan Nam, Xiao-Jian Wang, Yongning Zhou, and Xiao-Qing Yang
- **HTML Staff:** Jianming Bai

Brookhaven National Laboratory:

User project background of study

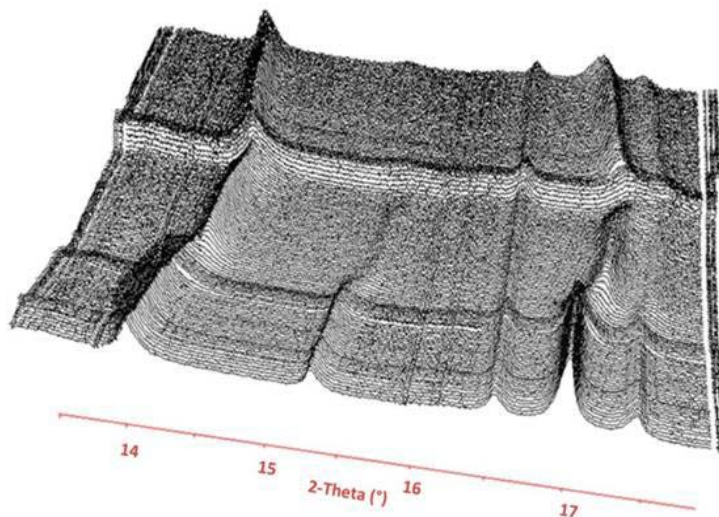


- Researchers from the Chemistry Department at Brookhaven National Laboratory and the HTML's Dr. Jianming Bai set up a cell for *in situ* x-ray diffraction studies of battery materials during charging and discharging at the X14A beam line at the National Synchrotron Light Source (NSLS). The X14A beam line is managed by the HTML User Program.
- The cell used for this study includes an olivine-structured lithium phosphate (or lithium transition metal oxide) as the cathode, a lithium foil as the anode, and LiPF_6 in EC-DMC as the electrolyte. This cell and a fast silicon strip detector were mounted on the six-circle Huber diffractometer.

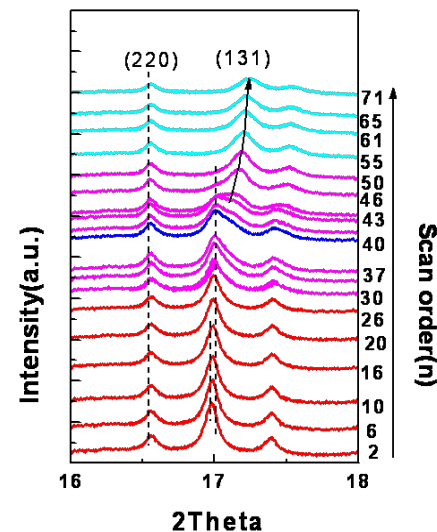
Brookhaven National Lab User Project:

Phase 1 study on effect of aliovalent dopants

- **Research problem:** To investigate the changes in electronic and crystal structures for both uncoated and carbon-coated olivine structured lithium phosphate cathode materials during charge-discharge cycling
- **Technical approach:** Powder diffraction patterns were taken in the transmission mode during charge-discharge cycling, with a typical time scale of a few minutes per scan.



In situ x-ray powder diffraction patterns of $\text{C-LiFe}_{0.6}\text{Mn}_{0.4}\text{PO}_4$ during the first charge-discharge cycle.



Detailed structure of the XRD pattern during the first charging process.

Brookhaven National Lab User Project:

What we learned and accomplished



- Detailed structure analysis of these phase transitions is ongoing, and more samples of LiMPO_4 -based cathode material with different transition metal doping will be studied using the same method.
- Temperature-dependent XRD studies will also be conducted on these samples at different charge states.
- These studies will enhance the understanding of the thermal stability of these cathode materials and the effects of their interaction with electrolytes, thereby supporting the Vehicle Technologies Program goal of safe batteries with improved energy and power density.



Timeline

- Start date: 6/1/2008
- End date: 9/30/2010
- % complete: 90%

Budget

- Included in the user center allocations from the annual budget of the HTML User Program; users cost-share as noted on slide #3.

Barriers

- Cost
- Durability
- Fundamentals

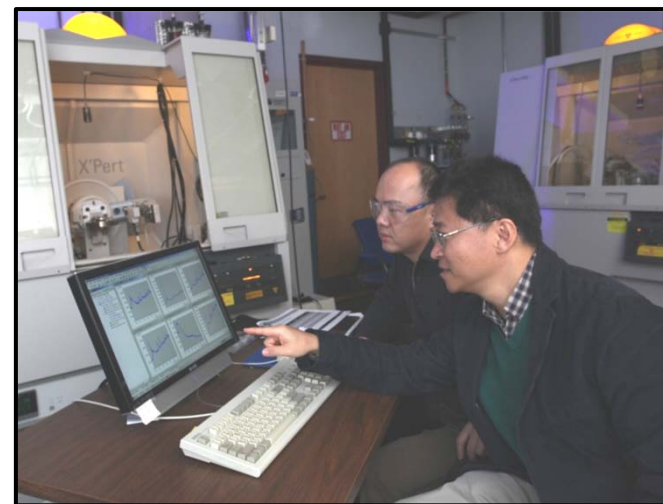
Collaborators

- **U. Mich Users:** Prof. A. M. Sastry, M. Park, H. Kim, H. Shin, X. Zhang
- **ORNL:** N. Dudney, S. Kalnaus
- **HTML Staff:** A. Payzant, R. Trejo, J. Howe, R. Peascoe-Meisner and Melanie Kirkham

University of Michigan User Project: Background of the study



- Understanding diffusion phenomena is one of the key factors to predict the performance of Li-ion thin-film batteries.
- Diffusion of Li-ion in thin-film cathode dictates overall battery capacity.
- Heat treatment is one of the main methods for tailoring microstructure in cathode thin film; it induces microstructure variation and thus changes in the diffusion coefficient of Li-ion.
- *In situ* XRD experiments on lithium cobaltate thin-film cathodes were designed to study heat treatment effects on the microstructure of cathode, including characteristics such as grain size, crystallinity, and phase transitions.

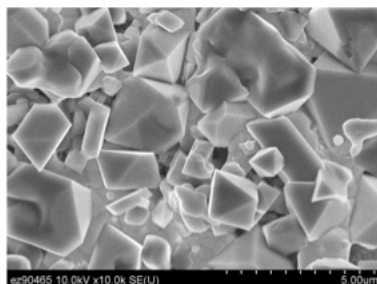
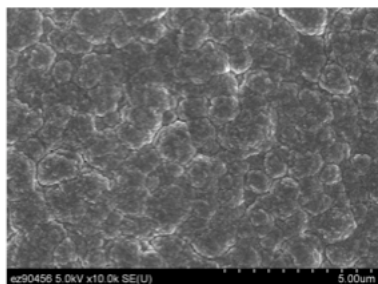
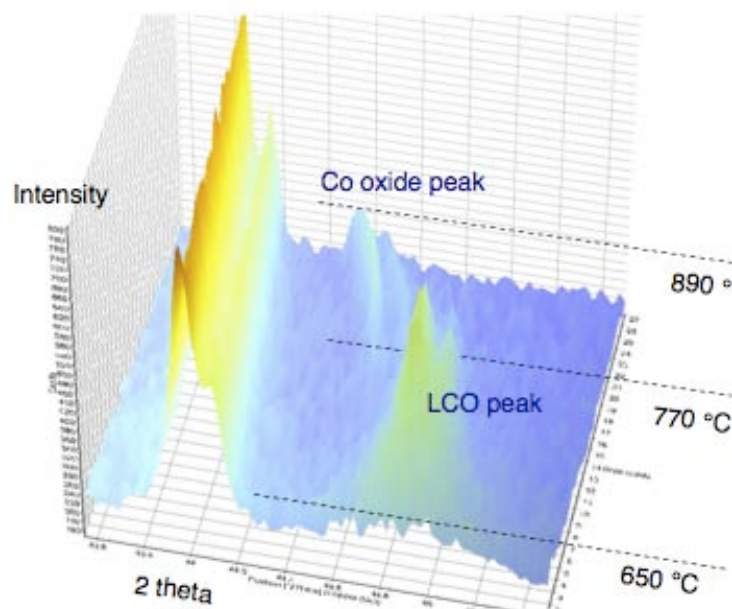
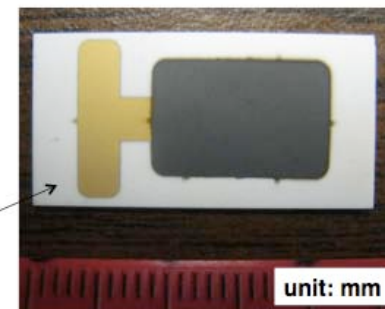
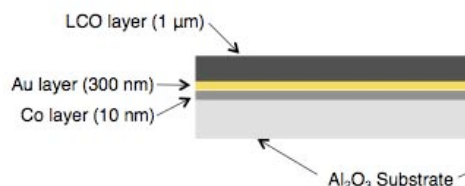


University of Michigan users Dr. Myounggu Park (foreground) and Dr. Honghyun Park analyze XRD data.

University of Michigan User Project: Experimental results



- Thin-film lithium lithium cobaltate cathode RF sputtered on alumina substrate with gold current collector and cobalt adhesion layer.
- In situ* XRD spectra (lower right) characterize thermal development from as-deposited amorphous layer to crystalline lithium cobaltate to crystalline cobalt oxide.
- Ex situ* SEM images (below) support interpretation of XRD data and characterize microstructure.



University of Michigan User Project: What we learned and accomplished



- continuous heat treatment
 - higher processing temperature induced Li loss and phase transformation!
 - final crystal structure was found to be cobalt oxide (FCC) consistent with SEM image
 - Cobalt oxide phase started to appear at 650 °C
- annealing (at 500 °C)
 - broad cobalt oxide peak started to appear immediately upon reaching 500 °C
 - peak height and width remained constant for 2 hrs of annealing, so phases were in equilibrium
 - grain size calculated to be 10 nm from XRD peak profile.

Heat treatment (time and temperature) need to be carefully controlled to ensure sufficient lithium cobaltate sintering and microstructure development without causing enough lithium loss to trigger decomposition to cobalt oxide.

Massachusetts Institute of Technology

“Structural analyses of battery materials for the electrification of vehicles”



Timeline

- Start date: 5/1/2008
- End date: 9/30/2010
- % complete: 95%

Budget

- Included in the user center allocations from the annual budget of the HTML User Program; users cost-share as noted on slide #3.

Barriers

- Cost
- Durability
- Fundamentals

Collaborators

- **MIT Users:** Prof. Y. M. Chiang, N. Meethong, Y. H. Kao
- **HTML Staff:** Jianming Bai

Massachusetts Institute of Technology:

User project background of study



- Olivine-based positive electrode materials are a potential component of high power, long-life lithium rechargeable batteries for vehicle applications.
- The reversibility and stability of electrochemically-induced phase transformations determine the energy, power, and life of battery systems.
- The reversibility and stability may be modified by aliovalent substitutions.
- There may be frequent application of electrical over- and underpotentials, the electrical analogs to undercooling and superheating.
- Overpotential effects on phase stability and transformation mechanisms have not been studied in detail and are not well understood.



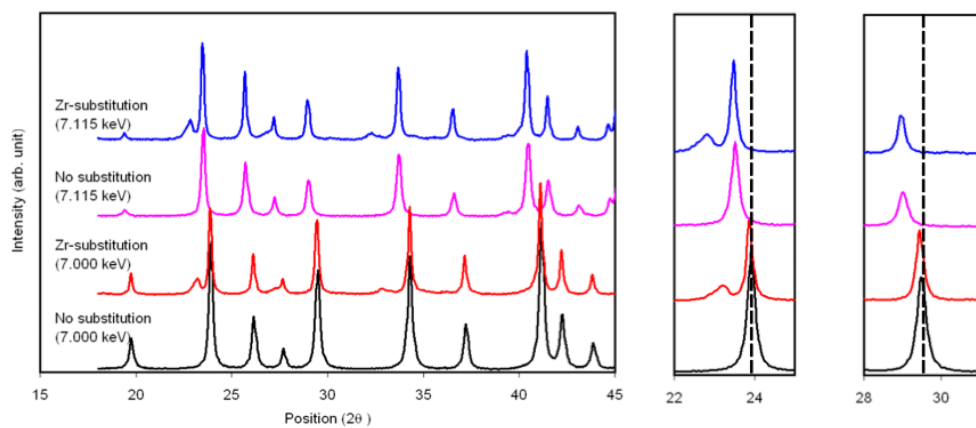
MIT graduate students, Nonglak Meethong (foreground) and Yu-Hua Kao at the HTML's X14A beamline (at the NSLS).

Massachusetts Institute of Technology

Phase 1 study: Effect of aliovalent dopants



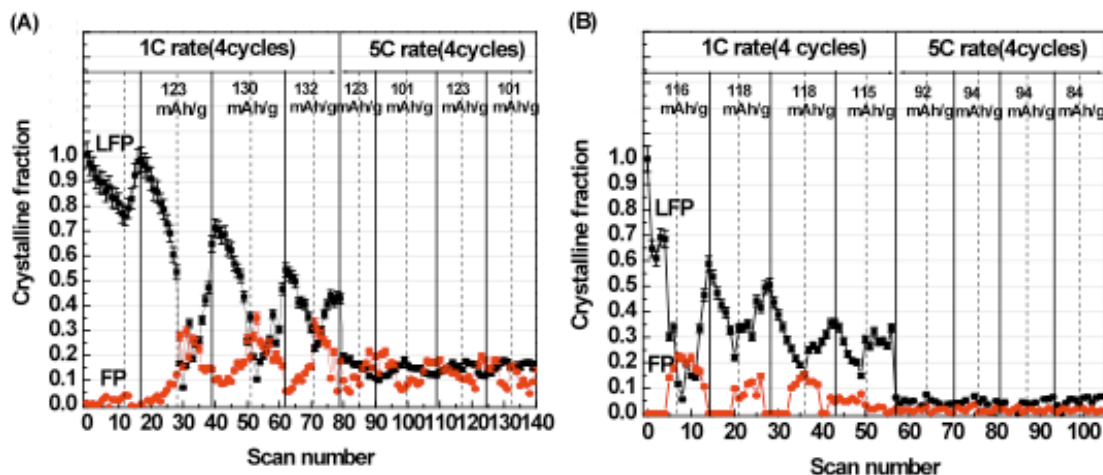
- **Research problem:** To determine the site occupancy of dopants in the olivine structure, with particular emphasis on identifying site mixing and site vacancies
- **Technical approach:** Resonant x-ray powder diffraction measurements were made on aliovalent cation (Mg^{2+} , Al^{3+} , Zr^{4+} , Ti^{4+} , Nb^{5+}) substituted olivine powders. This is a method unique to synchrotron x-ray sources. Two x-ray energies were selected, based on the x-ray absorption spectrum taken from the un-doped sample, to control the scattering factor contrast between Fe and other elements in the sample.



XRD patterns of Zr-substituted samples measured at both wavelengths clearly show shifting of peak positions toward low angles direction indicating unit cell dilation due to lattice-doping. A NASICON phase can also be observed for the Zr substituted samples.

Phase 2 study: Effect of cycling and overpotential

- **Research problem:** To determine overpotential effects on phase stability and transformation mechanisms in olivines.
- **Technical approach:** Synchrotron X-ray diffraction performed *in situ* during potentiostatic and galvanostatic cycling, combined with phase-field modeling, reveals a remarkable dependence of phase transition pathway on overpotential in the model olivine $\text{Li}_{1-x}\text{FePO}_4$. At both low (e.g., <20 mV) and high (>75 mV) overpotentials, a crystal-to-crystal olivine transformation is preferred, whereas at intermediate overpotentials, a crystalline-to-amorphous phase transition dominates.



Crystalline fraction determined from *in situ* XRD for 113nm (A) and 34nm (B) particle sizes under different charging conditions (four cycles at 1C followed by 4 cycles at 5C). It is the transformed amorphous phase that ends up being cycled.



What we learned and accomplished:

- Resonant synchrotron X-ray diffraction enabled detailed study of aliovalent dopant effects in olivine $\text{Li}_{1-x}\text{Fe}_{1-y}\text{A}_y\text{PO}_4$.
- Synchrotron X-ray diffraction performed *in-situ* during potentiostatic and galvanostatic cycling, combined with phase-field modeling, revealed a significant dependence of phase transition pathway on overpotential in the model olivine $\text{Li}_{1-x}\text{FePO}_4$.
- At both low (e.g., <20 mV) and high (>75 mV) overpotentials a crystal-to-crystal olivine transformation is preferred, whereas at intermediate overpotentials a crystalline-to-amorphous phase transition dominates.
- The overpotential-dependent phase transformation pathways seen in these experiments can be understood as an influence of driving force on nucleation and growth kinetics of competing phase transitions.

ORNL Materials Processing Group

“Development of an *in situ* XRD and acoustic emission technique for examination of fatigue behavior in lithium-ion battery electrodes”



Timeline

- Start date: 7/1/2009
- End date: 6/30/2011
- % complete: 60%

Budget

- Included in the user center allocations from the annual budget of the HTML User Program; users cost-share as noted on slide #3.

Barriers

- Cost
- Durability

Collaborators

- **Users:** Dr. Claus Daniel, Kevin Rhodes (UTK Ph.D. student)
- **HTML Staff:** E. Lara-Curzio

ORNL Materials Processing Group / University of Tennessee, Knoxville: User project background of study



- **Research problem:** To correlate acoustic emissions with damage processes induced during charging/discharging in lithium-ion cell electrodes
- **Technical approach:** Monitor acoustic emissions from battery electrodes during charging/discharging and utilize electron microscopy to characterize their damage.
- **Implications:** By developing an insight into both the mechanisms responsible for these occurrences of damage in battery electrodes and strategies to mitigate their effects, it will be possible to develop more durable and reliable batteries for hybrid and electric vehicles.



UT-Knoxville doctoral student Kevin Rhodes adjusts sample during acoustic emissions test.

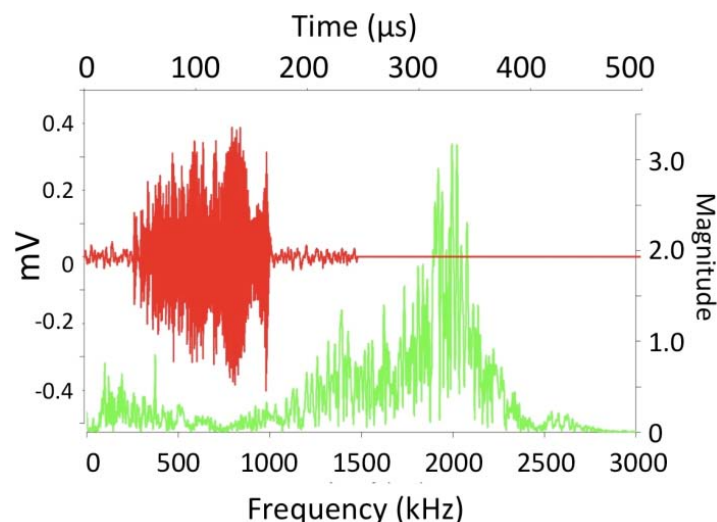
ORNL Materials Processing Group / University of Tennessee, Knoxville:

In situ AE spectra during battery cycling

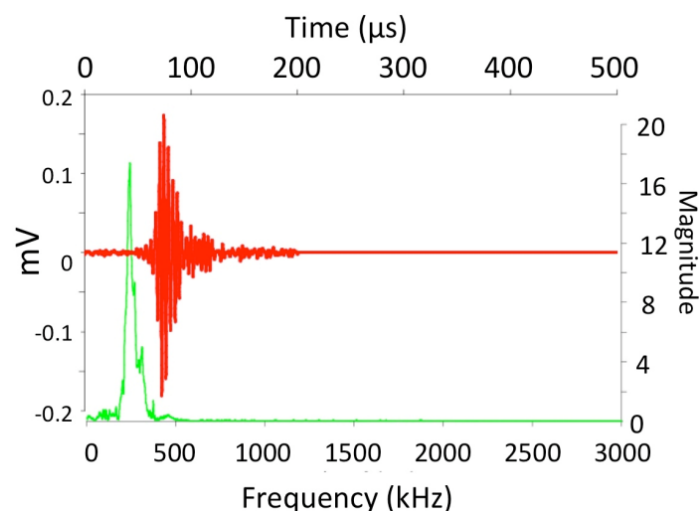


Part 1 objective – acoustic emission (AE) studies:

To characterize the acoustic emissions associated with the repeated charging-discharging cycling of lithium-ion half cells



Type I acoustic emission spectra. These were related to cracking events in the cell.



Type II acoustic emission spectra. These appear to be related to formation of carbon dioxide bubble in the electrolyte.

ORNL Materials Processing Group / University of Tennessee, Knoxville:

What we learned and accomplished



Acoustic emissions recorded during battery charging/discharging could be grouped into four classes, two of which are relevant to investigating damage processes.

Type I emissions were characterized by frequencies above 1 MHz and an amplitude of 27 dB, and are associated with cracking events.

Type II emissions had an average frequency of 238 kHz and were associated with the formation of CO₂ bubbles.

Examination of the cells at the end of the tests revealed the presence of cracks, which would be consistent with the occurrence of Type I emissions. Also, because CO₂ is a byproduct of the solid electrolyte interface formation, the occurrence of Type II emissions appears to be consistent with the formation of CO₂.

The potential of acoustic emission analysis as a tool to monitor the occurrence of damage in lithium-ion batteries has been demonstrated. This information provides insight into both the mechanisms responsible for these occurrences and the strategies to mitigate their effects, potentially contributing to the development of more durable and reliable batteries for hybrid and electric vehicles.

Summary

- The HTML User Program maintains world-class capabilities for materials characterization.
- During FY2009, the HTML User Program collaborated with 11 companies, 14 universities, and 3 national laboratories on 41 user projects addressing critical technical barriers to achieving the goals of DOE's Vehicle Technologies Program. HTML user projects typically last from a few months to two years and 6 of those projects were focused on Li-ion batteries.
- This poster presentation reviews HTML User Program projects with industry, universities and national laboratories that address fundamentals of operation, cost, performance, and life of lithium-ion batteries.