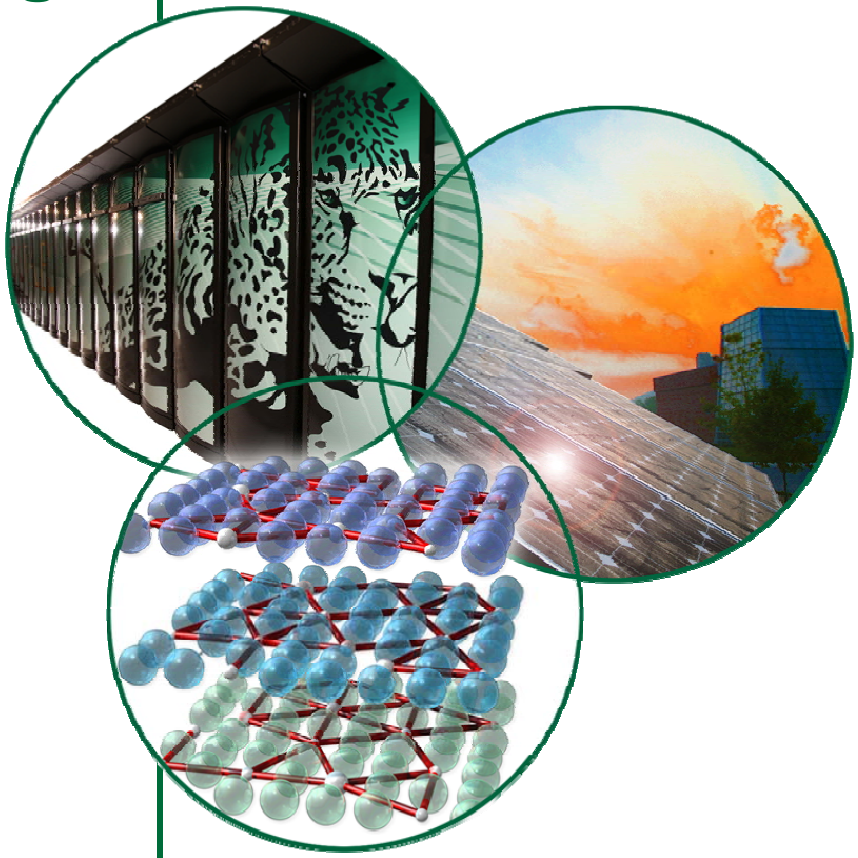
Project ID# Imp_02_payzant

Advanced Battery Materials Characterization: Success stories from the High Temperature Materials Laboratory (HTML) User Program



DOE 2009 Vehicle Technologies Annual Merit Review and Peer Evaluation Meeting

May 21, 2009

Dr. E. Andrew Payzant, ORNL

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U.S. DEPARTMENT OF ENERGY

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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 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. 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. 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. A nonproprietary project is complete when the results are published in the open literature and/or presented at a professional conference.

Project ID: IMP02, Payzant

The HTML User Program – FY2008 Activity

During FY2008, the HTML User Program managed 76 user projects from 53 different organizations.

The FY2008 budget for the HTML was $6,072,283 and was allocated as follows:

- $1,567,500 for capital equipment purchases
- $3,879,483 to support staff participation in user projects
- $626,000 for the operation of the user program

Users cost-share user projects through:

1) their direct involvement with HTML staff members during the development of the user project;
2) funding their travel to the HTML to perform research;
3) costs of materials provided by the user or the research performed prior to the user project;
4) their subsequent 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 FY2008, students and professors from 32 universities participated in the HTML User Program. Four of those students received their Ph.D. degree in FY2008 based in part on research performed through the HTML User Program.

Relevance to the VT Program

- The Vehicle Technologies Program supports the HTML User Program and provides an annual budget to address a wide range of materials-related issues in ground transportation systems arising from R&D needs in U.S. industry.

- The battery materials characterization user projects highlighted in this presentation address technology development issues associated with abuse-tolerance, durability and power density.

Overview

In this poster we highlight three HTML User Program projects focused on the characterization of materials for batteries.

- **Motorola Energy Systems Group**

- **Battery Research Group, Brookhaven National Laboratory**

- **Massachusetts Institute of Technology**

Project ID: IMP02, Payzant

Motorola Energy Systems Group

"Studying the effects of internal short circuit in Li-ion cells"

Timeline

- Start date: 5/16/08
- End date: 9/30/09
- % complete: 75%

Barriers

- Abuse tolerance
- Lack of standard method to test production cells

Budget

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

Collaborators

- User: Hossein Maleki
- HTML Staff: Hsin Wang

Project ID: IMP02, Payzant

User Project with Motorola Energy Systems

Research problem: Thermal runaway is an important safety and reliability issue for Li-ion batteries. The battery industry does not have a standard method to test production cells. The HTML is working with Motorola to develop a reliable method to test cells for potential of thermal runaway due to internal short.

Thermal conductivity of the cell materials determine how fast heat can be dissipated in an event of internal short. If local temperature reaches a critical point, thermal runaway will occur. High-speed infrared imaging was used to determine the temperature distribution in batteries.

Prismatic Li-ion cells were cut using a slow-speed diamond saw. A large piece (~1/3 of the cell) was used for through-thickness measurement and three 5-6 mm thick pieces in the middle section were used for in-plane measurements. The tests were done immediately with most of the electrolyte still in place.

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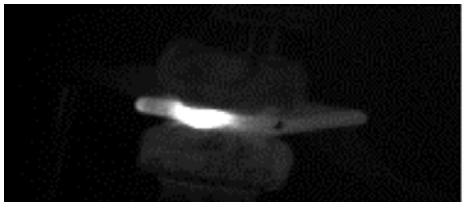
Motorola Energy Systems Group

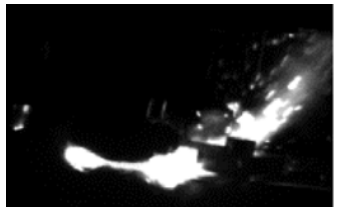
User Project with Motorola Energy Systems

A cross-section of a discharged cell showing the aluminum casing and the “jelly roll”.



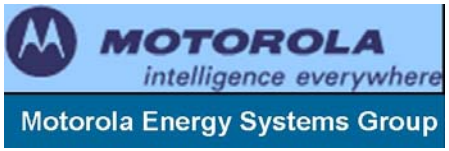
In a normal discharge shown in the above image, the cell heated up locally at the internal short location and the heat spread throughout the cell. The temperate rise was small (about 10ºC outside the aluminum can) and the cell was safe.

Cells from various manufacturers were charged up to 3.8V to 4.2V and subjected to mechanical pressure up to failure. Tested parameters included chemistry variations of the electrodes, separator materials, thickness, charging cycles. During every test, the IR imaging system was placed to view one side of the cell and record the temperature maps of the cell as a function of time. Depending on the test speed, the IR camera was set to take images at 60Hz or 30Hz.



During the thermal runaway shown at left, the initial local temperature rise could not be contained and was followed by a rapid temperature rise in the entire cell. The rise in temperature was much faster than normal and resulted in venting of hot gas and fire.

User Project with Motorola Energy Systems



- Thermal conductivity testing revealed that nearly all the heat transfer in a Li-ion battery is through the current collector, and it is extremely difficult to transfer heat through the “jelly roll”.

- We are working with Motorola to develop a reliable method to test the cells for potential of thermal runaway due to internal shorts. The initial testing method on charged cells was not supported with real-time monitoring sensors. Infrared imaging provided a convenient real-time measurement of cell temperature during the internal short and thermal runaway events.

- Such a test might be useful for future quality control evaluation of the potential for thermal runaway of Li-ion cells. More testing of cells are planned and thermal mechanical modeling efforts are underway in HTML and Motorola to better understand the process.

Battery Research Group: Brookhaven NL

"*In situ* XRD studies of cathode and anode materials for lithium-ion batteries"

BROOKHAVEN NATIONAL LABORATORY

Timeline

- Start date: 5/13/2008
- End date: 9/30/2008
- % complete: 75%

Barriers

- Testing fundamental theory and designing new diagnostic tools for exploratory battery development

Budget

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

Collaborators

- Users:
  Xiao-Qing Yang
  Kyung-Wan Nam
- HTML staff: Jianming Bai

Project ID: IMP02, Payzant

User Project with Battery Research Group, Brookhaven National Laboratory

Research Problem: Thermal stability during heating and structural stability during electrochemical cycling of battery materials.

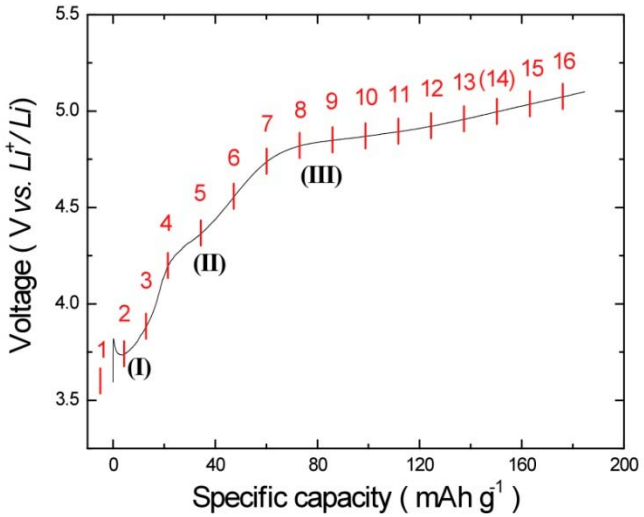
The changes in electronic and crystal structures for both uncoated and carbon coated $LiFe_{1/4}Mn_{1/4}Co_{1/4}Ni_{1/4}PO_4$ cathode materials during charge-discharge cycling were determined using the *in situ* x-ray diffraction capabilities of HTML's X14A synchrotron beamline at the National Synchrotron Light Souce (NSLS).

The work provides a deeper understanding of the charge-discharge process in Li-ion battery materials and provides essential data to improve the safety characteristics of lithium-ion batteries.

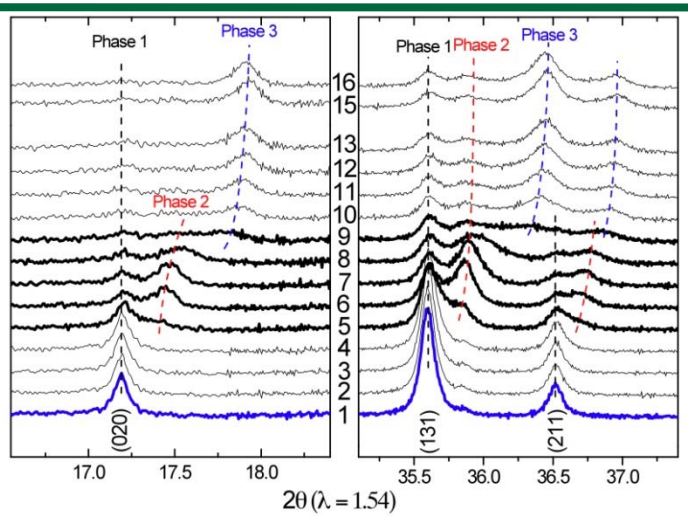
BROOKHAVEN NATIONAL LABORATORY

Project ID: IMP02, Payzant

User Project with Battery Research Group, Brookhaven National Laboratory



- First charge curve of carbon-coated $LiFe_{1/4}Mn_{1/4}Co_{1/4}Ni_{1/4}PO_4$, a new $LiMPO_4$ based cathode material synthesized by scientists at Beijing Institute of Physics, Chinese Academy of Sciences, who collaborate with the BNL researchers. Three voltage plateaus (marked as **I**, **II** and **III**) can be seen in the curve. X-ray absorption spectroscopy studies indicate that the plateaus I, II and III are attributed to the reduction-oxidation reactions of Fe^{2+}/Fe^{3+}, Mn^{2+}/Mn^{3+}, and Co^{2+}/Co^{3+}, respectively.



- *In situ* synchrotron x-ray diffraction (XRD) patterns of carbon coated **C** - $LiFe_{1/4}Mn_{1/4}Co_{1/4}Ni_{1/4}PO_4$ shown for the 2θ angle range which includes the (020), (131), and (211) reflections. The numbers marked between the patterns correspond to the scan numbers marked on the charge curve at left. Phase 1 is C-$LiFe_{1/4}Mn_{1/4}Co_{1/4}Ni_{1/4}PO_4$ before charging. Upon charging (i.e., Li de-intercalation), the reflections of the new intermediate phase 2 appeared at slightly higher 2θ values with growing intensities, and then the structure transforms to the final phase 3 of the fully de-lithiated compound (i.e., $Fe_{1/4}Mn_{1/4}Co_{1/4}Ni_{1/4}PO_4$).

Project ID: IMP02, Payzant

User Project with Battery Research Group, Brookhaven National Laboratory

- In the first phase of this project, a BNL-built charge-discharge cell, using lithium foil anode and $LiPF_6$ electrolyte, was used to test various cathode materials, e.g., lithium transition metal phosphates at different doping levels. Powder diffraction patterns were taken in transmission mode during the charge-discharge cycling, with a typical time scale of a few minutes per scan.
- Detailed analysis of these phase transitions is ongoing. 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 enhance our understanding of the thermal stability of these cathode materials and their interaction with electrolytes.

BROOKHAVEN NATIONAL LABORATORY

Massachusetts Institute of Technology

"Structural analyses of battery materials for the electrification of vehicles"

Timeline

- Start date: 5/13/08
- End date: 9/30/09
- % complete: 50%

Barriers

- Testing fundamental theory and designing new diagnostic tools for exploratory battery development

Budget

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

Collaborators

- Users:
  Yet-Ming Chiang
  Yu-Hua Kao
  Nonglak Meethong
- HTML Staff: Jianming Bai

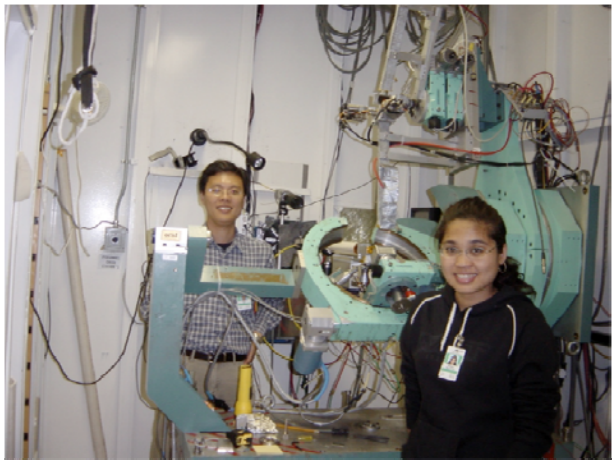
Project ID: IMP02, Payzant

User Project with Massachusetts Institute of Technology (MIT)

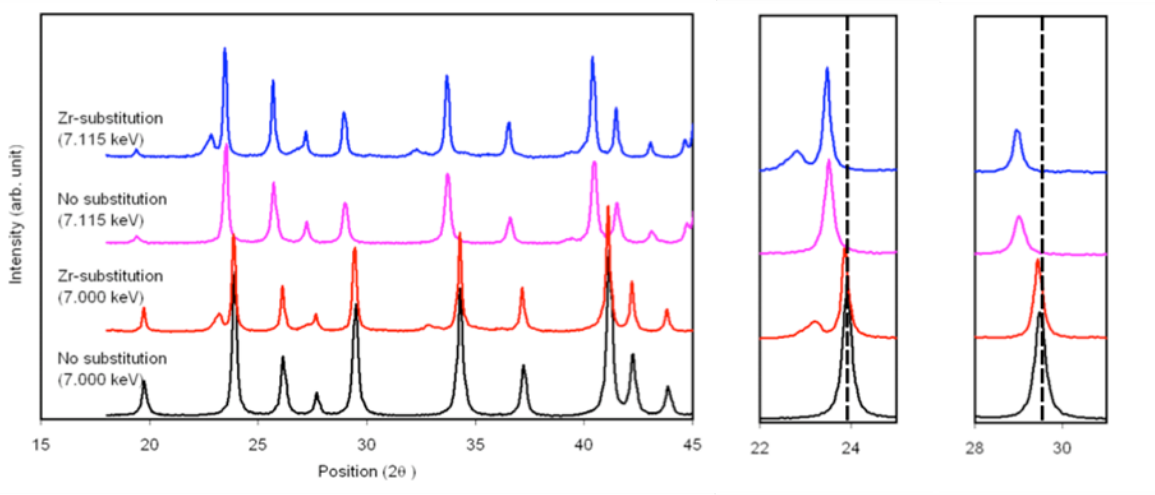
Research Problem: To investigate the crystal and defect chemistry of battery materials, including aliovalent substitutions and their effect on phase stability and transport properties, and on the thermodynamics and kinetics of electrochemically induced phase transformations. The reversibility and stability of these structural transformations determine the energy, power, and life of battery systems.

Implications: This research will provide important contributions to the development of high-performance rechargeable Li-ion batteries, by enabling fundamental understanding of the crystal and defect chemistry, including aliovalent solute substitutions and its effect on phase stability and transport properties of olivine-based $Li_{1-x}FePO4$ cathode materials. In addition, *in situ* studies may provide details of structural changes and its effect on electrochemical properties of this class of materials.

User Project with Massachusetts Institute of Technology (MIT)



Two graduate students, Nonglak Meethong (front) and Yu-Hua Kao (back) from the MIT Department of Materials Science and Engineering at the HTML synchrotron x-ray beamline at the NSLS.



Resonant XRD patterns at two different wavelengths of alivolavent cation substituted olivine powders. Example patterns are taken from Zr-substituted samples and control (No substitution) samples of similar particle size (< 50 nm). XRD patterns of the Zr substituted samples measured at both wavelengths clearly show shifting of peak positions toward low angles direction indicating unit cell expansions due to lattice-doping. A NASICON phase can also be observed for the Zr substituted samples.

User Project with Massachusetts Institute of Technology (MIT)

- In the first phase of this project, synchrotron x-rays were used to determine the site occupancy of dopants in the olivine structure, with particular emphasis on identifying site mixing and site vacancies
- Resonant x-ray powder diffraction measurements were made on alivolavent cation (Mg2+, Al3+, Zr4+, Ti4+, Nb5+) -substituted olivine powders.
- For each doped sample, two x-ray energies were selected to optimize the scattering factor contrast between Fe and other elements in the sample. This method enables determination of specific doping sites.
- Future tasks of the project to be completed in FY2009 include analyzing the average defect structure of the crystallites, determining crystallite size and microstrain, and studying the change in crystal structure with cycling under *in situ* conditions.

Future Work – Battery Materials Characterization Projects at the HTML

- **Complete work on projects highlighted in this poster presentation.**
- **During FY2009, three more user proposals dealing with characterization of Li-ion battery materials have been received. Some of these projects already have been initiated. These projects were submitted by:**
  - Massachusetts Institute of Technology
  - University of Texas, Austin (in partnership with MIT)
  - ORNL in partnership with University of Tennessee, Knoxville

Summary

- **Throughout FY2008, the High Temperature Materials Laboratory (HTML) User Program provided valuable characterization support for three User Projects investigating advanced battery materials. This support has continued into FY2009.**