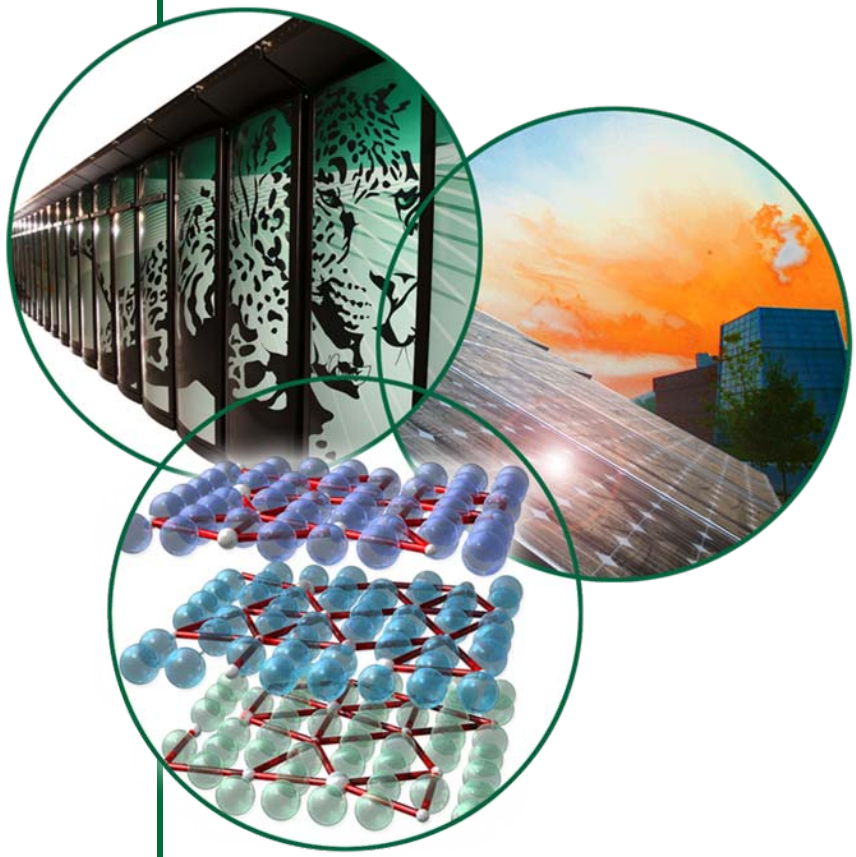
Materials Characterization Capabilities at the High Temperature Materials Laboratory and HTML User Program Success Stories

Project ID
Im028

DOE 2010 Vehicle Technologies Annual Merit Review and Peer Evaluation Meeting

Edgar Lara-Curzio
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

U.S. DEPARTMENT OF ENERGY

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

OAK RIDGE NATIONAL LABORATORY
MANAGED BY UT-BATTELLE FOR THE DEPARTMENT OF ENERGY

The HTML User Program – Objectives & Relevance

- The HTML is a DOE Designated National User Facility. 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 to address critical technical barriers to achieving the goals of DOE's Vehicle Technologies Program.
- User projects address technical barriers in most of the Vehicle Technologies Program technology areas.
- The HTML User Program capabilities are also being utilized to support Vehicle Technologies Program projects at ORNL in the program's technology areas of Lightweight Materials, Propulsion Materials, Energy Storage and Thermoelectric Conversion.

Overview

Timeline

Project Start Date: 1987
Project End Date: -

Barriers

HTML user projects address cost and technical barriers in most of the Vehicle Technologies Program technology areas.

Budget

The FY2009 budget for the HTML was $5,066,946

- $514,025 for capital equipment purchases
- $4,552,921 for the operation of user program

Users cost-share user projects through:

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

Partners

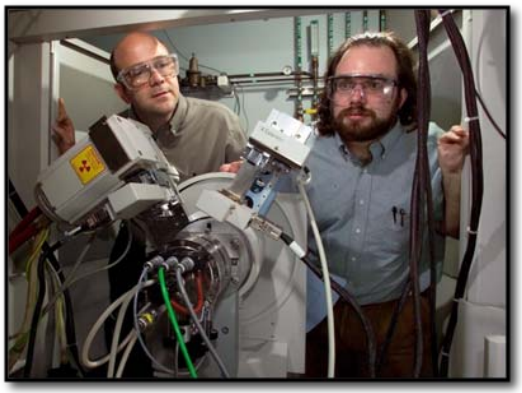
During FY2009, **11 companies, 14 universities and 3 national laboratories** participated in the HTML User Program on 41 projects. Participating organizations are listed in the appendix.

The HTML User Program also supports the education and preparation of a new generation of scientists and engineers. 27 students participated in the HTML User Program during FY2009. Six of those students received advanced degrees in FY2009 based in part on research performed through the HTML User Program.

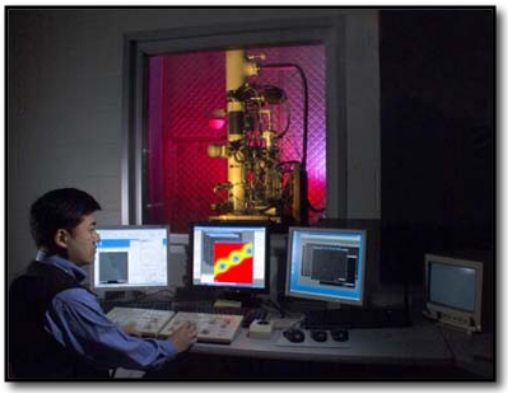
Approach

The HTML is organized into 6 User Centers,

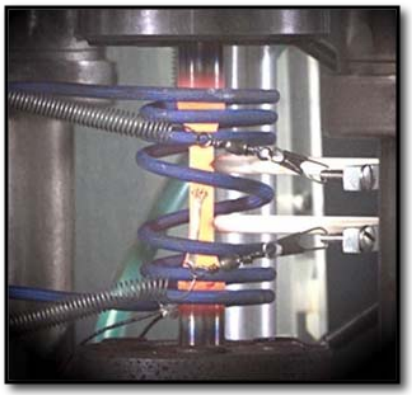
which are clusters of highly skilled staff and sophisticated, often one-of-a-kind instruments for materials characterization



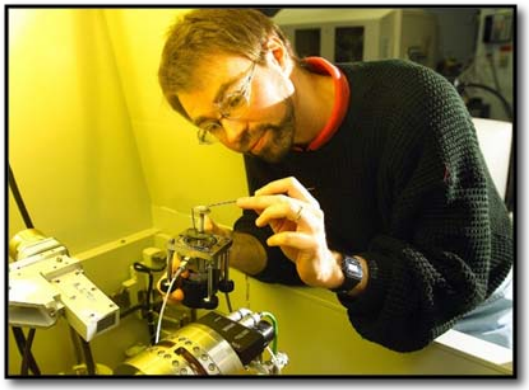
Diffraction



Materials Analysis



Mechanical Characterization

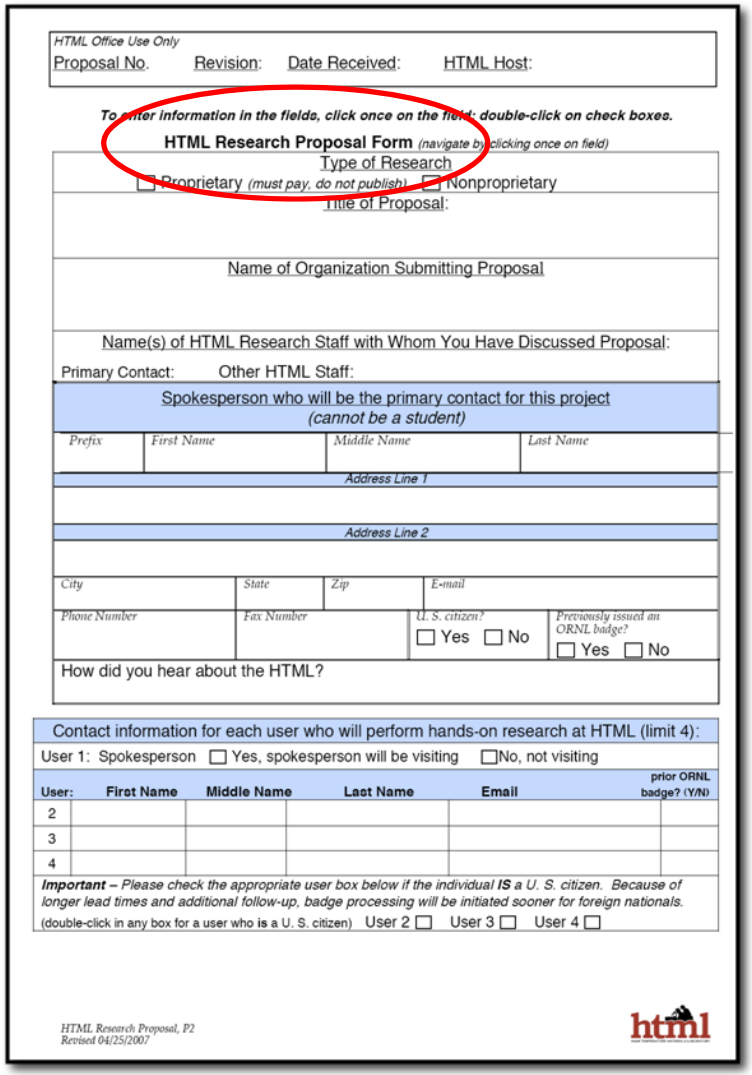


Residual Stresses

Thermography & Thermophysical Properties

Tribology Research

Approach: Access to the HTML



HTML Office Use Only
Proposal No. Revision: Date Received: HTML Host:

To enter information in the fields, click once on the field; double-click on check boxes.

HTML Research Proposal Form *(navigate by clicking once on field)*

Type of Research
☐ Proprietary *(must pay, do not publish)* ☐ Nonproprietary

Title of Proposal:

Name of Organization Submitting Proposal

Name(s) of HTML Research Staff with Whom You Have Discussed Proposal:

Primary Contact: Other HTML Staff:

Spokesperson who will be the primary contact for this project *(cannot be a student)*

Prefix	First Name	Middle Name	Last Name

Address Line 1

Address Line 2

City	State	Zip	E-mail

Phone Number	Fax Number	U. S. citizen?	Previously issued an ORNL badge?
		☐ Yes ☐ No	☐ Yes ☐ No

How did you hear about the HTML?

Contact information for each user who will perform hands-on research at HTML (limit 4):

User 1: Spokesperson ☐ Yes, spokesperson will be visiting ☐ No, not visiting

User:	First Name	Middle Name	Last Name	Email	prior ORNL badge? (Y/N)
2					
3					
4					

Important *– Please check the appropriate user box below if the individual **IS** a U. S. citizen. Because of longer lead times and additional follow-up, badge processing will be initiated sooner for foreign nationals.*

(double-click in any box for a user who is a U. S. citizen) User 2 ☐ User 3 ☐ User 4 ☐

HTML Research Proposal, P2
Revised 04/25/2007

html

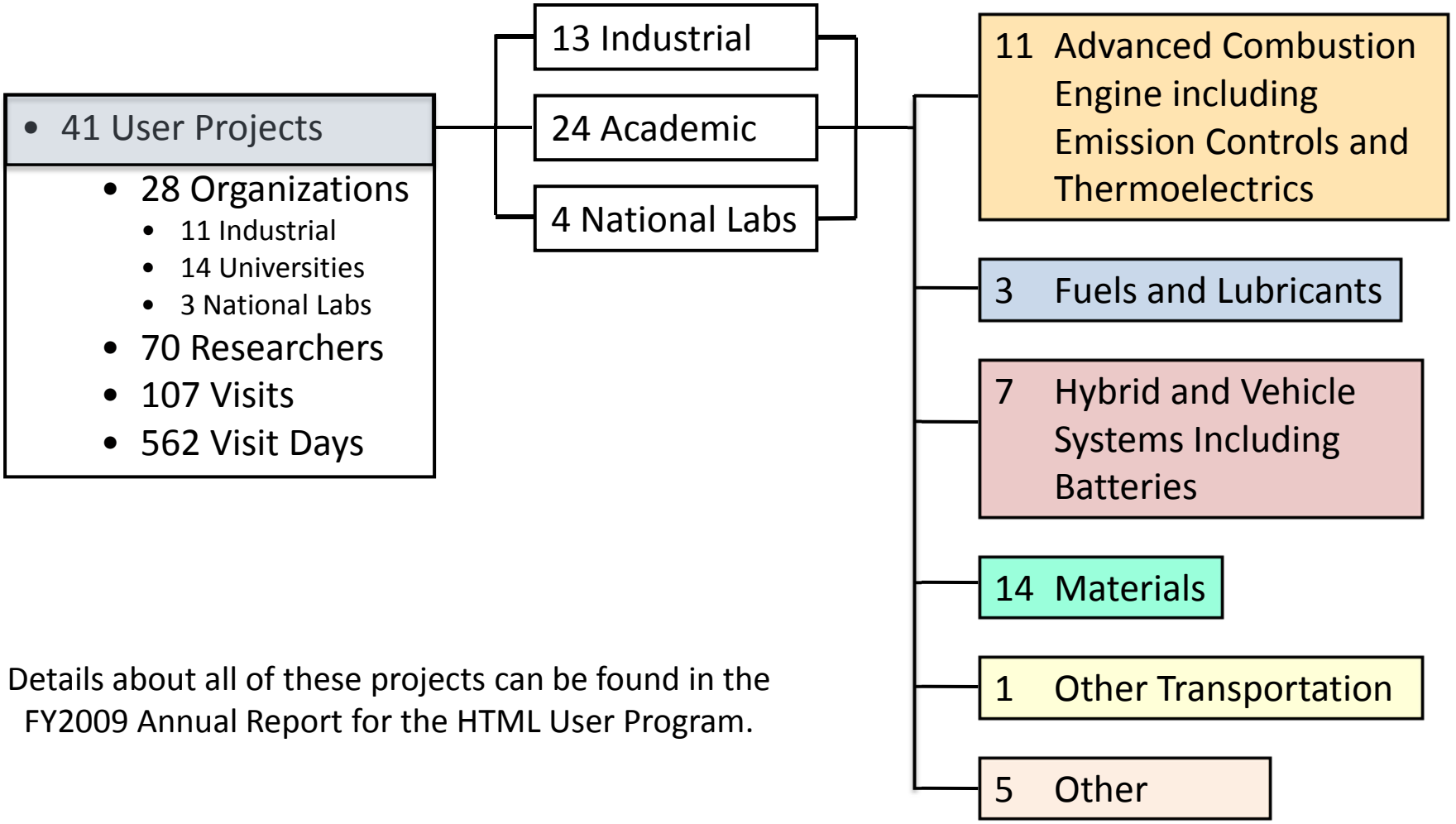
- Access to the HTML User Program is provided through a formal proposal process. Proposals are reviewed by an internal review committee and evaluated based on
  - Technical merit
  - Relevance of the proposed research to the mission of the Vehicle Technologies Program
  - Non-competition with the private sector
  - Organizations based in the U.S.
- Research is completed within 24 months, and it involves one or more user visits to the HTML.

A user agreement (proprietary or non-proprietary) is required prior to starting a user project.

Performance Goals and Milestones

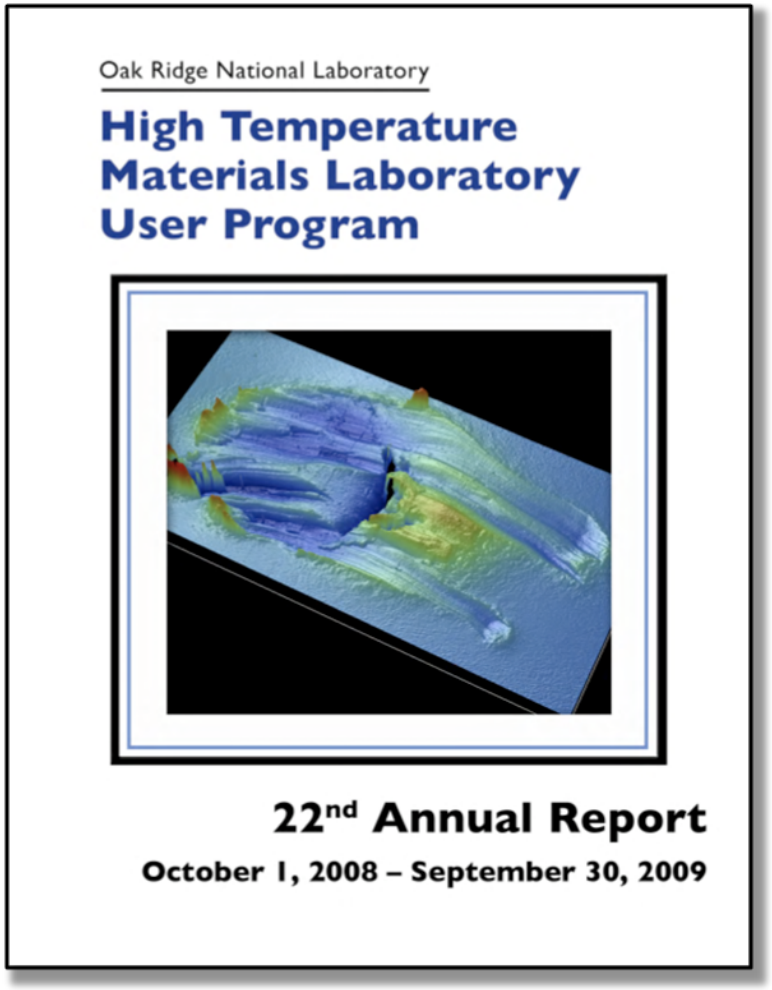
Milestones for FY2009		
1	Complete the installation of new state-of-the-art laser flash thermal diffusivity apparatus and differential scanning calorimeter used to determine the physical properties of materials.	Completed
2	Complete three user projects dealing with characterization of materials for Li-ion batteries.	Completed
3	Develop capabilities to perform *in situ* microstructural observations of materials for energy (e.g., Li-ion batteries, thermoelectrics) using electrons, X-rays and neutrons.	Completed

The HTML User Program - Accomplishments



Details about all of these projects can be found in the FY2009 Annual Report for the HTML User Program.

The HTML User Program - Accomplishments



HTML User Program FY2009 Annual Report

A copy of the annual report was provided to reviewers

The HTML User Program - Accomplishments

Examples of User Projects

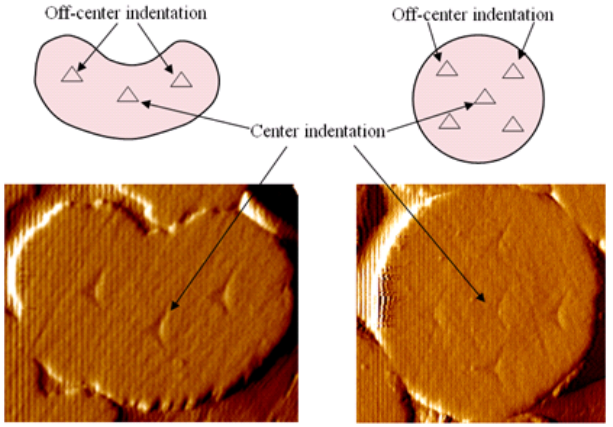
ORNL Polymer Matrix Composites Group

"Development of next generation low-cost carbon fibers: Microstructural analysis"

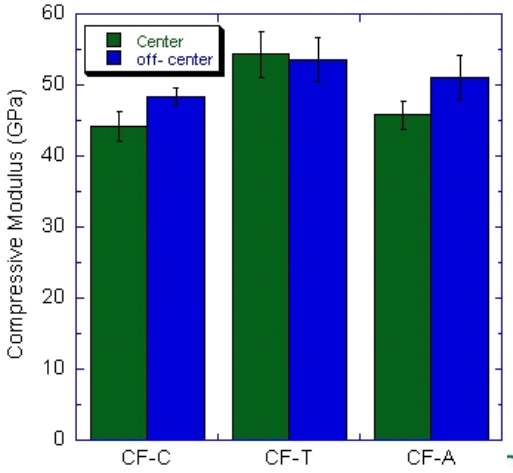
Research problem	To evaluate the micro-structure of carbonized fibers obtained from various precursors and processing conditions.
Technical approach	X-ray diffraction and nanoindentation were performed to determine the elastic modulus and crystallographic characteristics of carbon fibers.
Implications	High cost of carbon fibers is the greatest single barrier to their use in automotive and commercial vehicle applications. Also, adequate design data are necessary for the widespread application of these materials.
Barriers	Cost, Design Data, Manufacturability
Collaborators	**ORNL Users**: Soydan Ozcan and Felix Paulauskas **HTML Staff**: Rosa Trejo and Andrew Payzant

ORNL Polymer Matrix Composites Group Accomplishments

- The compressive elastic modulus of three carbon fibers from different precursors was determined from nanoindentation tests. Indents were made at on-center and off-center (close to fiber edges) locations of the fiber's cross-section.
- Elastic modulus values were found to be lower at the center of the fiber, which is believed to result from differences in the microstructure that arise from the kinetics of oxidation.
- Analysis of the X-ray diffraction data suggest that the elastic modulus of carbon fibers is a function of the orientation of crystallites but independent of the length and thickness of crystallites.
- The information obtained from this project will be used to optimize accelerated processing of carbon fiber precursor conversion to significantly reduce the cost of fiber production.



Schematic and images taken after indentation test, kidney shape textile-based carbon fiber (CF-T; left) and aerospace grade carbon fiber (CF-A; right).



Compressive elastic modulus results for commodity (CF-C), textile and aerospace grade fibers.

Innegrity, LLC

"Toughness of high performance Innegra™ S fibers at high strain rates"

Research problem	To characterize and understand the mechanical properties of Innegra™ S fibers, which are highly oriented polypropylene fibers and the lightest fibers currently available (0.67 g/cm^3).
Technical approach	Determined the effect of strain rate on the tensile strength of Innegra™ yarns using ORNL's high-rate servohydraulic testing machine. Special grips were developed for these tests.
Implications	Adequate design data (material property databases), test methods, and durability data are necessary for widespread application of advanced lightweight materials.
Barriers	Cost, Design Data, Performance
Collaborators	**Innegrity Users**: Michael Grah, Loren Chambers, and Brian Follo **HTML Staff**: Don Erdman and Barbara Frame

Michael Grah from Innegrity cuts a test specimen yarn prior to high-rate tensile testing.

Innegrity, LLC
User Project Accomplishments

Brian Follo inserts yarn into the high-rate tensile testing machine.

- Yarns with a gauge length of 25.4 cm were evaluated at strain rates of $0.1s^{-1}$, $1.0s^{-1}$ and $10.0s^{-1}$.
- The tensile strength of Innegra™S yarns was found to increase with strain rate from 8.69 g/denier at $0.1s^{-1}$ to 9.38 g/denier at $10s^{-1}$.
- The toughness of Innegra™S yarns decreased with strain rate.

Innegrity is developing hybrid composites using Innegra ™S fibers in combination with carbon, glass and aramid fibers. The mechanical properties of these hybrid composites will be evaluated as a function of strain rate in a future HTML User Program project.

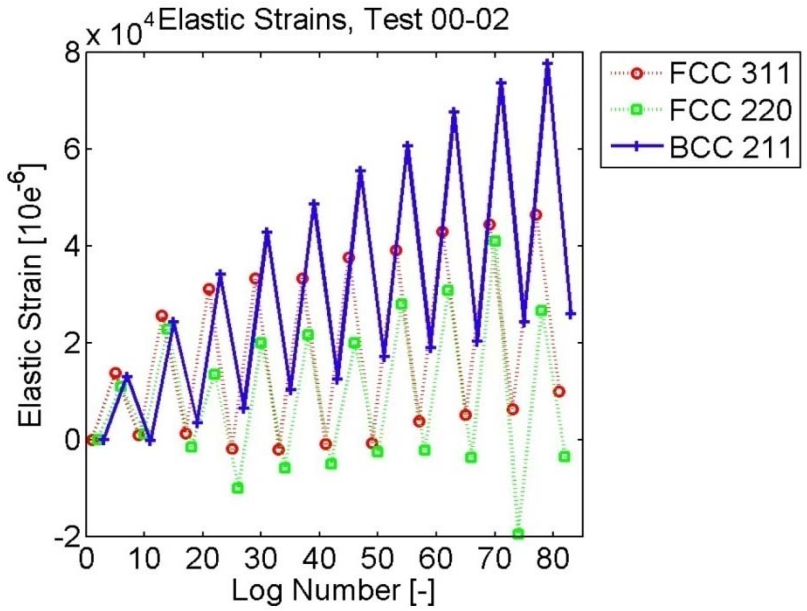
MIT's Impact and Crashworthiness Lab

"*In situ* neutron diffraction of residual strains and monitoring of martensitic phase transformation in austenitic stainless steel sheet"

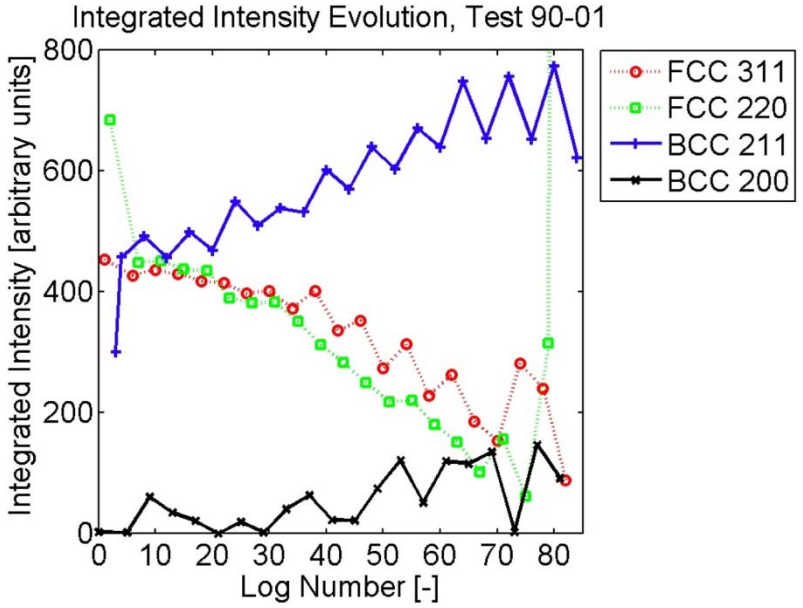
Research problem	To develop models for the transformation kinetics and plasticity laws of 301LN Advanced High Strength Steel (AHSS).
Technical approach	Collect *in situ* neutron diffraction data at the HTML User Program's neutron residual stress facility (NRSF2) to develop models for phase transformation, texture, and stress as functions of applied uniaxial load.
Implications	Constitutive and fracture models for AHSSs could lead to vehicle weight reduction without sacrificing safety.
Barriers	Design data (material property databases), test methods, analytical tools (i.e., models), and durability data.
Collaborators	**MIT Users**: Allison Beese and Scott Speakman **HTML Staff**: Camden Hubbard, Josh Schmidlin

MIT's Allison Beese prepares for an *in situ* loading neutron diffraction measurement at NRSF2

MIT's Impact and Crashworthiness Lab User Project Accomplishments



Measured diffraction elastic strain versus log number for two FCC and the BCC 211 diffraction lines for grains parallel to the loading direction. The load was step-wise increased and then released after each increase, leading to the saw-tooth patterns.



The drop of intensity of the two FCC lines and increase of intensity of the BCC lines provide quantitative data for monitoring transformation of grains parallel to the loading direction as plastic deformation increases. The BCC 200 lines have near zero intensity due to high texture in the as-prepared sample (log 0).

These *in situ* neutron diffraction results are contributing to the advancement of Advanced High Strength Steels for lightweighting vehicular structures.

Deere and Company, Moline Technology Innovation Center

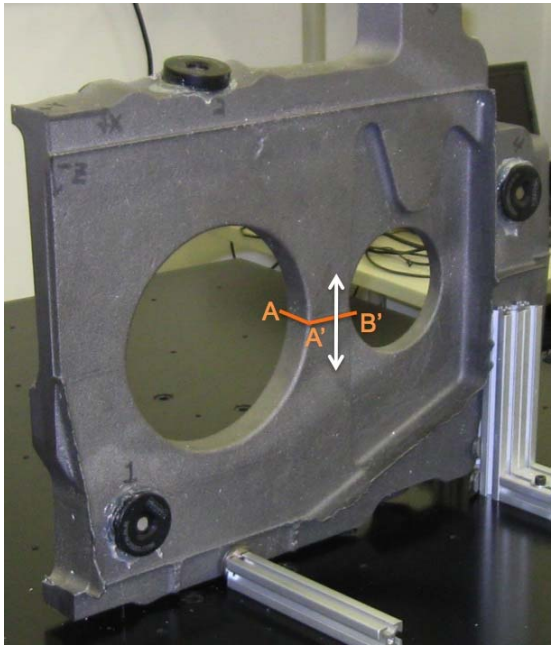
"Effect of cooling rate on residual stresses in gray cast iron"

Research problem	Build and validate computational tools for casting modeling in support of Deere's goal of implementing virtual design, testing and manufacturing of vehicles by 2015.
Technical approach	Measure residual stresses in cast ductile iron components using through-thickness mapping at the HTML User Program's neutron residual stress facility (NRSF2) and compare results with model predictions. A transmission housing and a stress-lattice test specimen were examined.
Implications	Data from this research will be used to validate models to increase casting rates in foundries, lower vehicle weight, and reduce production scrap rate.
Barriers	Design data (material property databases), test methods, analytical tools (i.e., models), and manufacturability.
Collaborators	**Deere Users**: Eric Johnson and Mohamad El-Zein **HTML Staff**: Tom Watkins, Amit Shyam, Josh Schmidlin, and Cam Hubbard

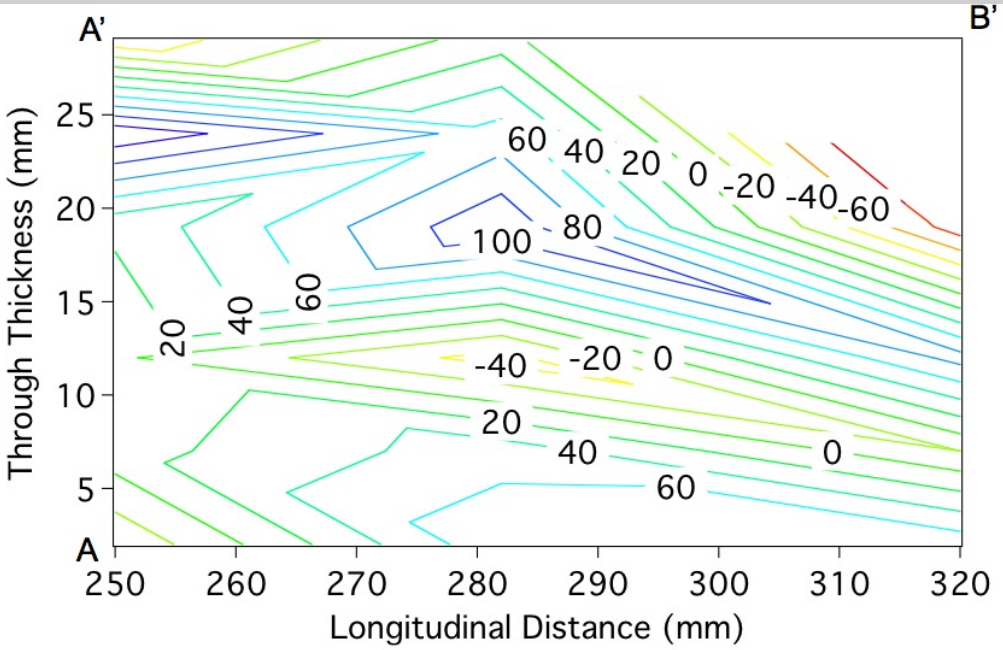
Eric Johnson uses laser scan arm to prepare for neutron diffraction residual stress measurements.

Stress-lattice test specimens

Deere and Company, Moline Technology Innovation Center: User Project Accomplishments



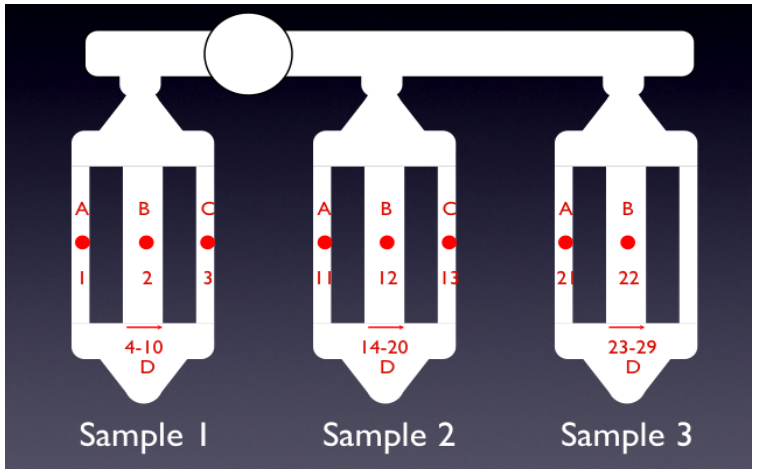
Close-up of transmission housing specimen showing the “knit line” or sample mid plane (plane AA’BB’) where two fronts of molten metal meet during casting.



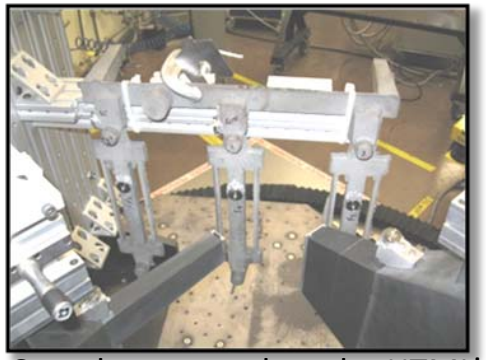
Map of the stresses (MPa) perpendicular to the “knit line”. The upper right corner is a cut-in portion of the casting.

Most of the stresses perpendicular to the “knit line” are tensile, which might result in reduced strength and fatigue life.

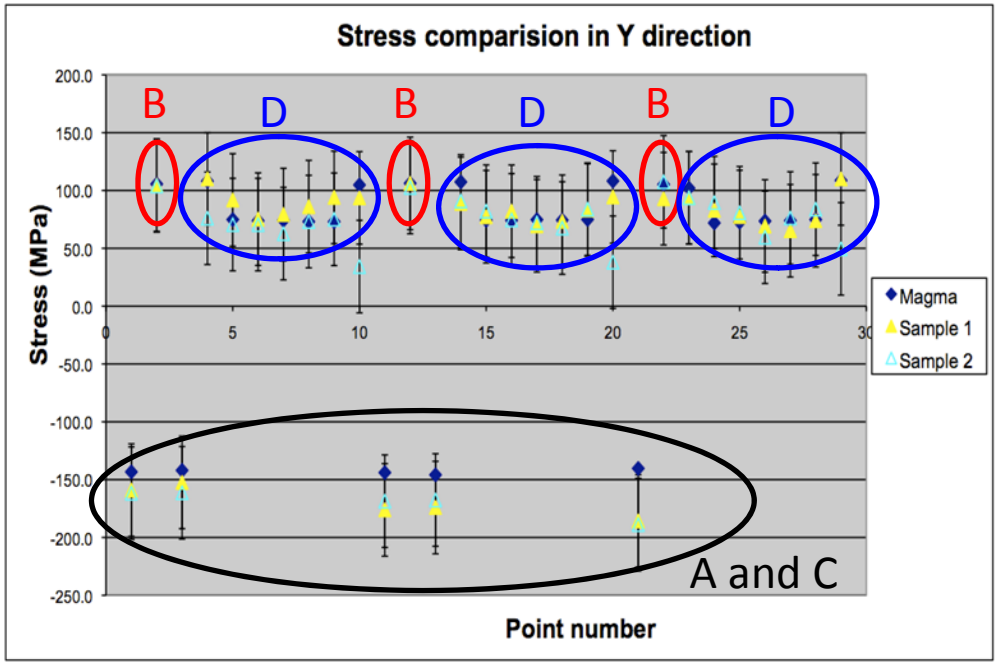
Deere and Company, Moline Technology Innovation Center: User Project Accomplishments



Stress-lattice test specimen measurement locations for neutron diffraction stress mapping.



Sample mounted on the HTML's neutron diffractometer.



Measured residual stresses for all three directions validate the stress predictions for the stress-lattice test specimen.

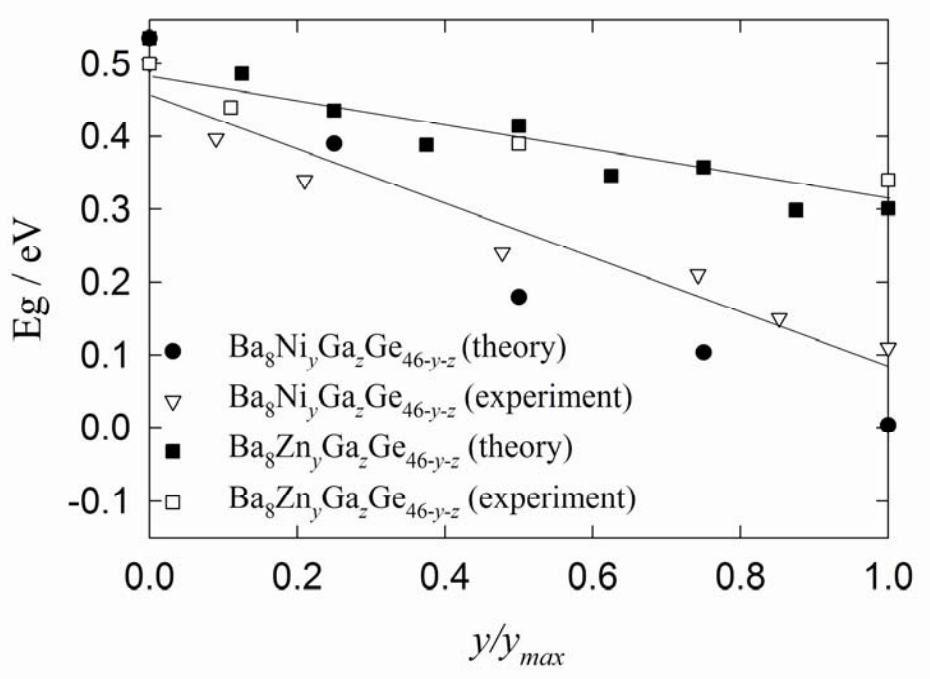
Deere found the correlation of the measured and predicted results for the two castings exceptionally good. Deere is using the validated models to optimize casting operations.

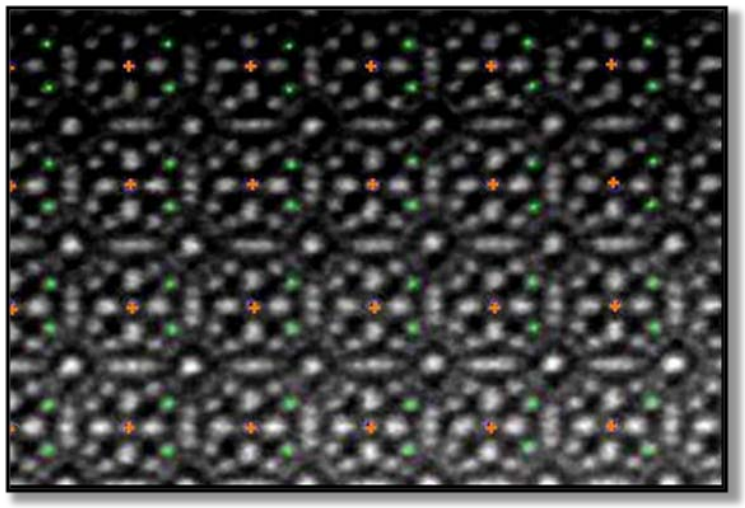
General Motors R&D Center User Project: "Thermoelectric properties of clathrates through a systematic cross-substitution of framework elements"

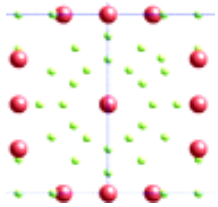
Research problem	Develop fundamental understanding of the structure-property relationships for clathrate thermoelectric materials.
Technical approach	Utilize advanced techniques to characterize the atomic structure of clathrate thermoelectric materials and their transport and electronic properties.
Implications	Thermoelectrics with a high figure of merit will enable the conversion of waste heat from engines into electrical energy to improve overall thermal efficiency and reduce emissions.
Barriers	Scale-up to a practical thermoelectric device, high figure of merit (ZT), and lack of standardized test methods
Collaborators	**GM Users**: Xun Shi, Jihui Yang, James Salvador **HTML Staff**: Hsin Wang, Miaofang Chi

Dr. Xun Shi from General Motors analyzes transport measurement data.

General Motors R&D Center User Project: Accomplishments







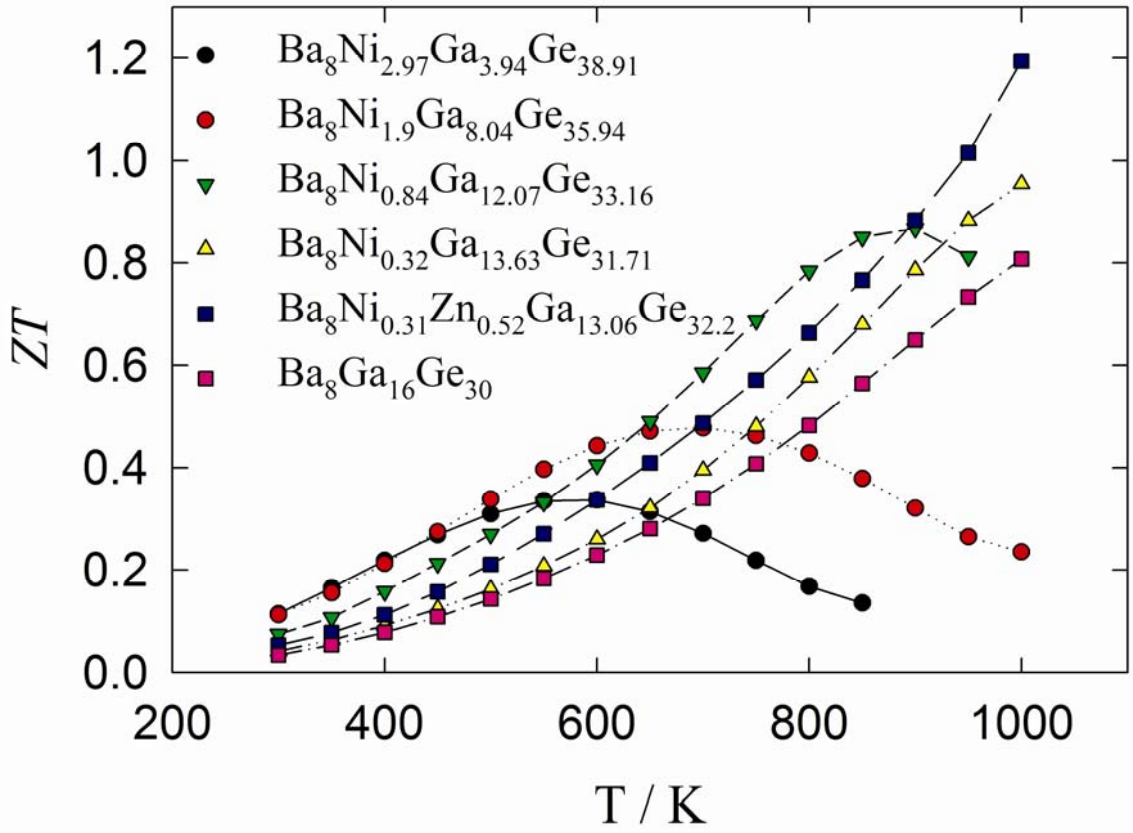
Ba
Ge/Ga

STEM image along the [100] direction for $Ba_8Ni_yGa_zGe_{46-y-z}$

- GM designed clathrates with composition that was changed by systematic cross-substitution of elements in the framework structure.
- Experimental measurements verified the ability to "tune" the band gap between 0.1eV and 0.5eV.

General Motors R&D Center User Project: Accomplishments

Temperature dependence of ZT for transition metal-substituted $Ba_8Ga_{16}Ge_{30}$. Maximum ZT is 1.2 near 1000K.



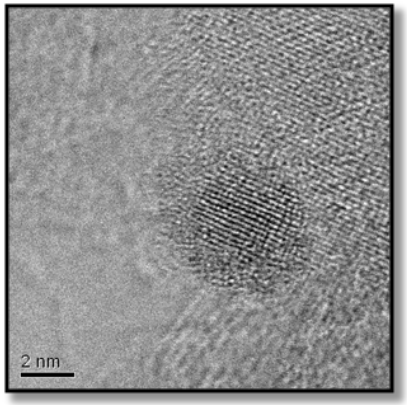
University of Michigan/Ford Research

"Characterization of Alumina-Supported Pt and Pt-Pd Alloy NO Oxidation Catalysts with Advanced Electron Microscopy"

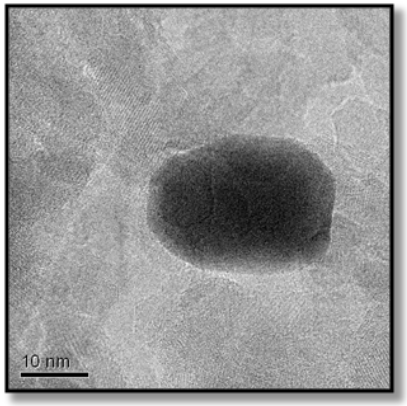
Research problem	To determine the relative efficacy of Pt/alumina vs. bimetallic Pt-Pd/alumina materials for the catalytic after-treatment of exhaust emissions in lean-burn gasoline and diesel engines.
Technical approach	Utilize the unique capabilities at the HTML for characterization of experimental Pt and Pt-Pd on alumina catalytic materials to obtain chemical and structural information at the atomic level, via aberration-corrected electron microscopy techniques.
Implications	Development of cost-effective, durable catalysts for emission control.
Barriers	Cost, Durability, Fundamentals of Catalysis
Collaborators	**Users**: X. Pan and O. Ezekoye (U. of Michigan) and A. Drews and G. Graham (Ford) **HTML Staff**: Larry Allard

University of Michigan Ph.D. student Obi Ezekoye at controls of the HTML User Program's ACEM at ORNL.

University of Michigan/Ford Research User Project



500°C Aging
particle size ~5nm



900°C Aging
particle size ~25nm

- Application of advanced electron microscopy techniques to characterization of alumina-supported Pt and Pt-Pd bimetallic catalysts has allowed us to understand the relation between alloying and particle coarsening aging under lean conditions .
- Some direct association between Pt and Pd was observed at the initial stage of bimetallic catalyst synthesis, but there is clearly a strong tendency for alloying to proceed *in situ* during the course of lean aging. This has a positive influence on limiting the growth of anomalously large particles typically found in pure Pt catalysts that have been harshly aged under lean conditions.
- We have also demonstrated that replacement of moderate amounts of Pt with Pd can be done with little or no loss of activity for NO oxidation. Further, standard catalyst precursors and synthesis methods have been shown to suffice.
- The use of Pd to both increase catalyst durability and decrease Pt loading in Pt-based catalysts for lean-burn engine exhaust-gas treatment thus appears even more favorable than before.

Pacific Northwest National Laboratory

"Morphological and Electronic Structure of Pt-Re Nanoparticles Supported on Carbon under Activation and Reaction Conditions for Aqueous-Phase Reforming of Bioliquid"

Research problem	To understand the mechanisms by which Re enhances the activity of Pt/activated carbon catalysts for aqueous phase reforming (APR) of oxygenated hydrocarbons for production of hydrogen and biofuels.
Technical approach	Characterize experimental Pt and Pt-Re on "real" activated carbon supports and on "model" thin film carbon supports, to obtain chemical and structural information at the atomic level, via aberration-corrected electron microscopy techniques
Implications	Development of cost-effective, durable catalysts for hydrogen and biofuel production.
Barriers	Cost, Durability, Fundamentals of Catalysis
Collaborators	**PNNL Users**: Liang Zhang and Yong Wang **HTML Staff**: Larry Allard

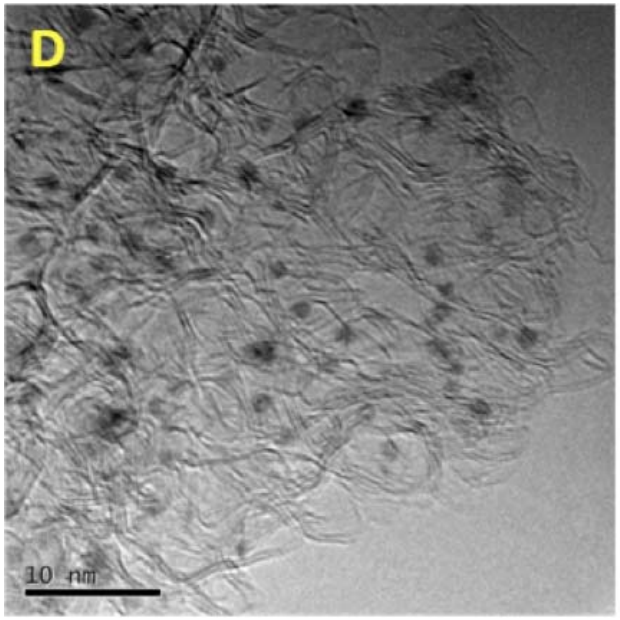
Dr. Liang Zhang at controls of the HTML User Program's ACEM at ORNL

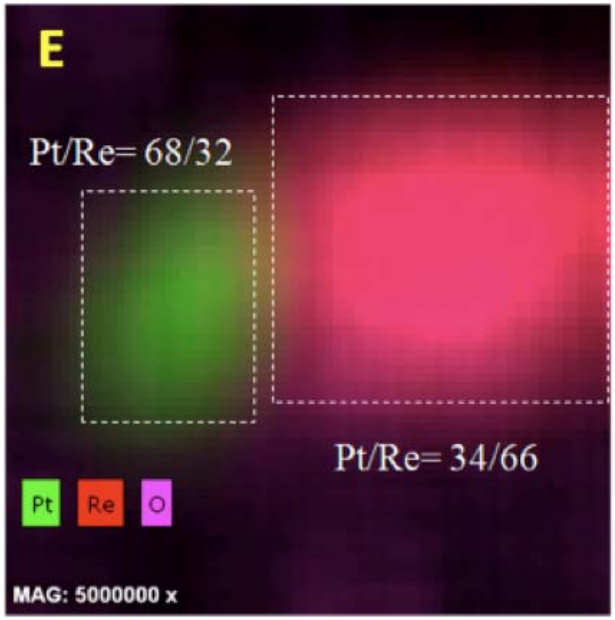
Pacific Northwest National Laboratory User Project

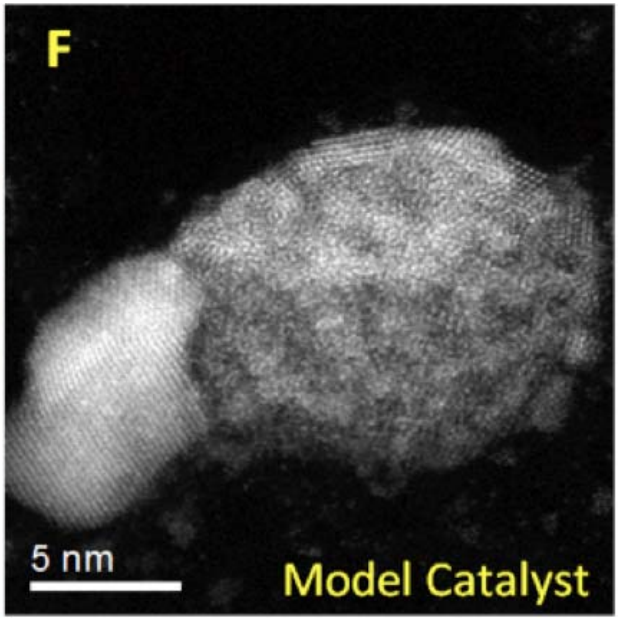
Pacific Northwest NATIONAL LABORATORY

"Real" APR catalyst

"Model" APR catalyst for *in situ* studies







D. PtRe nanoparticles retained in "turbostratic" carbon structure with graphite sheet fragments. EDS showed Pt-rich and Re-rich particles.

E, F: PtRe nanoparticle structure and chemistry studied by *in situ* heating of particles deposited on thin carbon film. Particle shown has left side with high Pt and right side enriched in Re with oxygen. ReOx phase occurs due to water molecules re-adsorbing dissociatively on the Re surface.

What we learned and accomplished:

Pacific Northwest NATIONAL LABORATORY

- The activated carbon support stabilizes the PtRe dispersion against cluster aggregation and coalescence during reduction treatments.

- After reaction, most of the single atoms or small clusters present in the reduced catalyst disappeared, leaving behind larger nanoparticles, likely due to agglomeration of neighboring clusters facilitated by water interaction or leaching out by liquid. This phenomenon likely leads to the decline in activity over time.

- Both Pt-rich and Re-rich nanoparticles were observed. EDS mapping showed the Re-rich particles were ReOx, suggesting the Pt-Re bond and/or the Pt-O-Re bond might be active sites in the APR reaction.

ACEM results significantly support PNNL studies of NOx–trap catalysts, as reported in *Science*.

(HTML User Program project with J.-H. Kwak, C.H.F. Peden et al. at PNNL)

Coordinatively Unsaturated Al^{3+} Centers as Binding Sites for Active Catalyst Phases of Platinum on γ-Al_2O_3

Ja Hun Kwak,[1]* Jianzhi Hu,[1] Donghai Mei,[1] Cheol-Woo Yi,[2] Do Heui Kim,[2] Charles H. F. Peden,[1]* Lawrence F. Allard,[3] Janos Szanyi[1]

In many heterogeneous catalysts, the interaction of metal particles with their oxide support can alter the electronic properties of the metal and can play a critical role in determining particle morphology and maintaining dispersion. We used a combination of ultrahigh magnetic field, solid-state magic-angle spinning nuclear magnetic resonance spectroscopy, and high-angle annular dark-field scanning transmission electron microscopy coupled with density functional theory calculations to reveal the nature of anchoring sites of a catalytically active phase of platinum o the surface of a γ-Al_2O_3 catalyst support material. The results obtained show that coordinatively rdinate Al^{3+} (Al^{3+}_{penta}) centers present on the (100) facets of the γ-Al_2O_3 Pt. At low loadings, the active catalytic phase is atomically dispersed on th $^{3+}_{penta}$ = 1), whereas two-dimensional Pt rafts form at higher coverages.

trol the dispersion and mor- al characteristics that de- formance of catalysts) of catalysts is a primary goal can be enabled by under- metal–support surface in- etals (e.g., Pt, Pd, and Rh) rfaces are the most widely materials. For these classes of the precious metal on especially critical factor e of the metal. ng metal-support interac- en as critical to sustaining

high catalytic activity under demanding cataly operation conditions (i.e., high temperature, hig water vapor pressure, etc.). Indeed, SMSI h been directly linked to the presence of electron defects that can be prepared with ease on the su faces of reducible oxides (e.g., CeO_2 and TiO (*1*). Anchoring the active metal components these electronic defects has been documente (*2*, *3*), with the strong interaction between th active metal and defects of reducible oxides fu damentally determining the dispersion, morpho ogy, and, therefore, the catalytic activity of met clusters. For example, the correlation between th number of oxygen defects on the TiO_2 suppo and the dispersion and morphology of nanosize Au particles has been clearly demonstrated b the results of density functional theory (DF calculations of Lopez *et al.* (*2*). Experimentall Chen and Goodman (*3*) have described the fo mation of stable, two-dimensional (2D) Au clu ters on a defect-rich TiO_2 thin film.

Electronic defects, however, are not prese on γ-Al_2O_3, a nonreducible oxide that is one of

alysis, Pacific Northwest National 999, MSIN K8-87, Richland, WA f Chemistry and Institute of Basic University, Seoul 136-742, Republic nal Laboratory, Oak Ridge, TN 37831, USA.

*To whom correspondence should be addressed. E-mail: Kwak@pnl.gov (J.H.K.); chuck.peden@pnl.gov (C.H.F.P.); janos.szanyi@pnl.gov (J.S.)

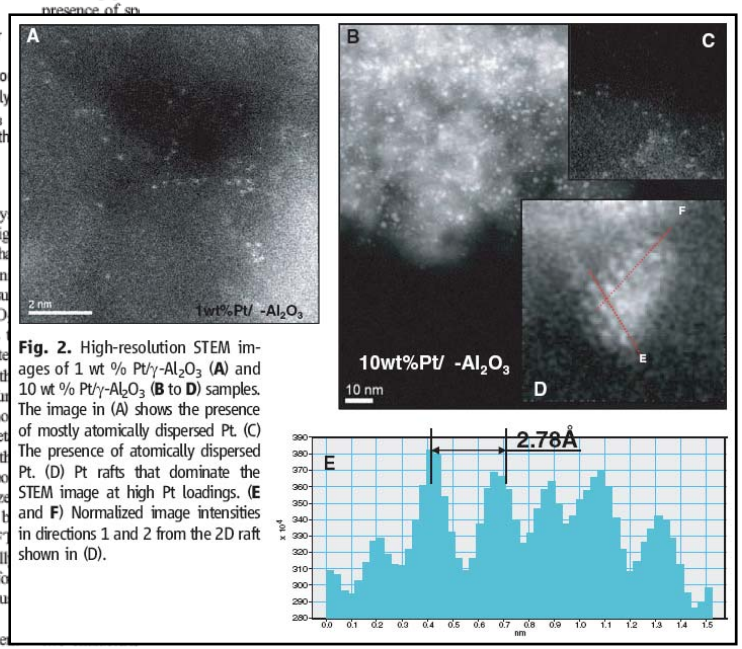


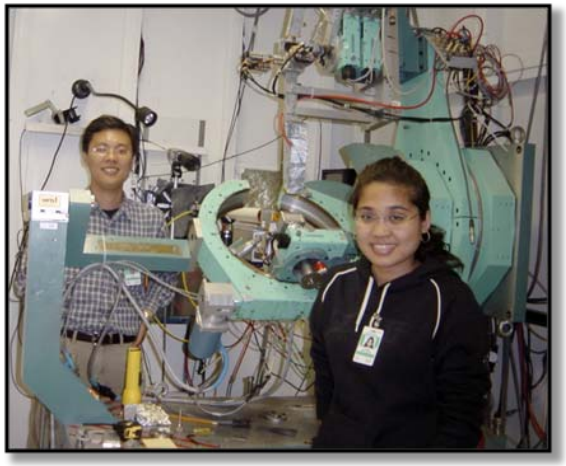
Fig. 2. High-resolution STEM images of 1 wt % Pt/γ-Al_2O_3 (**A**) and 10 wt % Pt/γ-Al_2O_3 (**B** to **D**) samples. The image in (A) shows the presence of mostly atomically dispersed Pt. (C) The presence of atomically dispersed Pt. (D) Pt rafts that dominate the STEM image at high Pt loadings. (**E** and **F**) Normalized image intensities in directions 1 and 2 from the 2D raft shown in (D).

Pacific Northwest NATIONAL LABORATORY

Massachusetts Institute of Technology

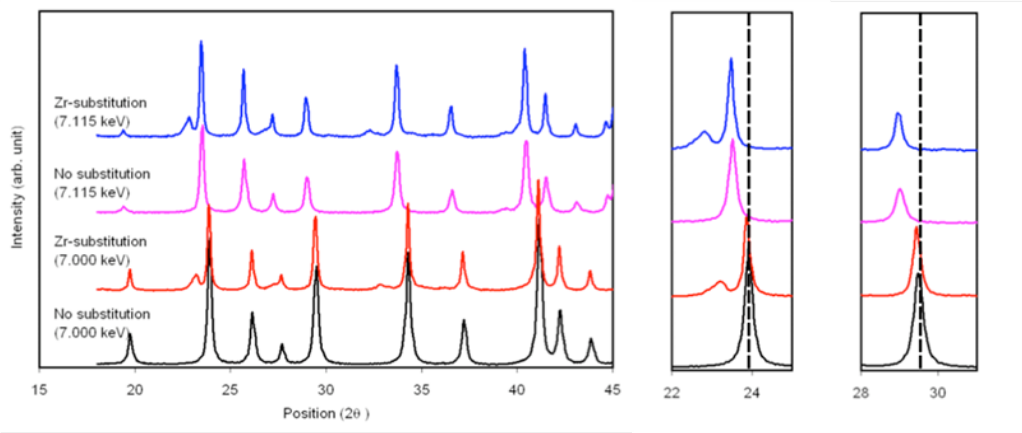
"Structural analyses of battery materials for the electrification of vehicles"

Research problem	To determine the site occupancy of dopants in the olivine structure, with particular emphasis on identifying site mixing and site vacancies. To determine overpotential effects on phase stability and transformation mechanisms.
Technical approach	Perform resonant x-ray powder diffraction measurements on alivolavent cation (Mg^{2+}, Al^{3+}, Zr^{4+}, Ti^{4+}, Nb^{5+}) substituted olivine powders. Perform *in situ* synchrotron XRD during potentiostatic and galvanostatic cycling.
Implications	Development of safe, durable batteries with high energy and power density.
Barriers	Cost, Battery Fundamentals, Performance, Life
Collaborators	**MIT Users**: Y. M. Chiang, N. Meethong Y.H. Kao **HTML Staff**: Jianming Bai

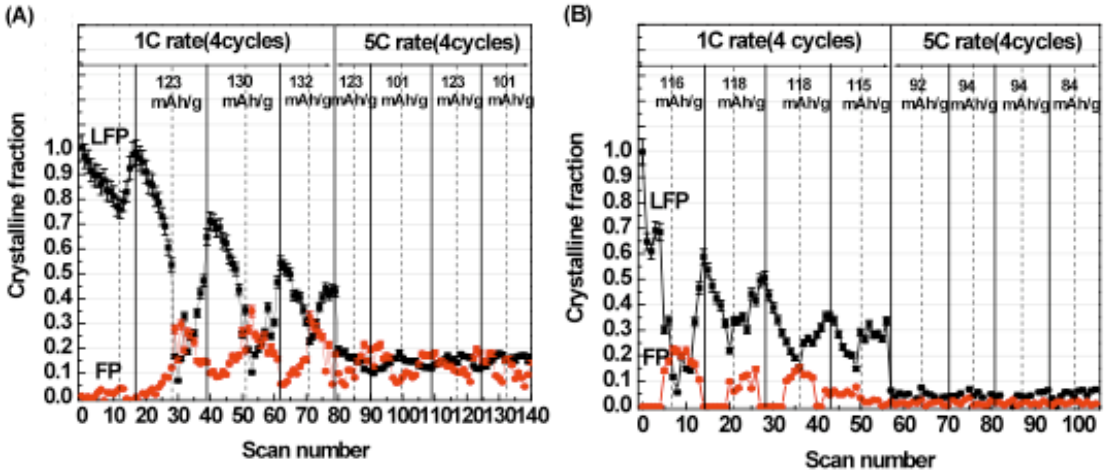


MIT graduate students Nonglak Meethong (foreground) and Yu-Hua Kao at the HTML's X14A beamline (at the NSLS).

Massachusetts Institute of Technology



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



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.

Massachusetts Institute of Technology:

What we learned and accomplished:

- Resonant synchrotron X-ray diffraction enabled detailed study of aliovalent dopant effects in olivine $Li_{1-x}Fe_{1-y}A_yPO_4$.
- 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 $Li_{1-x}FePO_4$.
- 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"

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.
Barriers	Battery Performance and Life
Collaborators	**Users**: Claus Daniel and Kevin Rhodes (UTK) **HTML Staff**: Edgar Lara-Curzio

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

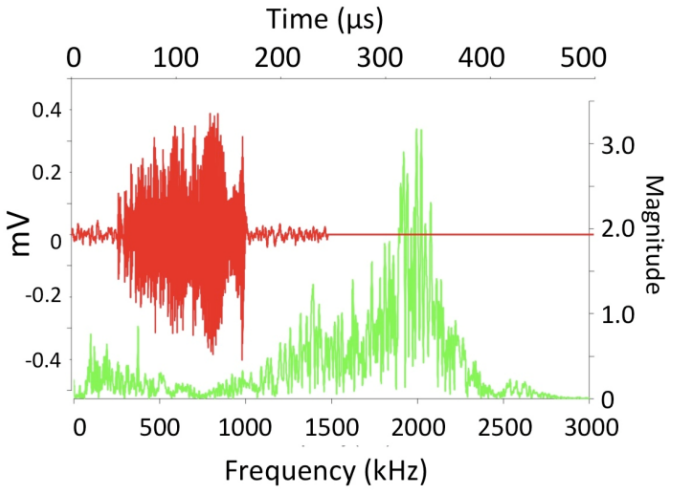
ORNL Materials Processing Group / University of Tennessee, Knoxville:

What we learned and accomplished

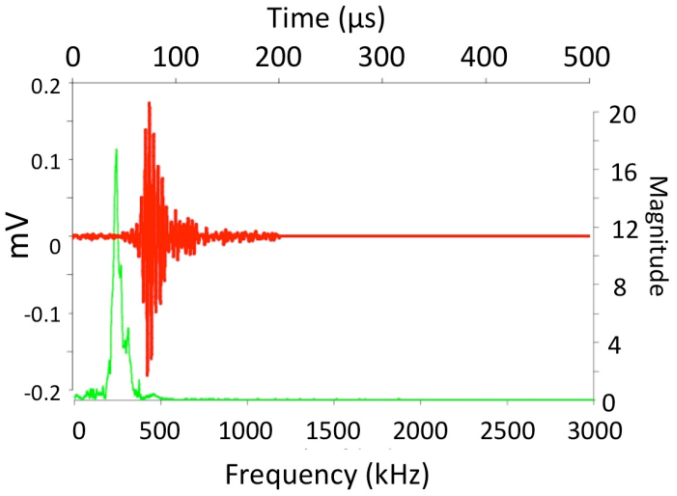
Acoustic emissions recorded during battery charging/discharging could be grouped into four classes, two of which are relevant to investigating damage processes.

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 CO_2 bubbles.



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 bubbles in the electrolyte.

ORNL Materials Processing Group / University of Tennessee, Knoxville:

What we learned and accomplished

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 CO_2 is a byproduct of the solid electrolyte interface formation, the occurrence of Type II emissions appears to be consistent with the formation of CO_2.

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

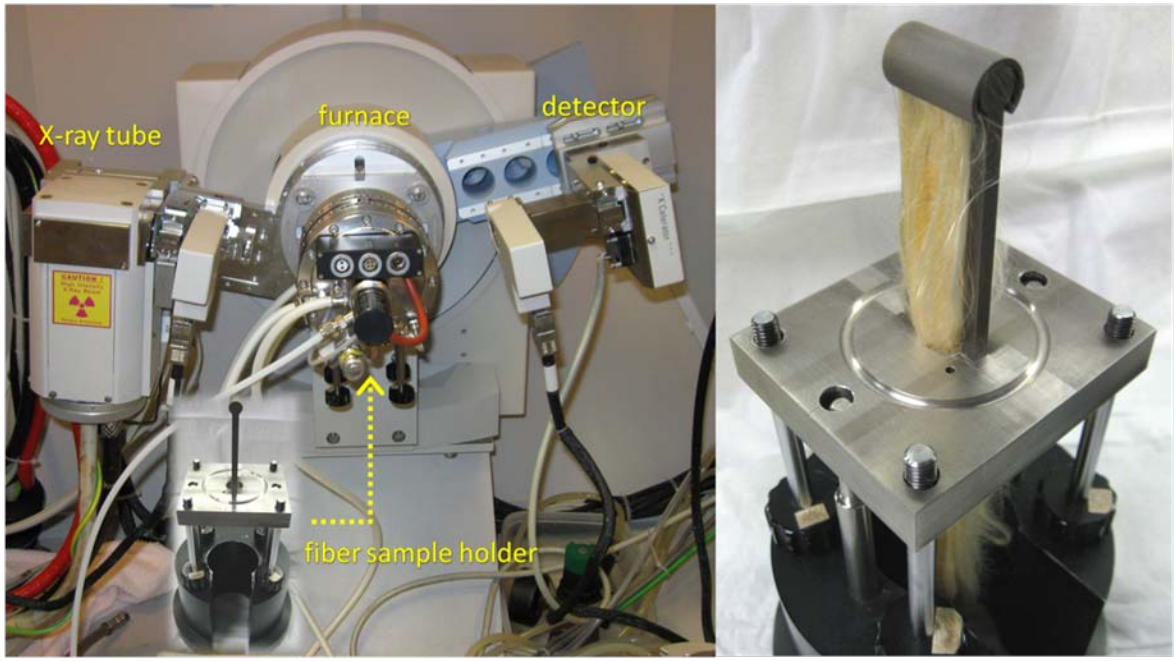
- The HTML is a National User Facility that supports the missions of the Vehicle Technologies Program, in particular by working with industry, universities and other national laboratories to develop energy-efficient technologies that will enable the U.S. to use less petroleum and reduce greenhouse gas emissions.
- The HTML User Program capabilities are also being utilized to support Vehicle Technologies Program projects at ORNL in the program's technology areas of Lightweight Materials, Propulsion Materials, Energy Storage and Thermoelectric Conversion.
- During FY2009 the HTML User Program collaborated with 28 different organizations (industry, universities, national laboratories) in the execution of 41 user projects. These projects addressed a wide range of materials technologies including materials for lithium-ion batteries, thermoelectric materials, catalysts, lightweight and structural materials, materials for thermal management, materials for propulsion and power generation, functional materials, and wear and tribology.

Future Work

- The HTML User Program will continue its collaborations with industry, universities, and national laboratories to address critical barriers to achieving the goals of DOE's Vehicle Technologies Program. More than 75 HTML User Program projects are currently active.
- Marketing efforts will continue to be focused on developing collaborations with Vehicle Technologies Program stakeholders.
- The development of special tools to enable the *in situ* characterization of materials and processes will continue. These include monitoring the microstructural evolution of carbon fibers under tensile loads during oxidation and carbonization, high-speed extensometry to measure deformation of materials and structures at high-strain rates, and hot stages and environmental cells to monitor the evolution of microstructures in physical processes, in real time, with atomic resolution, at elevated temperatures and controlled environments, using electrons, X-rays and neutrons for imaging and diffraction.

Example of developing HTML User Program capabilities to support VT projects:

In Situ XRD Capabilities for Characterization of Low-Cost Carbon Fiber Processing



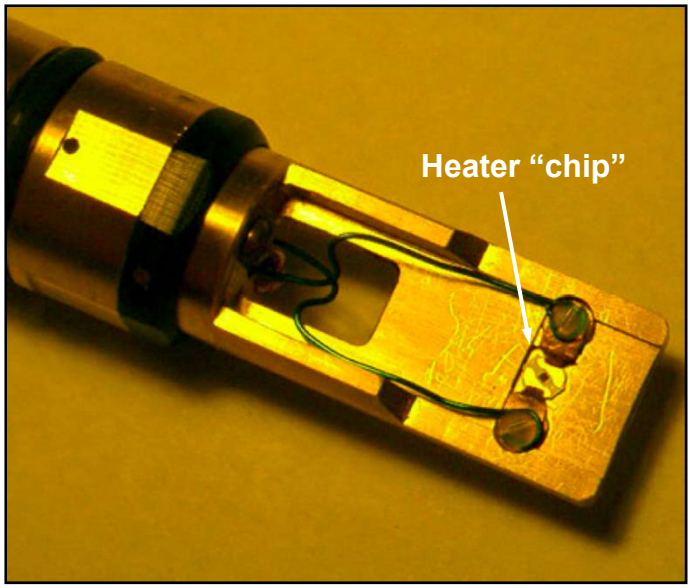
Unique *in situ* XRD attachment for carbon fiber processing characterization under development

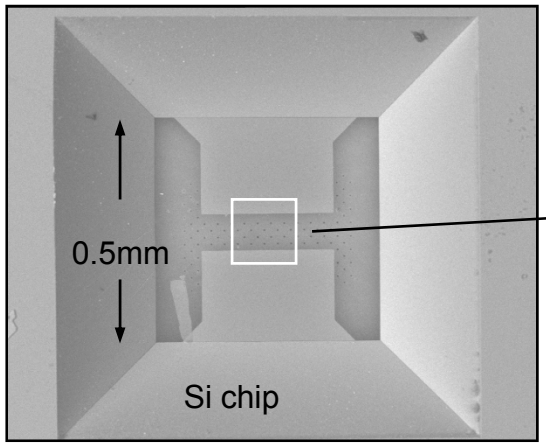
- **Fibers held in tension**
- **Furnace provides uniform temperature**
- **Extent of graphitization and texture determined by XRD as function of fiber precursor, process conditions such as tension and heating rates.**

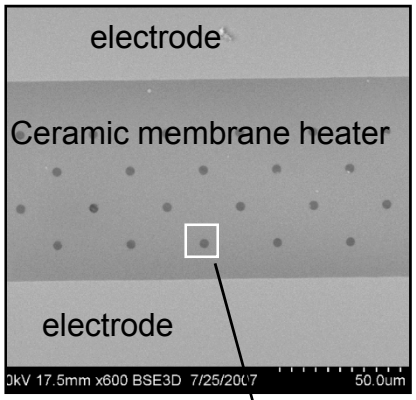
Barriers to be addressed:

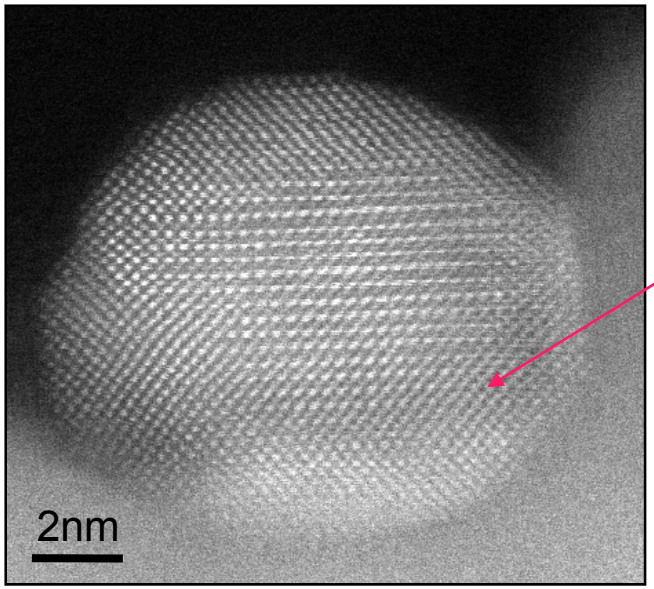
- Cost – by developing processing methods to significantly reduce the cost of producing carbon fibers.

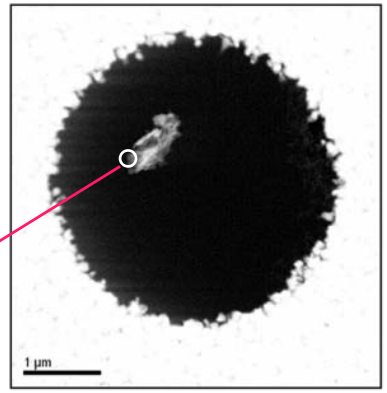
A new paradigm for *in situ* microscopy:
in situ heating with Protochips' MEMS* heater technology











lm028_laracurzio_2010_o

Protochips Co. provides novel heating elements fabricated using semiconductor technology. Thin ceramic membrane can be heated to >1000°C in 1 millisec!

*MEMS = micro-electromechanical system

Ultra-stable operation for sub-Ångström imaging