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

DOE 2011 Vehicle Technologies Annual Merit Review and Peer Evaluation Meeting

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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.

- 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, Power Electronics & Electric Motors, Emission Controls and Solid State Energy 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.

## Partners

During FY2010, the HTML User Program collaborated with 18 companies, 25 universities, and 6 national laboratories on 68 user projects addressing critical technical barriers to achieving the goals of DOE’s Vehicle Technologies Program. There were 96 researchers, 63% of them first-time users, who visited the HTML for a total of 716 research days.

The HTML also supports the education and preparation of the next generation of scientists and engineers. During FY2010, students and professors from 25 universities participated in the HTML User Program. **Five** of those students earned their Ph.D. degree and **one** earned her M.S. degree based in part on research they conducted through the HTML User Program.

## Budget

The FY2010 budget for the HTML was $5,312,400

- $881,959 for capital equipment purchases
- $4,430,441 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 time and 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.
## HTML User Program – FY2010 Participating Organizations

<table>
<thead>
<tr>
<th>Industry</th>
<th>Universities</th>
<th>National Labs</th>
</tr>
</thead>
<tbody>
<tr>
<td>• Applied Sciences, Inc.</td>
<td>• Columbia</td>
<td>• ORNL</td>
</tr>
<tr>
<td>• Atriax Components, Inc.</td>
<td>• Georgia Tech</td>
<td>• BNL</td>
</tr>
<tr>
<td>• Btechcorp.</td>
<td>• MIT</td>
<td>• NREL</td>
</tr>
<tr>
<td>• Capstone Turbine Corp.</td>
<td>• Michigan State</td>
<td>• National Res. Council, Canada</td>
</tr>
<tr>
<td>• Chromalloy</td>
<td>• New Jersey Tech</td>
<td>• PNNL</td>
</tr>
<tr>
<td>• Corning Incorporated</td>
<td>• Ohio State</td>
<td>• Sandia Nat. Laboratories</td>
</tr>
<tr>
<td>• Cummins, Inc.</td>
<td>• Pennsylvania State</td>
<td></td>
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<tr>
<td>• Fiberforge</td>
<td>• Purdue</td>
<td></td>
</tr>
<tr>
<td>• General Motors R&amp;D</td>
<td>• SUNY, Stony Brook</td>
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<tr>
<td>• GrafTech Int’l Holdings</td>
<td>• Tennessee Tech</td>
<td></td>
</tr>
<tr>
<td>• Hans Tech</td>
<td>• Virginia Commonwealth</td>
<td></td>
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<tr>
<td>• II-VI Incorporated</td>
<td>• Worcester Polytechnic</td>
<td></td>
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<tr>
<td>• Magnesium Elektron NA</td>
<td></td>
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<tr>
<td>• Marlow Industries, Inc.</td>
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<tr>
<td>• Metalsa Roanoke, Inc.</td>
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<tr>
<td>• The Timken Company</td>
<td></td>
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<tr>
<td>• Triton</td>
<td></td>
<td></td>
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<tr>
<td>• UOP, LLC</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

2010: 18 industry, 25 university, 6 nat. labs
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.

The concentration of these capabilities and expertise in one location make the HTML User Program a unique national asset.

Residual Stresses

Thermography & Thermophysical Properties

Tribology Research
Approach: Access to the 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

One milestone for the HTML User Program in FY2011 is to complete three user projects on the characterization of lightweight and lightweighting materials.

<table>
<thead>
<tr>
<th>Project ID</th>
<th>Organization</th>
<th>Project</th>
<th>Status</th>
</tr>
</thead>
<tbody>
<tr>
<td>2010-018</td>
<td>Atriax Components Inc.</td>
<td>Characterization of corrosion in heavy vehicle compressor components: Mg and Al casting and Al-MMC cylinder liner interface</td>
<td>Completed</td>
</tr>
<tr>
<td>2010-027</td>
<td>Virginia Commonwealth University</td>
<td>Characterization of lightweight materials for automotive applications</td>
<td>Completed</td>
</tr>
<tr>
<td>2010-028</td>
<td>University of Alabama-Birmingham</td>
<td>Effect of chemistry on the transformation characteristics of metastable austenite in intercritically austempered ductile iron for automotive applications</td>
<td>Completed</td>
</tr>
</tbody>
</table>
The HTML User Program - Accomplishments
The HTML User Program - Accomplishments

Examples of User Projects

Vehicle Technologies Program
## User Project with Virginia Commonwealth University “Surface treatment of dies for high strength steel forming”

<table>
<thead>
<tr>
<th>Research problem</th>
<th>To determine the relative wear resistance of coated and surface-treated die materials for use in forming high strength, automotive steel sheet materials.</th>
</tr>
</thead>
<tbody>
<tr>
<td>Technical approach</td>
<td>Utilized equipment for tribological measurements and microscopy to characterize worn surfaces.</td>
</tr>
<tr>
<td>Implications</td>
<td>Reduced material cost and increased die surface durability in metal stamping processes for high strength, dual-phase steels for lightweight automotive components.</td>
</tr>
<tr>
<td>Barriers</td>
<td>Cost, Manufacturing</td>
</tr>
</tbody>
</table>
| Collaborators | **VCU Users:** Professor Muammer Coç and Dr. Omer Cora, Virginia Commonwealth University  
**HTML Staff:** Peter Blau, Kevin Cooley |

Dr. Omer Cora (VCU) preparing a test using a reciprocating cylinder-on-flat configuration.
User Project with Virginia Commonwealth University “Surface treatment of dies for high strength steel forming”

- Cylinder-on-flat configuration under high contact forces.
- Two sheet steels, (DP 800 and DP 1000) were used as sliding partners against surface treated cylinders of die material.
- Die material: Type DC53, 8%Cr, 2%Mo, 1%C, 1%Si, 0.4%Mn, 0.3% V.

![Diagram of normal force and cylinder oscillation](image)

![Bar chart showing wear scar width](image)
User Project with Virginia Commonwealth University “Characterization of ultrasonically consolidated Ti-Al laminates”

<table>
<thead>
<tr>
<th>Research problem</th>
<th>To evaluate the mechanical properties of thin sheet lightweight metals, and to understand the stresses induced within lightweight composite alloys before and after warm hydroforming.</th>
</tr>
</thead>
<tbody>
<tr>
<td>Technical approach</td>
<td>Utilized X-ray diffraction to quantify residual stresses and an electromechanical testing machine to determine the tensile behavior of laminates as a function of rolling direction, temperature and strain rate.</td>
</tr>
<tr>
<td>Implications</td>
<td>Understanding the behavior of lightweight materials under certain forming conditions that will lead to determining their optimal forming limits as well as their requirements for mass production conditions.</td>
</tr>
<tr>
<td>Barriers</td>
<td>Cost, Manufacturing</td>
</tr>
</tbody>
</table>
| Collaborators    | **VCU Users:** İrfan Kaya and Muammer Coç, Virginia Commonwealth University  
**HTML Staff:** Rosa Trejo, Tom Watkins, Chris Stevens                                                                                                                                 |


User Project with Virginia Commonwealth University “Characterization of ultrasonically consolidated Ti-Al laminates”

VCU’s İrfan Kaya mounting a sample for high temperature tensile testing

Stress-Strain curves of thin Ti foil tested at (a) 0.13 1/s and (b) 0.0013 1/s. Samples were obtained (Type A) and normal (Type B) to the rolling direction.
User Project with Virginia Commonwealth University “Characterization of ultrasonically consolidated Ti-Al laminates”

Warm-hydroformed (200°C at a strain rate of 0.02/s), ultrasonically welded Ti-Al LMC (by Solidica Inc.)

The interplanar spacing as a function of $\sin^2 \psi$, where $\psi$ is the tilt angle at the center of the warm hydroformed portion of the sample. The spacing between the planes decreases with increasing square of the sine of the tilt angle, which indicates compression.
### User Project with Magnesium Elektron NA “Texture in asymmetrically rolled magnesium alloys”

<table>
<thead>
<tr>
<th>Research problem</th>
<th>To assess the influence of asymmetric shear rolling on the texture and microstructure of Mg sheet alloys (AZ31B and ZEK100) and in turn on their formability.</th>
</tr>
</thead>
<tbody>
<tr>
<td>Technical approach</td>
<td>Utilized X-ray diffraction and electron backscattered diffraction techniques to characterize microstructure and texture.</td>
</tr>
<tr>
<td>Implications</td>
<td>The development of methods for the cost-competitive production of automotive structures using magnesium alloys.</td>
</tr>
<tr>
<td>Barriers</td>
<td>Cost, manufacturability, lack of knowledge of advanced material properties and performance characteristics</td>
</tr>
<tr>
<td>Collaborators</td>
<td>Magnesium Elektron User: David Randman, HTML Staff: Tom Watkins, Ed Kenik, Don Erdman, Burl Cavin, Edgar Lara-Curzio</td>
</tr>
</tbody>
</table>

David Randman from Magnesium Elektron setting up a test in the X-ray Diffractometer
User Project with Magnesium Elektron NA “Texture in asymmetrically rolled magnesium alloys"

- Alloys AZ31B and ZEK100 processed by shear rolling under different preheat temperatures and reduction ratios
- Asymmetric rolling resulted in a weaker basal texture under all temperature conditions and rolling schedules
- Basal={0002} poles were observed to be tilted along the RD but toward the trailing edge.
- Rolling at lower temperatures resulted in cracking.
- Rolling at low temperatures results in shear band and recrystallization; at higher temperatures, grain growth.

Magnesium Elektron continues using the wide array of materials characterization capabilities available to industry users through the HTML User Program to develop methods for the cost-competitive production of automotive structures using magnesium alloys.
### HTML User Project with Fiberforge: “Crashworthiness of glass fiber reinforced PA6 and PET-PU tubes produced using a novel rapid preforming process”

<table>
<thead>
<tr>
<th>Research problem</th>
<th>To assess the feasibility of adhesively bonding hat-section profiles to produce composite tubular structures with high energy absorption</th>
</tr>
</thead>
<tbody>
<tr>
<td>Technical approach</td>
<td>Utilized the Test Machine for Automotive Crashworthiness and infrared imaging to determine the energy absorption of glass fiber-reinforced thermoplastic tubular structures. Tests were performed at different strain rates on specimens having different matrices and fiber architectures</td>
</tr>
<tr>
<td>Implications</td>
<td>The availability of structural materials for body and chassis applications that can significantly reduce the weight of passenger vehicles without compromising lifecycle cost, performance, safety or recyclability.</td>
</tr>
<tr>
<td>Barriers</td>
<td>Cost, Manufacturability, Performance, Joining</td>
</tr>
</tbody>
</table>
| Collaborators | **Fiberforge Users:** Benjamin Hangs and Andrew Burkhart  
**HTML Staff:** Don Erdman, Mike Starbuck, Ralph Dinwiddie |

Benjamin Hangs and Andrew Burkhart of Fiberforge reviewing the results from a TMAC test.
HTML User Project with Fiberforge: “Crashworthiness of glass fiber reinforced PA6 and PET-PU tubes produced using a novel rapid preforming process”
Tests were carried out at ambient conditions using ORNL's Test Machine for Automotive Crashworthiness (TMAC) at a crosshead speed of 4m/s.
HTML User Project with Fiberforge: “Crashworthiness of glass fiber-reinforced PA6 and PET-PU tubes produced using a novel rapid preforming process”

Tests were carried out at ambient conditions using ORNL's Test Machine for Automotive Crashworthiness (TMAC) at a crosshead speed of 4m/s.
HTML User Project with Fiberforge: “Crashworthiness of glass fiber reinforced PA6 and PET-PU tubes produced using a novel rapid preforming process”

• Specific energies up to 43 kJ/kg were obtained for PET-PU matrix composite tubes

• Specific energies of up to 50 kJ/kg were obtained for GF/PA6 matrix composite tubular structures

• These results demonstrate the potential of Fiberforge composite structures for energy management in automotive applications that could result in reduced vehicle weight, increased fuel economy, and better safety during crashes
## HTML User Project with Metalsa

**“Quenching Stresses and Distortions in Vehicular Structures”**

<table>
<thead>
<tr>
<th>Research problem</th>
<th>To assess and understand the thermal and transformation stresses induced in vehicle side-rails before and after quenching as a function of both plate thickness and steel supplier.</th>
</tr>
</thead>
<tbody>
<tr>
<td>Technical approach</td>
<td>Collect X-ray and neutron diffraction data at the HTML User Program’s neutron residual stress facility (NRSF2) as a function of heat treatment and steel supplier. Determined texture using X-ray diffraction.</td>
</tr>
<tr>
<td>Implications</td>
<td>Improved understanding of the origins of shape distortion will guide adjustments to the metals specifications and manufacturing processing to minimize distortion, reduce re-work, and improve process efficiency, helping to meet DOE’s goal of reduced energy consumption during manufacture and improved reliability of vehicular components.</td>
</tr>
<tr>
<td>Barriers</td>
<td>Cost, manufacturability, durability.</td>
</tr>
</tbody>
</table>
| Collaborators | **Metalsa User:** Joaquin del Prado Villasana  
**HTML Staff:** Camden Hubbard, Josh Schmidlin and Thomas Watkins |

Metalsa’s Joaquin del Prado Villasana prepares for an X-ray diffraction measurement.
HTML User Project with Metalsa
“Quenching Stresses and Distortions in Vehicular Structures”

- Twelve C-shaped channels 14” long, representing three thicknesses, two suppliers, and two stages of processing were examined.

- The through-thickness stresses for the as-rolled samples show little variation with depth, while the heat-treated and quenched C-channels exhibit considerable residual stress.

- Metalsa has begun analyzing the measured data and will use these results to determine the process adjustments needed to reduce distortion, leading to efficiencies in both production and energy use.
# User Project with NRC Canada

“Determination of residual stresses in V6 engine block”

<table>
<thead>
<tr>
<th>Research problem</th>
<th>To understand residual stresses in aluminum web and iron liners of a V6 engine block and their impact on distortion.</th>
</tr>
</thead>
<tbody>
<tr>
<td>Technical approach</td>
<td>Utilize neutron and X-ray diffraction techniques to obtain a distribution of residual stresses around and between cylinders.</td>
</tr>
<tr>
<td>Implications</td>
<td>By measuring residual stresses as a function of heat treatment and processing conditions, it will be possible to understand the origins of undesirable distortions in engine blocks and develop strategies to prevent them.</td>
</tr>
<tr>
<td>Barriers</td>
<td>Manufacturability</td>
</tr>
</tbody>
</table>
| Collaborators | **Users**: Dimitry Sediako, NRC-Canada  
**HTML Staff**: Camden Hubbard |
User Project with NRC Canada

“Determination of residual stresses in V6 engine block”

- GM 3.6L V6 gasoline engine block.
- Al 319 (Al-Si-Cu alloy) sand casting around Fe-liner cylinder inserts. The engine block is subsequently given a T7 heat treatment.
- Residual stresses along and between the Fe liners induce undesirable distortions and are a critical factor in determining the quality of the final product.
User Project with NRC Canada
“Determination of residual stresses in V6 engine block”

- Values of stress in the Al were found to exceed the alloy’s tensile yield stress. This suggests that while the Fe liners prevent fracture of the Al at the interbore regions, a high build-up of stress in the Fe liners and Al occurs, which results in dimensional distortions.
- The impact of variations in casting practices (e.g. cooling/solidification rate) on grain size and residual stress level is being considered for future studies
## User Project with Cummins

"Structure Property Relations for Different Nitriding Processes"

<p>| | |</p>
<table>
<thead>
<tr>
<th></th>
<th></th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>Research problem</strong></td>
<td>Determine the differences between white layers from two different nitriding processes.</td>
</tr>
<tr>
<td><strong>Technical approach</strong></td>
<td>Utilized X-ray diffraction, transmission electron microscopy, and nanoindentation to characterize the nitrided layers.</td>
</tr>
<tr>
<td><strong>Implications</strong></td>
<td>Nitriding is an important industrial process that needs to be better understood.</td>
</tr>
<tr>
<td><strong>Barriers</strong></td>
<td>Lack of knowledge of advanced materials properties and performance characteristics. Changing internal combustion engine combustion regimes</td>
</tr>
</tbody>
</table>
| **Collaborators**              | **Users**: Madeleine Smith and Lisa Behrens  
**HTML Staff**: Tom Watkins, Larry Allard, Rosa Trejo |

Madeleine Smith and Lisa Behrens of Cummins mounting a test specimen for X-ray diffraction measurements
User Project with Cummins
“Structure Property Relations for Different Nitriding Processes”

04-006-2533 Roaldite - Fe₄N
01-073-2101 Siderazot - Fe₃N

• X-ray diffraction and transmission electron microscopy are being used to identify the crystallographic phases in the while layer and their morphology. Nanoindentation is being used to determine their hardness and elastic modulus.

• By establishing structure-property relationships it will be possible to identify the optimum nitriding process for engine components.
**User Project with Atriax**

“Corrosion in magnesium compressor housings”

<table>
<thead>
<tr>
<th>Research problem</th>
<th>To assess and understand the nature and cause of apparent corrosion and casting defects between the cast Mg housing and the aluminum (A359) metal matrix composite (MMC) cylinder liner.</th>
</tr>
</thead>
<tbody>
<tr>
<td>Technical approach</td>
<td>Utilized X-ray diffraction and electron microprobe analyses for chemical and phase identification.</td>
</tr>
<tr>
<td>Implications</td>
<td>Understanding the interactions between magnesium castings and dissimilar materials.</td>
</tr>
<tr>
<td>Barriers</td>
<td>Cost, Manufacturing, Durability</td>
</tr>
</tbody>
</table>
| Collaborators | **Atriax Users**: Mike Black and David Weiss, Atriax  
**HTML Staff**: Thomas Watkins and Larry Walker |

Davis Weiss of Atriax placing a test specimen in an X-ray diffractometer.
User Project with Atriax
“Corrosion in magnesium compressor housings”

- Analysis of the interface between the AZ91 block and the Al MMC liner (SiC particulate + Ni-coated graphite particulate) using XRD identified the presence of silicon, aluminum, Mg$_2$Al, SiC and NiAl$_3$.
- Elemental maps using electron microprobe revealed the presence of Zr and O at that interface, possibly from a liquid dye penetrant, which might have facilitated corrosion.
- Cast A356 aluminum blocks with the same liner had no corrosion or interfacial issues.
- Lessons learned regarding the use of dye penetrants for inspection.
Effective use of waste heat from combustion engines would significantly increase overall engine efficiency and reduce emissions. The use of thermoelectrics for HVAC systems could result in additional fuel savings and reductions in GHG emissions.
The effect of Cu and Y doping on the thermoelectric properties of Ca₃Co₄O₉.

- Cu additions result in a significant increase in power factor caused by a reduction in electrical resistivity.
- Cu- and Y-doped doped Ca₃Co₄O₉ exhibited lower thermal diffusivity than Ca₃Co₄O₉.
- Doped Ca₃Co₄O₉ compounds exhibit greater ZT factor.

Collaborators

NJIT Users: Dr. Trevor Tyson and graduate student Tao Wu

HTML Staff: Hsin Wang
• The effect of Mg doping (1-10%) on the thermoelectric properties of hot-pressed CuAlO$_2$ with delafossite structure.

• Samples with 1% and 2% Mg exhibit greater power factor. For higher Mg concentrations the power factor decreased and for concentrations above 7.5% the material exhibited very high electrical resistivity.

• Good consistency was found for thermal conductivity data for CuAl$_{1-x}$Mg$_x$O$_2$ obtained under cryogenic conditions.

Collaborators

| MSU Users: Professor Don Morelli and graduate student Liu Chang |
| HTML Staff: Hsin Wang |
**HTML User Program Projects on Thermoelectrics**

- p-type Ce-filled skutterudite $\text{Ce}_{0.5}\text{Fe}_3\text{CoSb}_{12}$
- BNL-developed melt-spinning methods to reduce the processing time to obtain skutterudite materials (a few minutes vs. traditional processing routes, which involve long-term annealing periods (5-7 days)).
- The p-type skutterudite was formed by melt spinning, followed by grinding and sintering by SPS at $620^\circ$C under 50 MPa for 2 minutes.
- Another part of the quenched ingot was placed in a furnace and annealed at $700^\circ$C for 30h, followed by grinding and SPS sintering at the same conditions.
- The melt-spun material has lower thermal conductivity and higher power factor. The $\text{ZT}$ value was improved and a 15% peak enhancement was achieved.
- This project has demonstrated that non-equilibrium melt-spinning processing methods has the potential of producing materials with improved $\text{ZT}$.

**Collaborators**

- **BNL Users:** Dr. Qiang Li and Dr. Jie Qing
- **HTML Staff:** Hsin Wang
HTML User Program Projects on Thermoelectrics

- Thermal expansion and elastic moduli of antimony-based skutterudites and lead-telluride—lead-sulfide thermoelectric materials were determined as a function of temperature.

- Phase stability is being investigated as a function of time and temperature using X-ray diffraction.

**Collaborators**

**MSU Users:** Professor Eldon Case and graduate students Jennifer Ni and Robert Schmidt

**HTML Staff:** Rosa Trejo, Andrew Payzant, Melanie Kirkham and Edgar Lara-Curzio
• Temperature gradients in thermoelectric modules induce stresses that can lead to fracture of the legs or interface debonding.

• Used neutron diffraction techniques to map the distribution of strains in both n-type and p-type PbTe legs at one corner of a module.

• The analysis revealed a stress/strain distribution similar to the finite element simulation performed at Marlow. The successful strain mapping technique for thermoelectric modules will be applied by Marlow on the next-generation thermoelectric modules the company is developing for vehicle applications.
### User Project with General Motors

**“Characterization of Li-ion batteries Using Neutron Diffraction and Infrared Imaging Techniques”**

<table>
<thead>
<tr>
<th>Research problem</th>
<th>To determine the local temperature variation during charging and discharging and to explore phase changes in electrodes using in situ neutron mapping; information needed for GM to estimate life and reliability of full-scale battery system.</th>
</tr>
</thead>
<tbody>
<tr>
<td>Technical approach</td>
<td>Utilized the unique capabilities of the HTML User Program for <em>in situ</em> studies. A high-speed infrared camera was used for temperature mapping, and the neutron strain mapping facility was used for <em>in situ</em> phase monitoring during charging and discharging.</td>
</tr>
<tr>
<td>Implications</td>
<td>Batteries with higher energy density that can meet the requirement of 5,000 deep discharge cycles over the life of the battery.</td>
</tr>
<tr>
<td>Barriers</td>
<td>Performance, Life</td>
</tr>
</tbody>
</table>
| Collaborators | **Users:** Jihui Yang, Robert S. Conell, GM R&D Center  
**HTML Staff:** Hsin Wang, Cam Hubbard and Wei Cai |
Neutron diffraction peaks in Region #3 between 1.62 – 1.93 Å as a function of cell capacity. Data were collected in 9 steps during discharging.
User Project with General Motors
“Characterization of Li-ion batteries Using Neutron Diffraction and Infrared Imaging Techniques”

Temperature vs. time plots for two cycles

The results obtained from this User Project with General Motors project have enabled GM to develop a better understanding of cell performance, which will result in cells with improved performance and durability.
HTML User Project with Applied Sciences Inc/GM Team “Characterization of novel Li-ion battery anode”

<table>
<thead>
<tr>
<th>Research problem</th>
<th>To understand the effect of microstructure of Si/C composite anodes on the performance of Li-ion batteries.</th>
</tr>
</thead>
<tbody>
<tr>
<td>Technical approach</td>
<td>Utilized scanning-transmission electron microscopy and X-ray photoelectron spectroscopy to characterize the microstructure of Si/C composite anodes before and after cycling.</td>
</tr>
<tr>
<td>Implications</td>
<td>Si/C composite anodes could enable the development of Li-ion batteries with high capacity and durability, which are critical for the commercialization of electric vehicles.</td>
</tr>
<tr>
<td>Barriers</td>
<td>Battery Performance and Life</td>
</tr>
</tbody>
</table>
| Collaborators | **ASI User:** Max Lake  
**HTML Staff:** Jane Howe and Harry M. Meyer III |
ASI has produced anodes for Li-ion batteries consisting of low-cost hollow carbon nanofibers (CNF) coated with nanosized silicon (uniform coating about 12-nm thick, or an array of sub-20nm nodules that partially cover the surfaces).

By depositing silicon on both inner and outer surface of a hollow carbon nanofiber it is possible to maximize the efficiency of the Si/CNF composite during cycling.

Capacities in excess of 1000 mAh/g after 20 cycles and 500 mAh/g after 50 cycles in half-cell configuration and near 1000 mAh/g (full cell configuration) were achieved.

Battery cyclability varied from batch to batch.

Work is in progress to correlate the effect of processing conditions with the microstructural features of the coatings and the electrochemical performance of the composite anodes.
### Research problem

To better understand the interaction between active materials (metal oxide) and single-wall carbon nanotubes (SWNTs) in binderless composite electrodes for Li-ion batteries and to determine the optimum annealing temperature to obtain stable structures.

### Technical approach

Utilize X-ray diffraction technique to monitor, *in situ*, phase stability during annealing at different temperatures.

### Implications

Optimized electrode materials will enable high-performance, durable, and affordable Li-ion batteries for power-assisted HEVs and PHEVs that meet the DOE’s Vehicle Technologies targets.

### Barriers

Performance, Life

### Collaborators

**NREL User:** Dr. Chunmei Ban  
**HTML Staff:** Melanie Kirkham and Andrew Payzant

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NREL's Dr. Chunmei Ban preparing a test in the HTML's X-ray diffractometer
User Project with National Renewable Energy Laboratory “Annealing of composite electrodes for Li-ion batteries"

• A phase transition was observed in the iron oxide samples as the FeOOH precursor converts to Fe₂O₃ at around 250°C, whereas the carbon peak showed little change up to the maximum temperature of 550°C.

• No phase transition was observed in the LCO phase, although a change in lattice parameters upon cooling suggests that structural modifications might have occurred during annealing. Additionally, changes in the carbon peak suggest structural changes may also occur in the SWNTs.

• Work continues to understand the mechanisms responsible for these changes.

• Iron oxide/SWNT composite electrodes in a coin-cell configuration greatly improve performance, with the highest reversible capacity obtained using 5wt% SWNT, reaching 1000 mAh/g at C rate and 800 mAh/g at 5C.

• The performance of these iron oxide/SWNT composite electrodes has been observed to improve even further after annealing.
<table>
<thead>
<tr>
<th><strong>Research problem</strong></th>
<th>To characterize the microstructure and chemical composition of Fe$_{16}$N$_2$ thin films at the atomic level.</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>Technical approach</strong></td>
<td>Utilized X-ray photoelectron spectroscopy and transmission electron microscopy along with magnetic property measurements at the University of Minnesota.</td>
</tr>
<tr>
<td><strong>Implications</strong></td>
<td>The development of magnetic materials that do not contain rare earth elements.</td>
</tr>
<tr>
<td><strong>Barriers</strong></td>
<td>Rare Earth Minerals</td>
</tr>
</tbody>
</table>
| **Collaborators** | **University of MN Users**: Professor Jian-Ping Wang and Dr. Nian Ji  
**HTML Staff**: Larry Allard and Edgar Lara-Curzio |
• The combination of XPS and STEM results allowed verification of the presence of domains of Fe$_{16}$N$_2$, which has the highest saturation magnetization value ever reported.

• These results will enable the development of processing strategies for producing iron nitride materials with a high concentration of the metastable phase Fe$_{16}$N$_2$. The development of iron nitride magnets addresses an important barrier associated with the use of rare earth minerals in magnetic materials for multiple automotive components (e.g., electric motors, actuators).
### Research problem

To analyze the deactivation of diesel oxidation catalysts and lean NOx traps due to platinum group metal sintering.

### Technical approach

Utilize transmission electron microscopy and X-ray diffraction to characterize the structure and composition of fresh and aged catalysts.

### Implications

Improvements in diesel oxidation catalysts will enhance the durability of emissions control devices for biodiesel vehicles.

### Barriers

Lack of cost-effective emission controls; Durability

### Collaborators

**Users**: Dr. Todd Toops (ORNL) and graduate student Will Brookshear (University of Tennessee)

**HTML Staff**: Jane Howe and Andrew Payzant
User Project with ORNL’s Fuels Engines & Emissions Research Center

“Platinum catalyst particle growth in field-aged diesel oxidation catalysts and lean NOx traps”

- The periodic high temperatures that can be achieved in exhaust gases can cause platinum group metal (PGM) sintering, resulting in decreased PGM surface area. This leads to a drop in the maximum conversion of NOx to N₂ attained in LNTs.

- The sharper platinum peaks apparent in the engine-aged samples indicate PMG, which corresponds to a reduction of precious metal surface area for the oxidation of NO to NO₂. This is consistent with images obtained with scanning transmission electron microscopy.

- Analysis of the XRD data and STEM images have provided further understanding of the deactivation mechanisms associated with biodiesel fuels and can be used to improve the thermal durability of diesel after-treatment devices.
User Project with General Motors and Sandia National Laboratories
“Distribution of Hydrogen in Storage Media”

<table>
<thead>
<tr>
<th>Research problem</th>
<th>Quantify axial and radial hydrogen concentration gradients as a function of time during hydrogenation using sodium alanates.</th>
</tr>
</thead>
<tbody>
<tr>
<td>Technical approach</td>
<td>Utilize neutron scattering techniques at ORNL’s High Flux Isotope Reactor and Vulcan diffractometer to map hydrogen distribution.</td>
</tr>
<tr>
<td>Implications</td>
<td>Development of models to explain hydrogen transport mechanisms.</td>
</tr>
<tr>
<td>Barriers</td>
<td>Availability of alternative fuels</td>
</tr>
</tbody>
</table>
| Collaborators    | **Users**: Scott Jorgensen (GM), Terry Johnson (Sandia)  
**HTML Staff**: Andrew E. Payzant |

Scott Jorgensen (GM), Terry Johnson (SNL) and Andrew Payzant (ORNL) at the Vulcan diffractometer
H₂ depleted state: NaH + Al + \( \frac{3}{2} \)H₂

First step: \( \frac{1}{3} \)Na₃AlH₆ + 2/3 Al + H₂

Second step: NaAlH₄

(10 – 150 atm) and (120 – 180 °C)

Component mol % mass %

<table>
<thead>
<tr>
<th>Component</th>
<th>mol %</th>
<th>mass %</th>
</tr>
</thead>
<tbody>
<tr>
<td>Al</td>
<td>45.1%</td>
<td>49.9%</td>
</tr>
<tr>
<td>NaH</td>
<td>32.6%</td>
<td>32.0%</td>
</tr>
<tr>
<td>Carbon (graphite)</td>
<td>18.4%</td>
<td>9.1%</td>
</tr>
<tr>
<td>NaCl</td>
<td>2.9%</td>
<td>7.0%</td>
</tr>
<tr>
<td>Ti</td>
<td>1.0%</td>
<td>1.9%</td>
</tr>
</tbody>
</table>
Nominally NaH

- Hydride more crystalline near gas inlet/outlet but more amorphous at end.
- Graphite and NaCl phases evenly distributed.
Data revealed unexpected complexity of hydride phase distribution

- More crystalline hydride near gas inlet/outlet but more amorphous at end.
- Graphite and NaCl evenly distributed.
- Unexpected NaH phase near inlet.
- Hexagonal Na$_3$AlH$_6$ phase distributed throughout tube.
Data revealed unexpected complexity of hydride phase distribution

- More crystalline hydride near gas inlet/outlet but more amorphous at end.
- Graphite and NaCl evenly distributed.
- Tetragonal NaAlH$_4$ phase found mainly near inlet/outlet.
- Significant amount of hexagonal Na$_3$AlH$_6$ phase observed distributed throughout tube.
User Project with General Motors
“Forming Technologies for Al Intensive Automotive Body Panels"  

<table>
<thead>
<tr>
<th>Research problem</th>
<th>To characterize the kinetics of precipitation and aging in Aluminum alloy 6111 and evaluate the effect of loading rate and temperature on its mechanical behavior.</th>
</tr>
</thead>
<tbody>
<tr>
<td>Technical approach</td>
<td>Utilized <em>in situ</em> scanning electron microscopy and electron backscattered diffraction to study the kinetics of precipitation and aging. Used high-rate tensile testing to determine tensile properties</td>
</tr>
<tr>
<td>Implications</td>
<td>The development of production methods</td>
</tr>
</tbody>
</table>
| Barriers         | Manufacturability  
|                  | Lack of knowledge of advanced materials properties and performance characteristics |
| Collaborators    | **Users**: Raj Mishra  
|                  | **HTML Staff**: Larry Allard, Chad Parish, Chris Stevens, Edgar Lara-Curzio |

GM’s Raj Mishra and the HTML’s Larry Allard examining a test specimen in the scanning transmission electron microscope
User Project with General Motors
“Forming Technologies for Al Intensive Automotive Body Panels”
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 FY2010 the HTML User Program collaborated with 49 different organizations (industry, universities, national laboratories) in the execution of 68 user projects. These projects addressed a wide range of materials technologies including lightweight materials, propulsion materials, materials for lithium-ion batteries, thermoelectric materials, catalysis, magnetic materials and materials for the manufacture of vehicular structures.
Future Work

• Marketing efforts will continue to be focused on developing collaborations with Vehicle Technologies Program stakeholders and other sponsors to address the proposed budget reduction in FY12.

• The HTML User Program will continue its collaborations with industry, universities, and national laboratories to address critical barriers to achieving the goals of DOE and EERE.

• The development of special tools to enable the in situ characterization of materials and processes will continue. These include 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.