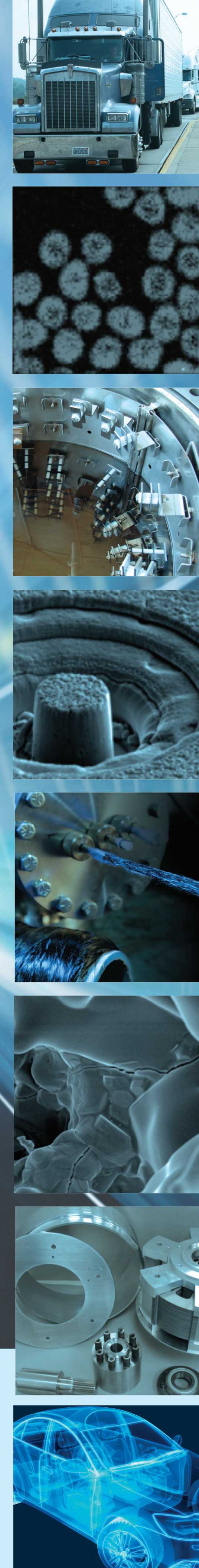
Sustainable Transportation Program

FY 2010 Annual Report



Oak Ridge National Laboratory
MANAGED BY UT-BATTELLE FOR THE DEPARTMENT OF ENERGY

Prepared for
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Prepared by
OAK RIDGE NATIONAL LABORATORY
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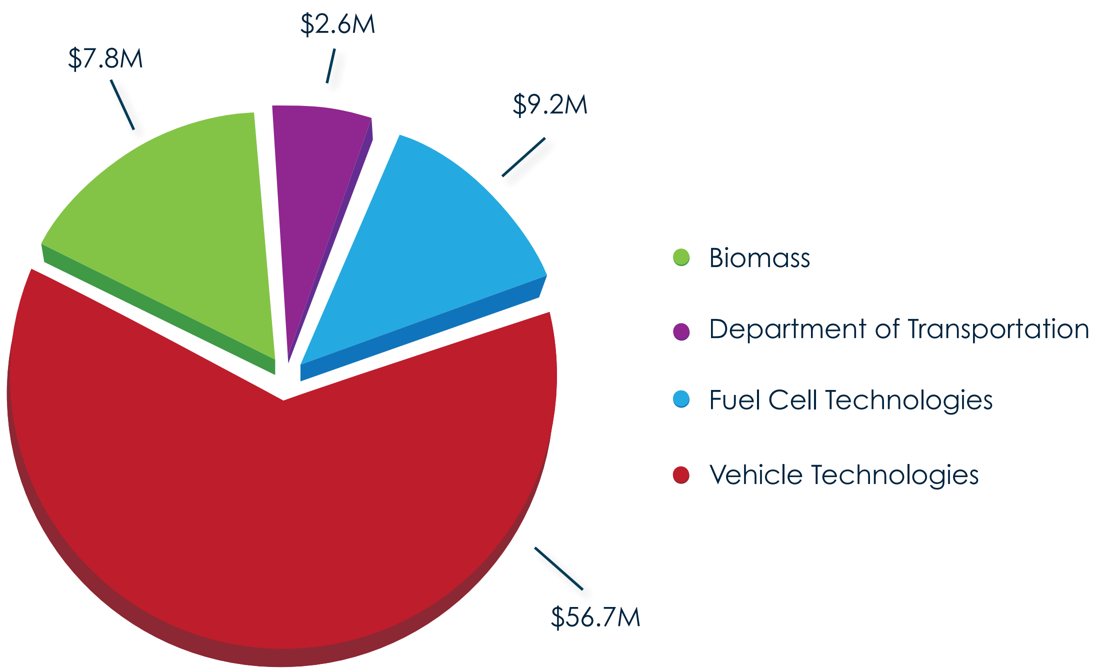
Contents

Introduction

Oak Ridge National Laboratory leverages its state of the art facilities and its renowned engineering and scientific staff to "attack the fundamental science challenges posed by DOE's missions and carrying out the translational work required to accelerate the delivery of solutions to the marketplace."[1] The Sustainable Transportation Program (STP) addresses the unique challenges being put forth by the Vehicle Technologies Program (VTP), Biomass Program (BMP), and the Fuel Cells Technologies Program (FCTP) within the U.S. Department of Energy (DOE), Office of Energy Efficiency and Renewable Energy (EERE); as well as the U.S. Department of Transportation (DOT); other U.S. governmental agencies; and private industry.

The STP received $76.3 million in new budget authority in FY 2010 from the DOE and DOT programs with the DOE VTP being the largest portion of the new budget authority (see below).



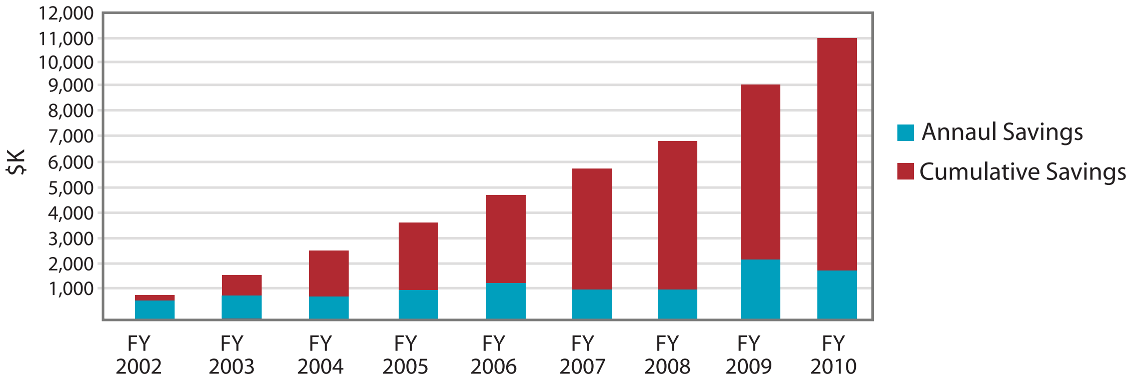
FY 2010 New Budget Authority

The STP involves scientists and engineers working together as interdisciplinary teams with the assistance of industry partners to address the DOE challenges. This report highlights some of the R&D work carried out in FY2010 as well as summarizing the recognition and awards given to the staff.

Oak Ridge National Laboratory Fact Sheet. ORNL2011-G00555/jcn. http://www.ornl.gov/ornlhome/docs/fact.pdf

Overhead Cost Savings

About half of the VTP-sponsored R&D at ORNL is conducted at the National Transportation Research Center (NTRC) in Knoxville, Tennessee.[2] R&D conducted at the NTRC is subject to a reduced ORNL overhead rate, as many of the ORNL support services—for example, physical security and grounds keeping—are not applicable at the NTRC because it is located away from the main ORNL campus. The figure below shows the approximate annual and cumulative cost savings resulting from the NTRC's off-site location since FY 2002, the first year of full occupancy and beneficial facility operation. These overhead cost savings allow a larger percentage of VTP funds to directly support programmatic R&D in the activities conducted at the NTRC.



Cumulative overhead savings of $11,000K have been applied to R&D at NTRC.

Patents

Sustainable Transportation Program staff members filed four patent applications and four invention disclosures during FY2010. Staff members were awarded twelve patents during the same time period. These items are detailed in the chart below.

Name	Invention Disclosures, Patent Applications, and Patents
J. Hsu and J. McKeever	Patent 7,683,264 B2 - High Pressure, High Current, Low Inductance, High Reliability Sealed Terminals
J. Hsu, L. Marlino, and C. Ayers	Patent 7,695,663 - Method of Making Hermetic Seals for Hermetic Terminal Assemblies
J. Hsu	Patent 7,719,153 - Permanent Magnet Machine and Method with Reluctance Poles and Non-Identical PM Poles for High Density Operations
G. Su	Patent 7,733,039 B2 - Vehicle System for Charging and Supplying Electrical Power
R Wiles, A. Wereszczak, C. Ayers, and K. Lowe	Patent 7,796,388 - Direct Cooled Power Electronics Substrate

Activities primarily conducted at the NTRC are advanced power electronics, education, safety codes and standards, technology validation, legislative and rulemaking, vehicle technologies deployment,

Name	Invention Disclosures, Patent Applications, and Patents
E. Lara-Curzio, K. An, J. Kiggans, N. Dudney, C. Contescu, F. Baker, and B. Armstrong	Patent Application 12/110,913 - Lightweight, Durable Lead-Acid Batteries
T. Yonushonis, R. Stafford, E. Lara-Curzio, and A. Shyam	Patent 7,701,231 - Apparatus, System, and Method for Detecting Cracking within an Aftertreatment Device
F. Paulauskas and D. Sherman	Patent 7,649,078 - Apparatus and Method for Stabilization or Oxidation of Polymeric Materials
F. Paulauskas, T. White, and D. Sherman	Patent 7,786,253 - Apparatus and Method for Oxidation and Stabilization of Polymeric Materials
F. Paulauskas, T. White, and T. Bigelow	Patent 7,824,495 - System to Continuously Produce Carbon Fiber via Microwave Assisted Plasma Processing
V. Kunc	Invention Disclosure 2377 - Curved Fibers Defintion and Measurement Fiber Length Measurement from Cross Section
H. Wang, Z. Feng, and W. Zhang	Invention Disclosure 2379 - Non-destructive Inspections of Welds and Joints Using Infrared Imaging and Induction Heating
J. Parks and B. Partridge	Patent Application ID-1962 - Oxygen Concentration Sensors and Methods of Rapidly Measuring of the Concentration of Oxygen in Fluids
R. Graves, S. Huff, J. Parks, and B. West	Patent 7,469,693 - Advanced Engine Management of Individual Cylinder for Control of Exhaust Species
S. Daw, J. Green, D. Edwards, and R. Wagner	Patent 7,431,011 - A Method for Diagnosing and Controlling Combustion Instabilities in Internal Combustion Engines Operating in or Transitioning to Homogeneous Charge Compression Ignition Modes
Z. Gao and J. Parks	Invention Disclosure - A Reverse-Flow Self-Cleaning Diesel Particulate Filter System
M Brady, B. Yang, and P. Maziaz	Patent 7,829,194 - Iron-based Alloy and Nitridation Treatment for PEM Fuel Cell Bipolar Plates
M. Yoon, S. Yang, Z. Zhang, and D. Geohegan	Invention Disclosure - Hydrogen Storage on Calcium Doped Nanostructures
J. Wang, K. Liu, and Z. Feng	Patent Application 12/498,877 - Apparatuses for Pre-stressing Rod-type Specimens in Tension for In Situ Passive Fracture Testing in an Extremely High-Pressure Environment of Hydrogen
S. Dai, G. Guiochon, and C. Liang	Patent Application 10/770,734 - Robust Carbon Monolith having Hierarchical Porosity

Awards and Professional Recognition

Our program staff is highly regarded by their peers. This is reflected by both the vast number and in the caliber of the awards and recognitions they received during FY 2010. Several staff members were appointed to serve on boards and in professional organizations. The chart below lists the most significant awards and recognitions.

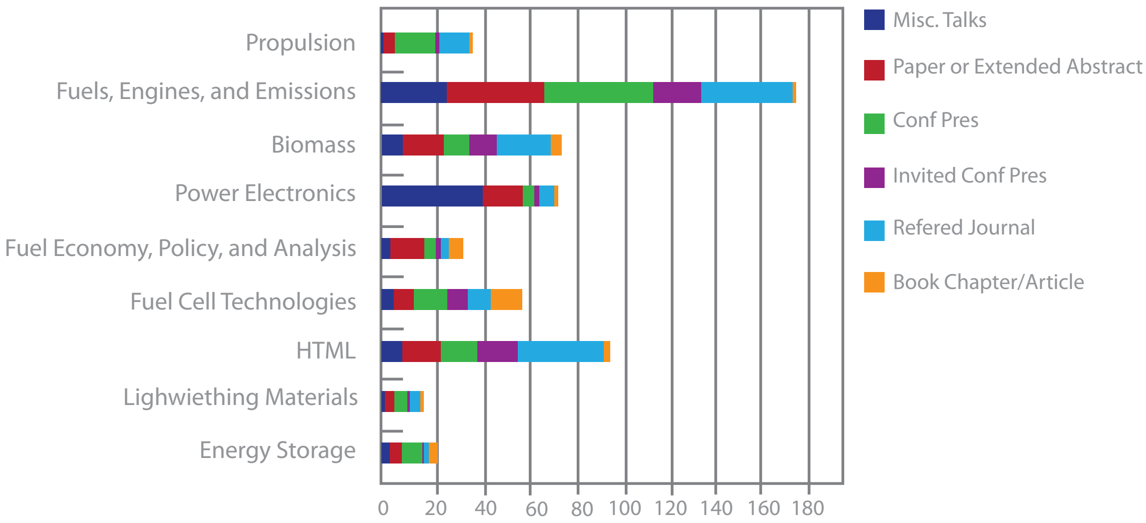
Name	Award or Recognition
J. Hsu	ORNL Top Patent Researcher for 2009 - Awarded 4 patents in 2009
F. Wang	IEEE Fellow
T. Burress	Outstanding Achievement Award presented at the 2010 DOE Vehicle Technologies Program Annual Merit Review and Peer Evaluation Meeting for his work in benchmarking power electronics and electric motor technologies
L. Allard	Microscopy Society of America Fellow
L. Allard	Elected Director, Physical Science for the Microscopy Society of America Council
P. Blau	Member of ASTM G2 committee on Wear and Erosion
P. Blau	Member of Board of Directors and Steering Committee for the 2011 International Conference on Wear of Materials
R. Dinwiddie	Chair of Thermosense XXXII Conference
E. Lara-Curzio, J. Wang, T. King, J. Chan, J. Graziano, and T. Goodwin III	R&D 100 Award for MELCOT:Methodology for Estimating the Life of Power Line Conductor-Connector Systems Operating at High Temperatures
E. Lara-Curzio	Arthur Federick Greaves-Walker Award presented by the American Ceramic Society and the National Institute of Ceramic Engineers
C. Rawn	Member of U.S. National Committee for Crystallography
L. Walker	Member of Advisory Board, Mechnical Engineering, Tennessee Technological University
H. Wang	Conference Organizer for the International Thermoelectric Society's 29th Internation Conference
H. Wang	Chairman of the Board of Governors of the International Thermal Conductivity Conference
W. Porter	Member of the Board of Governors of the International Thermal Conductivity Conference
Carbon Fiber Team	Gordon Battelle Award
F. Baker	Royal Society of Chemistry Fellow

Name	Award or Recognition
Z. Feng	2010 Forest R. McFarland Award for outstanding contributions to the SAE Engineering Meetings Board
B. West	Outstanding Achievement Award presented at the 2010 DOE Vehicle Technologies Program Annual Merit Review and Peer Evaluation Meeting for his leadership in assessing the impact of higher ethanol blends on the U.S. legacy vehicle fleet and all gasoline engines
R. Wagner	Society of Automotive Engineers Forest R. McFarland Award for outstanding contributions toward the work of the SAE Engineering Meetings Board
J. Parks, B. Partridge, and D. Simms	Excellence in Technology Transfer Award presented by the Federal Laboratory Consortium Southeast Region for their work on Laser-induced Fluroescence Fiber Optic Measurement of Fuel in Oil
J. Szybist	Society of Automotive Engineers Award for Outstanding Oral Presentation
R. Wagner	Member of Editorial Board for The International Journal of Engine Research
V. Dale	Appointed to the National Research Council's Committee on Environmental and Economic Impacts of Increasing Biofuels Production
S. Sokhansanj	Recognition Award from the American Society of Agricultural & Biological Engineers for Outstanding Leadership
T. Combs	Appointed to the National Nuclear Security Administration/DHS Aviation Security Enhancement Program Systems Analysis Group
T. Rose	Appointed to the National Nuclear Security Administration/DHS Aviation Security Enhancement Program Systems Analysis Group
P. Hu	Recognition Award from the TRB for her six years of service as the Committee Chairperson for TRB's Committee for National Transportation Data Requirements and Programs
G. Capps	DOE Office of Science Outstanding Mentor Award
M. Lascurain	DOE Office of Science Outstanding Mentor Award
T. Combs	Appointed to the Transportation Research Board Committee on Aviation Security and Emergency Management, AV090
J. Bielicki	Nominated for the Intergovernmental Panel on Climate Change (IPCC) Working Group II (Impacts, Adaptations, Vulnerabilities) and Working Group III (Mitigation)

Name	Award or Recognition
P. Hu	Reappointed to the Transportation Research Board's (TRB's) Expert Task Group (ETG) on Long Term Pavement Performance (LTPP) Traffic Data Collection and Analysis
P. Hu	Appointed to the Transportation Research Board's (TRB's) Strategic Highway Research Program (SHRP 2) Reliability Expert Task Group (ETG) focused on defining "A Framework for Improving Travel Time Reliability"
B. Knee	Reappointed to the Transportation Research Board's (TRB's) Committee on Vehicle-Highway Automation
D. Davidson	Appointed as a member of the Transit Rail Advisory Safety Committee (TRACS)
B. Peterson	Appointed as a member of the Steering Committee for the Transportation for the Nation Strategic Planning Effort
F. Southworth	Nominated to the TRB NCHRP Long Distance and Rural Travel Transferable Parameters for Statewide Travel Forecasting Models (Project 08-84 B-20) Panel
R. Goeltz	Served as Chairman of the TRB Expert Task Group
J. Dong	Servced as Young Member on the TRB Committee on Traffic Flow Theory and Characteristics (AHB45)
D. Geohegan	Co-Chair: SPIE Conference 7586 "Synthesis and Photonics of Nanoscale Materials
D. Geohegan	Co-Chair: Materials Research Society Spring Meeting, Symposium R

Publications and Presentations

ORNL R&D staff produced more than 584 papers, reports, and presentations on the ground breaking work funding by the STP. The figure below provides a breakdown by type.



Advanced Power Electronics and Electric Machines

High Power Density Integrated Traction Machine Drive

Background

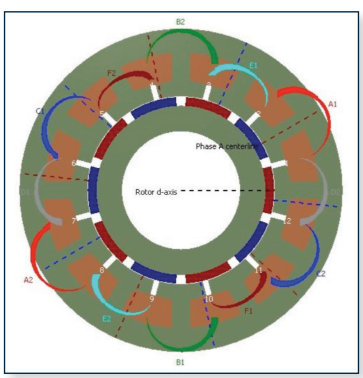
Today's electric vehicle traction drives cannot meet the aggressive U.S. DRIVE power density and cost targets for 2015 and 2020 because the electric machine and drive electronics are packaged as separate components, each with its own housing and thermal management system. Additionally, the connectors and cables needed to interconnect the machine and its drive add to the cost and lead to reliability issues. Integration of the motor and the electronics is highly desirable to reduce costs, size, and weight and optimize system performance.

Technology

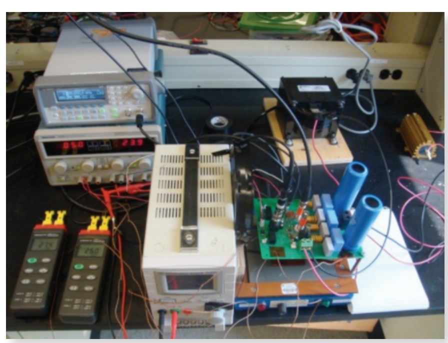
A promising long-term solution to meeting the power density and cost targets is to modularize both the machine and power electronics and integrate them into a single combined machine plus drive structure. The concept proposed to achieve this traction drive integration has been given the name "integrated modular motor drive" (IMMD). The basic building block of the IMMD consists of a single segmented stator pole with a concentrated stator winding that is energized by a dedicated single phase inverter and controller mounted at one end of the pole assembly. A number of these building blocks are interconnected in an annular configuration to form the complete stator plus drive assembly. In addition to power density advantages, this approach provides natural opportunities for introducing fault tolerance into the traction drive system, which significantly improves its ruggedness and reliability. Through the use of new packaging methods it is anticipated that silicon devices can be used in the drive electronics at elevated temperatures, affording cost advantages over higher priced wide bandgap devices.

Status

- A six-phase, 10-pole permanent magnet machine has been simulated and identified as the most promising motor configuration (bottom left).
- A heterarchical control architecture has been developed and simulated for achieving fault-tolerant operation.
- High temperature static and switching behaviors of candidate silicon devices have been tested and their performance characterized (bottom right).
- A baseline 10 kW phase-leg power module with 105°C cooling has been designed and simulated.



A six-phase, 10-pole permanent magnet machine.



Test setup for characterizing devices at high temperature.

Benefits

- This research will advance technology by
  - Increasing power density and reducing costs by modularizing both the machine and power electronics and then integrating them into a single combined machine-plus-drive structure
  - Extending silicon device operation to higher temperatures using advanced packaging approaches

High Temperature, High Voltage Fully Integrated Gate Drive Circuit

Background

Achieving the U.S. DRIVE target of $5/kW and 12 kW/kg for power electronics by 2015 largely depends on the development of high temperature control electronics that can work at up to 200°C with minimal heat sink and air cooling. Silicon carbide (SiC) based switches that will be used at elevated temperatures in the power conversion modules of hybrid electric vehicles (HEVs) need a different gate driver circuit from those used for silicon insulated gate bipolar transistors for proper switching, conduction, and blocking. To fully realize the advantages that SiC based power switches offer at high temperature, the associated gate driver circuits also need to operate reliably at high temperature.

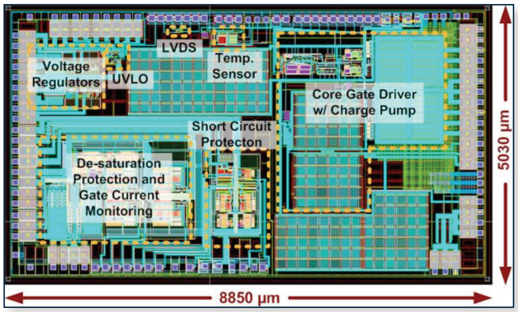
Technology

The goal of this research is to develop a silicon-on-insulator (SOI) based high temperature, high voltage gate driver integrated circuit with high drive current capability for wide bandgap (WBG) power switches, such as SiC and gallium nitride. Power electronics in future electric vehicles (hybrid, plug-in hybrid, and full electric) are expected to use WBG based power devices that are capable of working at much higher ambient temperatures than the conventional silicon based power switches. Implementation of WBG based power modules in automobiles will allow the use of air cooling for electronics under the hood. To obtain the full advantage of the high temperature capability of WBG devices, the associated control electronics (such as gate driver circuits) also need to operate at higher temperatures with minimal thermal management. By placing the gate driver circuit close to the power switches, system reliability as well as performance can be improved.

Status

A highly integrated SOI chip has been designed, fabricated, and packaged for use at ambient temperatures of up to 200°C (see below). The device features

- on-chip voltage regulator
- undervoltage lockout, short circuit, desaturation, and thermal shutdown protection
- gate current monitoring
- low-voltage differential signaling circuit
- drive current capability greater than 5 A at 200°C
- switching frequency greater than 100 kHz
- 100% high-side duty cycle with charge pump



SOI gate drive chip.

Benefits

- Combined with commercially available WBG based power switches, this SOI gate drive will help to realize high temperature dc-dc converters and inverters for traction drive systems for HEVs and plug-in HEVs.
- This is an enabling technology to reduce the cooling requirements of power electronics while achieving increased reliability at elevated operational temperatures.
- The reduction in the footprint for the traditional gate drive circuitry will realize substantial size and weight savings for the power electronics in these advanced vehicles.

Inverter Using Current Source Inverter

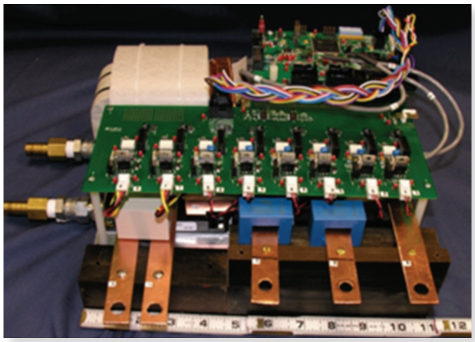
Background

Current hybrid electric vehicles (HEVs) and plug-in hybrid electric vehicles (PHEVs) use inverters that operate off a voltage source because the most readily available and most efficient energy storage devices (batteries) are inherently voltage sources. The voltage source inverter (VSI), however, possesses several drawbacks that make it difficult to meet the U.S. DRIVE goals in terms of volume, lifetime, and cost. It requires a very high performance direct current (dc) bus capacitor bank to maintain a near ideal voltage source. Also, currently available capacitors that can meet the demanding requirements are costly and bulky, taking up one-third of the inverter volume and cost. The reliability of the VSI is limited by the capacitors and further hampered by the possible "shoot-through" of the phase legs. In addition, steep rising and falling edges of the output voltage in the form of pulse trains generate high electromagnetic interference, impose high stress on the motor insulations, produce high frequency losses in the copper windings and iron cores of the motor, and generate bearing leakage currents that erode the bearings over time. Furthermore, the capacitor presents the most difficult hurdle to operating a VSI in automotive high temperature environments.

Technology

New Z-source current source inverter (ZCSI) topologies that combine the benefits of ORNL's current source inverter (CSI) efforts and Michigan State University's work on Z-source inverters are offered to eliminate or significantly relieve the aforementioned problems. The CSI significantly reduces the amount of bus capacitance required and uses only three small alternating current (ac) filter capacitors; the total capacitance of the ac filter capacitors is estimated at about one-fifth that of the dc bus capacitance in the VSI. The CSI offers many other advantages important for HEV applications, including (1) it doesn't need antiparallel diodes in the switches, (2) it can tolerate phase leg shoot-through, (3) it provides sinusoid shaped voltage output to the motor, and (4) it can boost the output voltage to a higher level than the source voltage to enable the motor to operate at higher speeds. These advantages translate into a significant reduction in inverter cost and volume with increased reliability, a much higher constant-power speed range, and improved motor efficiency and lifetime. Further, the CSI's capability to boost the output voltage could lead to smaller battery storage capacity requirements in PHEVs because the inverter can output the rated voltage over a wider discharge window. In other words, more energy can be drawn from the battery by discharging it to a deeper level. In comparison, the output voltage of the VSI drops with the decrease in battery voltage as discharging proceeds.

The proposed CSI (at right) includes a novel interfacing circuit to transform the voltage source of a battery or ultracapacitor bank into a current source to the inverter bridge to provide the capability to control and maintain a constant dc bus current. More importantly, the interfacing circuit also enables the inverter to charge the battery during dynamic breaking without the need for reversing the direction of the dc bus current.



55 kW ORNL CSI prototype.

Status

- ORNL has simulated two new ZCSIs with a reduced component count. Both have a higher boost ratio compared to the previous ZCSI (3 vs 2).

- A design for a 55 kW ZCSI has been completed using first generation reverse blocking–insulated gate bipolar transistor (RB-IGBT) technology. The design yields a specific power of 4.89 kW/kg and a power density of 15.5 kW/L.

- Simulation results confirmed the feasibility of using the ORNL CSI topology in series and power-split series/parallel HEV configurations. The CSI dual-motor-drive power-electronic using RB-IGBTs provides
  - specific power of 6.4 kW/kg,
  - power density of 9.9 kW/kg, and
  - cost of $15.4/kW.

Benefits

- Reduces dc link bus capacitor size and cost by 75% (capacitors represent about 20% of the cost and 30% of the volume of VSIs).
- Eliminates external boost converter by incorporating 3× the voltage boost in a VSI.
- Eliminates the uncontrolled permanent magnet regeneration failure mode.
- Increases motor reliability and efficiency by providing sinusoidal voltages and currents to the motor.
- Enhances inverter reliability by tolerating phase leg shoot-through and open circuit conditions.
- Can operate as a charger in electric vehicles and PHEVs.

New Class of Switched Reluctance Motors without Permanent Magnets

Background

Internal permanent magnet (IPM) motors are currently the technology of choice for vehicle electrification. However, there are notable problems associated with these motors, including the following.

- Cost and availability of rare earth magnets (predominantly controlled by China)
- Sensitivity of magnets to elevated temperatures
  - High temperatures reduce performance
  - Extreme temperatures can destroy the magnets

Other potential motor technologies such as the following exist but also come with tradeoffs.

- Induction motors—possess only moderate efficiency and power density
- Synchronous reluctance motors
    - Inherent rotor complexity—required for saliency/torque production
    - Speed limitations
    - Manufacturing costs
- Switched reluctance (SR) motors with conventional control schemes—low power density

Although SR machines traditionally must be designed larger for power ratings comparable to an IPM, they also have innate advantages. These include low manufacturing costs, simplicity of design, and the absence of permanent magnets in their rotors, which can lead to significantly reduced costs.

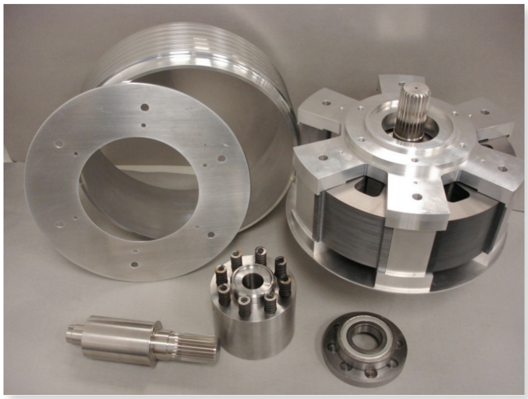
Technology

ORNL is performing research to design, develop, fabricate, and analyze the performance of an innovative hybrid electric vehicle traction drive prototype of at least 55 kW peak power that capitalizes on the benefits of conventional SR motors.

This research explores the possibilities of various novel SR motor design configurations coupled with a continuous conduction control algorithm. These designs will likely produce 2 to 3 times the power density of what is achieved with conventional SR motor designs and controls. Furthermore, if the implementation of an enhanced air gap design is feasible, it is possible that the power density of the motor can be increased by an additional 30% to 60%. Combining these techniques may improve the power density of the motor 2 to 4 times over that of a conventionally controlled SR motor.

Status

- Verified through simulations that the design meets 2015 performance targets and 2020 cost targets with less than 5% torque ripple.
- Developed custom software to interface to finite element analysis software and enable faster design turnaround time.
- Designed assembly and initiated fabrication of prototype (see figure).



SR motor prototype parts.

Benefits

- Eliminates rare earth permanent magnets in motors.
    - Reduces dependency on China for motor materials.
    - Reduces material costs through elimination of expensive rare earth materials.
- Novel configurations present opportunities to achieve low torque ripple, low acoustic noise, and low manufacturing costs while achieving permanent magnet synchronous motor-like performance without permanent magnets.

- Achieves the following goals.
  - Power density of 5 kW/L.
  - Specific power of 1.3 kW/kg.
  - Cost of $7/kW.

Power Device Packaging

Background

Existing commercial device packages introduce undesirable reliability, volume, and cost issues which contribute to the challenges in meeting the U.S. DRIVE 2020 targets. The current state-of-the-art packages used in automotive applications are only suitable for low temperature operation and the wire bonds currently used for signal and power interconnects introduce unwanted parasitic inductances and failure mechanisms. Some advanced concepts such as those used in the Toyota Lexus L600h show innovations in better cooling of the semiconductors but are still far too costly for attaining the FreedomCAR targets.

Technology

The proposed solution is to holistically evaluate existing large power device packaging technologies, including materials, processing, layout, interconnects, thermal management, and performance to determine the "weak links." Promising new packaging technologies will be identified for potential automotive applications through surveys, analysis, simulation, and testing. New packaging concepts will be developed beginning at the device level with die attach mechanisms to replace solders and wire bonds. Investigations into alternative substrate materials to increase material thermal and structural compatibilities will be performed as well as examinations of high temperature encapsulants and alternatives to conventional module level thermal management. This research will be expanded to other inverter components such as the capacitors and the inverter bus bar structure, resulting in new system level packages with improved performance, volume, and cost.

Packaging facility floor layout.

Status

- Multiple state-of-the-art commercial packaging technologies have been benchmarked.
- Advanced packaging approaches are being assessed with the objective of developing new module packages.
- A new packaging laboratory has been designed and outfitted.

Benefits

- Improved power density, thermal management, cost, and reliability.
- Complements other projects within the DOE Vehicle Technologies Program Advanced Power Electronics and Electric Motors Program through collaborations on packaging, thermal management, and module design research efforts.

Segmented Drive System with a Small dc Bus Capacitor

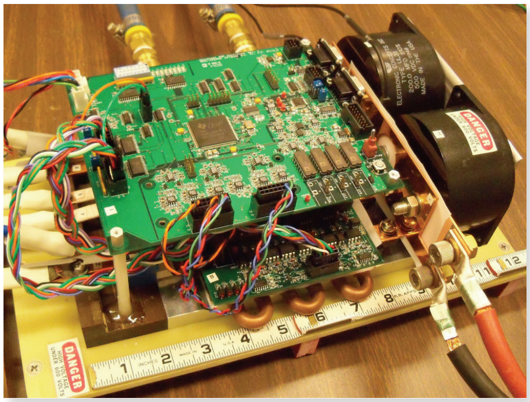
Background

The standard voltage source inverter (VSI) based traction drive is widely used in current hybrid electric vehicles (HEVs). The VSI, which is mainly composed of six power semiconductor switches, diodes, and a large bus capacitor (typically insulated gate bipolar transistors and a film capacitor), switches the battery voltage according to a pulse width modulation (PWM) scheme to regulate the motor current and voltage. In performing the switching operations, the switches generate a large ripple current in the direct current (dc) link, necessitating the use of a dc bus filter capacitor so that a relatively constant current flows into the battery. The capacitor ripple current can reach levels as high as 200 Arms. A bulky and costly dc bus capacitor is required to absorb this ripple current and prevent it from damaging and shortening the battery's life. The dc bus capacitor presents significant barriers to meeting the U.S. DRIVE targets for cost, volume, and weight for inverters. Currently, the dc bus capacitor contributes up to 23% of the cost and weight of an inverter and up to 30% of an inverter's volume.

The large ripple currents become even more problematic for the film capacitors (the capacitor technology of choice for electric vehicles/HEVs) in high temperature environments as their ripple current handling capability decreases rapidly with rising temperatures. There is thus an urgent need to reduce the ripple currents altogether or to divert them from the bus capacitor.

Technology

ORNL is currently performing research on a segmented drive system prototype design to respond to these issues (at right). The segmented prototype design does not need additional switches or passive components but enables the use of optimized PWM schemes to significantly reduce the dc link ripple current generated by switching of the inverter output currents. Unique aspects of this technology include the fact that while it significantly reduces the capacitor ripple current, it does not



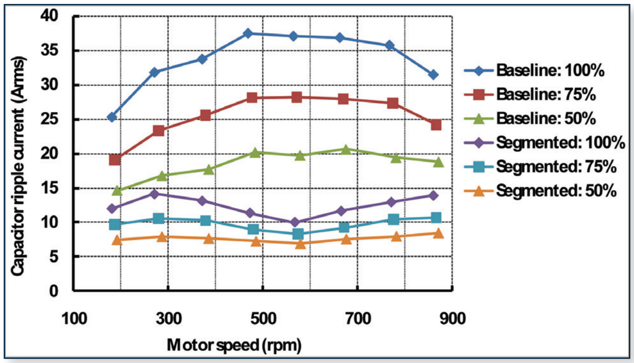
ORNL 55 kW segmented inverter prototype.

- need additional silicon or passive components,
- need additional sensors, or
- add control complexity.

Status

To date, ORNL has completed a 55 kW segmented inverter prototype with a 60% reduction of dc bus capacitance. It has been designed, built, and successfully tested with an inductor-resistor load and an induction motor. Test results (at right) show reductions of roughly

- 55%–75% in capacitor ripple current,
- 70%–90% in battery ripple current, and
- 60%–80% in motor ripple current.



Comparison of dc bus capacitor ripple current vs speed at various percentages of rated torque. (Motor ratings: torque, 91 Nm; current, 37.5 Arms).

Benefits

- Reduces cost and volume by 15% compared to standard VSIs.
- Reduces dc link bus capacitor size and cost by more than 60%.
- Reduces battery losses and improves battery operating conditions by reducing battery ripple current.
- Significantly reduces motor torque ripples (up to 50%).
- Reduces switching losses by 50%.
- Increases inverter reliability.
- Enables high temperature operation.

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Energy Storage Technologies

Materials and Processing for Advanced Batteries

Background

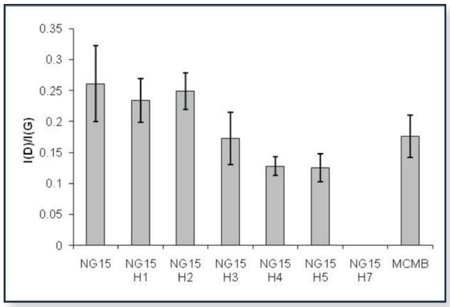
Lithium secondary battery technology is projected to be one of the energy storage leapfrog technologies for full electrification of automotive drivetrains. However, manufacturers currently have a poor understanding of the effects of processing parameters on battery performance, have difficulty preserving the required nanoscale features of components during scale-up, and are hampered by a limited understanding of the effects of different electrode formulations. The objective of this project is for ORNL to establish long-term partnerships with battery manufacturers to investigate, improve, and scale process methodology to manufacture high-performance lithium secondary batteries in industrial quantities. Using ORNL's expertise in process technology, quality control, and materials characterization, the laboratory is assisting these manufacturers in developing cutting-edge fabrication methods in the areas of anodes, cathodes, and separators and in enabling successful implementation of large-scale battery cells meeting performance needs and cost targets.

Technology

A cooperative research and development agreement (CRADA) with A123 Systems, Inc., is focused on identifying the relationship between the physical properties and cell performance of natural graphite-based anode materials required to achieve high-capacity and long-cycle-life lithium ion batteries. The results will guide decisions on powder selection for anode active materials. A CRADA with Dow Kokam, LLC, is investigating the microstructure, materials processing, and long-term performance of Dow Kokam's NANO-based cathodes for lithium ion batteries. The NANO material will be incorporated in the product mix of Dow Kokam's 1200-MWh/yr cell production. A CRADA with Planar Energy Devices, Inc., will assist in the development of large-scale electroless deposition and rapid thermal annealing (RTA) processes associated with making all-solid-state lithium ion battery cathode and electrolyte layers. This revolutionary processing methodology has the potential to transform the large-scale lithium secondary battery market with its safety and cycling improvements. A CRADA with Porous Power Technologies, LLC, will validate the performance, durability, and safety of a new type of composite lithium ion battery separator with improved ionic conductivity, which is produced by a new method of direct coating during electrode fabrication.

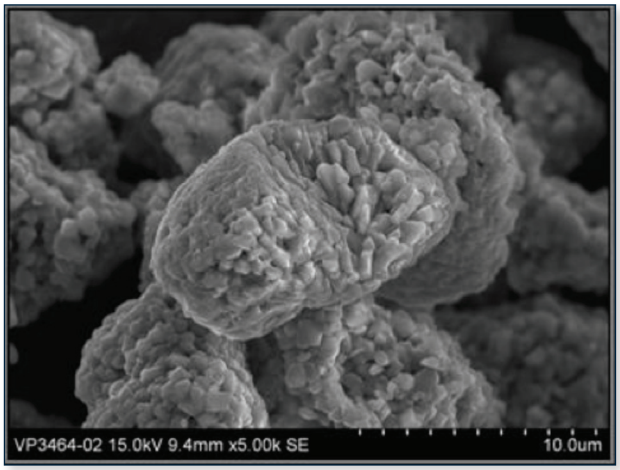
Status

Based on advanced materials characterization and coin cell performance data taken at A123 Systems, attention has been focused on temperatures of 950°C, 1050°C, and 2000°C. These temperatures represent a substantial reduction in the commonly used graphitization temperatures of 2500–3000°C. The figure at right shows Raman spectroscopy results for the ratio of the disordered band (D) to the graphitic band (G) of natural graphite samples heat treated to different temperatures. As shown, the D/G ratio, which should be ~0.2 for good lithium ion intercalation [i.e., mesocarbon microbead (MCMB)], of the samples treated to the lowest temperature (NG15-H1 and NG15-H2) is only about two times that of the sam-



Raman spectroscopy data for natural graphite samples heat treated to various temperatures compared to MCMB baseline.

ple treated to 1700°C (NG15-H5). Dow Kokam Gen I cathode NiMnCo (NMC) materials were found to be phase pure via x-ray diffraction (XRD) with a primary lithium manganate peak at about 2θ = 18.5°. X-ray photoelectron spectroscopy (XPS) confirmed the nominal compositions at the surface for lithium, nickel, cobalt, and manganese for the two different batches. The figure below shows a scanning electron microscope (SEM) image of the Gen I NMC material showing the secondary particle size of ~10–20 μm with primary crystallite sizes of ~500–1000 nm. Much progress has been made with Planar Energy in refining the processing conditions for RTA of the deposited Ni-Mn-Co-Al cathodes using both the ORNL plasma arc lamp and the PulseForge 3300. It was determined that conditions of much lower power (intensity) than initially thought are required to prevent sample damage during the RTA process. Continued characterization of baseline Porous Power SYMMETRIX HP and HPX separators has occurred, as we attempt to gain an understanding of how the thermal and mechanical properties of polyvinylidene fluoride based materials compare to those of state-of-the-art polyethylene and polypropylene based-separators.



SEM image of Gen I NMC cathode powder showing secondary particles and primary crystallites.

Benefits:

- Improvements in processing technology will reduce the energy used in battery manufacturing.
- Hybrid electric vehicles (HEVs) and plug-in hybrid electric vehicles (PHEVs) will reduce tailpipe emissions and reduce U.S. dependence on imported fuels.
- More reliable, less expensive, and longer lived batteries will increase deployment of HEVs and PHEVs and position the United States as a leader in the development of this technology.

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In Situ Acoustic Emission and X-Ray Diffraction of Lithium Ion Battery Materials

Objectives

- Develop cost-effective in situ characterization tools for the validation of degradation mechanisms.
- Develop an understanding of degradation mechanisms and the role of mechanical degradation of battery materials in capacity fade.

Technical Barriers

The primary technical barriers are a lack of development tools to support lifetime predictions, a lack of quality control procedures for plug-in hybrid electric vehicle batteries with 10 year lifetimes that meet or exceed all performance goals, and degradation mechanisms during formation cycling.

Technical Targets

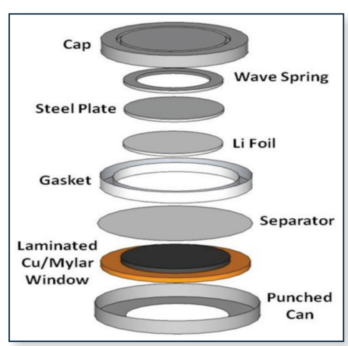
- Develop techniques to evaluate and understand quality and expected life of active electrode materials in experimental and real battery cells.
- Develop a formation-cycle analysis tool.

Accomplishments

- A laboratory-scale method was developed for using acoustic emission (AE) and x-ray diffraction (XRD) for monitoring degradation in lithium ion batteries (LIBs).
- In situ AE–XRD uses safe, inexpensive components that can be tailored to work with either anode or cathode materials, making the design useful in a wide variety of situations.
- Lattice strain in silicon was measured and correlated well with the observed AE activity.
- Lattice strain in $Li(NiMnCo)O_2$ (NMC) cathodes was monitored in situ for the first time with a standard diffractometer. The strain behavior was also monitored further into the cycling life of the cell than had been previously reported.

Introduction

Electrode materials for LIBs undergo many changes as they are cycled, including lattice strain and particle fracture. The role of mechanical degradation in overall LIB performance is not thoroughly understood but is likely to play an important part in the development of next-generation active materials and cell design. However, progress in this area is limited by current characterization techniques. A novel in situ technique that combines AE and XRD has been developed and tested on both anode and cathode materials.

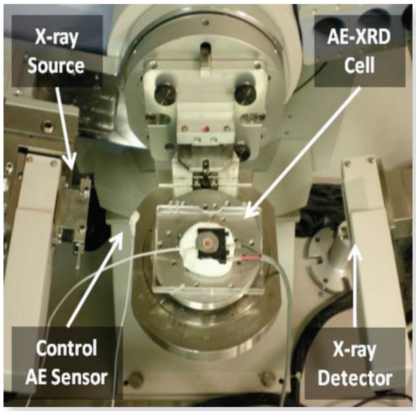


Schematic view of the in situ AE–XRD cell design used to study LIBs during cycling.

Approach

AE has been used to detect, sort, and classify mechanical events such as particle fracture inside cycling LIBs. To directly correlate the observed fracture events with strain in the active materials, special in situ methods of XRD can be used. A novel beryllium-free in situ AE–XRD cell has been devised that uses a metalized Mylar window to allow x-ray penetration during cycling in standard coin cell hardware.See schematic at right.

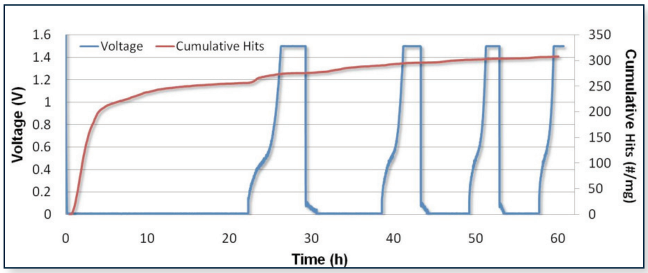
The picture at right shows a general experimental setup. This technique provides a safe, inexpensive alternative to current in situ XRD methods. It also provides data for a depth of understanding which before was possible only with special miniature cells and very short synchrotron beam time. The new cell allows for extended beam time in inexpensive laboratory-scale diffractometers. Mylar disks sputtered with copper can be used in direct contact with anode materials, and disks sputtered with aluminum can be used in contact with cathode materials. Studies using this combined technique will allow for further fundamental understanding of material degradation mechanisms and how they are correlated with capacity fade and cell failure.



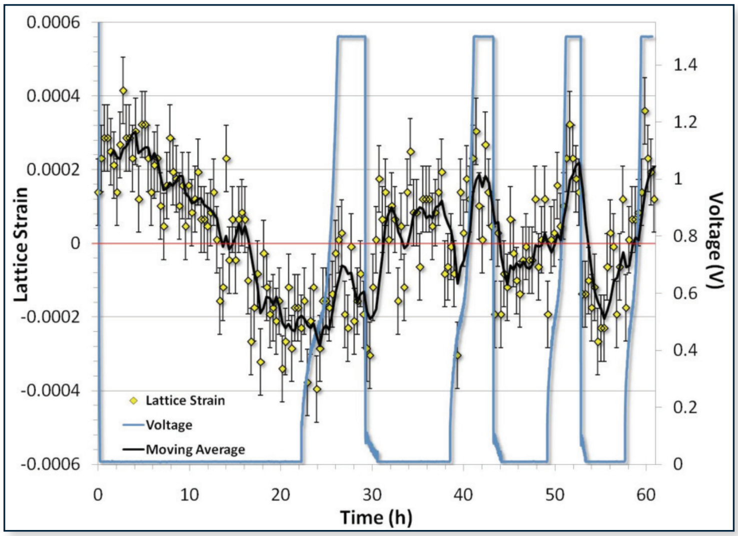
In situ AE–XRD experimental setup showing the cell connected to an AE sensor and current leads and sitting in the x-ray beam path.

Results

A study of silicon anodes was performed using the new characterization method; a plot of cumulative AE and voltage is shown below. These data correlated very well with previously reported results of AE from unmodified coin cells containing silicon electrodes. By performing Rietveld fits of XRD scans, the lattice strain in the crystalline region of silicon particles was determined (see below). The periods of highest AE activity overlap perfectly with major inflection points in the calculated strain, which directly shows the strain release occurring in the particles as they fracture.

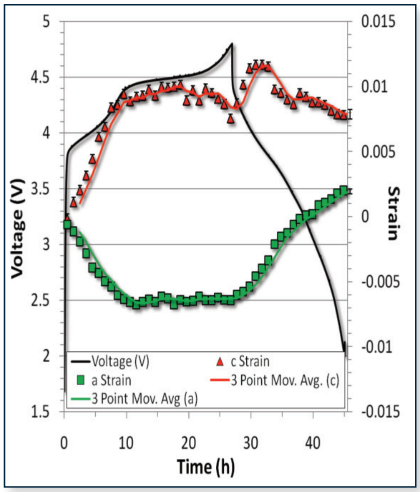


Cumulative AE and cycling voltage of in situ AE–XRD cell containing a composite silicon electrode.



Lattice strain in the crystalline region of silicon particles and voltage as a function of time.

When the technique was applied to NMC materials, a very clear picture of lattice strain was achieved. The results charted at right show very clearly the decrease in the "c" parameter during the voltage plateau, which correlates to cation rearrangement in the material. Results similar to those seen in the charge stage have been reported from synchrotron experiments, but this is the first time that ordinary laboratory XRD has successfully measured them. Additionally, this is the first attempt to look at lattice changes past the first charge stage.



Lattice strains "a" and "c" in NMC materials cycled in an in situ AE-XRD cell.

Conclusions and Future Directions

The developed in situ cell will be used to improve understanding of degradation mechanisms in cathode materials. In the next step, the understanding developed will be used in large-scale battery cells from U.S. manufacturers during formation cycling. Formation cycling is the key aspect of forming materials within the cell and obtaining the maximum performance from cells. It also provides insight into mechanical events during the formation of those materials. This information will be used to understand how mechanical response to formation cycling can be used as an early detection tool.

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Intercalation Kinetics and Ion Mobility in Electrode Materials

Objectives

- Develop fundamental understanding of deformation processes and stress generation during lithium intercalation (deintercalation) from active cathode material via experimental work on focused ion beam (FIB) micromachined samples.
- Develop and validate coupled kinetic, thermal, and mechanical model based on the experimental results.
- Understand the role of defects, texture, and mechanical damage in lithium ion kinetics in intercalation compounds.

Introduction

It is commonly accepted that lithium ion battery life is limited as a result of the degradation of electrode materials with repeated charging/discharging. One of the degradation mechanisms is related to the development of internal stresses in electrode particles because of repeated lithium insertion and removal, which ultimately leads to the appearance of cracks in and the fracture of particles. The current project targets the fundamental understanding, description through mathematical modeling, and controlled experimental validation of internal stress generation and the morphology change of electrode particles in a lithium ion battery. While the intercalation/deintercalation process induces the displacements, changing the overall dimension of the specimen, lithium diffusion should be investigated on the single-grain level. The second part of the project looks into texture and defect-dependent lithium ion mobility, which is the underlying process for diffusion-strain coupling.

Approach

The experiments are performed on model systems represented by micro-level specimens of electrode material. In this way, the modeling work is done on preselected geometries of specimens to validate the constitutive approach. Different cathode materials are investigated, including $LiCoO_2$, $LiMn_2O_4$, and $Li_4Ti_5O_{12}$.

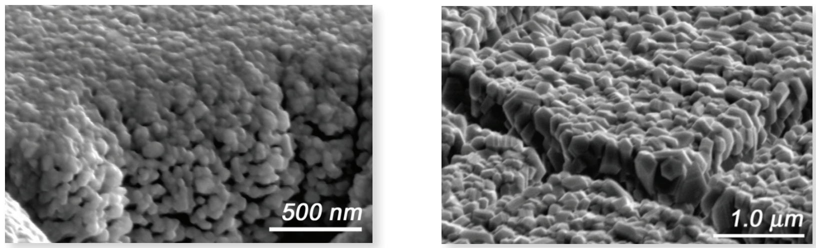
The specific distribution of tasks is as follows. Thin-film battery systems with thicknesses suitable for FIB machining are synthesized at ORNL. Subsequent micromachining of electrode samples is done at ORNL using dual-beam FIB/scanning electron microscopy (SEM). Micro-samples are tested in a half-cell setup at the University of Michigan. The setup is equipped with an atomic force microscope (AFM) with a tip serving as a current collector, which allows for simultaneous cycling and investigation of morphological changes in the specimen. The experimental results will be used to validate the proposed coupled kinetic, thermal, and mechanical model.

In addition, electrochemical strain microscopy (ESM), recently developed at ORNL, was applied to study lithium ion concentration gradients in thin-film $LiCoO_2$ electrodes. The method is based on strain-bias coupling used for detection of local electrochemical activity.

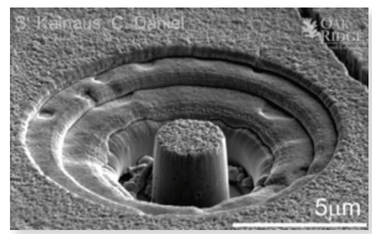
Results

Physical vapor deposition preparation of thin film systems. Thin-film samples with a $LiCoO_2$ cathode were prepared by radio frequency magnetron sputtering of a cold-pressed and sintered $LiCoO_2$ target. Layers were deposited on the Al_2O_3 substrate. A $LiCoO_2$ cathode was deposited over a thin layer of gold as a current collector.

Annealing was done at 700°C and 800°C. The lower temperature provides a fine grain size specifically suitable for FIB milling, and the higher temperature provides larger crystals for ESM analysis (see below).



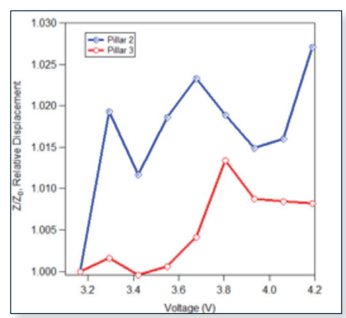
Thin-film $LiCoO_2$ cathode annealed at (a) 700°C and (b) 800°C.



FIB machined pillar.

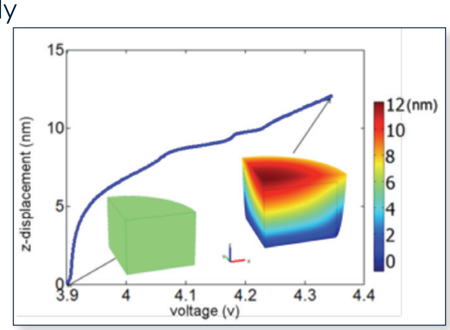
Micromachined electrodes. Samples were fabricated using a Hitachi NB5000 dual-beam FIB/SEM. Runs with decreasing apertures were applied, with the final run having a current of 0.07 nA in order to remove the layer of gallium implantation. A SEM image of the milled samples is shown at right.

In situ AFM. A Veeco electrochemical AFM (Veeco Instruments, Inc.) with a Z-direction noise level of less than 0.035 nm was used in the experiments. The system was equipped with a wet cell for in situ mapping of the electrode sample. A nonconductive silicon nitride AFM tip with a radius of 10 nm was used for scans in contact mode. A Bio-Logic VMP3 (Bio-Logic USA, LLC) potentiostat with a current ranging from 1 nA to 400 mA was used for cycling. The height change of the pillars was measured as a function of applied voltage (at right).



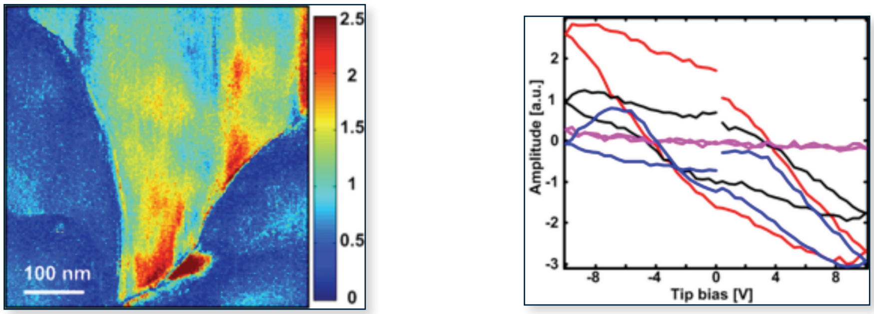
Relative vertical displacement of FIB micromachined cylinders.

Modeling. The finite-element method (FEM) was applied for numerical solution of differential equations incorporated into the model. The pillar was simulated as rigidly attached at the bottom surface, and the flux of ions was allowed as a boundary condition along the remaining surfaces. The figure at right depicts the results, showing the vertical displacement of the pillar as the voltage increases following the cyclic voltammetry (0.05 mV/s) scan.



FEM modeling of $LiCoO_2$ micro-pillar.

Micro-pillar compression. The effect of mechanical damage on the form of compressive pre-straining was investigated using nanoindentation techniques. At the preliminary stage, several FIB micromachined cylinders were compressed in an MTS Nanoindenter XP system using a flat tip indenter 20 µm in diameter. The results allowed for a preliminary estimate of Young's modulus, which was determined to be close to 30 GPa. In future investigations, the effect of precompression on electrochemical strain will be determined by using AFM scans of the pillars. Work is also under way to introduce damage to the thin films using a spherical tip indenter for further investigation of damage to local ion mobility by ESM.



ESM of $LiCoO_2$ grains: (left) amplitude and (right) hysteresis loops at different locations.

Electrochemical strain microscopy. ESM was applied to 800°C annealed $LiCoO_2$ thin-film samples to map the strain induced by lithium concentration gradients. A high-frequency, low-voltage pulse was applied via the AFM tip, which redistributed lithium in the tip vicinity, causing local displacements in the grains. The results show the significant dependence of electrochemical activity on the crystallographic features of the sample. Bias-induced strain amplitude (above left) and a corresponding hysteresis loop area (above right) are functions of the location of the pulse application. The technique is very promising for revealing preferential locations for lithium ion diffusion in cathode material.

Conclusions and Future Directions

The diffusion-stress coupling model shows the capability to predict strains in electrode micromachined specimens. The model awaits improvement based on the experimental data obtained from electrochemical cycling of electrode samples. Work will continue on application of the developed technique to other cathode materials. The newly developed ESM technique is a powerful and promising method for investigation of lithium mobility within the electrode as a function of defects, grain boundaries, introduced damage (slip lines), and state of charge. At present, the work has been done in ambient air, when the ions are moving within the material as a result of a locally applied pulse. At the next stage, it is proposed that the experiments be performed in an electrolyte in order to study lithium ion transport across a solid/electrolyte interface. Future efforts may also focus on developing an understanding of microstructural features for low state of charge power enhancements and on future materials processing routes to maintain those microstructures in large-scale batteries.

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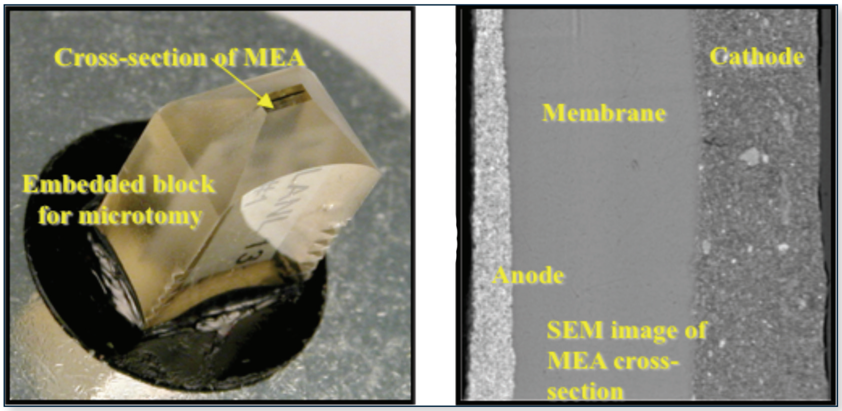
Fuel Cell Technologies

Advanced Imaging and Compositional Analysis Techniques to Evaluate Micron-Ångstrom-Scale Membrane Electrode Assembly Microstructures

Background

The membrane electrode assembly (MEA) is the core of a polymer electrolyte membrane (PEM) fuel cell. Examination of the aging of MEA materials under load for thousands of hours is critical to evaluate their durability in fuel cell environments. Understanding MEA structural and chemical degradation mechanisms will be critical for implementation of MEAs in future power sources. This project uses high-resolution imaging and compositional/chemical analysis techniques for characterization of the material constituents of as-processed and electrochemically aged PEM fuel cell MEAs.

(a) (b)



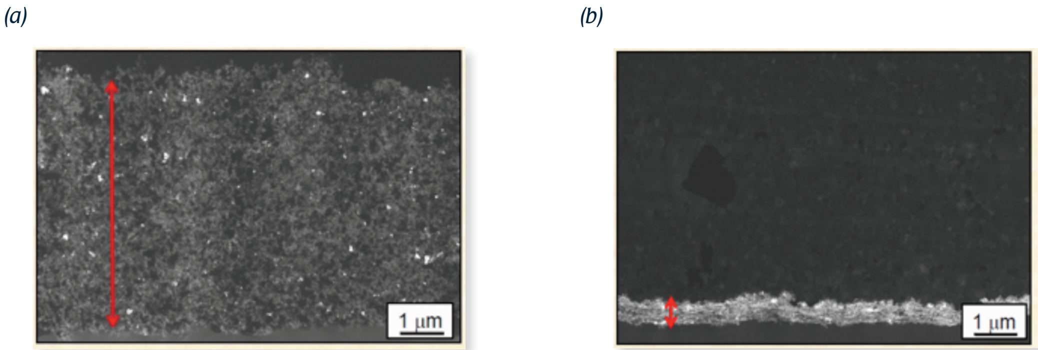
Trimmed block of embedded MEA cross section (a) is used initially for scanning electron microscope imaging (b) and then for transmission electron microscope thin-section preparation.

Technology

This project applies state-of-the-art electron microscopy techniques for the analysis of MEA material constituents including catalyst nanoparticles, membranes, carbon supports, and gas diffusion/microporous layers and makes this technology available to partners to correlate structure/composition with MEA processing and/or life-testing studies. State-of-the-art electron microscopy techniques used for the analysis of MEA materials include high-resolution field emission gun (FEG) scanning electron microscopy, high-resolution FEG transmission electron microscope tomography imaging, and high-angle annular dark field imaging (Z-contrast imaging) in an aberration-corrected scanning transmission electron microscope. These techniques are enabled by improvements in specimen preparation including the use of partial embedding for microtomy and cryomicrotomy/cryotransfer for membrane analysis (see above).

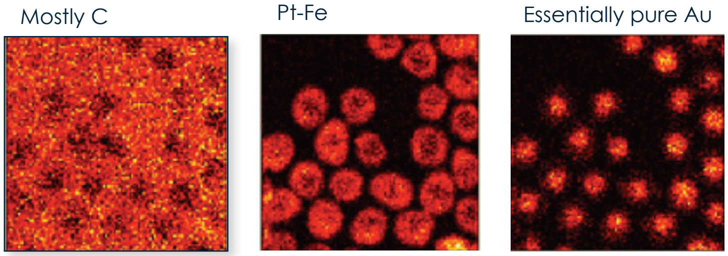
Results

Investigation of carbon-support corrosion mechanisms in electrochemically aged MEAs has shown that during electrochemical aging under adverse conditions the cathode can collapse, compress, or thin, resulting in significant performance loss. This work has also demonstrated the migration of platinum from the cathode into the adjacent membrane. These platinum migration profiles can be complex, comprising numerous platinum bands composed of different size platinum particles distributed across the membrane.



Carbon corrosion of cathodes before (a) and after (b) electrochemical aging.

Principal component analysis (PCA) of Ångstrom-scale elemental/compositional analyses of catalyst nanoparticles has extracted the primary elements and their primary location within the structure of catalyst nanoparticles. For example, in platinum-shell/gold-core structures determined from raw dark-field energy dispersive x-ray spectroscopy data, PCA indicates that iron in these structures correlates with the platinum in the shells of the catalyst nanoparticles (see below).



Three primary element groups determined from PCA and their distributions with catalyst nanoparticles.

Benefits

- Identify and optimize novel high-resolution imaging techniques, compositional/chemical analysis techniques, and unique specimen preparation methodologies for the micron-Ångstrom-scale characterization of fuel cell materials.
- Apply advanced analytical and imaging techniques for the evaluation of microstructural and microchemical changes that correlate with fuel cell performance.
- Elucidate microstructure-related degradation mechanisms contributing to fuel cell performance loss.
- Make techniques and expertise available to researchers outside of ORNL.

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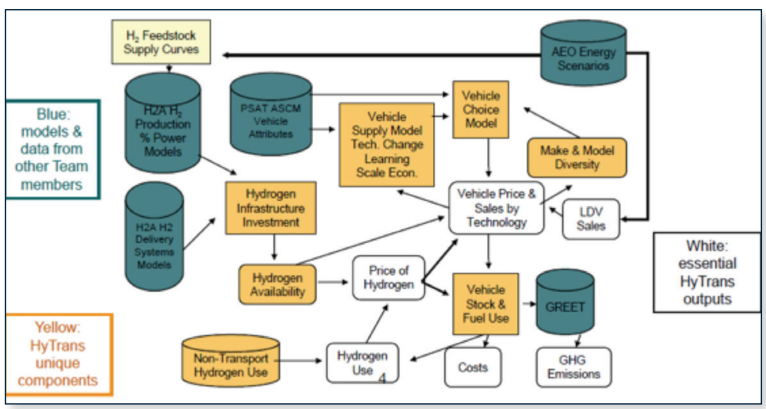
Analyzing the Potential for Stationary Fuel Cells to Augment Hydrogen Availability in the Transition to Hydrogen Vehicles

Background

Understanding how the transition to hydrogen can be achieved efficiently and effectively is critically important to the success of the DOE Fuel Cell Technologies Program. This project supports that program through development of the Hydrogen Transition (HyTrans) model, a tool for simulating market transitions of advanced light-duty vehicle (LDV) systems from conventional petroleum-powered internal combustion engines to hydrogen, and application of the model to develop and analyze scenarios of the early transition to fuel cells and fuel cell vehicles. By incorporating other established models such as DOE's Hydrogen Analysis (H2A) Program hydrogen production and delivery models, HyTrans is able to consistently represent all key interdependent factors affecting the transition.



Components of the advanced vehicle and fuel market integrated in HyTrans.

Technology

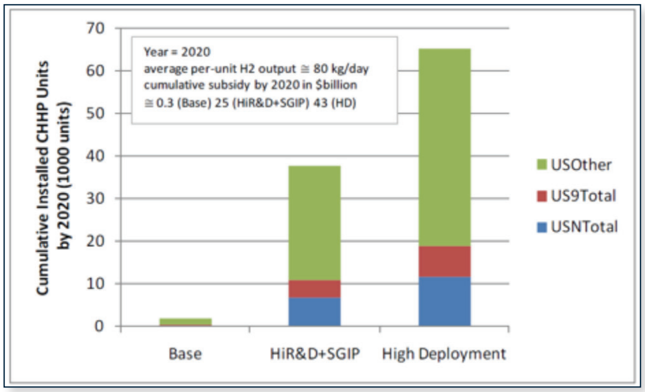
The HyTrans market-equilibrium model represents interdependent decisions of hydrogen suppliers, vehicle manufacturers, and consumers for the period from 2000 to 2050. It finds competitive market solutions by maximizing producers' profits and consumers' welfare. HyTrans incorporates reduced form representations of production, delivery, and forecourt technologies from the models developed by the H2A working group (see above). It uses vehicle technology characterizations from the Argonne National Laboratory (ANL) Power System Analysis Toolkit (PSAT) model and cost estimates developed with the Automotive System Cost Model (ASCM) developed by ORNL in collaboration with Ibis Associates, Inc. Greenhouse gas (GHG) emissions estimates are from the ANL Greenhouse Gases, Regulated Emissions, and Energy Use in Transportation (GREET) model. HyTrans is calibrated to the National Energy Modeling System's Annual Energy Outlook (AEO) projections extrapolated to 2050. HyTrans models the impacts of the accomplishment of FCTP technical goals and the effects of policies that could increase the baseline numbers of fuel cells and fuel cell vehicles in the early years of transition. Current research focuses on adding internal combustion engines and hydrogen plug-in hybrid electric vehicles to the model; analyzing the role that combined heat, hydrogen, and power (CHHP) could play in increasing hydrogen refueling; and determining potential synergies between stationary and mobile hydrogen fuel cell applications.

Results

HyTrans was used to examine the impact of CHHP on hydrogen production and distribution for a variety of policy scenarios including accelerated research and development (R&D), government incentives such as self-generation incentive programs (SGIPs), and favorable markets (top figure). With the kind of strong incentives for CHHP offered by national and California policies, up to 60,000 CHHP sites could potentially be active by 2020. Without CHHP, nearly all hydrogen production and retail outlets will be large steam methane reforming (SMR) installations. With CHHP, some SMR stations would be replaced by CHHP stations, resulting in more hydrogen stations, smaller average station size, and better fuel availability for hydrogen vehicles. Increased R&D commitments and government incentives could further reduce the share of hydrogen produced by SMR and greatly increase the availability of CHHP retail outlets (bottom figures).

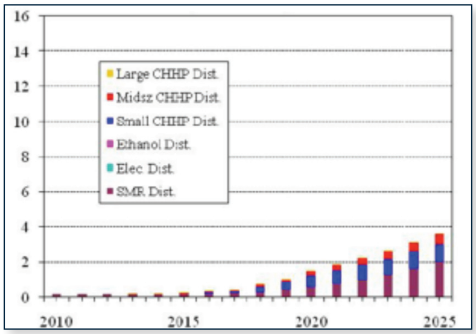
Benefits

- Identifies important synergies between stationary and mobile fuel cell markets.
- Incorporates and integrates established models developed previously by other groups.
- Successfully analyzes problem areas to facilitate streamlining transition to a hydrogen economy (e.g., by determining that widespread deployment of CHHP could greatly reduce the problem of hydrogen availability in the early stages of transition to fuel cell vehicles).

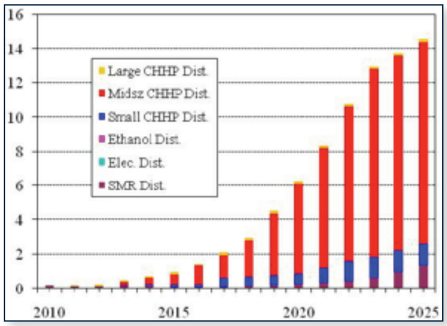


Effect of R&D and incentives on future CHHP sites.

(a)



(b)



Thousands of distributed retail stations in base (a) and high R&D plus SGIP (b) cases.

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Cost-Effective Metallic Bipolar Plates through Innovative Control of Surface Chemistry

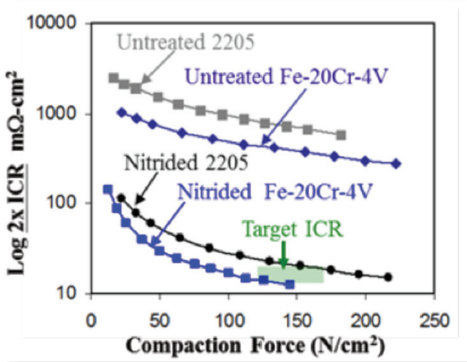
Background

The bipolar plates in proton exchange membrane fuel cells serve to electrically connect the anode of one cell to the cathode of another in a stack to achieve a useful voltage. They also separate and distribute reactant and product gas streams. Thin stamped stainless steel bipolar plates offer the potential for (1) significantly lower cost than currently used machined graphite bipolar plates, (2) reduced weight/volume, and (3) better performance and amenability to high volume manufacture than developmental polymer/carbon fiber and graphite composite bipolar plates. However, despite high bulk electrical conductivities, stainless steels have unacceptably high interfacial contact resistance (ICR) due to the presence of passive oxide layers which afford corrosion protection.

The goal of this effort is to scale up and demonstrate the technological and economic viability of thin (≤0.1 mm) stamped metallic bipolar plates protected by a thermal (gas) nitridation surface treatment. In this approach, a low contact resistance electrically conductive and corrosion-resistant nitride surface layer is formed on the bipolar plate component by heating a specially designed bipolar plate alloy to high temperatures in a nitrogen containing environment.

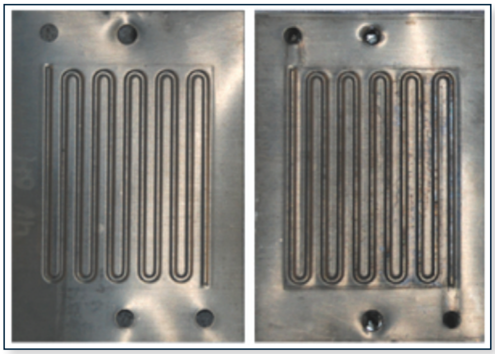
Technology

Extensive studies led to the development of Fe-20Cr-4V wt %. This alloy exhibits a combination of low alloy cost and amenability to stamping while also forming a low ICR and corrosion-resistant surface on thermal treatment. Surface treatment was accomplished by pre-oxidizing to form a chromium- and vanadium-rich oxide surface and then converting the surface to nitride. Compared to conventional stainless steels such as type 2205 (Fe-22Cr-5Ni wt % base), the vanadium in Fe-20Cr-4V aids in transformation of the initial oxide surface to nitride, resulting in through surface layer conductive vanadium-nitride paths that result in the good electrical behavior (top right).



Nitridation significantly lowers ICR of commercial 2205 stainless steel and Oak Ridge National Laboratory developmental Fe-20Cr-4V alloy foils.

Single-cell fuel cell testing was conducted under cyclic conditions, including excursions to open circuit. More than 1,000 h of single-cell fuel cell testing was accomplished for the stamped and pre-oxidized–nitrided Fe-20Cr-4V foils (bottom right) and benchmark graphite and 904L plates (a highly alloyed stainless steel benchmark; not shown). The best voltage-current (V-I) performance curves were exhibited by pre-oxidized, nitrided Fe-20Cr-4V, which was moderately better than untreated 904L stainless steel and machined graphite.



Stamped and pre-oxidized, nitrided Fe-20Cr-4V foils before and after fuel cell testing.

The graphite plate V-I performance behavior was moderately lower than Fe-20Cr-4V due to minor differences between the machined graphite and stamped stainless steel flow fields. No significant degradation in V-I performance curves was observed.

Analysis of the membrane electrode assemblies (MEAs) from the 1,000 h durability tests indicated levels of iron contamination of only 0.1–0.3 × 10^{-6} g/cm^2 for both the stamped and pre-oxidized–nitrided Fe-20Cr-4V and graphite plates. This level of iron contamination is in the range of the fresh MEA starting levels and indicates excellent resistance to metal ion dissolution by the stamped and nitrided Fe-20Cr-4V foil. In contrast, iron levels in the 1.1 × 10^{-6} g/cm^2 range were observed in the MEAs from the 904L plates.

Benefits

- Nitridation forms protective, pin-hole-defect-free nitride surface coatings.
- Stamping and nitriding are industrially established manufacturing techniques.
- Thin metallic bipolar plates translate into high power density fuel cell stacks of interest for automotive applications.
- Materials and manufacturing methods are low cost and can potentially deliver power at the bipolar plate program goal of $5/kW.
- Fe-20Cr-4V alloy provides a low ICR and corrosion-resistant surface with no observed performance decline after more than 1,000 h testing.

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Fuel Economy, Policy, and Transportation Analysis

Biomass Energy Data Book

Background

In 2006 the biomass industry grew rapidly, and the need for data and information did as well. At that time, DOE's Office of Energy Efficiency and Renewable Energy had four energy data books—transportation, buildings, power technologies, and hydrogen. A fifth energy data book, a compilation of data and information on biomass, was necessary not only to give biomass researchers access to consistent and reliable data, but also to inform the general public whose curiosity was piqued by recurring biomass references in the news.

The first edition of the *Biomass Energy Data Book* was published in October 2006 as an online document (http://cta.ornl.gov/bedb). That version was replaced online in April 2009 with the second edition of the document. From the first to the second edition, more than 30 tables, 15 figures, and 80 glossary entries were added to the book. The third edition was posted online in December 2010.

Technology

The purpose of the data book is to draw together, in one place, biomass data from diverse sources to produce a comprehensive document that supports anyone with an interest or stake in the biomass industry. Designed for use as a reference website, the data book is an assembly and display of statistics and information that characterize the biomass industry. The website presents relevant statistical data in the form of tables and graphs. Data from the book are available via the Internet (http://cta.ornl.gov/bedb) in both Excel and PDF formats.

Status

Edition 3, which is the most recent, is divided into five chapters. The first chapter is an introduction to the biomass industry. Chapter 2 concentrates on biofuels such as ethanol and biodiesel. Chapter 3 includes information on biopower (i.e., the use of biomass for electric power generation and heating). Chapter 4 contains data on biorefineries, and Chapter 5, the largest, displays maps and data on biomass feedstocks. A glossary of more than 275 biomass terms is also included. Over the last year, the *Biomass Energy Data Book* website has served more than 5,000 unique visitors each month.

The *Biomass Energy Data Book* is growing with the biomass industry and is becoming, like other DOE energy data books, a go-to resource for researchers, analysts, and the general public.

Benefits

- Provides one-stop resource for biomass information needs.
- Reflects the information needs of users in both scope and organization.

- Provides a means for obtaining historical trend information.
- Provides links to other online sources of biomass information.
- Provides conversion tables.
- Provides an acronym list and glossary.

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Commercial Motor Vehicle Roadside Technology Corridor

Background

DOT's Federal Motor Carrier Safety Administration's (FMCSA's) Office of Analysis, Research, and Technology (ART) is pursuing a strategic initiative to accelerate FMCSA's mission and ART's goal of expediting the deployment of safety technologies by developing and using a commercial motor vehicle roadside technology corridor (CMVRTC) to test and evaluate new safety technologies and procedures.

FMCSA launched CMVRTC in 2007 in partnership with the Tennessee Departments of Safety and Transportation, ORNL, and the University of Tennessee to further enable FMCSA testing of current, new-to-market, and emerging commercial motor vehicle (CMV) safety technologies and to promote their usage and acceptance by stakeholders.

CMVRTC is a series of specially equipped testing facilities at weigh stations in Tennessee to demonstrate, test, evaluate, and showcase innovative CMV safety technologies under real-world conditions to improve commercial truck and bus safety. It is located in Tennessee on a 70-mile stretch of I-81 and I-40 in Knox, Greene, Hamblen, Jefferson, and Sevier Counties. Currently, there are plans to expand the corridor to I-65 near Nashville. It is anchored on the west end by the Knox County CMV Inspection Station (IS) and on the east end by the Greene County CMV IS.

CMVRTC is located on a 70-mile stretch of I-81 and I-40 in Knox, Greene, Hamblen, Jefferson, and Sevier Counties.

Since 2007, ART has established internal partnerships with the FMCSA Offices of Bus and Truck Standards and Operations, Enforcement and Compliance, and Safety Programs at FMCSA headquarters and with the Southern

Service Center in the field. CMVRTC is available to these and other FMCSA offices with management support provided by ORNL. ART has established an external partnership with DOE to collect CMV safety sensor data from a DOE partner fleet. These data will be used to support CMVRTC objectives.

Technology

Since its commissioning in 2007, testing has been conducted within the CMVRTC to

Performance-based brake testing technology provides a safe, accurate, and objective assessment of a vehicle's brake force and overall brake performance.

- study the wear and performance of brake drums/rotors and lining/pads of four different vocations of Class-8 CMVs;
- correlate Performance-Based Brake Tester (PBBT) (at right) results with North American Standard (NAS) Level-1 inspection results relative to CMV brakes;
- support the substitution of the PBBT test in lieu of physical brake stroke measurements in the NAS Level-1 inspection;
- determine the out-of-service (OOS) rate of the mainline on I-81 southbound (Greene County CMV IS);
- determine and contrast OOS rates for the other fixed inspection sites with that of the Greene County site;
- support the development of functional specifications for a smart infrared inspection system for brakes, tires, and bearings;
- prove the viability of the wireless roadside inspection (WRI) concept (see below); and
- test system loading, end-to-end functioning, and end-user acceptance of WRI using commercial mobile radio services.

Using a fixed site or mobile vehicle, WRI is designed to conduct up to 25 times more vehicle inspections a year than the current, in-person inspection process. In real time, an inspector can obtain driver and carrier identity, vehicle condition, and hours-of-service violations while the vehicle is traveling at highway speed.

A newsletter describing current research within CMVRTC, *Technology Corridor News*, is published by ORNL/FMCSA and posted to the CMVRTC web page (http://www.fmcsa.dot.gov/facts-research/art-CMV-Roadside-Technology-Corridor.htm).

Benefits

- Showcases inspection technologies and highlights their systematic integration with existing enforcement operations and highway information systems by partners at the Tennessee Department of Safety and Tennessee Department of Transportation.
- Collects data on CMV safety technologies of interest to FMCSA and assesses their viability for deployment.
- Provides a technology transfer function for new-to-market and emerging technologies by collecting operational data for the development of functional specifications to support FMCSA Motor Carrier Safety Assistance Program grant applications.

- Collects data to support FMCSA enforcement and compliance programs, state safety programs, policy research, and future rulemaking activities.
- Facilitates accelerated deployment of proven safety technologies.

Status
The vision for CMVRTC going forward is to expand the corridor to additional inspection sites in Tennessee and other states as program level efforts such as WRI and Smart Roadside mature and require a larger test bed and multisite, multistate participation. Additionally, CMVRTC plays a prominent role in supporting FMCSA's technology transfer activities enabling the accelerated deployment of proven safety technologies.

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Freight Analysis Framework Version 3

Background
The Freight Analysis Framework version 3 (FAF^3) database is a DOT Federal Highway Administration (FHWA) freight data product composed of U.S. domestic and international freight flows. FAF integrates data from a variety of sources to create the most comprehensive publicly available picture of freight movements among states and major metropolitan areas by all modes of transportation. FAF^3 provides estimates for tonnage and value by commodity type, mode, origin, and destination for 2007, the most recent year, and forecasts through 2040. Also included are truck flows assigned to the highway network for 2007 and 2040.

In 1997 FHWA, in cooperation with other DOT modal administrations with freight responsibilities and ORNL's Center for Transportation Analysis (CTA), developed the first FAF. CTA assisted FHWA with database improvements resulting in the 2002 FAF or FAF^2; assisted in harmonizing the 2002 data with the 1997 FAF; and currently is responsible, with staff at the Battelle Memorial Institute and MacroSys, Inc., for FAF^3. FAF answers the following freight questions:

- How much is moving?
- What is moving?
- How is it getting there?
- When does it move?

FAF provides the only comprehensive national picture of freight flows and major corridors. It shows where states and localities fit in the national and global freight system. This is essential in most places where the majority of freight is inbound and outbound rather than local.

Technology

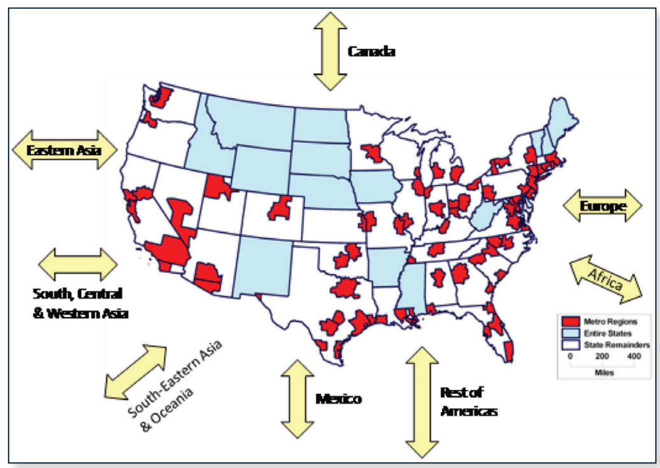
In developing FAF, CTA constructed a set of commodity class and mode specific annual origin-to-destination flows for the entire United States, covering to the extent feasible all domestic as well as all imported and exported goods. Inputs include data from the U.S. Commodity Flow Survey (CFS) and a number of supplemental data sources out of which a single commodity flow matrix is constructed. The product of this effort is a four-dimensional matrix of flows that can be reported in annual tons, annual dollar value, and annual ton-miles, with the principal dimensions being

- shipment origination region (O),
- shipment destination region (D),
- the class of commodity being transported (C), and
- the mode of transportation used (M).

The complete FAF^3 origin-destination-commodity-mode (ODCM) freight flow matrix is made up of 131 O × 131 D × 43 C × 7 M category data cells or 103,466,944 flow estimates in total.

FAF^3 Geography

The figure at right shows the boundaries of the 123 domestic FAF^3 flow analysis regions, also referred to as FAF^3 analysis zones. These are the same freight analysis zones used by the 2007 CFS. Three subsets of regions are highlighted: 74 regions determined by metropolitan areas; 33 regions made up of state remainders, representing a state's territory outside these metropolitan regions; and 16 regions identified as entire states, within which no single FAF^3 metropolitan region exists.



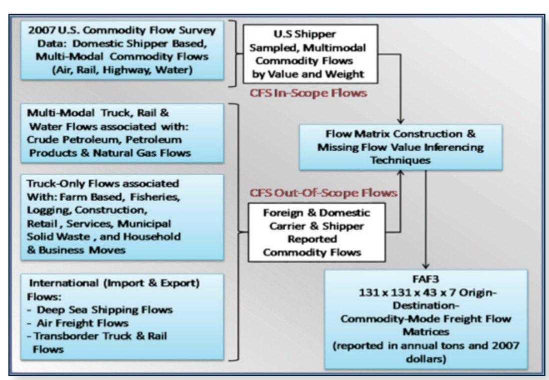
FAF geography.

Commodity and Mode Classes

FAF^3 reports annual tonnage and dollar valued freight flows using the same forty-three 2-digit Standard Classification of Transported Goods classes used by the 2007 CFS. These flows are also broken down by seven modes of transportation.

Modeling

The figure at right provides a high-level overview of the major data modeling steps involved in generating the FAF^3 ODCM annual freight flows matrix. The approach combines the results of filling gaps in the CFS (using a variety of missing value inferring techniques) with the results of applying spatial interaction and other data models to a variety of carrier reported and economic activity data to estimate the 40% or so of U.S. freight movements that are not captured by the CFS.



FAF modeling overview.

The data products from the FAF include the following.

1. A set of ODCM matrices of annual tons and dollar valued trades.
2. Based on these flows, a set of spatially disaggregated ODCM flow matrices suitable for freight and related economic activity forecasting.
3. An assignment of spatially disaggregated freight flows to specific links on the U.S. transportation network for the purpose of ton-mileage computations and infrastructure capacity analysis.

Status

The ORNL team is currently preparing a time series to harmonize the 1997 and the 2002 FAF matrices and will develop the 2010 provisional FAF update in summer 2011. All the data products, the documentation, and the data extraction tool are available on the FAF website (http://www.ops.fhwa.dot.gov/freight/freight_analysis/faf/index.htm).

Benefits

- Useful in planning, operating, and managing the nation's freight transportation system.
- Helps the public and private sectors to better understand the structure and dynamics of the multimodal and intermodal freight transportation system.
- Provides essential information for the development of capacity solutions for the U.S. highway, rail, water, and air freight systems.

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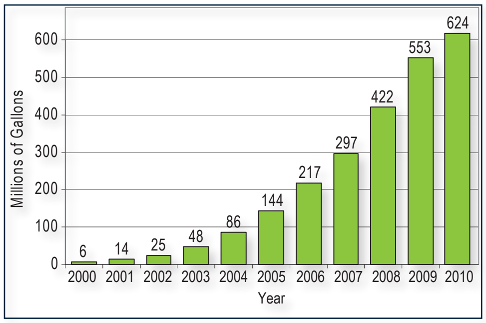
Fuel Economy Program

Background

The United States depends on foreign oil for more than half (52%) of its petroleum needs, costing the country $217 billion in imports annually. The transportation sector is especially dependent. It relies on petroleum for 94% of its energy needs and accounts for 72% of the petroleum that Americans use. The mission of the Fuel Economy Information Program is to reduce U.S. oil dependency by promoting highway vehicle fuel economy and helping consumers make informed fuel economy choices when they purchase vehicles. ORNL estimates that the Fuel Economy Information Program reduced U.S. petroleum consumption by about 624 million gallons in 2010 (at left).



Estimated fuel savings by year from the Fuel Economy Information Program.

Technology

The Fuel Economy Information Program, funded by the DOE Office of Energy Efficiency and Renewable Energy, provides information to consumers through two primary products: fueleconomy.gov and the *Fuel Economy Guide*. Fueleconomy.gov is an online resource that provides the following information.

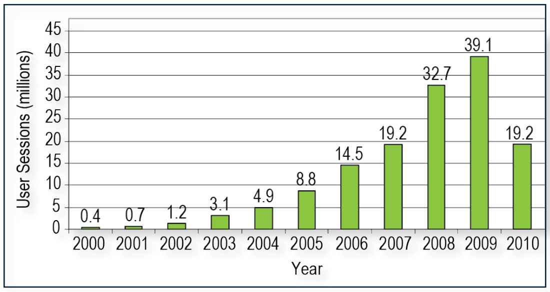
- U.S. Environmental Protection Agency (EPA) fuel economy ratings for passenger cars and trucks, 1985–present.
- User-provided, real-world fuel economy estimates.
- Energy impact scores (petroleum consumption).
- Fuel economics.
- Carbon footprint and air pollution ratings.
- Information on vehicles that can use alternative fuels (e.g., E85 and compressed natural gas).
- Fuel-saving tips.
- Information on tax incentives for hybrids, plug-in hybrids, diesels, electric vehicles, and alternative fuel vehicles.
- Downloadable *Fuel Economy Guide*.

Benefits

- Provides fuel economy information to tens of millions of consumers each year (more than 19 million user sessions in 2010).
- Estimated to have reduced U.S. petroleum consumption by more than 624 million gallons in 2010.
- In 2010, more than 350 television, Internet, radio, and print sources shared site information, providing reliable fuel economy information to their audiences. Media outlets include CNN, CBS News, and *USA Today*.
- The Fuel Economy Guide, accessible on fueleconomy.gov, is an annual publication produced by DOE and EPA that lists the estimated miles per gallon, both city and highway, for all new model year vehicles. It is distributed to all new car dealerships in the United States, as well as libraries, credit unions, and several other entities.

Status

Fueleconomy.gov is in its 12th year of providing fuel economy data to the public and is a nationally established resource for fuel economy information. The visibility and influence of the site have increased dramatically since it was introduced in October 1999 (figure at right). It reached a peak of more than 39 million user sessions in 2009 (October 2008–November 2009), a period when gas prices were high and the site was supporting the government's Car Allowance Rebate System (also known as "Cash for Clunkers"). User sessions declined in 2010, likely due to low fuel prices and decreased car sales, but are on pace to reach about 28 million in 2011. In 2010, more than 350 television, Internet, radio, and print articles featured the site or information from the site.



Fueleconomy.gov user sessions by year, showing dramatic increases in use since its launch in 1999.

Fueleconomy.gov implemented a major site redesign in 2010, upgrading the site visually and functionally and making it easier to use. In addition, new information and features were added to the site, including new tax incentive information for electric vehicles and plug-in hybrids; top ten lists; and updated information on electric vehicles, plug-in hybrids, and fuel cell vehicles.

The site is currently in the process of enhancing the personalization feature that provides consumers with personalized fuel economy, fuel cost, petroleum use, carbon footprint, and emissions estimates based on their driving habits, location, and other factors. It will also implement a model that provides personalized fuel economy, fuel cost, and environment-related estimates for plug-in hybrids.

Fueleconomy.gov's mobile site is being enhanced to provide personalization features and additional vehicle information not previously available via mobile device.

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Fuel Tax Evasion Detection

Background

Revenues from motor fuel and other highway use taxes provide the primary source of funding for our nation's transportation system, and ensuring all of these taxes are collected, remitted, and credited to the Highway Trust Fund is a priority for the Federal Highway Administration (FHWA). Loss of revenue due to tax evasion has been estimated to be as much as 25% of total revenues.

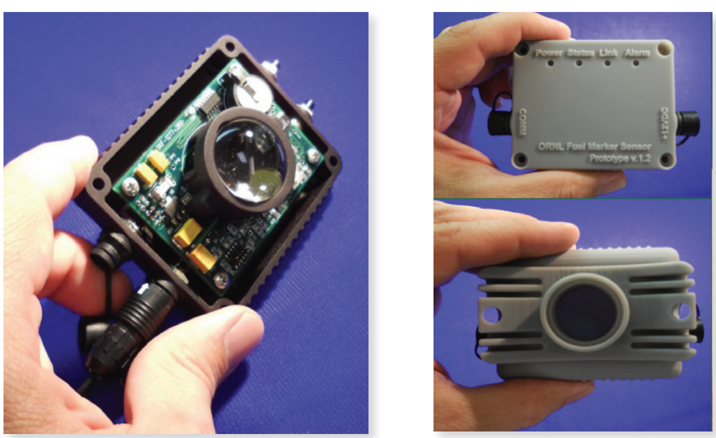
Diesel dedicated to residential heating, industrial use, or other off-road purposes is nontaxable, while diesel used for on-road transportation is taxed. Currently nontaxable fuel is distinguished by having red dye added at terminal rack facilities as fuel is loaded from bulk storage tanks into tanker trucks for delivery to retail stations or bulk users. Despite the dye, bootleg mixing and distribution continues, and commercial fuel supplies are being corrupted by blending taxed and untaxed fuels and even adding waste streams such as used engine oils.

Through funding from FHWA and support from Pilot Travel Services, LLC, researchers at ORNL are helping develop a system to reveal incidents of fuel dilution and mixing. This research project will use evidential reasoning techniques, fuel markers, sensor devices, and vehicle tracking devices to monitor, track, and detect the transfer and movement of petroleum products between different locations and determine the "legitimacy" of the movements and fuel loading/unloading, thus enabling shippers and regulators to better track the disposition of taxed and nontaxed petroleum based products.

The system under development will be capable of identifying dilution occurrences where taxable fuel is diluted with nontaxable fuel products to reduce the amount of taxes paid. Because taxes collected from taxable fuel are allocated to the Highway Trust Fund that in turn is apportioned to states for highway projects, the system can make an immediate, positive impact on consumer transportation.

Technology

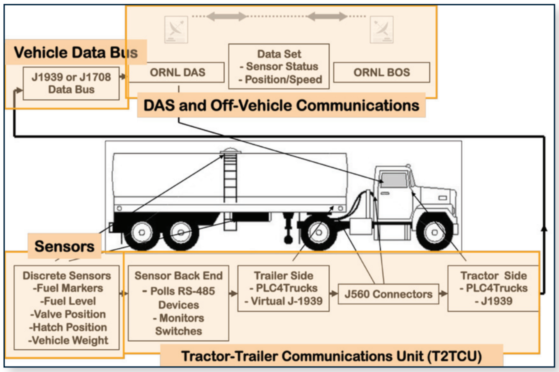
A suite of sensors (i.e., hatch, pressure, valve, and weight sensors) will detect when the hatch and valves have been opened or a change in fuel level has occurred. An optical fuel marker sensor developed by the ORNL Measurement Science and Systems Engineering Division (MSSED) (at left) will be mounted on a fuel tanker along the outlet pipe. As the marked fuel passes through the outlet pipe, the optical sensor will measure the concentration of the unique fluorescence marker that has been blended into the fuel. This suite of monitoring devices will connect to an ORNL developed sensor control unit (SCU) that



ORNL prototyped fuel marker sensor with front (top right), rear (bottom right), and internal views (left).

feeds data to a data acquisition system (DAS) that will be mounted unobtrusively in the cab of the tanker truck (below left). The DAS collects the data generated continuously by the SCU and wirelessly uploads it to a server where rule based and evidential reasoning algorithms are applied. These algorithms are designed to look for any illegitimate occurrences associated with the fuel blend or the tanker route. If an illegitimate incident is detected, the system is capable of notifying the appropriate parties. Together these devices enable the system to track vehicles and petroleum movement in near real time. The diagram below at right depicts the system communication flow.

DAS that is installed in a truck cab.



Communication flow from the sensors to the back-office system (BOS) web system.

Status

Currently the project is in the field testing phase, and tests are being conducted at the Transportation Research Center Inc. (TRC) in East Liberty, Ohio. TRC is equipped with professional drivers, fuel handling and dye mixing equipment, and miles of private roads to test the fuel tax evasion system.

Benefits

- Assists in the detection of tax evasion schemes.
- Potentially increases the collection of fuel tax revenue that is credited to FHWA Highway Trust Fund.
- Potentially increases the resources available to build and maintain the U.S. transportation infrastructure.

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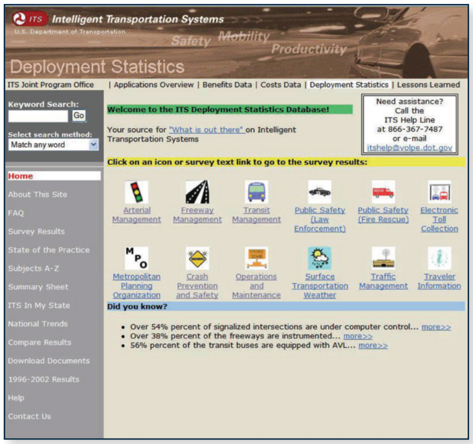
Intelligent Transportation Systems Deployment

Background

The Intelligent Transportation Systems (ITS) Deployment Tracking Project collects and disseminates information on the level of deployment and integration of ITS technology nationally. Information is gathered through a series of national surveys covering metropolitan and rural deployment. Since 1997, nine national surveys have been conducted, the most recent being 2010. These surveys typically cover transportation agencies in 108 metropolitan areas involved with freeway, arterial, and transit management; public safety; and toll collection, as well as state departments of transportation in each state. The surveys involve from 1,800 to 2,100 agencies, and response rates have ranged from 85% to 92%. The information gathered through these national surveys is used by the U.S. Department of Transportation in support of the national ITS program. Understanding the rate of ITS deployment in various metropolitan areas can lead to insights regarding future program changes, redefinition of goals, or maintenance of current program direction. In addition, the data are made available online for agencies wanting to know more about ITS deployment, researchers, private vendors, and the general public.

Technology

The ITS Deployment Statistics website provides access to deployment data gathered from the national surveys summarized nationally, by metropolitan area, or by individual agency. The site (at right) can be accessed at http://www.itsdeployment.its.dot.gov.



ITS Deployment Statistics website.

Deployment information provided by the site covers 12 broad ITS application areas. Seven of these application areas are primarily metropolitan: Arterial Management, Freeway Management, Transit Management, Public Safety (Law Enforcement and Fire/Rescue), Electronic Toll Collection, and Metropolitan Planning Organizations. The remaining five application areas are primarily statewide or rural in scope: Crash Prevention and Safety, Operations and Maintenance, Surface Transportation Weather, Traffic Management, and Traveler Information.

The website supports online searches for information and provides the capability to download a variety of reports and summaries covering metropolitan and statewide/rural deployment. The website features quick access to data broken out by three different views: national, metropolitan, or individual agency. Users can employ a keyword search or select individual items from a survey outline to access information on individual technologies, application areas, or geographic areas. A variety of reports are available for download, including summaries for each survey type, individual metropolitan site reports, one page fact sheets covering key deployment results for each metropolitan area and state surveyed, and a national summary report for metropolitan and statewide deployment. The site also provides trend information and access to results from previous surveys.

Status

The 2010 national survey was completed in December 2010. The deployment tracking website currently reflects data gathered through 2007 and will be updated with results from the 2010 survey in the summer of 2011. A national summary report for the 2010 data will be included, as well as individual survey summaries. New for the 2010 survey data, the website will provide access to the complete survey results for download and use by researchers and others. Also new is an effort currently under way to gather data on locations of individual technologies, referenced to the national interstate system using geographic information systems technology. It is anticipated that these data will be released in the fall of 2011.

Benefits

- Provides comprehensive ITS information in one place.
- Provides information for ITS deployment planning.

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MA^{3}T Model of the Plug-In Electric Vehicle Market

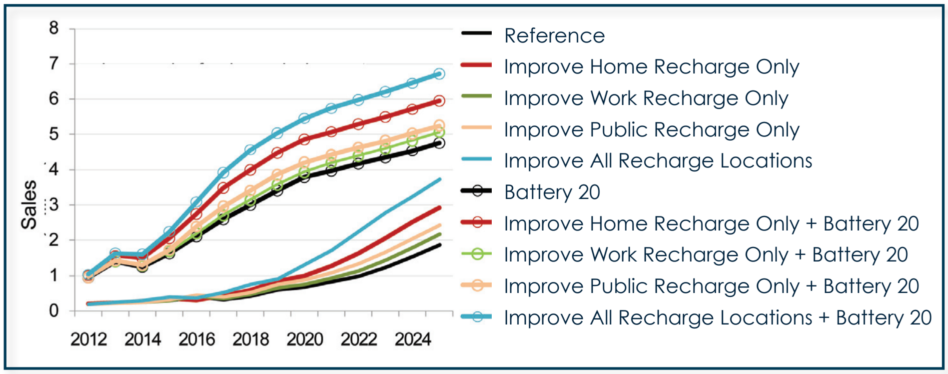
Background

In 2010 the Obama administration called for 1 million plug-in hybrid electric vehicles (PHEVs) on the road by 2015. The goal presents many challenges, including the need to identify factors such as the charging infrastructure that might impede or enhance progress toward the goal and the need to accurately represent the impacts of PHEVs such as their potential to reduce petroleum use and greenhouse gas (GHG) emissions. These and many other policy questions call for market simulation models that endogenously predict sales and usage of competing vehicle technologies. One example is ORNL's Market Acceptance of Advanced Automotive Technologies (MA^{3}T) model. Sponsored by the DOE Vehicle Technologies Program, the model was developed to project PHEV demand and its impact on energy and the environment.

Technology

MA^{3}T features 26 vehicle technologies, including conventional gasoline, diesel, hybrid electric, plug-in hybrid electric, battery electric, and fuel cell; 1,458 different market segments within the United States; multiple inputs such as fuel prices, vehicle performance, charging infrastructure, and purchase subsidies; and application flexibility. The model can provide oil displacement estimates, GHG emissions, electricity demand, the market share for each vehicle technology, and much more. A nested multinomial logit model coded in Excel/Visual Basic for Applications, MA^{3}T is ready, easy, and free to use for policy analysis on PHEVs.

Projections generated by the ORNL MA^3T model for plug-in hybrid electric vehicle (PHEV) sales by scenario of recharge deployment are identified in the chart below. Note: (1) "Reference" assumes existing policies, recharge availability, and moderate technological progress; (2) "Battery20" stands for 20 years earlier reduction of battery cost; (3) deployment of each recharge option is assumed to be aggressive from 2017 through 2025; and (4) temporary kinks are due to expiration of the American Recovery and Reinvestment Act PHEV subsidies.



Projected PHEV sales in millions by scenario of recharge deployment..

Status

Development of the model is ongoing. A copy of the model can be provided upon request.

Benefits

- Facilitates policy analysis related to advanced vehicle technologies.
- Provides a logical, transparent, flexible modeling platform.
- Estimates potential impact of advanced vehicle technologies (AVTs) on energy use and GHG emissions.
- Provides a tool for evaluation of program benefits and research and development directions.
- Is open for update and recalibration as more information on AVTs accumulates.

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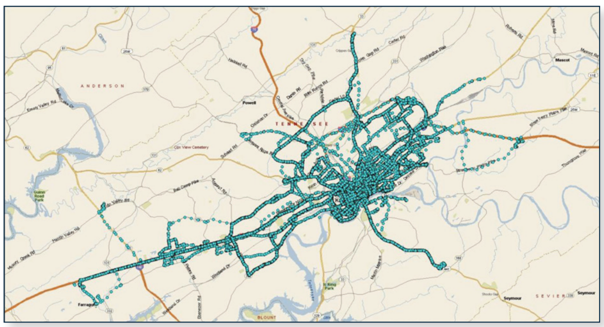
Medium Truck Duty Cycle

Background

DOE's Medium Truck Duty Cycle (MTDC) project is a follow-on effort to the Heavy Truck Duty Cycle (HTDC) project that was completed in FY 2008. This program involves efforts focused on the collection, analysis, and management of data and information related to medium truck operation in real-world highway environments. Data collected within the HTDC and MTDC efforts come from commercial fleets operating in real-world environments. Special data analysis tools have been developed, in prototype form, which allow parsing of the data to support modeling and fuel efficiency analysis needs.



Routes of participating transit buses covering the Knoxville, Tennessee, area.

The MTDC project is collecting 60 channels of data from four Class-6/Class-7/Class-8 vocations: local delivery, urban transit, towing/recovery, and utilities. During a 12-month period in 2009–2010, duty cycle data were collected from three H.T. Hackney vehicles during local delivery routes and three Knoxville Area Transit Authority vehicles during normal routes (see above). Data are currently being collected from towing and recovery vehicles owned by Fountain City Wrecker Service and utility vehicles owned by Knoxville Utilities Board (see below). Data and information from this project will be useful for (1) supporting development and evaluation of the heavy and medium truck modeling efforts; (2) generating customized, real-world-based data for the heavy truck energy efficiency research community; (3) conducting real-world-based energy efficiency studies related to heavy truck performance-shaping factors; and (4) making investment decisions.

(a)

(b)

Instrumented test vehicles: (a) Fountain City Wrecker Service test vehicle and (b) Knoxville Utilities Board test vehicle.

Technology

The MTDC project uses the six data collection platforms developed in the HTDC portion of the program. These data acquisition systems include the ability to wirelessly download the collected data on a daily basis and the ability to access near-real-time data for any of the instrumented vehicles. The Duty Cycle Generation Tool (DCGenT) prototype was developed to generate a characteristic duty cycle from multiple database segments that meet user specified criteria. Improvements in DCGenT were achieved through the addition of new algorithms that greatly decreased the required time to decompose duty cycles into acceleration and deceleration segments. Also, improved file reading has decreased load time on usually large duty cycle files. Both improvements help contribute to the overall end-user experience and increase efficiency while using DCGenT.

Status

Part 1 of the field operations test, which involved collection of duty cycle data from the delivery and urban transit vehicles, was completed in February 2010. As part of this effort, DOT's Federal Motor Carrier Safety Administration collected 20 additional performance measures related to tire pressure and brake usage for the combination tractor-trailer vocation. About 109 GB of data were collected, consisting of more than 95,000 miles of duty cycle data. Analysis of the data contrasted the driving and idle times for the two vocations studied, focusing on factors affecting the fuel usage patterns for the more than 17,000 gallons of fuel consumed during the data collection period. The efforts and associated analysis are documented in the interim report (http://info.ornl.gov/sites/publications/Files/Pub26777.pdf).

In early FY 2011, the remaining six vehicles from the utility and towing/recovery vocations were instrumented, tested, and launched for data collection purposes.

Benefits

- Provides a fundamental understanding of the operations of selected Class-6, Class-7, and Class-8 vocations to support future energy efficiency technology investment decisions.
- Provides real-world data as a baseline for assessing the benefits of new and emerging truck-based energy efficiency technologies.
- Provides data sufficient for characterizing duty cycles associated with the selected Class-6, Class-7, and Class-8 vocations.
- Provides a real-world-based data source for evaluating and validating models of engine and vehicle performance.

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National Household Travel Survey

Background

Policy makers rely on transportation statistics, including data on personal travel behavior, to formulate strategic transportation policies and to improve the safety and efficiency of the U.S. transportation system. Data on personal travel trends are needed to examine the reliability, efficiency, capacity, safety, and flexibility of the nation's transportation system to meet current demands and accommodate future demands; to assess the feasibility and efficiency of alternative congestion alleviating technologies; to evaluate the merits of alternative transportation investment programs; and to assess the energy-use and air-quality impacts of various policies.

To address these information needs, DOT initiated an effort in 1969 to collect detailed data on personal travel. Known originally as the Nationwide Personal Transportation Survey (NPTS), the surveys are conducted roughly every 5 to 7 years and are the only data source in the country that links individual personal travel behavior, household demographic and socioeconomic attributes, vehicle ownership, and vehicle characteristics. The survey tools are regularly evaluated, and before the 2001 survey, the DOT Federal Highway Administration and Bureau of Transportation Statistics, which lead the survey effort, funded a comprehensive pretest to determine whether NPTS (focused on daily travel) should be combined with the American Travel Survey (ATS) (focused on long-distance travel). Both survey instruments were redesigned to better suit the objectives of the data collection effort. The findings of this pretest resulted in the 2001 survey being a combined NPTS/ATS survey, and the survey name was changed to the National Household Travel Survey (NHTS) in recognition of that content change.

In 2010 DOT once again made changes to NHTS based on presurvey findings, contracting with the ORNL Center for Transportation Analysis (CTA) to enhance the quality of the 2009 survey data and to develop the NHTS website, the associated documents, and the online analysis tools.

Technology

The NHTS website (http://nhts.ornl.gov) is maintained by CTA. The website serves as a central facility to obtain information on NHTS; status updates on the dataset or publications; publications using NHTS data; and the disaggregate NHTS data, which are available for download and analysis by the user community. The Online Analysis Engine on the website allows users to create customized tables from the NHTS data using only a web browser—without any knowledge of statistical software or programming capability.

Status

The 2009 NHTS, the most recent survey, provides information to assist transportation planners and policy makers who need comprehensive data on travel and transportation patterns in the United States. NHTS serves as the nation's inventory of daily travel. Data are collected on daily trips taken in a 24-hour period and include

- purpose of the trip (work, shopping, etc.);
- means of transportation used (car, bus, subway, walk, etc.);
- how long the trip took (i.e., travel time);
- time of day when the trip took place;
- day of week when the trip took place;
- fuel use, by vehicle type (based on Energy Information Administration data); and
- density of surrounding land use.

These data are collected for all

- trips;
- modes;
- purposes;
- trip lengths; and
- areas of the country, urban and rural.

Following are some of the types of information that can be obtained from NHTS.

- Average vehicle occupancy by mode and purpose
- Number of households by household driver count
- Number of drivers by age and gender
- Number of vehicles by household income
- Number of person trips by mode and purpose
- Fuel consumption by household and trip characteristics
- Fuel consumption and trip lengths by density of land use

Benefits

- Provides a tool for DOT officials and other policy makers to assess program initiatives, review programs and policies, study mobility issues, and plan for the future.
- Helps identify trends in travel over time.
- Provides national benchmark data to measure local programs against.
- Supports municipal planning organizations and statewide planning processes and policy decision making.
- Provides information for planning purposes on the travel needs/patterns of special groups such as the elderly, children, and the poor.

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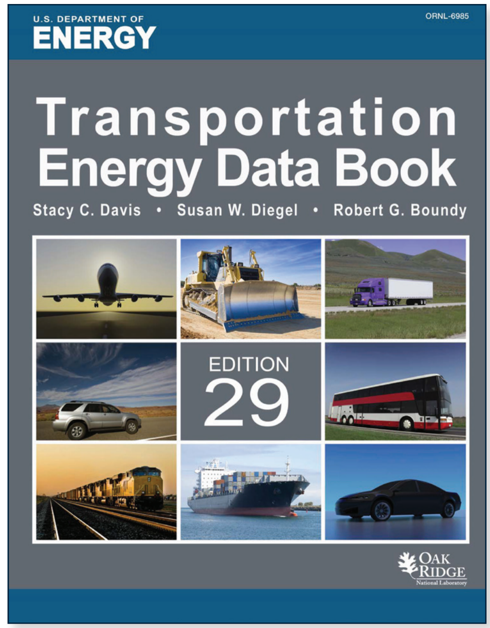
Transportation Energy Data Book



Background

In January 1976, the Transportation Energy Conservation Division (TEC) of the Energy Research and Development Administration (ERDA) contracted with ORNL to prepare a transportation energy conservation data book to be used by TEC staff in their evaluations of current and proposed conservation strategies. The main purposes of the data book were to draw together, under one cover, transportation data from diverse sources; to resolve data conflicts and inconsistencies; and to provide comprehensive coverage of the field. The first edition of the *Transportation Energy Conservation Data Book* was published in October 1976. After DOE was established, work formerly under the purview of ERDA and TEC, including the data book, was transferred to DOE, which has been responsible for all editions since the third. The renamed *Transportation Energy Data Book* is now produced by ORNL for DOE's Office of Energy Efficiency and Renewable Energy. Twenty-nine editions of the book have been published since 1976.

Technology

Designed for use as a desktop reference, the data book is an assembly of statistics and information that characterizes transportation activity and also presents data on other factors that influence transportation energy use. The book is also available via the Internet (http://cta.ornl.gov/data), and tables and figures are available online in both Excel and PDF formats.

Status

Information for the data book is taken from the latest available data. Edition 29, the current edition, has 12 chapters that focus on various aspects of the transportation industry. Chapter 1 focuses on petroleum; Chapter 2, energy; Chapter 3, highway vehicles; Chapter 4, light vehicles; Chapter 5, heavy vehicles; Chapter 6, alternative fuel vehicles; Chapter 7, fleet vehicles; Chapter 8, household vehicles; Chapter 9, nonhighway modes; Chapter 10, transportation and the economy; Chapter 11, greenhouse gas emissions; and Chapter 12, criteria pollutant emissions. Much of the information that is found in previous editions has been updated for Edition 29, thus preserving important historical trends.

There are also three appendixes which include detailed source information for some tables, measures of conversion, and the definition of census divisions and regions. A glossary of terms and a title index are also included for the reader's convenience.

Currently, hardcopies of the *Transportation Energy Data Book* are mailed domestically to about 1,500 users, including federal and state government agencies, universities, libraries, automobile manufacturers, oil companies, and private consultants. The book is not currently mailed overseas, but over the years people from 31 different countries have requested copies of the report and now have access through the online version.

Some countries, such as Canada and Japan, have modeled transportation data compilations for their countries based on this time-honored book.

Since its inception in 1976, the *Transportation Energy Data Book*, online or in hard copy, has been where the transportation community goes for energy data.

Benefits

- Meets the need for a comprehensive information source on the transportation industry.
- Provides accurate baseline data for models and predictions.
- Provides information on trends and relationships in the transportation industry.
- Provides a means for obtaining historical trend data.
- Includes links to other online transportation data sites.
- Includes a comprehensive glossary.

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Fuels, Engines, and Emissions

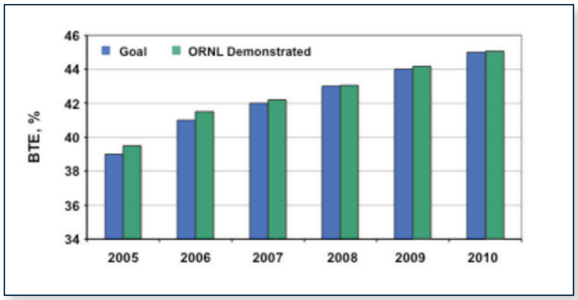
Achieving and Demonstrating the FreedomCAR Efficiency Milestones for Advanced Combustion Engines

Background

The U.S. DRIVE roadmap has established efficiency and emissions goals for the next several years, one of which is achieving a 45% peak brake thermal efficiency (BTE) in 2010 while meeting the Tier 2 Bin 5 emissions levels. The objective of this activity is not to develop all the necessary technology to meet these goals but rather to serve as a focus for the integration of technologies into a multicylinder engine platform and to provide a means of identifying pathways for improved engine efficiency.

Technology

Substantial improvements in engine efficiency will require a reduction in thermal energy losses to the environment and a better understanding of thermodynamic loss mechanisms associated with the combustion process. With less than half of fuel energy converted to useful work in a modern engine, opportunity exists for significant advancements in engine efficiency. A fundamental thermodynamics perspective, simulations, and laboratory experiments are being used to provide guidance on developing and evaluating a path for meeting 2010 milestones and to provide longer-term insights into the potential of future high efficiency engine systems.



On path to demonstrating FY 2010 U.S.DRIVE engine and efficiency milestones including 45% peak BTE.

A peak BTE of 45% has been demonstrated on a light-duty diesel engine through a combination of engine shaft power and electrical power generated from the exhaust heat of the engine with an organic Rankine cycle. This is the final milestone for the 2010 U.S. DRIVE goal of 45% peak BTE and Tier 2 Bin 5 emissions (at left). Advanced engine technologies identified and investigated in FY 2010 include thermal energy recovery, electrification of auxiliary components, advanced lubricants, and fuel properties. In addition, a flexible microprocessor based control system was used for reoptimization of engine parameters to make better use of these technologies.

Organic Rankine cycle which is being used to convert exhaust heat to electrical power on a 1.9 L General Motors diesel engine.

The organic Rankine system produced 3.9 kW of net power from the exhaust heat. A picture of the system is shown at left. The potential impact of recovering this discarded thermal energy on fuel economy improvements over a light-duty vehicle drive cycle has been investigated with vehicle simulations. The models indicate potential fuel savings between 2% and 5% over standard driving cycles when using the organic Rankine cycle on the exhaust gas recirculation and exhaust heat streams.

This activity makes use of research results from internal ORNL activities, other national laboratories, universities, and industry. Internal ORNL activities include those focused on advanced combustion processes, aftertreatment, fuels, and unconventional approaches to improve combustion efficiency. The progress and results of these activities are regularly shared with external sources through government-industry technical meetings, professional conferences, and one-on-one interactions with industry teams.

Status

The final milestone of 45% peak BTE was demonstrated on a light-duty GM 1.9 L diesel engine with exhaust thermal energy recovery. In addition, the potential of this type of system over vehicle drive cycles was explored with full vehicle simulations. This goal was reached through the application of modeling and experiments and through interactions with the scientific community. Several efficiency enabling technologies, including thermal energy recovery, advanced combustion processes, and aftertreatment systems, were used to achieve the milestone.

Benefits

- Improved fundamental understanding of fuel efficiency losses in internal combustion engines and identification of promising strategies for reducing these losses.
- Demonstration of U.S. DRIVE fuel efficiency and emissions milestones.
- New insights into systems integration of advanced transportation technologies to expand the boundaries of engine efficiency and emissions improvements.

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Combustion and Emissions Characterization of Reactivity Controlled Compression Ignition on a Multicylinder Light-Duty Diesel Engine

Background

Advanced compression ignition combustion concepts have been shown to reduce both oxides of nitrogen (NO_X) and particulate matter (PM) while improving thermal efficiency. Many of the concepts have only been modeled and some have been demonstrated on single cylinder engines. Some of these techniques are dependent not only on the engine operating conditions but also on the characteristics of the fuel.

Dual-fuel reactivity controlled compression ignition (RCCI) controls fuel reactivity in the combustion cylinder by simultaneously direct injecting diesel fuel and fumigating gasoline by multiport fuel injection. ORNL worked with the University of Wisconsin (UW), which provided modeling for the initial operating condition, to run dual-fuel RCCI on a modified multicylinder engine.

Initial Experiments

Stable dual-fuel RCCI combustion has been demonstrated on a multicylinder light-duty diesel engine at an operating condition of 5.5 bar net indicated mean effective pressure accomplished through port fuel injection of gasoline and direct injection of diesel fuel (see below).

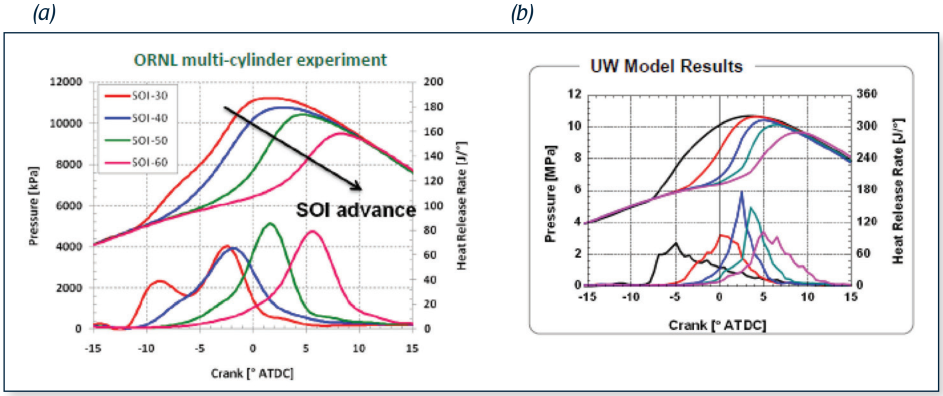
(a) *(b)*

Modified intake manifold installed on engine (a) and with gasoline injectors installed (b).

The initial experiments focused on (1) the combustion characteristics and performance of dual-fuel RCCI compared to the UW model and conventional diesel combustion at the same load and (2) emissions characterization and catalyst effectiveness in dual-fuel RCCI mode compared to conventional diesel combustion and diesel premixed charge compression ignition.

The ORNL multicylinder experiments mirrored the trends predicted by the UW modeling (see below). Compared to conventional diesel combustion at the same load, dual-fuel RCCI showed a 4.5% improvement in brake thermal efficiency, a more than 90% reduction in NO_X, and a nearly 99% reduction in PM. There were corresponding increases in carbon monoxide (CO) and hydrocarbons (HCs) and lowered exhaust temperatures. These findings motivated the third part of the study examining the exhaust species including PM and investigating the effectiveness of a diesel oxidation catalyst at reducing the increased HCs and CO. Favorable results were shown for reductions in particle number from RCCI, and a diesel oxidation catalyst was shown to be effective at reducing HC and CO emissions even at the lower exhaust temperatures.
This activity is the result of collaboration across ORNL, universities, and industry. Internal

(a) *(b)*



Comparison of ORNL multicylinder RCCI (a) with (b) UW modeling.

ORNL activities include those focused on advanced combustion processes, aftertreatments, fuels, and various approaches to improving combustion efficiency. The progress and results of this work have been shared with external sources through government-industry technical meetings, professional conferences, and one-on-one interactions with industry teams.

Status

Currently the next set of experiments for multicylinder dual-fuel RCCI looking at higher loads is being planned at ORNL. There will again be collaboration with UW, which has already provided modeling at a higher load point.

Benefits

- Demonstration of the transition of an advanced combustion concept from modeling and single cylinder experiments to a multicylinder engine.
- Increased understanding of the emissions characteristics of dual-fuel RCCI.
- More widespread implementation of high efficiency engines.

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Ethanol Blends Reduce Particulate Matter Emissions 30%–45% for Lean and Stoichiometric Direct Injection Spark-Ignition Vehicles

Background

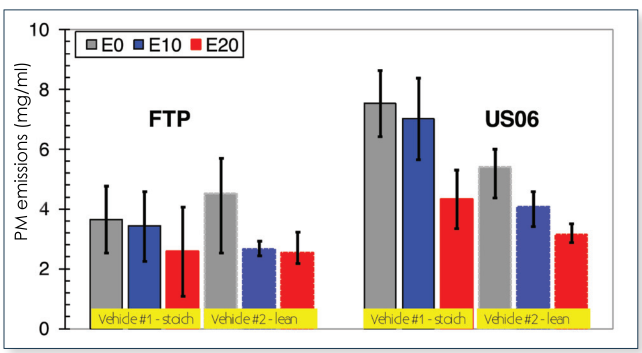
Direct injection spark-ignition (DISI) gasoline engines can offer better fuel economy and higher performance over their port fuel-injected (PFI) counterparts and, thus, are appearing increasingly in U.S. vehicles. Small displacement turbocharged DISI engines are likely to be used in lieu of large displacement engines, particularly in light-duty trucks and sport utility vehicles, to meet the more challenging fuel economy standards for 2016. In addition to changes in gasoline engine technology, fuel composition may increase in ethanol content beyond the 10% allowed by current law due to the Renewable Fuels Standard passed as part of the 2007 Energy Independence and Security Act. An improved understanding of the combined effects of DISI and ethanol blends on particulate matter (PM) emission levels is necessary to address DOE goals of better fuel efficiency and energy security.

Technology

Unlike PFI engines, DISI gasoline engines inject the fuel directly into the cylinder, much like modern diesel engines. The air-fuel mixture is then ignited by a spark. DISI engines have been in commercial production since the late 1990s but have become increasingly common in the U.S. light-duty vehicle fleet in the past 5 years. DISI engines can be more fuel efficient, in particular under fuel-lean operating conditions, and also offer a performance benefit due to the higher volumetric efficiency at high load.

In the United States, all DISI vehicles operate within a stoichiometric air-fuel ratio to enable the use of a three-way catalyst for nitrogen oxide (NO_X) emissions control. In Europe, NO_X emissions regulations are less strict, so many DISI vehicles operate in a fuel-lean, stratified charge mode which can be as much as 15%–20% more fuel efficient than stoichiometric operation. All DISI engines tend to make more PM than their PFI counterparts, with PM mass levels exceeding those of diesel vehicles equipped with diesel particulate filters. One of the goals of the DOE Vehicle Technologies Program Health Impacts activity is tracking the effects of the convergence of the two advanced technologies, DISI and ethanol blends, on emission levels.

In this research, two production DISI vehicles were characterized over transient drive cycles (see figure below). These vehicles included a turbocharged, stoichiometric vehicle certified for ethanol-free gasoline (E0) in the United States and a normally aspirated, lean stratified vehicle certified for gasoline in Europe. The two vehicles both meet the U.S. light-duty PM emissions standard (10 mg/mile) with gasoline. Both vehicles showed a reduction in PM mass emissions of 30%–45% with a 20% blend of ethanol-gasoline (E20). The highest reductions were associated with accelerations and high speed operation for both vehicles; PM formation is thought to occur in fuel-rich combustion zones. The additional fuel-bound oxygen in E20 may increase the air-fuel ratio in these zones, reducing PM formation.



PM mass emissions for both study vehicles over the urban transient driving cycle (FTP or federal test procedure) and a more aggressive cycle (US06) with three ethanol blends [E0, 10% ethanol (E10), and E20]. For comparison, typical post-2002 PFI vehicles emit less than 1 mg/mile of PM, and diesel-DPF vehicles emit 1–2 mg/mile over the FTP cycle.

This activity makes use of earlier results from ORNL Health Impacts activities involving exhaust particle characterization and Mobile Source Air Toxics measurement. An industrial partner loaned ORNL the European vehicle used in the study, and progress and results are shared regularly with a wide audience.

Status

The path forward on DISI PM characterization will include measurements on hybrid vehicles as well as advanced engines in FY 2011. Because of high PM emissions identified during cold start events, particular attention will be paid to hybrids during idle, shutdown, and launch. Additional biofuel blends will be added as needed.

Benefits

- Improved understanding of PM mass and number levels from DISI vehicles to minimize the emissions impact of the more fuel efficient technology.
- Analysis of the impact of increased biofuel usage on new spark-ignited engine technology.
- New insight into PM formation during advanced combustion regimes.

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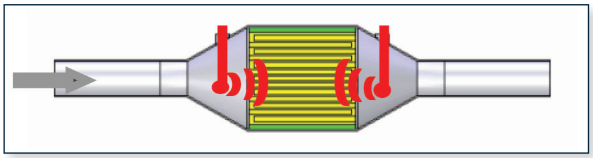
Improved Diagnostics of Particulate Loading on Diesel Particulate Filter Demonstrated with Radio Frequency Technology

Background

At the CLEERS (Cross-Cut Lean Exhaust Emissions Reduction Simulations) Workshop in April 2009, a panel discussion was held on onboard diagnostics (OBD) for emission control technologies. Industry representatives invited to the panel expressed the need for more robust sensing of particulate loadings on diesel particulate filters (DPFs). The need derived from increasing requirements for OBD based on upcoming emission regulations and the general need for improved sensing to better manage DPF regeneration, which results in a fuel penalty for the engine system. To address this need, ORNL studied a radio frequency (RF) based diagnostics technology developed by Filter Sensing Technologies, Inc., (FST) on a modern diesel engine platform at ORNL.

Technology

The RF sensor operates by transmitting an electromagnetic wave at radio frequencies through the DPF monolith (see below). An antenna at the opposing end of the DPF collects the RF signal, which is analyzed to determine the loading of particulate matter (PM) on the DPF. The FST RF sensor does not operate at a fixed RF frequency; instead, the RF frequency is swept over a range that spans several resonance modes associated with the DPF size and shape. PM on the DPF changes the resonance mode central frequency and magnitude; thus, analysis of the RF signal leads to measurement of the PM loading on the DPF.



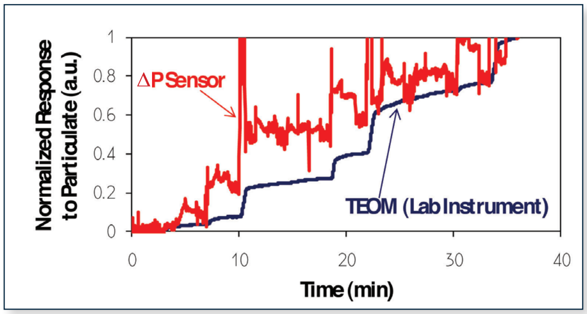
Schematic of the RF sensor transmitter and receiver antenna on the inlet and exhaust side of the DPF.

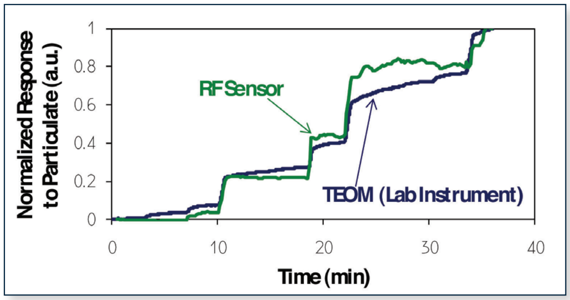
Status

Experiments were conducted at ORNL with a GM 1.9 L diesel engine fitted with a cordierite substrate DPF. The RF sensor was installed on the DPF system, and a delta pressure (ΔP) sensor was also used on the system for comparison. The ΔP sensor is commonly used in vehicle applications where DPFs are installed and measures the increase in backpressure on the DPF as it becomes loaded with PM. The ΔP sensor is known to be affected adversely by changes in the exhaust flow across the DPF, which commonly occurs during transient driving conditions. In comparison to the ΔP sensor and a laboratory tool for measuring PM emissions (Tapered Element Oscillating Membrane or "TEOM"), the RF sensor was much more accurate in characterizing the PM loading of the DPF under various engine loads and speeds (see below).

Benefits

- The RF sensor provides more accurate measurement of PM loading on a DPF in comparison to the commonly used ΔP sensor.
- The improved sensing of the DPF state by the RF sensor can enable better controls which can lead to lower fuel consumption during DPF regeneration (the periodic heating of the DPF to temperatures at which the trapped PM will oxidize).
- The RF sensor is also an excellent candidate for meeting new OBD requirements for emissions regulations.





Comparison of PM loading measured by the ΔP sensor and TEOM laboratory instrument (top) and the RF sensor and TEOM laboratory instrument; the RF sensor tracks PM loading much better than the ΔP sensor (bottom) commonly used currently for DPF loading diagnostics on vehicles.

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Load Expansion of Stoichiometric Homogeneous Charge Compression Ignition Using Spark Assist and Hydraulic Valve Actuation

Background

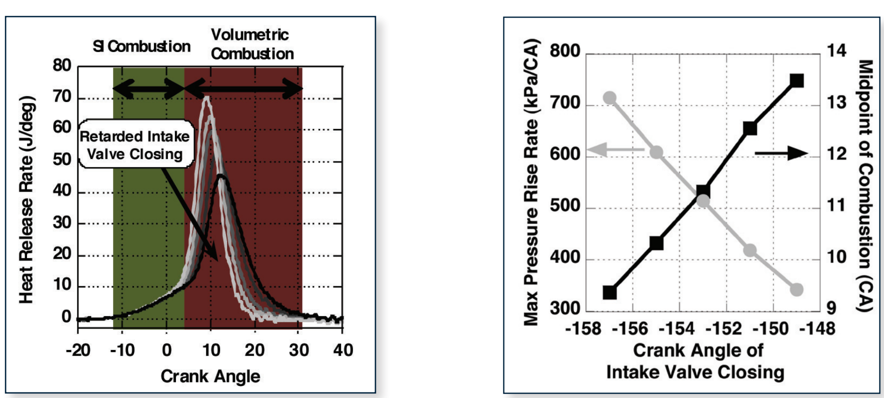
Because advanced combustion strategies have the potential to improve the efficiency of gasoline engines, the goal of this research is to expand the advanced combustion operating range. Advanced combustion strategies such as homogeneous charge compression ignition (HCCI) are typically limited to low loads because of excessive combustion noise at higher loads. This study uses a combination of spark timing and variable valve actuation to control combustion noise to acceptable levels, thereby expanding the operable engine load. Further, unlike most HCCI studies which operated fuel-lean, this investigation used a stoichiometric air/fuel ratio at all operating conditions to maintain compatibility with a standard automotive three-way catalyst (TWC) for nitrogen oxide (NO_X) aftertreatment.

Technology

Numerous experimental investigations have shown that engine loads above about 4 bar indicated mean effective pressure (IMEP) are not possible with lean-burn HCCI combustion because of high rates of in-cylinder pressure rise. Unlike previous HCCI investigations, where the advanced combustion load limit is typically about 4 bar IMEP, we demonstrate that by using advanced controls it is possible to reduce the engine noise and achieve engine loads of 7.5 bar IMEP from 1,000–3,000 rpm. By expanding the load range, real-world efficiency is increased because the engine spends more time in advanced combustion regimes.

With this combustion strategy the combustion process has two modes: (1) an initial slow, spark-ignited mode of combustion followed by (2) a volumetric HCCI-like mode of combustion. At low engine loads, volumetric heat release dominates the combustion event, so much so that at some operating points spark is not required. As engine load increases, a large fraction of the fuel energy is released during the spark-ignited combustion mode. With this dual-mode combustion, the rate of pressure rise and combustion noise is controlled by a combination of spark timing, which controls the start of combustion, and variable valve actuation, which can vary the effective compression ratio. Control of pressure rise rate with the intake valve closing (IVC) angle is illustrated below.

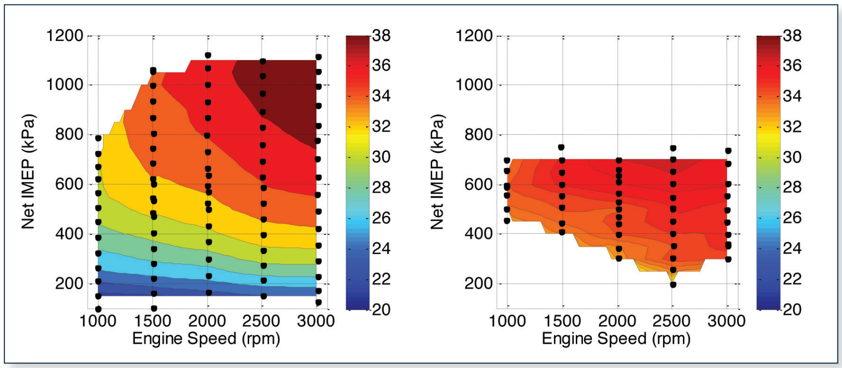
(a) *(b)*



Effects of IVC angle during spark assisted HCCI combustion at 2,000 rpm and 500 kPa IMEP: (a) effect of IVC angle on heat release rate and (b) effect of IVC angle on maximum pressure rise and the phasing of the midpoint of combustion.

Compared to conventional spark ignition (SI) combustion, this combustion strategy reduces engine-out carbon monoxide, unburned hydrocarbon emissions, and NO_X emissions. While they are lower than with SI combustion, NO_X emissions for this combustion strategy can still be substantial enough to require aftertreatment, which is why a stoichiometric air/fuel ratio is used to maintain compatibility with conventional TWC technology. Thus, rather than being a detriment to this combustion strategy, the NO_X emissions can be easily treated and do not represent a barrier to implementation.

This combustion strategy does provide an increase in engine efficiency compared to conventional SI combustion, as shown below. Efficiency improvements are realized at nearly all operating conditions, with the largest efficiency improvements occurring at the lowest engine loads and translating to a fuel consumption reduction of up to 9%. And importantly, the increase in engine efficiency is attained while producing no increase in tailpipe-out emissions because compatibility with TWC technology is maintained.



Indicated thermal efficiency (%) for (a) conventional SI combustion and (b) spark assisted HCCI combustion.

Status

A strategy of spark-assisted HCCI combustion has been developed and characterized for high octane certification gasoline. Continuing research will focus on fuel effects with low octane gasoline as well as ethanol and butanol blends.

Benefits

- Increased high load limit for advanced combustion.
- Reduced emissions of unburned hydrocarbons, carbon monoxide, and NO_X compared to conventional SI combustion.
- Compatibility with mature TWC technology for NO_X aftertreatment maintained.
- Efficiency advantage compared to conventional SI combustion at nearly all operating points, translating to a fuel consumption reduction of up to 9%.

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Materials Compatibility Investigations for Mid-Level Ethanol Blends

Background

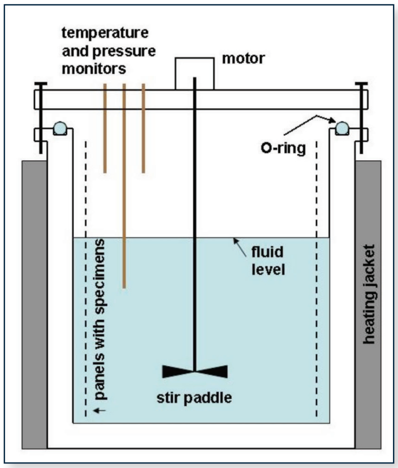
DOE and others have been assessing the viability of using intermediate ethanol blends (E15 or E20) as a way to accommodate growing volumes of ethanol. Before intermediate blends can be introduced into the nation's fueling infrastructure, their effects on the emissions and performance of vehicles and nonroad engines and the fueling infrastructure must be determined. ORNL has conducted several vehicle and nonroad engine studies that will allow an informed decision by the Environmental Protection Agency on whether to allow the use of E15 or E20 in vehicles.

Another critical link to expanded use of ethanol is the compatibility of the refueling infrastructure with increased ethanol levels. Metals, plastics, elastomers, and sealants are materials that can potentially be affected by ethanol-gasoline blends. ORNL has been working with the National Renewable Energy Laboratory (NREL) and Underwriters Laboratories (UL) to evaluate the compatibility of fuel dispensers and intermediate ethanol blends. Although there has been much internal research with the automotive companies regarding ethanol compatibility, there has been no coordinated effort to evaluate the effects of intermediate ethanol blends on fuel dispensers.

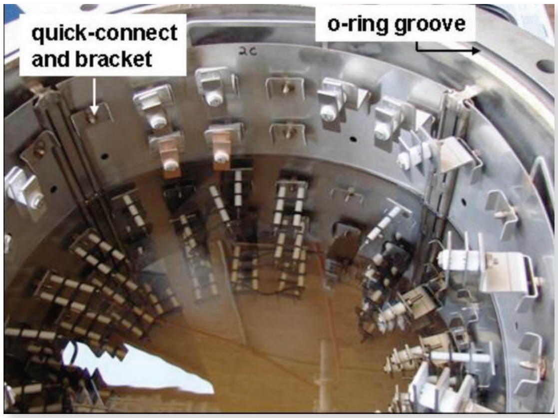
Technology

ORNL in collaboration with NREL and UL is evaluating the compatibility of individual dispenser materials with ethanol blend test fuels under controlled and accelerated conditions. ORNL developed a unique stir tank facility to expose material samples to various test fuels (see below). The tanks are sealed, held at constant temperature, and continuously stirred for 2–16 weeks. A representative array of dispenser polymers, metals, and sealants was evaluated for fuel compositions containing 0, 10%, 17%, and 25% aggressive ethanol. Samples are removed periodically and analyzed for mass loss, volume swell, hardness, and elasticity. The results will be used to identify potential compatibility concerns and will further the development of fuel compatible seals and structural polymers.

(a)



(b)



ORNL stir tanks are used to expose materials samples to various fuels under controlled conditions: (a) is a schematic of internal features of a stir tank; (b) is a photograph looking down into the tank (lid is removed) showing mounted specimens immersed in the test fuel along with specimens above the fuel line for vapor exposure.

Status

ORNL and NREL are analyzing data from both the dispenser and materials experiments and are currently preparing reports summarizing the results and highlighting key findings.

Benefits:

- Dissemination of large data sets describing the impact of intermediate fuel blend chemistry with typical dispenser materials.
- Identification of compatibility issues associated with intermediate blends.
- Development of more durable fuel dispensers and components.

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Understanding Diesel Particulate Oxidation and the Impact of Biodiesel Blends

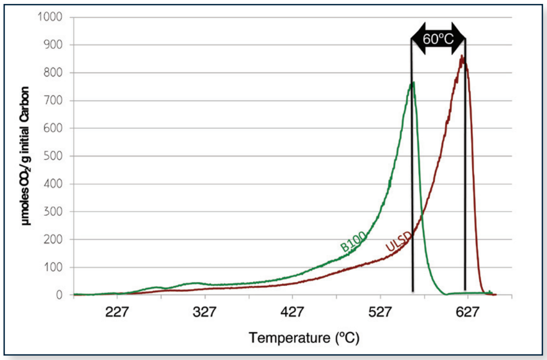
Background

The modern diesel-powered vehicle is equipped with a diesel particulate filter (DPF) to remove harmful particulates from the exhaust. While this advanced technology has been very successful in the reduction of emissions from these fuel efficient engines, the introduction of the DPF can lead to a decrease in fuel economy of as much as 4%–9%. This reduction is primarily due to the periodic requirement to increase the exhaust temperature to actively regenerate the DPF (i.e., high temperatures are required to oxidize the carbon-based particulate to gaseous CO_2). While this process is understood well enough to allow DPFs to be implemented in current vehicles, improved understanding of particulate oxidation is required to reduce the fuel penalty. This is especially true as the increased introduction of biodiesel is pursued. Blending petroleum-based ultralow-sulfur diesel (ULSD) with this renewable fuel has been shown to considerably impact the reactivity of the particulate.

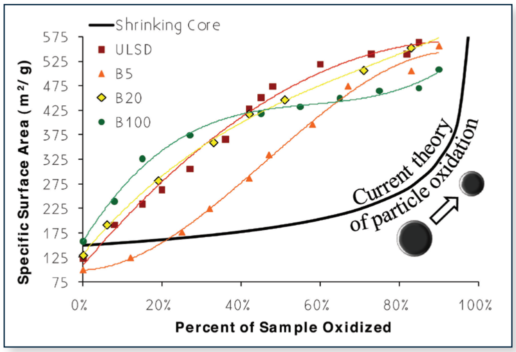
Technology

The efforts described here are an investigation of the reactivity of ULSD–biodiesel blends [ULSD (i.e., no biodiesel), B5 (5% biodiesel), B20 (20% biodiesel), and B100 (100% biodiesel)] using O_2 as the oxidant, which is a representation of the active regeneration of the DPF. All particulates were generated on a late model Mercedes Benz diesel engine at a single engine operating condition. Particulates were collected in a DPF and later removed for kinetic studies, which were performed in a microreactor system. This system allowed us to precisely control the conditions and environment that the soot was exposed to such that the kinetics of oxidation was measured rather than the diffusion of the gases to the soot particle. Additionally, this system was configured to allow the periodic measurement of the exposed surface area of the particulate using a flowing BET technique.

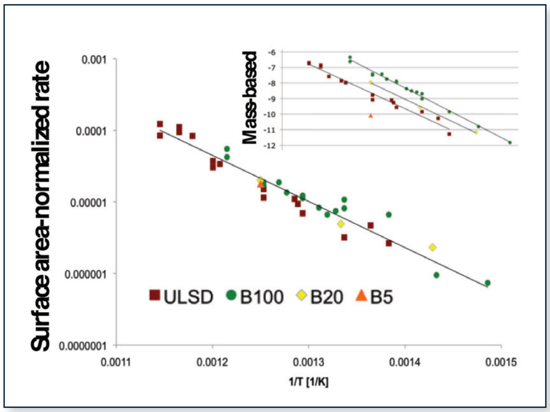
As shown in the temperature programmed oxidation profile in the top left figure below, the reactivity of the particulate varies significantly depending on the fuel being used. While measuring oxidation in a separate, more controlled configuration, we also monitored the rate of oxidation and evolution of the surface area as a function of burnout. The resulting trends are plotted in the top right figure below for all fuel blends and compared to the current theory of particle oxidation. Results show that the specific surface area of the particulate increases significantly throughout the oxidation sequence, and this increase in surface area begins at the onset of oxidation. These observations contradict the current theory of particle oxidation, which suggests that the particulate proceeds through a "shrinking core" oxidation sequence. If this mode were followed the surface area would not change significantly until 60%–80% of the particle had been oxidized. Taking this analysis a step further, the rates of oxidation were then normalized to surface area to determine whether this feature was dictating the oxidation behavior of the particulate. The bottom figure below is an Arrhenius plot of this normalized rate that illustrates the reactivity can be described by a single set of kinetic parameters. This simplification when combined with the contribution of the volatile hydrocarbon content allows a more accurate model of soot oxidation that can account for different fuel blends.



Temperature programmed oxidation profiles of ULSD and B100 particulate showing the difference in reactivity.



Evolution of particulate surface area as a function of the extent of reaction. For comparison the current theory of shrinking core is also plotted to illustrate the differences in theory compared to experimental data.



Arrhenius plot demonstrating that the reactivity of the four fuel blends can be captured when the rate is normalized to surface area rather than particulate mass.

Status

Having established the reactivity of particulate from a range of biodiesel blends using O_2 as the oxidizing agent, we will direct future efforts toward establishing the reactivity using NO_2. The use of O_2 represents an active regeneration pathway to DPF regeneration, while using NO_2 will convey the passive regeneration reactivity.

Benefits

- Improved fundamental understanding of particulate oxidation for a range of fuel types.
- Demonstration of improved reactivity of particulate generated with biodiesel blends above 5%.
- Development of a surface area based model that can account for the oxidation behavior of particulate from a wide range of fuels and can include the effects of hydrocarbon content.

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High Temperature Materials Laboratory

The High Temperature Materials Laboratory (HTML) at ORNL is a DOE User Facility that specializes in materials characterization and conducts collaborative materials research with industry, universities, and other research organizations. The HTML User Program's mission is to enable the development of materials-based, energy-efficient, and environmentally friendly highway transportation technologies.

User Projects on Batteries

Background

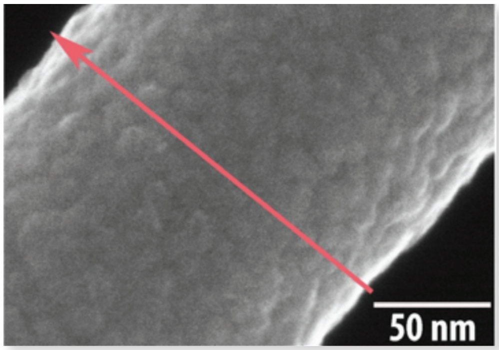
In support of the DOE Office of Energy Efficiency and Renewable Energy Vehicle Technologies Program (VTP) goals, projects in the HTML User Program are characterizing new materials for rechargeable batteries with the objective of reaching VTP energy storage goals for electric vehicles (EVs) and hybrid EVs (HEVs).

Benefits

- Improved safety and performance characteristics of lithium ion batteries for EVs and plug-in HEVs.
- Enhanced charging characteristics of batteries.
- Development of multiphysics models of battery electrodes that account for thermomechanical and electrochemical phenomena.
- More durable and reliable batteries for EVs.
- Development of diagnostic tools to better predict the performance and lifetime of cells.

User Projects

1. Applied Sciences, Inc. (ASI) has produced a high-performance anode for lithium ion batteries by depositing nanosized silicon-based materials onto low cost carbon nanofibers (CNFs). The silicon-CNF anode materials (see below) were assembled into battery cells at General Motors, where it was found that battery cyclability varied from batch to batch. To investigate the mechanisms responsible for these differences, Max Lake from ASI worked with HTML User Program researchers Jane Howe and Harry Meyer using the remote capabilities of the HTML scanning transmission electron microscope and x-ray photoelectron spectroscopy. Anode materials were characterized before and after the battery cycling tests. It was found that silicon-CNF composites have amorphous silicon coatings on both the internal and the external surfaces of the hollow CNFs. Depending on the deposition conditions, silicon may form either a uniform coating about 12 nm thick or an array of nodules less than 20 nm thick that partially covers the surfaces. The thickness of the silicon coatings provides fast mass transport of lithium ions while the graphite core offers high electrical conductivity. Work is in progress to correlate the effect of processing conditions with the microstructural

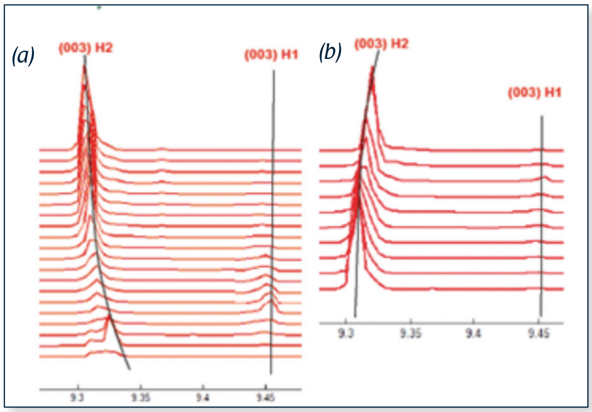


A micrograph of the ASI silicon-CNF used in lithium ion battery anodes.

features of the coatings and the electrochemical performance of the composite anodes. Such findings will enable the development of durable lithium ion batteries suitable for transportation applications.

2. Using the HTML operated X14A synchrotron beam line at the National Synchrotron Light Source (NSLS) at Brookhaven National Laboratory (BNL), BNL's Xiao-Qing Yang and HTML's Jianming Bai are investigating the relationship between the particle size of $Li_{1-x}FePO_4$ cathode materials and their phase transition behavior during charge-discharge cycling using in situ x-ray diffraction (XRD). Under equilibrium conditions, the $Li_{1-x}FePO_4$ cathode contains two coexisting phases, $LiFePO_4$ and $FePO_4$, throughout the voltage plateau during the charging process. It has been generally assumed that the mole composition is $(1-x)LiFePO_4 + xFePO_4$ for a state of charge “x.” However, the quantitative analysis of in situ XRD data (charged at C/10 rate) obtained as part of this project and analyzed with Rietveld refinement shows that the $FePO_4$ phase fraction is not linear to the state of charge as generally assumed but rather dependent on particle size. The phenomenon appears to be related to diffusion-controlled processes for lithium ion transport in cathodes during charge-discharge cycling. The longer diffusion length of lithium in larger particles causes a more significant delay in phase transition. The results are being used to refine a more sophisticated model to quantitatively explain the phase fraction evolution in the $Li_{1-x}FePO_4$ cathode and provide information to develop lithium ion batteries with greater energy and power density and durability.

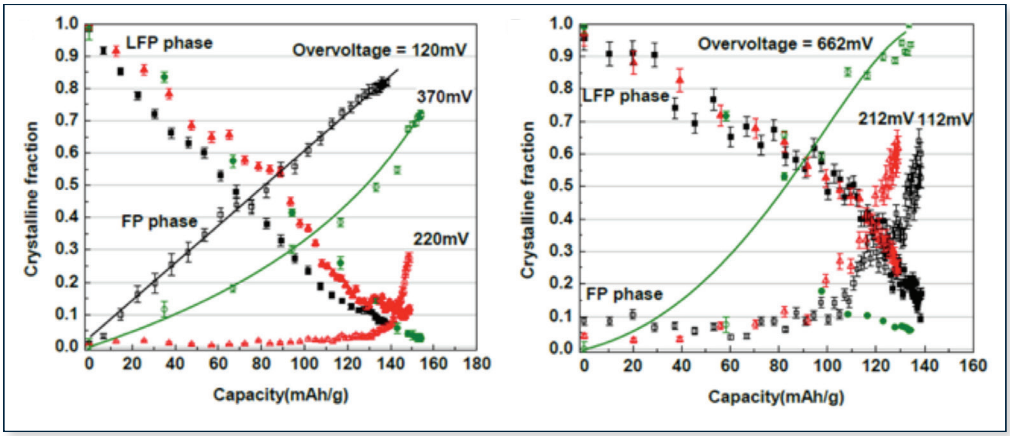
3. A University of Michigan team led by Prof. Ann Marie Sastry is using the NSLS to investigate the effect of processing parameters on the phase and structural characteristics and electrochemical performance of two commonly used cathode materials, $LiCoO_2$ (LCO) and $LiMn_2O_4$ (LMO). In one synchrotron XRD experiment phase transitions due to fast discharge in the high voltage region of LMO were characterized, phases existing at different states of charge in LCO were identified, and lattice parameter changes in LCO were observed. Preliminary results obtained from these experiments revealed C-axis expansion and contraction during charge and discharge of the H2 phase in the LCO cathode material, as shown in the figure below. It has been reported that LCO cathodes undergo a transition to hexagonal phase from monoclinic phase upon first charge, and as the applied voltage increases, a series of hexagonal phases, conventionally labeled as H1, H2, O1a, and O1, will emerge. The observation of the H1 to H2 phase transition in the voltage range from 3.3 V to 4.3 V indicates a successful in situ XRD measurement. In addition to the XRD work at NSLS, the University of Michigan team visited the HTML User Facility at ORNL to characterize LMO test specimens via scanning and transmission electron microscopy. The results from these investigations will provide information to develop safer, more durable lithium ion batteries with greater energy and power density for EV applications.



In situ XRD data showing the C-axis expansion and contraction during (a) charge (deintercalation) and (b) discharge (intercalation) of the H2 phase in the LCO cathode material.

4. Lithium ion cells degrade in capacity over their service lifetime; however, currently there is a lack of advanced nondestructive phase-sensitive tools with high spatial resolution to probe cell performance in commercially available lithium ion batteries. The ability to study a cell nondestructively and predict its long-term performance is critical to EV applications. To address this situation, researchers Jihui Yang and Robert Conell from the General Motors Research and Development Center teamed with HTML's Cam Hubbard, Hsin Wang, and Wei Cai to determine whether two advanced techniques, neutron diffraction and infrared (IR) thermography, could be effectively used for nondestructive, spatially resolved, in situ characterization of full scale EV batteries. The neutron diffraction technique was shown to be a valuable tool for nondestructive characterization of the changes in lithiation/delithiation of the cathode and anode phases within large format EV batteries. The technique can be used to verify that production batteries behave in the way that laboratory-based materials studies predict and that the phases are homogeneous throughout a large format battery. Sensitivity to temperature within the battery was best characterized by the IR method.

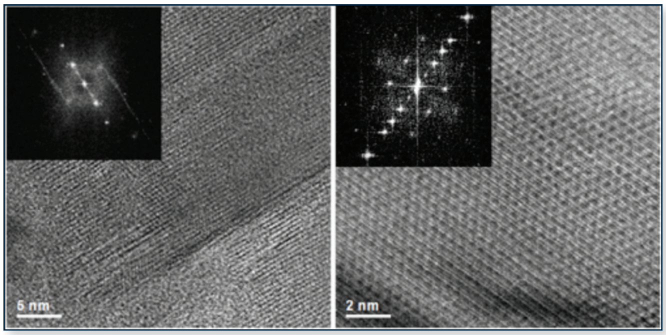
5. In worldwide efforts to replace the current petroleum-based transportation infrastructure with EVs, lithium-iron-phosphate ($LiFePO_4$) batteries have been identified as among the most promising onboard electric power sources because of the abundance of their raw materials and their good thermal stability, low environmental impact, and long cycle life. However, there are still many unsolved problems related to the charge-discharge process, and a better understanding of these electrochemical processes will help improve energy and power density and extend the cycle life of $LiFePO_4$ batteries. For the past 2 years, Professor Yet-Ming Chiang and students Nonglak Meethong and Yu-Hua Kao from the Massachusetts Institute of Technology (MIT) have been working with the HTML User Program's Jianming Bai at the BNL NSLS to carry out in situ experiments on electrochemically driven phase transitions in $LiFePO_4$ battery cathodes. This past year the team focused on an interesting yet unexplored problem in the charge-discharge process of the $LiFePO_4$ battery: overpotential effects on phase stability and transformation mechanisms. They found that for a particle size of about 113 nm, at both low and high overpotentials, a crystal-to-crystal olivine transformation dominates, whereas at intermediate overpotentials a crystalline-to-amorphous phase transition is favored (see below). As particle sizes decrease to the nanoscale, amorphization is further emphasized. Overpotential-dependent phase transition behavior has significant consequences which can impact battery durability. Greater knowledge



Phase fraction changes as a function of the state of charge.

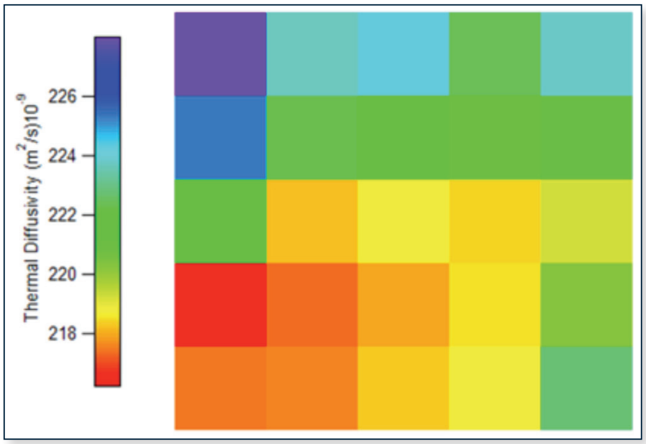
about the overpotential- and time-dependent phenomena could permit phase states and transition pathways to be electrochemically controlled and thus improve the stability and cycle life of EV batteries.

6. MIT post-doctoral researcher Chris Carlton is working with the HTML User Program's Larry Allard to study materials for the positive electrodes of lithium ion batteries to increase electrode stability under cycling. Using the HTML's aberration-corrected electron microscope, they have discovered some novel atomic arrangements (at right). Understanding these structural phenomena is critical to developing the next generation of battery materials. In particular, results from this research project will have a major impact on developing novel positive electrode materials with high cyclability and high thermal stability. These materials will be crucial to improve energy storage efficiency and to ensure a safer operating condition for lithium rechargeable batteries.



Bright-field aberration-corrected scanning transmission electron microscope images of layered-layered composite positive electrode materials for lithium ion batteries: (left) a pristine electrode and (right) a cycled electrode.

7. For the past 2 years Ohio State University (OSU) Prof. Sudarsanam Babu, doctoral student Shrikant Nagpure, and HTML researchers have been studying material degradation and aging mechanisms in lithium ion batteries. This past year the focus was on investigating the feasibility of using thermal diffusivity measurements to quantify aging. HTML staff member Ralph Dinwiddie traveled to OSU with a high-speed IR camera to conduct tests on six $LiFePO_4$-based lithium ion batteries that had been aged to about 80% of their capacity with varying charge-discharge rates. A new battery was also included in the studies as a baseline. After the cells were fully discharged and disassembled, thermal images of a 2 x 2 in. area of the cathode were taken according to the ASTM 1461 standard test method for flash thermal diffusivity. For analyzing the data and calculating the thermal diffusivity, each image was divided into a 5 x 5 matrix. Thermal diffusivity was then calculated for the 25 sites on each thermal image. Using these values, a corresponding thermal diffusivity map was created for each thermal image taken, as shown above. The extensive data obtained in these experiments are being analyzed to correlate these maps with battery performance.



Sample thermal diffusivity map.

8. The batteries in typical EVs or HEVs will be subjected to many charge-discharge cycles, leading to electrode damage and decreased cell life. ORNL Materials Science and Technology Division researchers Sergiy Kalnaus and Claus Daniel are working with HTML User Program researchers Amit Shyam and Edgar Lara-Curzio to better characterize the state of damage in lithium ion battery cathodes using resonant ultrasound spectroscopy (RUS) to determine the elastic modulus of electrode materials at different stages of battery cycling and relate changes to the state of charge. The experimental data will be further used for development and validation of a brittle damage model for life prediction of electrode materials. Initial testing has been carried out to determine the elastic constants of a 99.6% alumina disk using the RUS technique. The disk will serve as a lithium ion half cell electrode, and a finite element model for the multilayered structure is currently being constructed for further resonance modal analysis.

User Projects on Catalysis

Background
HTML supports the DOE Office of Energy Efficiency and Renewable Energy Vehicle Technologies Program emissions reduction goals through collaborations with users to characterize catalytic materials used in aftertreatment devices, fuel cell technologies, and biofuel production. As a result of these collaborations and the unique in situ heating and spectroscopic capabilities at HTML (described below), HTML users are gaining a fundamental understanding of the behavior of these materials, which may lead to more effective emissions controls as well as new energy sources.

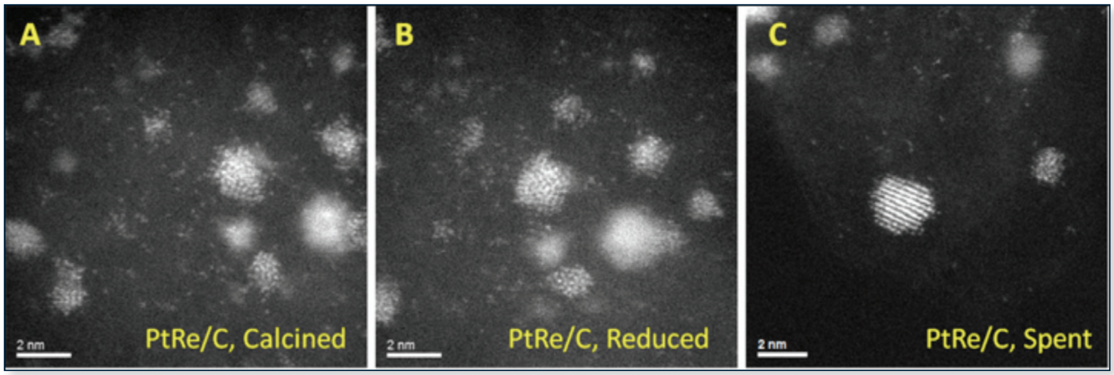
Benefits
- Development of more effective catalytic materials for use in automotive exhaust aftertreatment devices.
- Improved fundamental understanding of the thermodynamics and kinetics of nucleation, growth, and sintering in precious metal catalysts.
- Enhanced catalysts for lean-burn diesel engines, resulting in their greater use in automotive vehicles.
- Development of advanced catalysts for biofuel production.
- Development of advanced catalysts for fuel cell applications.

Technology
Production of hydrogen and biofuels from renewable biomass-derived feedstocks has attracted great interest in recent years as a result of increasing environmental concerns and U.S. energy security policy. One promising alternative to conventional production methods is aqueous-phase reforming (APR) of oxygenated hydrocarbons such as sugars, sugar alcohols, and polyols. Platinum-rhenium on activated carbon (Pt-Re/C) has proven to be an effective catalyst for the APR process due to its high hydrothermal stability and activity. Formation of a PtRe alloy, or close contact between the Pt and Re phases, has been proposed to account for the phenomenon of Re-enhanced activity. However, more definitive evidence is needed to clarify the structure of PtRe nanoparticles, reaction mechanisms, and support-particle interactions. Atomic-level structural characterization of Pt-Re will advance understanding of the interaction within the catalyst system and its role in APR and therefore contribute to design and development of an advanced catalyst for renewable energy applications. Studies to date have been limited to reduced catalysts; no work has been reported on catalysts under working conditions.

A new Pacific Northwest National Laboratory (PNNL)-HTML user project is addressing this through investigation of the structure of a PtRe/C catalyst activated and exposed to hydrothermal environments that are close to actual APR reaction/working conditions.

Status

Liang Zhang of PNNL has been working with the HTML User Program's Larry Allard using aberration-corrected scanning transmission electron microscope dark-field imaging at atomic resolution. Micrographs A and B below show that activated carbon helps stabilize the PtRe particles against sintering during in situ reduction by anchoring clusters with oxygen-containing functional groups and confining movement of clusters by the unique physical structure of activated carbon. The dark-field images of reduced PtRe/C reveal the presence of many single atoms, small clusters, and nanoparticles. After APR, most of the single atoms or small clusters present in the reduced catalyst disappeared, leaving behind larger nanoparticles, as seen in micrograph C. This is possibly due to agglomeration of neighboring clusters facilitated by water interaction or leaching out by liquid. This phenomenon could be one of the reasons, in addition to blocking pores and active sites by polymerized hydrocarbon through aldol condensation, for decline of activity over time.



Transmission electron microscope images of real PtRe/C for APR reaction: (A) calcined PtRe/C; (B) in-situ reduced PtRe/C in the same area showing little evidence of sintering; and (C) spent PtRe/C after APR, showing loss of fine clusters and growth of larger nanoparticles.

User Projects on Automotive Lightweighting Materials

Background

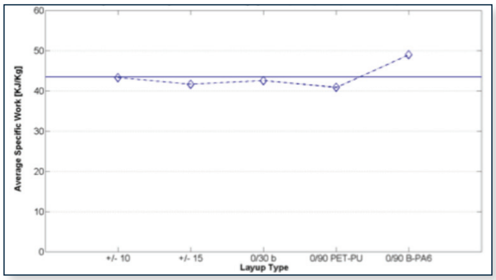
HTML supports the DOE Office of Energy Efficiency and Renewable Energy Vehicle Technologies Program automotive lightweighting activity through collaborations with users to characterize structural materials for applications that significantly reduce the weight of passenger vehicles without compromising vehicle performance, safety, life-cycle cost, or recyclability. As a result of these collaborations and the unique measurement and test capabilities at HTML (described below), HTML users are gaining a better understanding of and contributing to the knowledge base on the properties of polymer composites, high-strength steel, carbon fibers, and lightweight metals for automotive and heavy truck components.

Benefits

- Models for lightweight structural materials that enable producing lightweight materials with improved properties yet with unchanged vehicle life-cycle cost, performance, safety, or recyclability.
- Development of low cost carbon fibers and recovery of carbon fibers from scrapped or recycled composites at a 50% cost savings over producing new carbon fibers.
- New component designs that enable technologies to predict the response of materials after long-term loading, under exposure to different environments, and in crash events.
- Confirmation of the advantages of electromagnetic pulse welding, an attractive low cost joining technology for automotive applications.

User Projects

1. Fiberforge, a manufacturer of thermoplastic composites, has developed a novel low-cost, high-volume process to produce advanced composite structures from glass fibers (GFs) and thermoplastic matrices such as polyethylene terephthalate-polyurethane (PET-PU) and polyamide (nylon) 6 (PA6). During 2010 Fiberforge researchers Benjamin Hangs and Andrew Burkhart worked with HTML User Program staff members Don Erdman, Mike Starbuck, and Ralph Dinwiddie to test the automotive crashworthiness of GF reinforced PA6 and PET-PU tubes produced using the process. Tests were carried out using ORNL's test machine for automotive crashworthiness (TMAC) at a crosshead speed of 4 m/s. Force and deflection data were collected along with high-speed and infrared videos to support data analysis. From the force-deflection curves, absorbed energy was calculated and normalized by the crushed tube mass. Results are plotted at right. The results show 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.



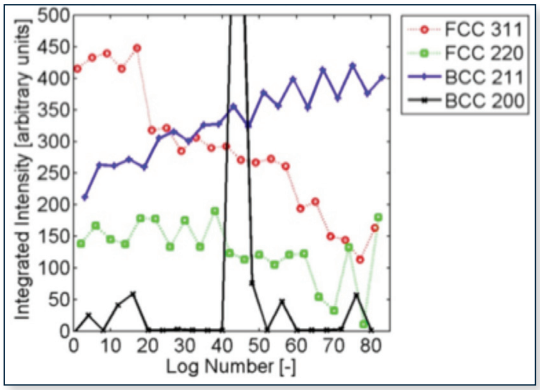
Plot of specific energies obtained for PET-PU matrix composite tubes with different layups.

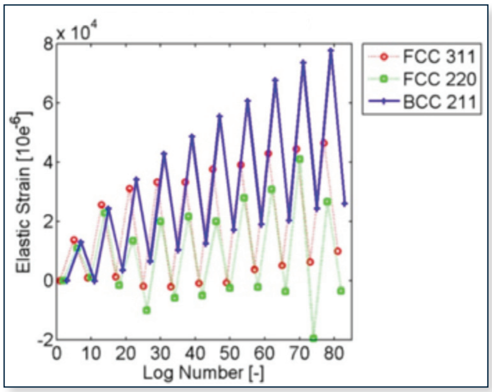
2. Metalsa Roanoke, Inc., a Tier 1 supplier to the U.S. automotive industry, manufactures side rails, a key component of a heavy truck chassis, for several customers in the heavy truck industry in North America. The materials used to produce the side rails come from various suppliers; come in various sizes, thicknesses, and compositions; and have been exposed to different processing conditions, leading to quality problems for Metalsa. In two separate but related programs, Metalsa's Joaquin Del Prado Villasana is teaming with HTML User Program's Wallace Porter, Tom Watkins, Josh Schmidlin, and Cam Hubbard to (1) assess and better understand the thermal and transformation stresses induced in vehicle side rails before and after quenching as a function of both the plate thickness and the steel supplier (see above) and (2)

Metalsa's Joaquin Del Prado Villasana aligns a side rail sample for x-ray residual stress measurement.

develop an understanding of the variability seen in the heat treat transformation kinetics of steel alloys used for side rails. Improved understanding of the origins of shape distortions by stresses in quenched side rails and transformation kinetics and dilatation behavior of steel alloys will guide adjustments to the metals specifications and manufacturing processes to minimize distortion, reduce rework, and improve process efficiency, which in turn will lead to reduced energy consumption during manufacturing, less waste, and improved reliability of finished vehicular components.

3. Better understanding of phase transformations in steels and the development and implementation of constitutive and fracture models for advanced lightweighting steels will increase confidence in them and thus enable greater use of these materials in automobile structures, thereby reducing vehicle weight and improving fuel efficiency without sacrificing safety. In pursuit of this goal, Professor Tomasz Wierzbicki and graduate student Allison Beese from the Massachusetts Institute of Technology's (MIT's) Impact and Crashworthiness Laboratory are developing plasticity and fracture models for metastable austenitic stainless steel 301LN sheets for incorporation in commercial finite element analysis codes. The MIT team collaborated with HTML's Cam Hubbard to collect in situ neutron diffraction data from 301LN samples under applied uniaxial load using HTML's second generation neutron residual stress mapping facility (NRSF2), a unique world-class facility. It was found that fcc austenite transforms to bcc martensite when tensile loading results in plastic deformation (bottom left), and the changes in fcc d-spacings (bottom right) indicate compression in the austenite due to other grains transforming to martensite. Based on the position of the bcc (211) peaks, the fraction of martensite increases with increasing plastic deformation, and the martensite is in tension after plastic deformation. These results will aid in developing models for phase transformation, texture, and stress as a function of applied load.





Results of stress-strain mapping: ((left) intensity of the four diffraction lines as a function of log number showing the transformation of fcc grains parallel to the loading direction to bcc 211 oriented grains as plastic deformation increases (the data for bcc 200 are unreliable due to low intensity arising from texture); (right) elastic strain in parts per million versus log number for two fcc and the bcc 211 diffraction lines.

4. The engine block of the General Motors (GM) 3.6 L V6 gasoline engine consists of an Al 319 (Al-Si-Cu alloy) sand casting around iron liner cylinder inserts. The engine block is subsequently given a T7 heat treatment. One of the critical factors determining the quality of the final product is the type, level, and profile of residual stresses along and between the iron liners. Such stresses and the resulting liner distortion are always present in this type of cast component and likely are very dependent on process conditions. Greater understanding of such stresses as a function of heat treatment and processing could lead to processing changes to alleviate undesirable distortion. Demitry Sediako, representing a team from the National Research Council of Canada, GM, and Ryerson University, used the HTML NRSF2 neutron beamline to characterize residual stresses and strains in the aluminum web and iron liners of the engine block. To date values of stress in the aluminum were found to exceed the alloy's tensile yield strength. This suggests that while the iron liners prevent fracture of the aluminum at the interbore regions, a high buildup of stress in the iron liners and aluminum occurs that results in dimensional distortion. Further investigation is warranted to characterize the residual stresses in the engine block following the T7 heat treatment process. In addition, the impact of variations in casting practice (e.g., cooling/solidification rate) on grain size and stress level is being considered for future studies.

User Projects on Thermoelectric Materials

Background

In support of the DOE Office of Energy Efficiency and Renewable Energy Vehicle Technologies Program (VTP) goals, HTML User Program projects are assisting facility users in the development of thermoelectric materials with a high figure of merit to recover waste heat from internal combustion engines. Because 35% to 40% of a fuel's energy potential is lost in the exhaust gases, recovering this energy would be one way to improve engine efficiency and increase vehicle fuel economy.

Benefits

- Potential for 10% or more improvement in overall engine efficiency as well as significantly increased vehicle fuel economy.
- Improved transport properties to increase figure of merit, ZT.
- Improved design of reliable waste heat recovery devices.
- Design information for developing durable, reliable thermoelectric generators.

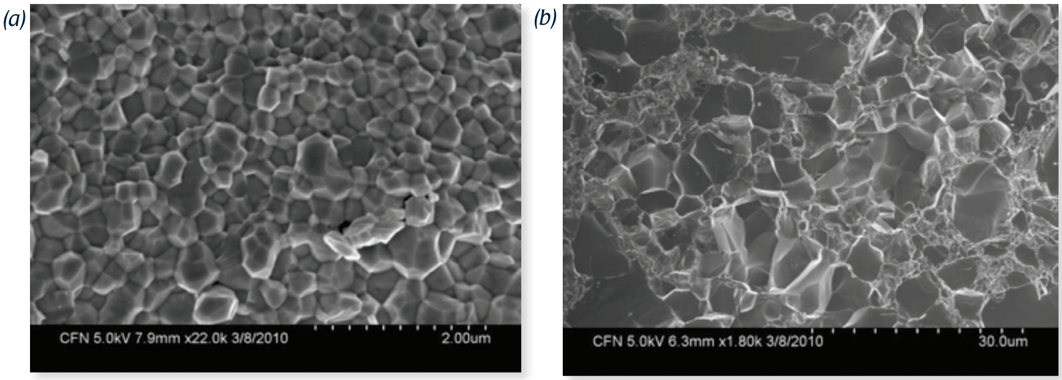
User Projects

1. While the figure of merit (ZT) of n-type skutterudites has reached values as high as 1.5, those of its counterpart p-type materials have values of ZT less than 1. Therefore, the development of p-type skutterudites with greater figure of merit could accelerate their use in vehicular waste heat recovery applications.

   Qiang Li's Advanced Energy Materials Group at Brookhaven National Laboratory (BNL) has developed melt-spinning techniques to obtain skutterudite materials of the desired phase in several minutes. This is in contrast to traditional processing routes for these materials, which involve long-term annealing periods (5-7 days). In addition to greatly reducing processing time, melt-spinning techniques produce ribbon-like microstructures with potentially improved transport properties.

Jie Qing, a member of Li's group at BNL, worked with the HTML User Program's Hsin Wang to characterize the transport properties of p-type Ce-filled skutterudite $Ce_{0.9}Fe_3CoSb_{12}$ using an array of instruments at the HTML's Thermography & Thermophysical Properties User Center. Materials processed by conventional methods and by melt-spinning followed by SPS were studied. Results show that the melt-spun material has lower thermal conductivity and higher power factor than the material processed according to conventional methods. The ZT value was improved over the temperature range from 26°C to 527°C and exhibits a 15% peak enhancement. Although the overall ZT value is still below 1, this project has demonstrated that non-equilibrium melt-spinning processing methods have the potential of producing materials with improved ZT.

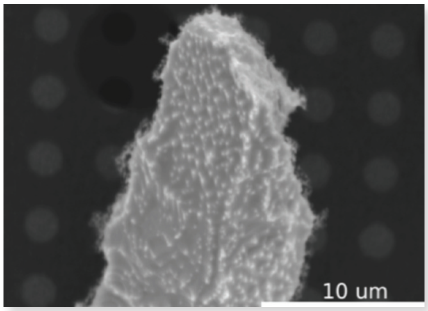
2. There is increasing interest in developing power generators using thermoelectric (TE) materials, which can convert waste heat into electrical energy. However, the successful application of TE materials depends on their thermal stability.



Scanning electron micrographs of the fracture surface of (a) non-equilibrium (MS) and (b) equilibrium (AN) synthesized samples.

Furthermore, because powder processing has become an emerging processing technique, it is necessary to understand the thermal stability of powders at conditions similar to those used for the densification of TE materials.

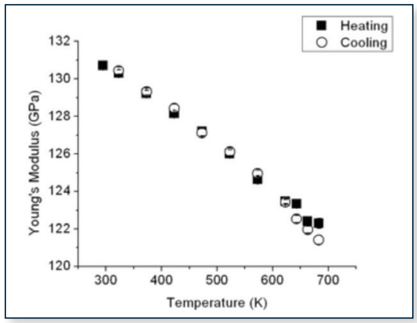
LAST (Pb-Sb-Ag-Te) is one of the best bulk thermoelectric materials because of its high energy conversion efficiency. In this HTML User program project, Professor Eldon Case from Michigan State University worked with HTML researchers Jane Howe and Fei Ren to study the phase and chemical composition of LAST powders obtained from cast ingots. The evolution of both powder morphology and chemical and phase composition was studied under vacuum via in situ scanning electron microscopy between room temperature and 550°C. Preliminary results indicate Sb-rich inclusions are less stable than the PbTe matrix, while evaporation of Pb from the matrix resulted in a new phase containing Ag and Te (see image at right).
This study suggests that powder processing of LAST materials should be performed in inert atmospheres and under pressures greater than the highest vapor pressure of the constituents. Also, if TE devices that utilize LAST are operat-



A scanning electron micrograph showing the morphology of a LAST powder particle at 550°C, where the surface roughness is due to evaporation of element Pb.

ed at temperatures above approximately 230°C, a protective environment such as an inert atmosphere with appropriate pressure should be provided to diminish the thermal degradation of LAST and hence extend the useful lifetime of the device.

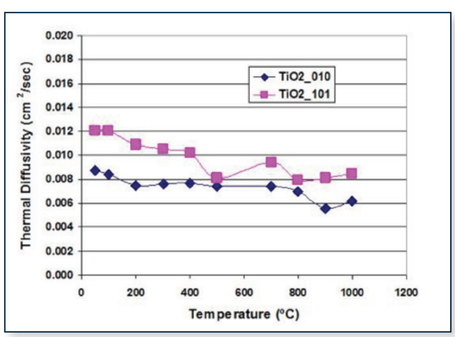
3. The use of thermoelectric generators to recover energy from internal combustion engine exhaust represents a potential for at least a 10 percent improvement in overall engine thermal efficiency. Michigan State University's Professor Eldon Case and graduate students Jennifer Ni and Robert Schmidt worked with HTML User Program staff members Edgar Lara-Curzio, Rosa Trejo, Melanie Kirkham, and Andrew Payzant to characterize the thermal expansion and elastic moduli of antimony-based skutterudite and lead-telluride—lead-sulfide thermoelectric materials as a function of temperature. The thermal expansion coefficient was determined by dilatometry using a thermo mechanical analyzer and by x-ray diffraction, while the temperature dependence of the elastic constants was determined by resonant ultrasound spectroscopy (RUS). It was found that there is a reversible linear relationship between the Young's modulus of these materials and temperature up to 330°C (see figure at right). During operation in vehicular applications thermoelectric generators will be subjected to mechanical vibration and temperature gradients. Therefore the information obtained in this project is essential to assess the structural integrity of these materials and to estimate thermally induced stresses as a function of temperature.



Elastic modulus as a function of temperature of n-type skutterudite without cerium dopant.

4. The Magnèli phases in reduced TiO_2 can be effective barriers to block phonon propagation, thus reducing thermal conductivity at high temperatures. Therefore, oxide thermoelectrics show potential as lower cost thermoelectric power generators that can withstand high temperatures. In their HTML User Program project with Hsin Wang, the University of Wyoming's Prof. Jinke Tang and graduate student Corin Chepko are characterizing the transport properties of TiO_2 test specimens with different concentrations of oxygen vacancies. In particular, they are investigating preliminary data reveal that phonon scattering by point defects and defect planes could play an important role in restricting heat flow. To verify that such a mechanism can contribute to a reduction in thermal conductivity at high temperature, where TiO_2's potential as a viable thermoelectric material lies, it is essential that its thermoelectric properties be examined.

Chepko and Wang measured the thermal diffusivity of two reduced TiO_2 samples (10mm x 10 mm x 1 mm) prepared at the University of Wyoming and cut along different crystal orientations. Data were gathered from room temperature to 1000°C in argon. The data in the figure at right indicate that the thermal diffusivity varied significantly over the entire temperature range. For example, at room temperature, thermal diffusivity in the <101> direction was 0.0121 cm^2/sec and 0.0087 cm^2/sec in the <010> direction. Since the den-



Thermal diffusivity of reduced TiO_2 in two crystal orientations: <010> and <101>.

sity and specific heat used to calculate thermal conductivity are the same in both directions, the same variations are present in measuring thermal conductivity. These preliminary results confirmed that phonon blocking effects depend on crystal orientation in reduced TiO_2.

User Projects on Thermal Management for Power Electronics

Background

The HTML User Program supports the U.S. Department of Energy Office of Energy Efficiency and Renewable Energy Vehicle Technologies Program goals for power electronics development through characterization of thermal management materials for products that lower thermal resistance or enhance thermal diffusivity. Applications include graphite heat spreaders for lithium-ion batteries and films for automotive power electronics.

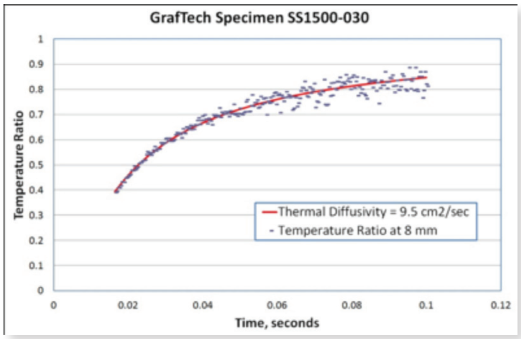
Benefits

- Precise measurements of thermal diffusivity in graphite foils, which are used widely for thermal management in a variety of automotive components.
- Development of adhesive films with low thermal resistance.
- Validate thermal testing methods and instruments.

User Projects

1. GrafTech, a graphite material company with more than 100 years' experience, manufactures a line of graphite heat spreaders with thermal conductivities ranging from about 300 to 1,500 W/m K, and the company is currently working to develop and commercialize a portfolio of expanded natural graphite thermal management products that improve the performance, durability, and safety of lithium ion batteries. Although the developed products will be applicable to all sizes of battery packs, they are expected to be of greatest benefit to larger systems such as those used in motive, vehicular, backup power, and utility energy storage applications.

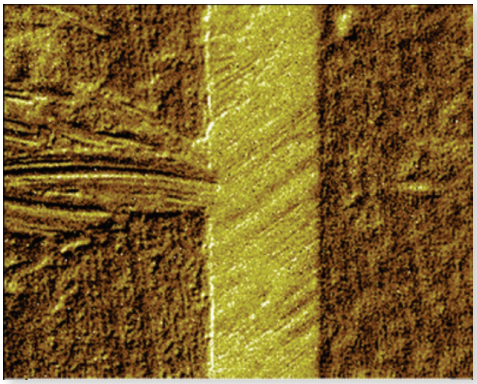
   Graftech's John Southard, Julian Norley, and Ryan Wayne collaborated with the HTML User Program's Ralph Dinwiddie to measure the in-plane thermal diffusivity of their thin graphite foils intended to be used as heat spreaders in the thermal management of lithium ion batteries. Both a LaserPit system and high-speed thermography yielded consistent in-plane thermal diffusivity results. In the case of high-speed thermography, the front face of a 50 mm by 50 mm specimen was pulse-heated by a flash lamp through a mask with a small rectangular hole. An IR camera records the temperature profile of the rear face of the specimen as a function of time after the flash. A model is then fit to the ratio of temperatures at a known distance away from the mask hole to the temperature directly at the center of the hole. The result is a heat-loss corrected in-plane thermal diffusivity measurement of the specimen (see at right). The determination of the thermal properties of GrafTech's graphite foils will facilitate their commercialization to help overcome barriers that limit the service life of batteries and efficiency of power electronic components.



Curve fit of the in-plane thermal diffusivity model to the temperature ratio of the signal at 8 mm to the signal at 0 mm from the center of the mask hole.

2. Btechcorp's HM-2 adhesive film consists of high thermal conductivity graphite fibers embedded and aligned in the normal direction of a nylon film. When used to bond two substrates together, it exhibits the lowest known thermal resistance of any polymeric adhesive and is therefore being evaluated for several applications, including automotive power electronics. However, Btechcorp has been using very expensive vapor-grown carbon that makes the cost of the adhesive film prohibitive for the auto industry. Thus, the company is investigating commercially available graphite fibers that will meet cost objectives and at the same time lower the bond thermal resistance to less than 0.04°C cm^2/W to meet DOE Vehicle Technologies Program objectives.

   Btechcorp's James Brown and HTML User Program staff member Ralph Dinwiddie evaluated the thermal interfacial characteristics of dozens of specimens consisting of two metal substrates bonded together with the adhesive film (below) in their investigation of several approaches to lowering the thermal resistance of the film. Data from a Xenon flash instrument and a high- speed infrared camera with a microscopic lens conclusively determined that a promising candidate for lowering the thermal resistance was actually increasing it. Thus the work at HTML prevented months of wasted effort pursuing a false lead. Testing also eliminated several other promising theories on how to lower the thermal resistance, although the research did provide a control group of specimens and data that have already been used to verify other thermal testing methods and instruments.



Infrared image of the Btechcorp interface material sandwiched between two aluminum plates. Carbon fibers appear as diagonal lines in the bright interface material.

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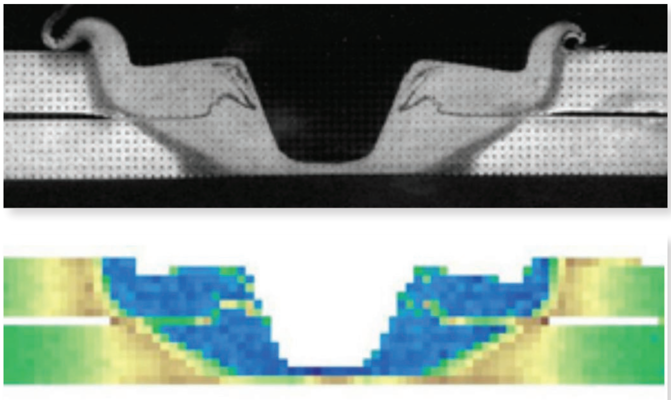
Lightweighting Materials

Friction Stir Spot Welding of Advanced High-Strength Steels II

Background

An initial project on friction stir spot welding (FSSW) of advanced high-strength steels (AHSSs) confirmed that FSSW of AHSSs could be accomplished with currently available tool materials and that the process could make spot welds with high tensile lap-shear strengths. High joint strengths were obtained through systematic investigations into weld process parameters and tool design. The figure below shows an example of the micro-structure and hardness distribution in an FSSW in a hot-stamp boron steel.



Cross-sectional views of FSSW in hot-stamp boron steel: optical image (top); image representation of hardness measurements (bottom).

Two important conclusions of the initial project relate to process cycle time and tooling costs. For FSSW to be accepted as a viable alternative to resistance spot welding (RSW) in automobile manufacturing it must not require too large of a penalty in weld cycle time. Resistance spot welds on steels like DP780 can be made in a fraction of a second. This is because RSW relies on melting to create bonds. In contrast, FSSW relies on the combined effects of time, temperature, pressure, deformation, and recrystallization to create a metallurgical bond. It is unlikely that this process will ever have spot welding times competitive with those of RSW. However because it avoids melting, FSSW has the potential to overcome important technical challenges related to using RSW on AHSSs. This is the fundamental reason for continuing the study of FSSW of AHSSs.

The second important conclusion was that reducing the cost of tooling or significantly increasing durability appears to be critical for FSSW to compete directly with RSW of AHSSs. In the interest of minimizing tooling costs the performance of various hard materials such as metal-matrix composites (right) was evaluated. If tooling costs are not significantly reduced, then there must be other compelling technical reasons to use FSSW rather than RSW on AHSSs (e.g., better control of microstructures and properties).

Stir tools made from metal matrix composites.

Technology

This follow-on project is designed to specifically focus on FSSW of alloys like high-strength TRIP (transformation-induced plasticity) hot-stamped boron steels that cannot be acceptably resistance spot welded. Compared to previous work, the overall approach will involve the following.

- More comprehensive characterization of mechanical behavior including fatigue strength, T-peel strength, cross-tension strength, and possibly impact behavior.
- More comprehensive microstructure characterizations.
- Identification and characterization of liquid metal embrittlement phenomena.
- Development of a consensus approach for comparing FSSW joints to those made by other processes like RSW, clinching, and adhesive bonding.
- Concentrated evaluation of candidate materials for friction stir tools.
- Interaction with equipment suppliers so that their constraints help guide decisions about welding parameters and tooling.

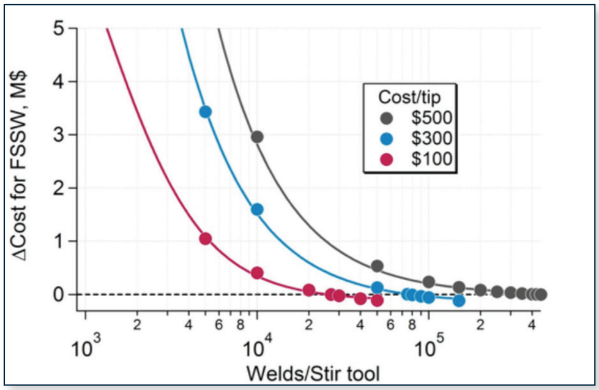
An initial experiment involved making several series of spot welds on a 1.5 mm thick TRIP steel provided by General Motors (GM). The stir tools used for these welds included existing designs of polycrystalline cubic boron nitride (PCBN) and newly acquired tools manufactured from Si_3N_4. As with previous evaluations, welds were made using both one- and two-step procedures and tool rotation speeds of 800 and 1,600 rpm. The welding time was fixed at 4 so that strength results could be compared with existing datasets. The various welding details and lap-shear strength results are presented in the table at right.

Tooling	rpm	Steps	kN
BN97	800	1	9.7
	1,600	1	11.3
	1,600	2	15.1
BN46	1,600	1	8.1
	1,600	2	12.5
SN77	1,600	1	6.14
SN97	1,600	2	5.3

Initial results for FSSW of uncoated TRIP steel.

The tabulated strength values represent averages for the four specimens. The BN tools are made of PCBN; the SN tools are made of silicon nitride. This TRIP steel had a nominal strength of 780 MPa; thus, the BN97 welds at 1,600 rpm and the two-step BN46 welds exceeded American Welding Society D8.1 minimum values.

Analysis of FSSW total process costs (at right) indicated that as the cost of stir tools approaches that of RSW electrode tips the difference in process costs decreases provided stir tools last as long as RSW tips. The current cost of PCBN tools is considerably higher than $100/tool. Reducing the cost of tooling or significantly increasing durability appears to be critical for FSSW to compete directly with RSW of steels. Alternatively, there must be other compelling technical reasons to use FSSW rather than RSW on AHSSs.



Variations of cost of friction stir spot welding (FSSW) relative to resistance spot welding depending on stir tool cost and life.

Status

The project includes a committee of consultants from Chrysler, Ford, GM, Kawasaki (robot manufacturer), MegaStir (producer of PCBN friction stir tooling), and Ceradyne (producer of Si_3N_4 tooling). The technology is not restricted by intellectual property rights.

Benefits

- Solid-state process that avoids melting.
- Concerns about cracks and porosity associated with solidification are eliminated.
- Potential for interactions with zinc coatings that degrade joint properties and tooling are minimized.
- Very low manufacturing energy use.
- Low heat input may minimize processing effects on heat treatable microstructures.

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Fundamental Study of Austenite-Ferrite Transformation Details for Austenite Retention in Carbon Steels

Background

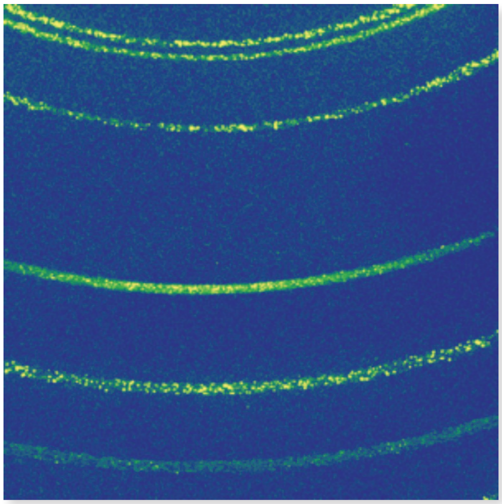
About 80% of all the materials used for passenger and other light vehicle construction are metals, and by a wide margin, the largest fraction of the metals is steels. Steels represent about 62% of average vehicle weight. Of the various steel mill products used for auto construction, about 70% of the total, or 839 kg of the 1,970 kg average light vehicle weight, is supplied as flat-rolled carbon steel for chassis parts and body panels.

The traditional sheet steels used for chassis and body constructions are the so-called "mild" steels. The combined interests of improving crash worthiness and reducing vehicle weights were at least partially responsible for the development of the first generation of advanced high-strength steels (AHSSs). What is now desired is a third generation of AHSSs that borrows from previous alloy development efforts to achieve intermediate strengths and ductilities but at costs that would make acceptance for automotive construction feasible. Controlling costs will likely require that Gen 3 AHSSs be no more than modestly alloyed compared to Gen 1 AHSSs and capable of being produced within existing steel mill infrastructures.

It is well known that retaining austenite in automotive sheet steels can markedly improve ductility at high strength through transformation-induced plasticity (i.e., the TRIP effect). Better fundamental understanding of austenite-ferrite transformations will enable a more scientific approach to improving properties through novel processing that can be achieved with existing infrastructure.

Technology

Most of the experiments are being conducted with the uncoated dual phase steel DP780 (from ArcelorMittal Steel). Diffraction experiments are being conducted on the UNICAT X-33 bending magnet beam line at the Advanced Photon Source (Argonne National Laboratory, Argonne, Illinois). X-ray data are captured by a charge-coupled device (CCD) on which the diffracted beams were integrated over a 1 s exposure. Diffraction patterns are acquired at a maximum rate of about 1/s. Data analysis begins by converting the two-dimensional images recorded by the CCD detector (at right) into one-dimensional (1D) plots of diffracted intensity versus d-spacing. The 1D plots were then analyzed for texture effects and ferrite and austenite phase volume fractions using published methods.



CCD image of synchrotron diffraction pattern from DP780 steel held at 800°C.

Technical issues being addressed include the following.

- Making direct, in situ observations of the time dependence of austenite-ferrite transformation behavior at elevated temperatures, during rapid heating/cooling, and during low temperature treatments designed to maximize retained austenite.
- Measuring partitioning of carbon between austenite and ferrite during processing.
- Understanding effects of critical alloying elements such as carbon, manganese, and silicon on transformation behavior and retention of austenite.

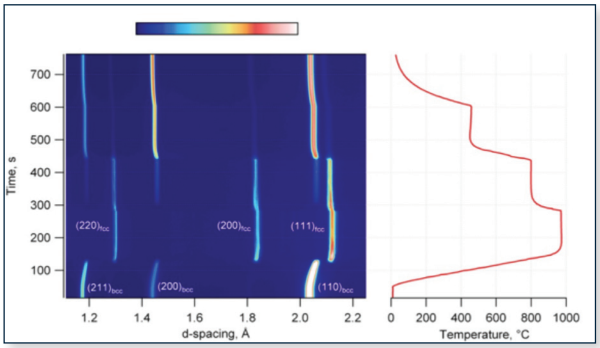


Image representation of diffracted intensity shows the transformation behavior of a carbon steel during austenitizing and cooling to room temperature.

The figure at left shows the overall response of DP780 to being heated to 970°C and held for 2 minutes followed by holding at 800°C for 2 minutes, holding at 460°C for 2 minutes, and then cooling to room temperature. This time-temperature heat treatment basically simulates what could be used to produce a dual phase steel. The transformations between the ferrite (body-centered cubic crystal structure) and austenite (face-centered cubic crystal structure) phases are clearly evident, and austenite is retained in the final microstructure. Recent improvements to experimental techniques significantly improved the consistency of the diffraction results with corroborating data from independently conducted experiments and thermodynamic calculations of equilibrium. We are performing additional experiments and analyses to refine the diffraction results and to extract additional information from the experimental diffraction data that would establish this approach as a unique capability in the development of Gen 3 AHSSs.

Benefits

- Detailed description of ferrite-austenite transformations during the rapid heating-cooling conditions that characterize commercial steel production.
- Continuous monitoring of austenite retention during cooling.
- Possible method for developing processing routes to maximize austenite within existing steel plant infrastructures.
- Transformation behavior and lattice parameter results will support development of new steel alloys with improved strength-ductility relationships.

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Polymer Composites Underbody Attachment Development

Background

ORNL is developing testing and modeling methods to predict the effects of mechanical loadings and environmental exposures on the durability of an automotive composite-to-metal (multi-material) joint. The focus application is the joining of a polymer matrix composite (PMC) underbody to the rest of the vehicle structure.

Significant automobile weight reductions and corresponding increases in fuel economy could be achieved by replacing dense materials such as metals with strong lightweight composite materials. Technologies for attaching or joining PMC parts with other metallic components enable the widespread integration of composites into a predominantly steel vehicle's design and manufacture. This design strategy requires reliable technologies for joining components made of dissimilar materials.

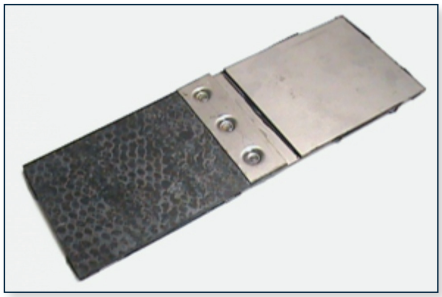
Issues associated with multi-material joint design include long-term reliability (durability) and manufacture. Generic tools for predicting the performance of any composite joint design do not exist, so validated modeling tools must be created to allow original equipment manufacturers to predict the durability of composite structures with the same level of confidence as metal assemblies. Consequently, the joint and materials to be used in the PMC underbody must be studied for this particular application.

One of the principles of automotive structural joint design is that the limiting factor should be the strength of the materials composing the vehicle structure, not the joint strength. Identifying the location of failures and understanding failure mechanisms is therefore as important as the joint strength and durability. Once these factors are understood, it can be determined where in the vehicle the joint will be most effective based on the different types of loads the structure will experience at various locations. Using modeling and analysis, the appropriate factors for designing the joints (materials, material properties, geometry, etc.) can be established.

The Composite Underbody Attachment project addresses several critical technology barriers identified by the Automotive Composites Consortium (ACC) Underbody Design and Joining teams to reliably manufacturing a vehicle with a PMC underbody.

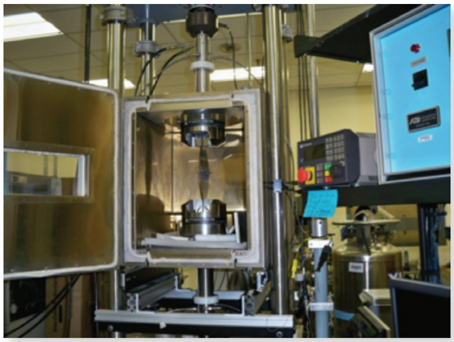
Technology

ORNL, Multimatic Inc., and ACC are collaborating to develop testing and modeling methods to predict the effects of mechanical loadings and environmental exposures on the durability of an automotive composite-to-metal (multi-material) joint. This research directly supports the ACC Composite Underbody project (Focal Project 4: Automotive Components from Structural Composites).



Weld bonded PMC-to-steel multi-material joint.

The research focus is evaluation and comparison of PMC-to-steel joint specimens prepared with weld bonded (at right) and adhesive bonded joint configurations. The specimens are manufactured using the same fabric sheet molding compound material that has been selected for the ACC composite underbody.



Tension-tension fatigue testing with the MTS Systems Corporation (MTS) test machine/oven chamber.

Status

Quasi-static and cyclic fatigue testing are being conducted for the load cases of tension, torsion, and bend (figures at left). Environmental stressors include ambient, 80°C, and -40°C temperature conditions. These load cases have been identified by the automotive industry as significant to the performance and durability of a composite underbody joint. The development of a dynamic (high strain rate) tensile test has been initiated using the ORNL Test Machine for Automotive Crashworthiness to simulate joint loading during crash. Nondestructive evaluations using infrared thermography are being used in the identification of initial failure locations and mechanisms.

Cyclic torsion fatigue test with the MTS axial-torsional test machine.

The Multimatic Engineering Services Group is using computer-aided engineering modeling of the underbody joint using existing tools to determine the applicability of these models to this material system and geometry. The validity of these models will be established by comparing the predicted results to the test data generated using the multi-material joint specimen and testing method.

This project will generate the coupon-level durability data needed for project model development and validation efforts. In addition, the data will also provide important joint durability information on design hardware to the automotive community. By directly supporting these ACC team goals, this project facilitates the demonstration and deployment of the composite underbody and demonstrates the viability of this and other PMC components that are designed to carry crash loads in vehicle structures. Increased deployment of PMC composites decreases vehicle weight and thus supports a key DOE Vehicle Technologies Program objective.

Benefits

- Weight savings in automotive structures translates into energy savings.
- Technologies for attaching/joining PMC parts with other metallic structures enable integration of composites into a steel vehicle's design and manufacture.
- Understanding joint strength, durability, and failure mechanisms across a range of loading scenarios is crucial to effective joint design in a vehicle.
- These testing and modeling methods can be applied to other types of multi-material joints, including other material combinations.

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Projects in Low Cost Carbon Fiber…

Significant vehicle weight reduction and corresponding increases in fuel economy can be achieved by replacing dense materials like metals with strong, lightweight materials such as those made with carbon fiber composites.

As the load-bearing component in these composites, carbon fiber offers significant weight saving potential because of its remarkable high strength, high modulus, and low density. Carbon fiber strength is higher than that of steel at about the same stiffness and about one-fifth of steel's density. It is estimated that vehicle structure weights could be reduced by 50% if carbon fiber composites were used in passenger automobiles.

While carbon fiber composites have proven themselves in high performance aircraft and other high performance applications, the large volume use of carbon fiber in automotive production is currently restricted because of its high cost—$8 to $15 per pound. About 50% of that cost is attributable to the cost of the precursor used to make the carbon fiber, and a significant portion of the balance is attributable to processes needed to convert the precursor into carbon fiber.

Working with government and industry, ORNL conducts extensive carbon fiber research and development with a focus on bringing down the cost of carbon fiber to $5–$7 per pound to enable large-scale application of carbon fiber in transportation and other energy industries. The remaining five Lightweighting Materials projects discussed here detail ORNL work toward achieving this goal.

Carbon Fiber Matrix Interface Adhesion

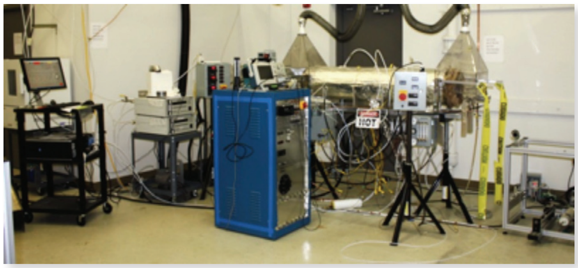
Background

The quality of the fiber-matrix interface is often a critical factor in determining composite mechanical properties and durability. The compatibility of commercially available carbon fiber with candidate lower cost matrix materials such as vinyl esters, polyesters, and thermoplastics is poor. Traditional surface treatments and sizing materials will not provide sufficient bonding between fibers and the new generation matrix polymers. Because of this, it is likely that the interface with experimental carbon fibers will also be of low quality as will initial composite manufacturing trials with them. Conventional carbon fibers are too expensive to be used in large volume applications, yet their superior properties would enable lightweighting in current glass fiber based industrial composite applications. Because of this cost barrier, carbon fiber producers have not developed their products for large volume processes such as sheet molding compounding and injection molding. Thus, the goal of this research is to address the fiber-matrix compatibility barrier to use of next generation low cost carbon fibers with lower cost matrix materials such as automotive resins.

Technology

Novel gaseous surface treatments and sizing materials are being developed at ORNL to use in carbon fiber production processes addressing the need for large volume low cost composites (see figures at top of next page). Present common practice is to surface treat carbon fibers in an electrooxidative bath. After surface treatment, the fibers are sized with a water-borne polymer (usually epoxy) by immersion in a sizing bath. Electrooxidative treatments form a wide range of acidic and basic oxygen containing moieties on carbon surfaces including ethers, hydroxyls, lactones, ketones, carboxylic

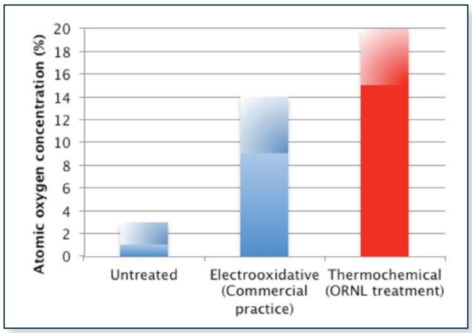
(a)



(b)

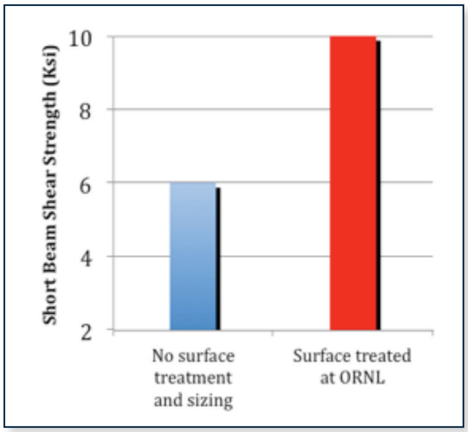
ORNL laboratory-scale experimental carbon fiber reinforced composite processing line: (a) continuous thermochemical surface treatment applicator; (b) continuous sizing line.

acids, and carbonates at crystallite edges and defects. The electrooxidative process cannot be controlled to emphasize only a particular surface species. For this reason, it cannot be tailored for forming acid-base or chemical bonds with vinyl esters.



Comparison of surface atomic oxygen concentration of untreated fibers (measured), fibers treated using a commercial electrooxidative surface treatment process (compiled from literature), and fibers treated using the ORNL thermochemical treatment process (measured).

Research at ORNL is targeting the control of surface functional groups and the creation of highly energetic surfaces (figure at left), which not only changes the type of surface treatment used, but also presents requirements for sizing techniques that diverge from the traditional approach. Carbon fiber surfaces can be functionalized with narrow distributions of moieties centered on desired groups by properly choosing source gases and application parameters. The flexibility of the surface treatment method that is being developed at ORNL permits the use of a variety of sizing chemistries and components. It also will allow an array of surface functionality designs to be used with various reactive coupling agents, film forming polymers, radical inhibitors, and surfactants.



Short beam shear strength test results for composites prepared from polyacrylonitrile based carbon fiber with vinyl ester resin matrices before and after surface treatment at ORNL.

Several approaches to a vinyl ester compatible sizing are being considered. They include thermoplastic sizing, film-forming polymers, specialty surface modification (functionalization), application of reactive finishes, or a combination of these. Based on results to date (shown at left), we anticipate developing a final surface treatment and sizing process that will dramatically increase the short beam shear strength of composites made with low cost carbon fiber and low cost resin systems and will meet a key need in ORNL's low cost carbon fiber program—the use of low cost resin systems in carbon fiber composite structures.

Commercialization

ORNL is developing novel gas phase thermochemical and plasma based surface treatments and sizings compatible with vinyl esters, polyesters, and automotive thermoplastics. Development of specific surface treatments and sizings will be focused on use of next generation low cost carbon fiber technology.

Benefits

- Development of specialty surface treatments and sizings for low cost carbon fiber and resin systems of interest to automotive and other emerging energy industries will accelerate the use of low cost carbon fiber precursor and technology in those industries and applications.
- Improved adhesion at the carbon-fiber–resin interface will enable the fabrication of thinner parts with comparatively higher mechanical performance, resulting in weight reduction and cost savings.
- Optimized interfacial bonding will improve the mechanical properties, and hence the quantity of carbon fiber required to meet design targets will be reduced, further reducing costs.

Carbon Fiber Precursors from Polyolefins

Background

Currently, common commodity grade carbon fibers are produced from polyacrylonitrile (PAN) based precursors. PAN based textile precursor is a potential candidate for low cost carbon fibers, with projected cost savings of about $2 per pound of finished carbon fiber.

Polyolefin based fibers (polyethylenes and polypropylenes) are industrially produced in the United States and are very low cost commodity plastic fibers ($0.50–0.75/lb). The cost of these precursor fibers is less than half that of PAN based precursor fibers. However, because polyolefin fibers are melt spun, a stabilization route, without melting, needs to be developed before carbonization of the precursor fiber. In the past, conversion of polyolefin precursors was attempted by a few research groups via sulfonation of the precursor fibers. Although the reported practical carbon yield was very high for the polyolefin fibers in comparison to that of the PAN based fibers (~70% and ~50%, respectively), unfortunately the residence time requirement for the stabilization step was very high. ORNL researchers have developed a conversion technology for polyolefin precursors that requires less than 1 h stabilization time and direct carbonization without a further oxidation step.

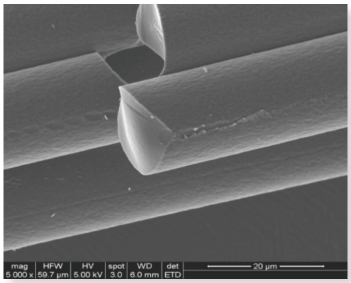
Technology

ORNL melt spun polyolefin fibers in collaboration with a U.S. industrial melt-spinning equipment manufacturer. Mechanical properties of the filaments can be tailored depending on the degree of filament draw down ratio. A systematic investigation was used to determine optimal stabilization conditions for 100 to 1,500 filament tow of 10 to 20 mm diameter fibers. A semicontinuous operation was established for those tows using a simple reactor. Optimization of conversion parameters is under way, with an overarching goal to produce polyolefin-precursor–based lower cost carbon fiber.

To date carbonized fibers with 150 ksi strength and 15 Msi modulus have been produced. Almost 70% carbon yield was observed from the said precursor materials. As a result, ORNL researchers are building a partnership with one of the industrial precursor manufacturers.

Benefits

- Polyolefin based precursors are significantly lower in cost compared to PAN based precursors.
- Melt spinning is less expensive than solution spinning.
- Fibers can be spun at high speed.
- Total saving in carbon fiber cost could exceed $2/lb.
- Polyolefin based precursor technology has a lower unit investment cost.
- Melt-spun polyolefin fiber is available in the market.
- Polyolefins offer significantly high carbon yield (~70%).



Scanning electron microscope image of polyolefin based carbon fibers.

Setup for semicontinuous functionalization of filaments.

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Low Cost Carbon Fiber Production Advanced Oxidation Technique

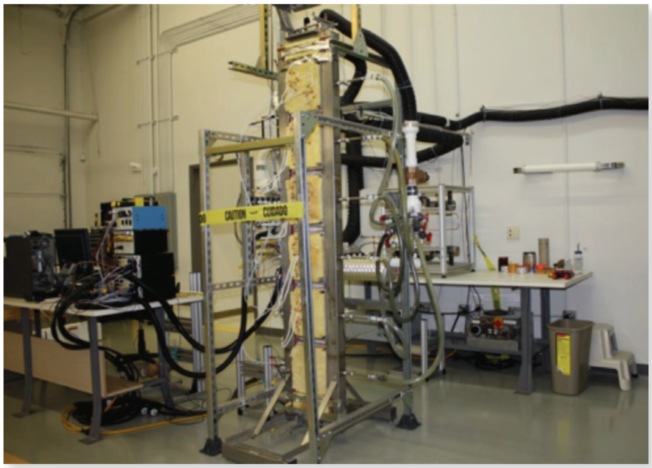
Background

ORNL and Sentech, Inc., are developing a plasma based processing technique that rapidly and inexpensively oxidizes polyacrylonitrile (PAN) precursor fibers. Conventional oxidation is a slow thermal process that typically consumes more than 80% of the processing time in a conventional carbon fiber conversion line. A rapid oxidation process could dramatically increase the conversion line throughput and appreciably lower the fiber cost. This technology will integrate with other advanced fiber conversion processes to produce low cost carbon fiber with properties suitable for use by the automotive industry. This technique has successfully oxidized both aerospace grade and textile grade PAN and will be tested with other precursors as well.

Technology

The approach currently being pursued is based on a new stabilization technique that uses advanced thermochemical mechanisms to speed up the effective radial bulk diffusion of the physical and chemical changes required to prepare PAN for carbonization. This approach would not be economical with conventional processing techniques. However, with proprietary industrial plasma technology, this process not only enhances oxidation and diffusion rates, thereby lowering reactor residence times, but does so with lower energy consumption.

This research program has progressed from bench-scale batch processing to laboratory-scale continuous processing of multiple tows using lower processing temperatures and residence times than are currently seen in the industry. Multiple tow reactor is pictured at right. Concurrently, the chemical mechanisms involved have been refined and characterized using Fourier transform infrared spectroscopy and quantitative gas monitoring equipment. Issues related to very rapid oxidation diffusion from skin to core led to fiber damage, which has been addressed through optimized processing parameters and better understanding of the chemical and physical mechanisms at work.



Laboratory-scale multiple tow reactor.

An inherent concern with a new thermochemical process is the chemical compatibility of all materials involved. To address this, a materials compatibility test stand (MCTS) was built to conduct long-term materials compatibility testing with the candidate plasma based advanced oxidation process. This system includes an automated data acquisition system, a sealed inert test chamber inside a remotely controlled convection oven, and independent plasma generation for independent chemistry control. The test chamber was designed to withstand the higher temperature range required in the advanced oxidation process. This flexible, independent system will generate many hundreds of hours of data over the course of the oxidation research and will assist in understanding what materials can be used in industrial-scale ovens and reactors.

Commercialization

During the current fiscal year several important objectives were met that produced valuable knowledge on the scaled-up advanced oxidation process and brought the technology closer to demonstrating that it is adequately robust for further development and eventual commercialization. The relationship between fiber density and quality and process parameters in the main reactor was better defined. A wider range of chemical parameters was explored and understood. Textile PAN was processed for the first time. The MCTS that will provide essential information on material compatibility with the advanced oxidation process became operational. Energy demand and residence time factors were evaluated and summarized.

This project is currently beginning a scale-up phase of development with the end goal of producing specifications for a demonstration-scale oxidation reactor to be used in ORNL's Carbon Fiber Technology Center (CFTC). At the conclusion of this project, the researchers will be positioned to procure, install, test, and operate a pilot-scale plasma oxidation module in an advanced technology pilot line. The follow-on of this project will be the design and construction of the advanced technology pilot line that will be installed in the CFTC. It will be used to validate system performance and scalability and to produce the required quantities of advanced technology carbon fibers to support the Lightweight Materials program's advanced development activities.

Benefits

- Fully continuous process.
- Conventional residence times are less than half.
- Process could be incorporated into existing conversion lines.
- Does not use expensive source gases.
- Stabilizes both standard grade and textile grade PAN.
- Higher speed conversion of the precursor into carbon fiber yields cost savings.

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Low Cost Carbon Fiber Production Precursor and Fiber Evaluation Systems

Background

As part of the Low Cost Carbon Fiber (LCCF) Program, ORNL and its partners are evaluating a variety of alternative precursor materials and advanced processing techniques.

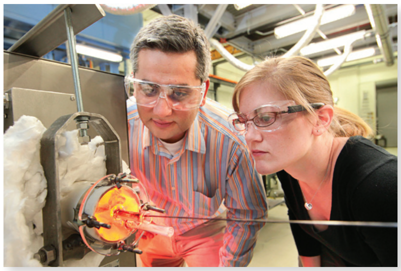
Technology

The ORNL precursor and fiber evaluation system (below), 1/20-scale pilot line, and microwave assisted plasma (MAP) carbonization unit facilitate the evaluation of materials and processes for the LCCF initiative. This equipment plays a key role in advancing technology development and providing the critical information necessary for planning and executing production scale-up. The capabilities of these facilities include

- evaluations of new concepts,
- demonstrations of technical feasibility,
- demonstrations of cost-effectiveness,
- evaluations of alternate precursor convertibility,
- production of fibers for evaluation by the Automotive Composites Consortium and other interested parties, and
- resolution of processing/operation/equipment issues.

Precursor evaluation system.

The precursor evaluation system is designed to complement the conventional pilot line in that it is designed for single-shift evaluation of very small precursor quantities. During precursor development, initial batches tend to be a few short filaments or a single tow up to about 80 K filaments. The precursor evaluation system is useful for evaluating the feasibility and process parameters for converting those precursors into carbon fibers. After the conversion process parameters are determined, the conversion protocols can be validated on the pilot line and larger quantities of fiber produced there.



Carbon fiber tow exits the high temperature carbonization furnace.

ORNL's conventional pilot line enables the production of a few pounds/day of 50 K tow. Therefore, it is useful for making small quantities of fiber for tow and composite evaluations. It can also be used to conventionally oxidize or carbonize tows for which the balance of the conversion is accomplished by advanced processes. The pilot line requires at a minimum hundreds of feet of at least 1 K tow, and the start-up time for the high temperature carbonization furnace (at right) is at least 10 hours.

The MAP carbonization unit was developed in the MAP carbonization project and continues to be maintained and operated for demonstration purposes. Proper maintenance, intelligent upgrading, and wise use of these critical facilities, which were developed during previous or current projects, continue to be important factors in the success of the related technology development projects.

Status

The precursor evaluation system and pilot line continue to function as essential tools for the development and validation of new precursor technologies, having been used for the initial evaluation and/or development of polyolefin, textile polyacrylonitrile, and proprietary precursors. Significant new capabilities have been acquired for the precursor evaluation system, with installation under way. Important upgrades to the pilot line are scheduled for near-term implementation to provide higher speed capability, additional stretching capability, surface treatment and sizing capabilities, and enhanced controls and data acquisition systems. Future plans for the MAP carbonization unit include making it the focal point for development of an advanced technology demonstration line. An atmospheric plasma oxidation unit currently under development will be a part of this advanced technology demonstration line. All of these facilities will continue to be maintained and operated as needed to support the development of LCCF.

Benefits

- Precursor Evaluation System
  - Scientific development of precursors.
  - Conversion process development.
  - Conversion trials on single- or few-filament precursor samples up to a large tow (thousands of filaments).
  - Processes isolated into very fine stages or subsets for temperature and/or stretching studies.
  - Batch or continuous mode.
  - Precise tension control and stretching capability.
- Pilot Line
  - Multiple tow capability (up to eight tows).
  - Fully integrated operations.
  - Can validate precursor development and conversion protocols.
  - Facilitates scale-up studies and advanced conversion process module interchanges.
- Advanced Conversion Processes (development funded separately)
  - MAP carbonization.
    - Utilizes modification to traditional low pressure plasmas to enhance carbonization speeds thereby reducing residence time, energy consumption, and production costs.
    - Significant progress has been demonstrated; scale-up of the technology for continuous operation is in progress.
    - Existing current generation technology unit at ORNL is utilized for both demonstration and developmental purposes.
  - Atmospheric plasma for oxidative stabilization
    - Utilizes atmospheric pressure plasmas to enhance oxidation speeds thereby reducing residence time, energy consumption, and production costs.
    - Proof of principal has been demonstrated; scale-up to multiple tows and continuous processing is in progress.

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Low Cost Carbon Fiber Production Textile Based Precursors

Background

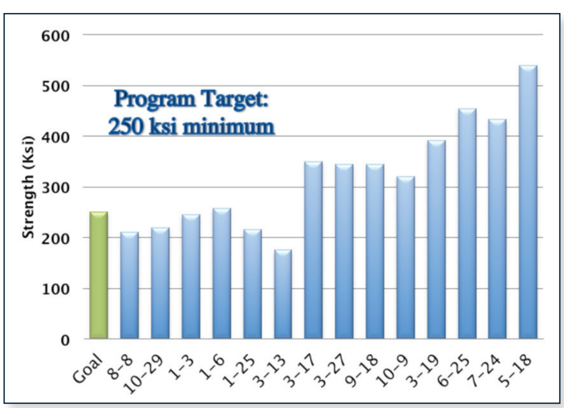
Hexcel Corporation and ORNL have developed the baseline technology necessary to use textile based polyacrylonitrile (PAN) fiber as a very low cost precursor for making carbon fiber. The key to using textile PAN precursors (shown at right) is the application of a chemical pretreatment during manufacture of the precursor fiber. ORNL and Fibras Sinteticas de Portugal, S.A. (FISIPE) are working to complete development and commercialize this precursor to make it available to current and potential carbon fiber manufacturers. Use of textile fiber, which sells for significantly less than the cost of conventional carbon fiber PAN precursors, would result in a savings of more than $2 per pound in the finished carbon fiber manufacturing costs.

Textile grade PAN precursors.

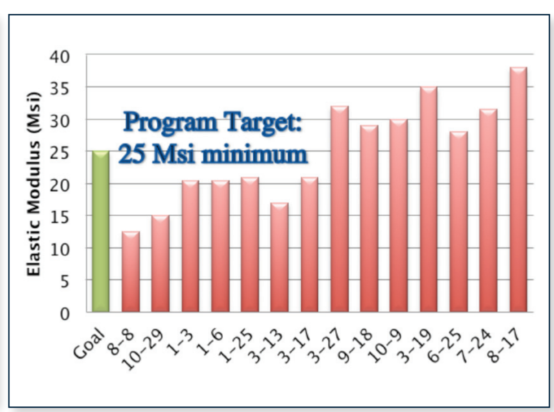
Technology

ORNL and FISIPE have defined several textile formulations that yield suitable carbon fibers. They are modifying materials that can be oxidized near the oxidation temperature of conventional carbon fiber precursors. In addition, they have developed a way to modify the chemistry of the starting materials by the addition of a small amount of a third component and have defined a chemical pretreatment protocol for further altering the fiber chemistry.

Different levels and conditions of the pretreatment were also evaluated. Key to incorporating these changes has been the ability to perform the chemical modification in current production facilities and at current production speeds and temperatures. Mechanical properties now well exceed the program requirement, as shown below.



Improvement in fiber strength during the project.



Improvement in fiber modulus during the project.

The oxidative stabilization of the modified textile precursors requires only about 70 minutes compared to a time of 80–120 minutes for conventional carbon fiber precursors. Oxidative stabilization is the low speed bottleneck in the carbon fiber conversion process. As a result, modified textile precursors may be carbonized at much higher speeds and a significant production cost reduction achieved.

Commercialization

FISIPE, a commercial fiber production company, intends to offer this new fiber as a lower cost precursor to current and future carbon fiber manufacturers. ORNL has other parallel efforts to develop new production technologies that will enable manufacturers to develop high volume, commercial carbon fiber plants that use textile based PAN precursors along with other advanced manufacturing methods.

Benefits

- Textile based PAN precursor will provide for a considerable (or substantial) price reduction when compared with the traditional PAN precursor.
- Chemical pretreatment is easily incorporated into existing textile mills.
- Textile mill volumes can support the large increases in fiber quantity required for automotive applications.
- Total saving in carbon fiber cost could exceed $2/lb.
- Higher speed conversion of the precursor into carbon fiber yields additional cost savings.

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Propulsion Materials

Catalysis by First Principles

Background

This research focuses on an integrated approach to computational modeling and experimental development, design, and testing of new catalyst materials that we believe will rapidly identify the key physiochemical parameters necessary for improving the catalytic efficiency of these materials.

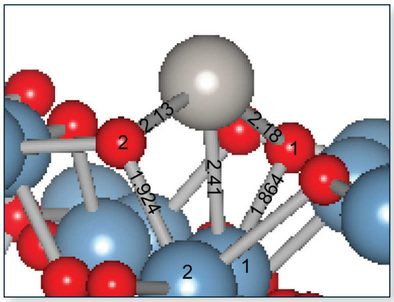
The typical solid catalyst consists of nanoparticles on porous supports. The development of new catalytic materials is still dominated by trial and error methods, even though the experimental and theoretical bases for their characterization have improved dramatically in recent years. Although it has been successful, the empirical development of catalytic materials is time consuming and expensive and brings no guarantees of success. Part of the difficulty is that most catalytic materials are highly nonuniform and complex, and most characterization methods provide only average structural data. Now, with improved capabilities for synthesis of nearly uniform catalysts, coupled with state-of-the science characterization methods, including those that allow imaging of individual catalytic sites, we have a compelling reason to markedly accelerate the advancement of the science and technology of catalysis.

Computational approaches, on the other hand, have been limited to examining processes and phenomena using models that had been much simplified in comparison to real materials. This limitation was mainly a consequence of limitations in computer hardware and in the development of sophisticated algorithms that are computationally efficient. In particular, experimental catalysis has not benefited from the recent advances in high performance computing that enable more realistic simulations (empirical and first principle) of large ensemble atoms, including the local environment of a catalyst site in heterogeneous catalysis. These types of simulations, when combined with incisive microscopic and spectroscopic characterization of catalysts, can lead to a much deeper understanding of the reaction chemistry that is difficult to achieve with experimental work alone.

Thus, a protocol to systematically find the optimal catalyst for a particular application can be developed that combines the power of theory and experiments for the atomistic design of catalytically active sites and can translate the fundamental insights gained directly to a complete catalyst system for deployment.

Technology

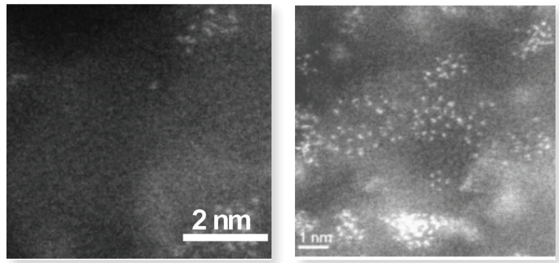
The theoretical modeling is based on density functional theory (DFT) studies of platinum supported on θ-alumina. We used the Vienna Ab-initio Simulation Package to carry out first principle total energy calculation within the supercell DFT framework. Generalized gradient approximation in the Perdew-Wang-91 form was used for electron exchange and correlations. The Kohn-Sham equations were solved using the projector augmented wave approach for describing electronic core states. The plane-wave basis set was truncated at a kinetic energy cutoff of 500 eV. We have completed the study of single atoms of Ni, Pt, Pd, Cu, Au, and Ag supported on the (010) surface of θ-alumina.



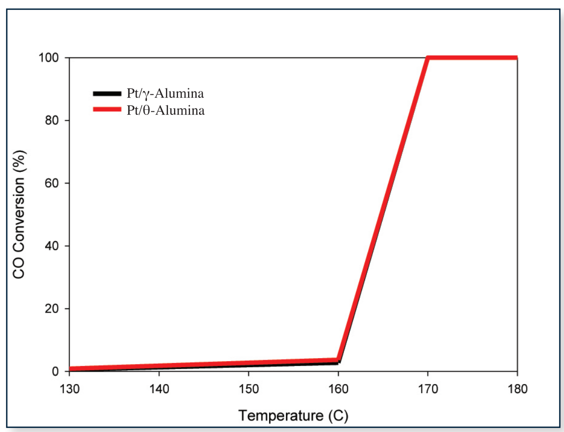
Platinum atom on θ-alumina surface.

Experimentally, we have synthesized a series of platinum clusters/particles of different sizes supported on γ alumina (images at right) and evaluated the catalysts' CO and NO oxidation activity. We monitored the microstructural changes throughout the CO and NO oxidation process to correlate microstructure and activity. We have also carried out a preliminary study of HC oxidation processes. Our experimental studies show that CO oxidation is identical on platinum supported on γ-alumina, θ-alumina, and α-alumina (chart at right). This suggests that CO oxidation by itself is not an adequate probe for catalyst sites as the nanostructure of platinum is identical when supported on γ-alumina or θ-alumina but different when supported on α-alumina.

(a) *(b)*



High-angle annular dark field–scanning transmission electron microscope images of fresh Pt/γ-Al_2O_3 (a) and Pt/θ-Al_2O_3 (b) using the ORNL aberration-corrected electron microscope.



Complete CO conversion as a function of temperature.

Status

- Our theoretical studies show the following.
  - Single atoms of platinum on the (010) surface of θ-alumina are in the zero oxidation state. This result is in stark contrast to previously reported models where the platinum atom is reported to be d9s1 on α-alumina.
  - We found that Pt, Pd, Au, and Ag single atom adsorption is in the order of Pt>Pd>Au>Ag. The surface mapping and nudged elastic band method allowed us to find the lowest energy location for platinum and its reaction pathway to the highest energy site.
  - The bimetallic clusters of Pt-Pd are not energetically more stable than Pt-Pt clusters. Furthermore, energetically there is no significant difference between a Pt atom bonded to PdO_2 or PtO_2.

- Experimentally, we have shown the following.
  - Previously we had shown that platinum supported on γ-alumina or θ-alumina exhibited identical CO, NO_x, and HC oxidation behavior.
  - We found the following under lean burn conditions.
    - CO conversion became quantitative at about 170°C while NO_x conversion reached a maximum of 45% at about 250°C.
    - The bimetallic clusters of Pt-Pd, carefully synthesized to obtain various ratios of Pt and Pd, were deposited on γ-alumina. Upon aging under lean burn conditions, the Pt-Pd clusters were more stable than platinum alone at high temperatures.

Benefits

- Understanding the structures of supported nanoclusters.
  - Theoretical models to understand cluster oxidation state (oxidized, reduced, in equilibrium), dependence on cluster size, and the kinetics of oxidation.
  - Nanostructure of platinum on supports determined by aberration-corrected electron microscopy.
- Understanding interaction of the support with supported clusters and its impact on the structure and reactivity of catalysts.
  - Cationic or zero-valent metals or both.
  - Cationic metals at the metal–support interface.
- Understanding reactivity of the clusters.
  - Theoretical studies of CO, NO_x, and HC reaction on supported clusters.

Advanced Materials Development Through Computational Design for Applications in Homogeneous Charge Compression Ignition Engines

Background

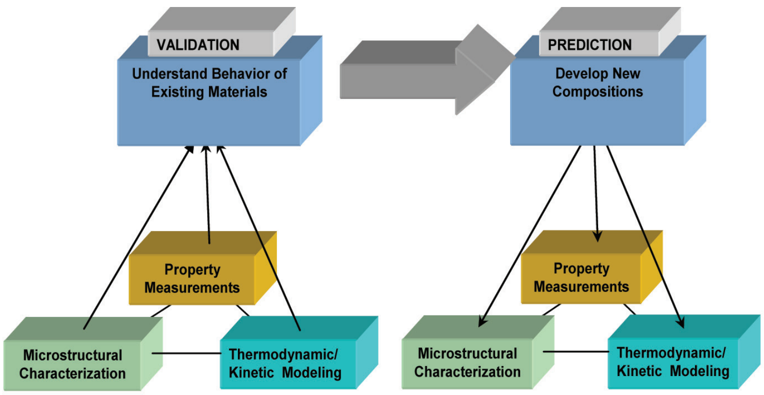
The goals of the DOE Office of Vehicle Technologies Advanced Combustion Engine Research Program are to develop and demonstrate an emissions compliant engine system for Class 7-8 highway trucks that improves the engine system fuel efficiency by 20% (i.e., from about 42% thermal efficiency today to 50%) and to develop technologies that will achieve a stretch thermal efficiency goal of 55% in prototype engine systems, leading to a corresponding 10% gain in over-the-road fuel economy relative to the 2010 goal. One of the important strategies for achieving these goals is advancing technologies that increase engine combustion efficiency such as lean-burn operation (high efficiency clean combustion), exhaust gas recirculation, turbocharging, variable valve actuation, and/or variable compression ratios. Materials performance must improve before the advantages of such advanced combustion technologies can be realized. This project deals with identification of material requirements for homogeneous charge compression ignition engines in automotive and truck applications and development of advanced, yet cost-effective, materials through computational design.

Technology

"Materials-by-design" is an ORNL concept that encompasses a variety of materials related techniques including modeling, correlation, and materials modification. The premise behind the materials-by-design approach is that mechanical properties can be correlated to microstructures and phase compositions. Variations in microstructures and phase compositions can be achieved through variations in alloy chemistry; thermal treatment at high temperatures; and thermomechanical processing techniques such as quenching, rapid casting solidification, and mechanical working. The observed microstructural characteristics can be correlated with mechanical properties and predictions from equilibrium thermodynamic and kinetic modeling through advanced correlation techniques. Results from such correlations allow untested compositions or treatments to be modeled so that desirable trends in microstructures and phase compositions can be rapidly established. Small heats of targeted materials can then be processed to confirm the modeled properties and to broaden the correlation database.

Benefits

- Targeted, on-demand development of new materials for specific applications.
- Reduced development cost due to selective experimental alloy development work.
- Cost-effective design of suitable materials with varying alloying element additions.

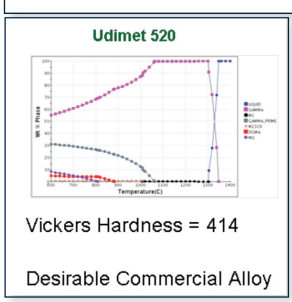


Overall approach for computational design of materials (materials-by-design).

Status

Based on discussions with various companies, exhaust valves were identified as one of the highest priority components. New valve materials are needed to operate at temperatures up to 1,600°F, significantly higher than the current operating temperature of 1,400°F. High temperature fatigue life was identified as a critical property for valve materials at this temperature.

Several candidate Ni-based alloys with the potential to have the required high temperature properties at 1,600°F were identified for further testing and evaluation. Fatigue properties of these alloys have been measured using fully reversed fatigue tests at 1,600˚F. Thermodynamic calculations have been performed to understand the equilibrium microstructures of the alloys as a function of temperature. Detailed evaluation of the microstructures and high temperature mechanical properties of these alloys were carried out to develop a database on the relationship between composition of alloys, microstructures, and high temperature fatigue properties. Computational modeling tools were used to identify an initial set of alternate alloys which could have similar mechanical properties at the desired temperature but would potentially be lower in cost. Microhardness tests in the aged condition show that some of the alternate alloys have hardness values comparable to those of the previously identified alloys (figures at left); further work to characterize the long-term properties of these alloys is under way.



Thermodynamic calculations showing predicted microstructure of two commercial alloys and a newly designed alloy along with microhardness values in the aged condition.

Durability of Diesel Particulate Filters

Background

The advantages of diesel engines are well known: greater fuel efficiency, longer engine life (vs other internal combustion engines), less waste heat (vs other internal combustion engines), and minimal CO emissions. However, the advantages come with a price: increased emissions of nitrogen oxides (NO_X) and particulate matter (PM)—both regulated by the Environmental Protection Agency. Prominent among the technologies for PM control are diesel particulate filters (DPFs). More stringent regulation of PM went into effect in 2007, and efficient DPFs are essential to meeting these requirements.

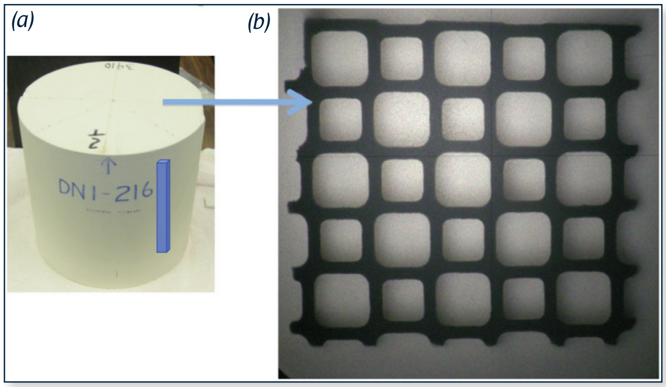
Typically ceramic devices are used as DPFs to collect PM in the exhaust stream. Because ceramics are highly heat resistant, they can withstand the high temperatures of the exhaust, allowing the heat to break down or oxidize the PM inside. DPFs reduce emissions of PM and hydrocarbons by 60% to 90%. Most DPFs consist of a ceramic honeycomb with hundreds of cell passages partitioned by walls. Increasing the porosity of the filter materials can heighten filtration efficiency to more than 90% and reduce gas-flow resistance for better engine performance.

One of the main problems of DPFs is that the trapped PM can eventually clog the filters. The key to the successful application of DPFs, therefore, is to reliably regenerate the filter (i.e., to clean up the PM that the filter continues to trap or collect). There are a number of ways to do this, including both passive and active methods; however, again each of these has inherent problems, some of which can actually damage the filters/ceramic material.

Better understanding of the ceramic materials used in DPFs can lead to better filters and ultimately greater acceptance of diesel engines.

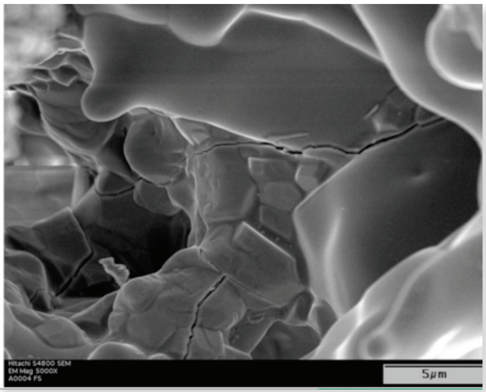
Technology and Status

Techniques to assess the elastic and fracture properties of virgin or unexposed DPF substrates have been identified, implemented, reported, and adapted for new materials and product forms. For example, the asymmetric cell nature of the Al_2TiO_5 based DPF (shown at right) is designed to allow ash to accumulate in the larger channels (inlet side) of the DPF without plugging the channels. This asymmetry resulted in modifications to the corresponding moment of inertia calculations.

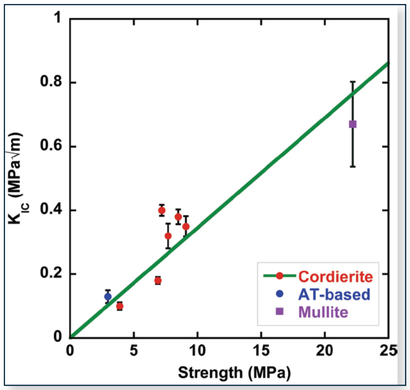


Typical honeycomb DPF: (a) an Al_2TiO_5 based DPF with nominal dimensions of 26.5 by 25.5 cm (D X H); (b) expanded view of the cross section showing two channel sizes. The nominal dimensions of the cells are 1.4 by 1.4 mm and 1 by 1 mm.

The porous (~50%) and microcracked nature of the Al_2TiO_5 (AT-based) dominates the physical properties of these materials (shown below left). The figure below at right shows the fracture toughness, K_{IC}, of three ceramic DPF materials increasing as a function of strength. The strength values were corrected for the moment of inertia of the honeycomb structure for the three materials. Both the fracture toughness and strength increase with decreasing porosity for the cordierite; the lowest and highest strength samples have relative porosities of 68% and 50%, respectively. The mullite based material possessed an unusual microstructure of interpenetrating needles, which results in the high strength and toughness with high porosity (63%).



Scanning electron microscopy micrograph of an Al_2TiO_5 based DPF showing rectangular grains in a porous, microcracked microstructure.



The fracture toughness as a function of strength for three DPF materials.

Benefits

- Better understanding of the microstructure-property relationship of the ceramic materials and its impact on the performance of DPFs.
- Development of new ceramic materials for DPFs.
- Improved DPFs.
- Greater acceptance of diesel engines by the public.

Engine Materials Compatibility with Alternate Fuels

Background

With the experience in Brazil over the past 10 years with fuel blends up to E100[2] and more recent experience in the United States and Europe with fuel blends up to E85, observations of corrosion problems not previously observed with ethanol-free gasoline have begun to accumulate. Like water, ethanol is a proton-bearing medium capable of sustaining electron transfer, so it is potentially corrosive. Absolutely pure ethanol is not generally corrosive toward many metallic engineering materials, but depending on the carbohydrate source and processing variables used in the production and handling of ethanol, contaminants such as water, oxygen, organic acids, and salts can accumulate and lead to general or localized corrosion of a variety of common engine materials. This has been observed, in particular, in the crevice between the aluminum cylinder head and the ferrous alloy valve seat of some engines. In addition, corrosion of fuel pump and fuel injector components and issues with hot corrosion have been reported.

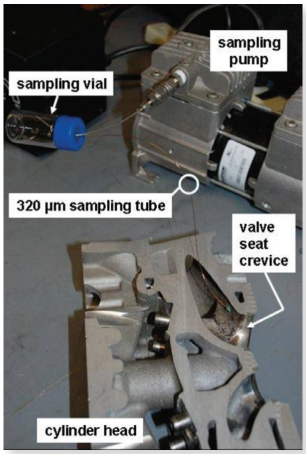
When discussing alternative fuels, the "E" in the E-number stands for "ethanol," and the two digits following stand for the percentage of alcohol in the fuel. For example, E85 = 85% ethanol blended with 15% gasoline; E100 = 100% ethanol; E15 = 15 % ethanol blended with 85% gasoline.

From a potential corrosion perspective, the addition of ethanol to traditional gasoline changes two important fuel properties. Firstly, ethanol is several orders of magnitude more electrically conductive than gasoline, so even small additions of ethanol can substantially increase conductivity and the potential for corrosion problems (including galvanic attack). Secondly, the affinity of ethanol for water (and its associated solubility) is many orders of magnitude greater than the affinity/solubility of gasoline for water, and thus various aqueous corrosion issues may be expected in ethanol fuel blends that are not observed in traditional gasoline.

To conduct a systematic assessment of engine material corrosion in ethanol fuel blends, a Cooperative Research and Development Agreement (CRADA) has been established between participants at ORNL and domestic automobile manufacturers. †

Technology

Information will be gathered to enable development of relatively rapid electrochemical test protocols to assess potential susceptibility to corrosion of engine materials in ethanol fuel blends. Methods to gather information will include advanced surface analysis, comparison of corrosion products formed on actual engine parts to laboratory test specimens, in situ extraction of liquid/gas constituents from behind the valve seat crevice during engine operation, and laboratory corrosion testing of engine material coupons to assess the role of material composition and structure as a function of fuel blend variables.



Proof-of-principle device for sampling gas/liquid from the valve seat crevice region.

Status

Cylinder heads for evaluation of structure and corrosion products have been received and prepared for analysis at ORNL, and microprobe and Auger examinations of surfaces associated with the valve seat crevice are under way.

A proof-of-principle technique for evaluation of the valve seat crevice environment has been demonstrated (above). Cylinder heads for testing are being machined to incorporate the required capillary tube inserts

Autoclave test chambers were specified and procured for use in evaluation of corrosion as a function of ethanol-blend composition–material composition variables. Static testing has been initiated to assess the role of material structure and composition of engine and valve seat materials as a function of fuel blend variables.

Benefits

- Develop a mechanistic understanding of performance boundaries and material selection requirements for engine materials used in flex fuel vehicles.
- Develop a rapid corrosion assessment technique to assess engine material corrosion potential via correlation of forensic analysis (materials returned from actual engine operation) with laboratory corrosion test results.
- Improve the performance of flex fuel vehicles and thus their acceptance.

Materials for Control of Exhaust Gases and Energy Recovery Systems

Background

To meet the 2010 Environmental Protection Agency emission requirements for diesel exhaust, aftertreatment in diesel engines may be necessary and aftertreatment technologies will have to be integrated with engine control systems. Currently, no commercial off-the-shelf technologies are available to meet these standards. Consequently, Cummins Inc. is working to understand the basic science necessary to effectively use aftertreatment catalyst systems. ORNL is assisting with the materials characterization effort. This summary will focus on the study of materials used in ammonia oxidation (AMOx).

Ammonia containing compounds may be added to diesel exhaust to reduce nitrogen oxides (NO_X) to nitrogen gas (N_2), as in selective catalytic reduction (SCR). The reductant reduces NO_X to H_2O and N_2. Excess ammonia is often needed, resulting in ammonia escaping to the atmosphere (referred to as "ammonia slip"). While ammonia slip currently is not regulated, it is a concern, and proactive steps are taken to mitigate even small amounts of ammonia slip by using a selective oxidation catalyst.

Oxidation catalysts are usually present in aftertreatment systems to oxidize ammonia that is not being oxidized upstream by the SCR catalysts. These oxidation catalysts, which ensure that ammonia release to the atmosphere is minimal, are referred to by several names: AMOx catalysts, selective catalytic oxidation catalysts, or ammonia slip catalysts. Candidate catalysts are typically zeolite-based, alumina-supported metal catalysts or alumina-supported metal oxide catalysts. Hydrothermal conditions, temperature, and water content strongly influence the functioning of these catalysts by changing or aging the catalytic materials. These changes and their impact on performance are not well understood.

Technology

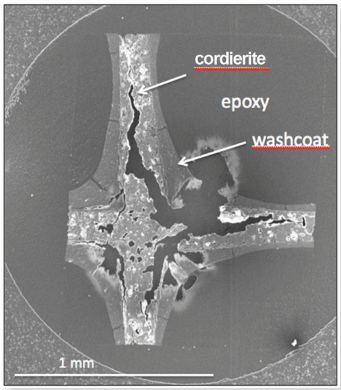
In previous work, both ORNL and Cummins personnel have collaborated to understand various catalysts. The crystal structure, morphology, phase distribution, particle size, and surface species of catalytically active materials supplied by Cummins have been characterized at ORNL using transmission electron microscopy (TEM), x-ray diffraction (XRD), x-ray photoelectron spectroscopy (XPS), and Raman spectroscopy. Several of the above tools were expected to be suitable for characterization of the less understood platinum group metal-containing catalysts such as AMOx catalysts.

The initial plan was to use the above advanced tools to qualitatively (and if possible quantitatively) understand how the oxidation and SCR functions were integrated into the AMOx catalysts. This summary presents the initial results. It is expected that AMOx catalysts can come from all stages of the catalyst's life cycle: as received, calcined, aged, etc., and in the second stage of the project we will analyze field returned or simulated catalysts.

Status

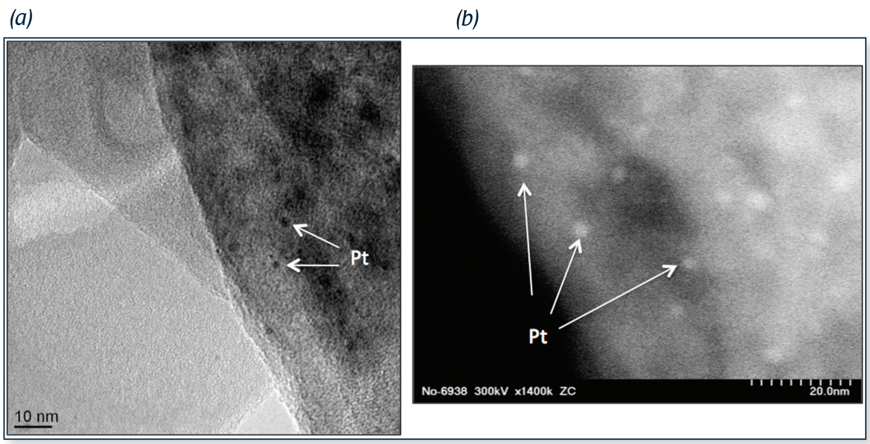
The as-received AMOx catalyst has been characterized using XRD, TEM, and XPS. "Cross" cross-section samples for TEM analysis were prepared by grinding; polishing; dimpling; and, finally, ion-beam milling until the middle of the cross was perforated, providing electron-transparent regions intersecting the cordierite/washcoat interfaces.

The figure at right shows a low magnification secondary electron image of an entire cross, recorded on a Hitachi S-3400 scanning electron microscope purchased and maintained in the ORNL High Temperature Materials Laboratory. It should be noted that the nature of the phases in this sample makes such TEM cross sections extremely fragile. It is not uncommon to lose some of the initial thin regions while handling the samples and loading them into the TEM holder.



Secondary electron image of a typical TEM thin foil specimen showing the cordierite "cross" structure embedded in epoxy. Electron transparent edges at the cordierite interface, center, are imaged at higher magnification in the TEM.

The figures below show a region of the washcoat in bright-field TEM and a higher magnification view of a nearby region in annular dark-field scanning TEM mode. Platinum particles are in bright contrast when imaged in annular dark-field mode. The bright contrast of the nanoparticles is consistent with the higher atomic number of platinum relative to the average atomic number of the washcoat. The effect of hydrothermal conditions on the AMOx catalyst will be characterized next to continue evaluation of the feasibility of the advanced tools available at ORNL for quantitative analysis of the material changes underlying the AMOx catalyst performance degradation with age.



Section of a cross at higher magnification: (a) bright-field image of a region of the washcoat and (b) annular dark-field image at higher magnification showing the nanoparticles in bright contrast, as expected from the higher atomic number platinum species present.

Benefits

- Determination of utility of advanced characterization tools to interrogate AMOx catalysts.
- Greater understanding of the catalyst systems used in diesel exhaust aftertreatment systems and the effects of changes such as aging on their performance.
- Potential improvements to current diesel engine aftertreatment technologies.
- Enhanced ability to meet emission requirements for diesel engines while maintaining performance/energy efficiency.
- Greater acceptance of diesel engines and consequent reduction in petroleum use.

Modeling of Thermoelectric Materials and Devices

Background

Successful implementation of thermoelectric (TE) devices will only result if they are designed to overcome the thermomechanical limitations (e.g., brittleness) inherent in the TE materials that make up their core. A TE material with a combination of low thermal conductivity, high coefficient of thermal expansion, and poor strength can readily fail in the presence of a (needed) thermal gradient thereby preventing the exploitation of the desired thermoelectrical function.

This seemingly insurmountable problem can be overcome with the combined use of established probabilistic design methods developed for brittle structural components, good thermoelastic and thermomechanical databases for the candidate TE materials, and iteratively applied design sensitivity analysis.

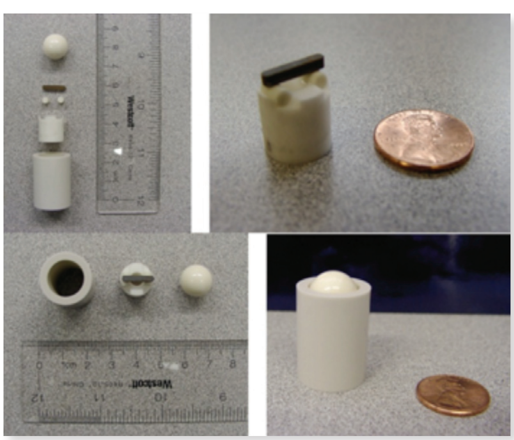
Technology

The use of TE devices is of great interest for potential waste heat recovery in the transportation and industrial sectors. TE devices have been around for decades now; however, current devices have insufficient efficiencies and temperature capabilities for waste heat recovery. Newly developed TE materials offer the potential for improved efficiencies, but their incorporation in devices for (higher temperature) transportation and industrial applications has been hindered by their poor mechanical properties.

ORNL is collaborating with Marlow Industries, Inc., a world leader in the design and manufacture of TE materials, to better characterize these materials. ORNL is responsible for the mechanical evaluation of the candidate high-temperature-capable TE materials that are under consideration and is also assisting in the design optimization of TE devices. The thermomechanical modeling of TE devices in this study provides guidance on what strengths and fatigue resistances of TE materials will be needed for long-term successful operation of TE devices.

Status

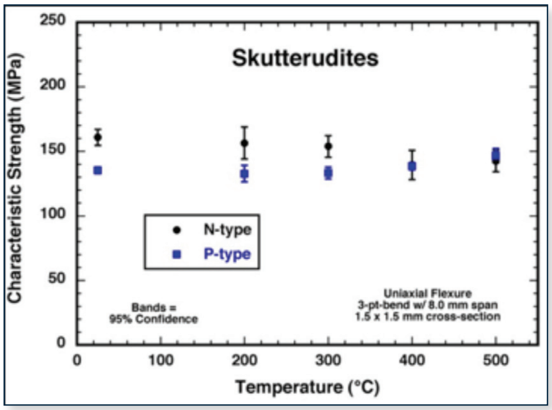
To successfully design TE devices, validated mechanical property databases must be established for the TE materials that compose them, so much of the present work is devoted to that.



Different views of a high temperature bend fixture developed to test small prismatic bars of thermoelectric materials.

A custom designed high temperature fixture is being used for flexure strength testing up to at least 500°C. The fixture, shown at left, is self-contained, has built-in provisions for semi-articulated loading (i.e., passive self-alignment), and is made of an aluminum oxide ceramic. Its simple design allows for rapid insertion and extraction of the test specimen, so high productivity specimen testing can be achieved. Perhaps most importantly, it tests coupons (prismatic bars) whose cross sections would be the same as TE legs used in prospective TE devices. The strengths of high-temperature-capable n- and p-type TE compositions (e.g., skutterudites) are now being quantified using this fixture.

An example of fast-fracture (or inert) strength as a function of temperature for n- and p-type skutterudites is illustrated at right. No statistically significant change in strength occurred between 25°C and 500°C.



Example of measured strength as a function of temperature for n- and p-type skutterudites.

Benefits

- Improved strength of TE materials.
- Better paradigm for community to design TE devices.
- Setting the state for durable high-temperature-capable TE devices.

Modeling/Testing of Environmental Effects on Power Electronic Devices

Background

A complex relationship exists between environment (temperature, humidity, and vibration) and the performance and reliability of the material constituents within automotive power electronic (PE) devices and in support systems. There is significant interest in developing more advanced PE devices and systems that are capable of sustained operation to 200°C for transportation applications (e.g., hybrid electric vehicles, plug-in hybrids). Advances in packaging materials and technology can achieve this but only after their service limitations are better understood via modeling and testing.

Technology

Three key areas need to be addressed to advance automotive PE devices and support systems.

1. Interest exists to operate PE devices up to 200°C for electric and hybrid vehicles. However, many contemporary devices such as insulated gate bipolar transistors cannot sustain continuous operation above 125°C because of limits of their material constituents.

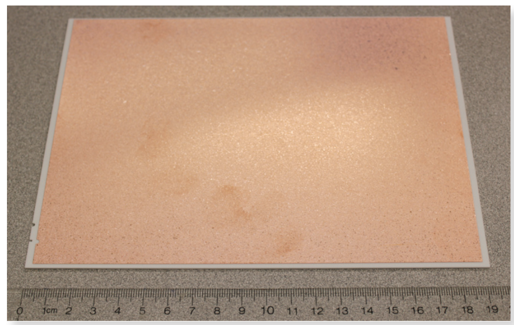
2. Accurate life prediction and accelerated test methods are not available to the PE device community, and this hinders more rapid development of devices. This is critical because advances in PE devices must address needs for greater ruggedness and improved thermal management.

3. Other electronic components in electric and hybrid vehicles (e.g., permanent magnetic materials used in motors) are too expensive or are increasingly scarce. Some could be more efficiently designed to lessen weight and volume. Therefore, identifying and developing alternative material constituents that help overcome those limitations has rationale.

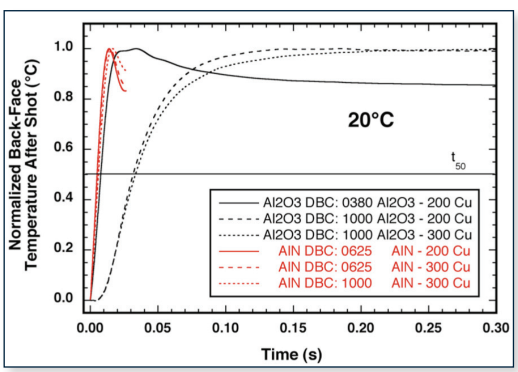
Status

A patent for a "direct cooled ceramic substrate" was published. The development was a consequence of collaboration among the Advanced Power Electronics and Electric Machines and Propulsion Materials Programs and the National Transportation Research Center. Thermomechanical analysis of candidate ceramics was performed using finite element and material strength probabilistic analyses. The analyses were used to iteratively redesign the ceramic substrate until the maximum tensile stress in the aluminum oxide substrate was minimized.

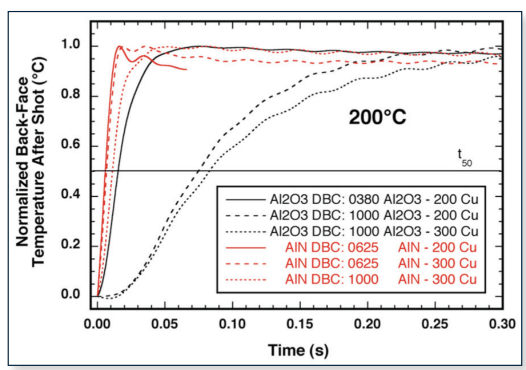
As a second primary effort, the apparent thermal diffusivity and coefficient of thermal expansion of six different direct bonded copper (DBC) substrates were investigated. An example of such a DBC substrate is shown at right. These DBC substrates are the foundation of many PE devices because they are responsible for serving at least two key roles. First, they are a platform for the actual power devices that are attached to them. Second, DBC substrates are a key thermal conduction pathway for the cooling and overall thermal management of those devices.



Example of an aluminum-oxide-containing DBC substrate.



Thermal transfer response at 20°C for several DBC substrates. Numbers in legend represent thicknesses in micrometers of the DBC substrate constituents.



Thermal transfer response at 200°C for several DBC substrates showing slower response than at 20°C. Numbers in legend represent thicknesses in micrometers of the DBC substrate constituents.

The DBC substrates must be able to stand up to long-term thermal cycling and thermal transients, and this project supports the improved understanding of their responses to temperature changes. An example for several different DBC substrates is illustrated in the figures above, where the 200°C thermal responses are shown to be more sluggish than at 20°C. Such temperature-dependent thermal response changes need to be taken into account to optimize the thermomechanical reliability of DBC substrates.

Benefits

- Higher-temperature-capable PE devices.
- More reliable PE devices.
- Alternative methods to achieve improved thermal management in PE devices.

Non-Rare Earth Magnetic Materials

Background

The strategic importance of rare earth elements (REEs) and the associated potential problems are receiving increased attention as a result of their use in permanent magnets for electric motors. Currently there are no alternative permanent magnet materials competitive with $Nd_2Fe_{14}B$ which do not contain REEs. The development of such materials would allow progress toward lowering the cost of electrical propulsion systems toward the performance goals for the Hybrid and Electric Propulsion subprogram set forth by the U.S. Drive Partnership and Vehicles Technologies Program. The usefulness of a permanent magnet material can be characterized by the maximum energy product $(BH)_{max}$. The best rare earth (RE) magnets have energy products of about 50 MGOe. The most competitive non-RE material is AlNiCo, which has an energy product near 10 MGOe. The other most commonly used permanent magnets are ferrites, with energy products limited to about 5 MGOe. Bearing in mind that AlNiCo and ferrites have been studied and optimized for many decades, these numbers suggest that incremental advances in current non-RE permanent magnet materials will not result in the significant improvements required to compete with $Nd_2Fe_{14}B$. Thus, new families of hard ferromagnetic materials are needed.

Technology

Progress is enabled by our combined experience and expertise in solid state synthetic chemistry, materials processing and characterization, and state-of-the-art first principles calculations. Relevant experimental capabilities include arc melting; reactions in vacuum, inert, or reactive atmospheres; numerous single crystal growth techniques; melt spinning; magnetic field annealing; and crystallographic magnetic and thermal properties measurements over a wide range of temperatures and applied magnetic fields.

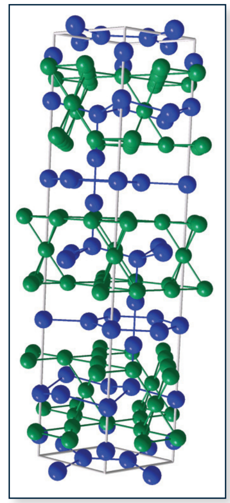
Status

In FY 2010 we began our investigation of RE-free chemical systems for new strong ferromagnets in an effort to identify materials with potential applications in permanent magnet motors. Some understudied known materials have been investigated, and their analysis is ongoing. Assessment of currently used permanent magnet materials indicates that the most likely path toward advanced non-RE permanent magnets is through the investigation of new materials. We believe that the most promising chemical systems will combine light (3d) and heavy (4d or 5d) transition metals in ternary compounds which adopt anisotropic crystal structures. This will allow for strong magnetocrystalline anisotropy in the absence of REEs.

Among known materials, the $(Zr/Hf)_2Co_{11}$-based alloys may hold some promise (at right). However, systematic improvement of properties must await a better understanding of their true compositions, crystal structures, and microstructures. In the end, the cost of cobalt may limit the utility of these materials.

A typical melt-spinning crucible and two melt-spun ribbons of Hf_2Co_{11}-based hard ferromagnetic materials.

The μ-phases typified by W_6Fe_7 (at right) combine several of the targeted attributes (heavy transition metals, light transitions metals, anisotropic structure). The chemical versatility of the structure type suggests that a wide range of behaviors may be expected. To date, only antiferromagnetism has been clearly identified, although hints of weak ferromagnetism have been observed in one ternary system. Further experimentation and theoretical calculations are under way to determine whether good permanent magnet properties are likely to be found in these materials.



μ-phase crystal structure. In the prototype W_6Fe_7, green spheres represent iron atoms, and blue spheres represent W.

The ideas and experience developed in FY 2010 will continue to guide the experimental and theoretical work as the project progresses. The investigation of materials discussed here will continue, as well as the identification of other promising known materials and the search for entirely new RE-free compounds with interesting permanent magnet properties.

Benefits:

- Understanding magnetocrystalline anisotropy in non-RE ferromagnets will benefit efforts to design alternative materials for permanent magnet motors.

- The availability of lower cost alternative permanent magnet materials would allow progress toward lowering the cost of electrical propulsion systems toward the performance goals of $12/kW by 2015 and $8/kW by 2020 for the Hybrid and Electric Propulsion subprogram set forth by the DOE Vehicles Technologies Program.

Titanium Friction and Wear: Surface Engineering of Connecting Rods and Other Bearing Components

Background

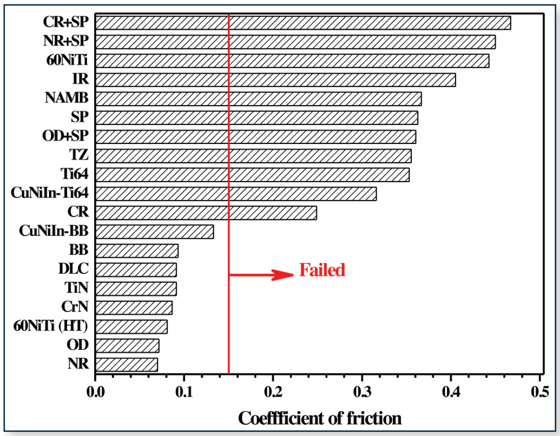
Titanium (Ti) alloy parts are strong, corrosion-resistant, and lighter weight than similarly sized steel or cast iron parts. Once used mainly in aerospace, Ti's applications have expanded into areas like human joint replacements, dental implants, sports equipment, and industrial machinery. Recent developments in processing Ti raw materials by nontraditional routes promise to make its alloys more affordable for use in fuel-efficient heavy vehicles to achieve the targeted 50% increase in freight efficiency (measured in ton miles per gallon).

Despite their advantages, Ti alloys also have a propensity for scuffing, galling, and adhesive wear. Lubricant formulations that were designed for ferrous alloys do not work for Ti surfaces. This project attacks those shortcomings through surface engineering. The objective is to enable new opportunities to use lightweight Ti alloys for pistons, cam shafts, crank shafts, tappet shims, fuel injector needles, and connecting rods containing integral bearing surfaces instead of traditional inserts.

Technology

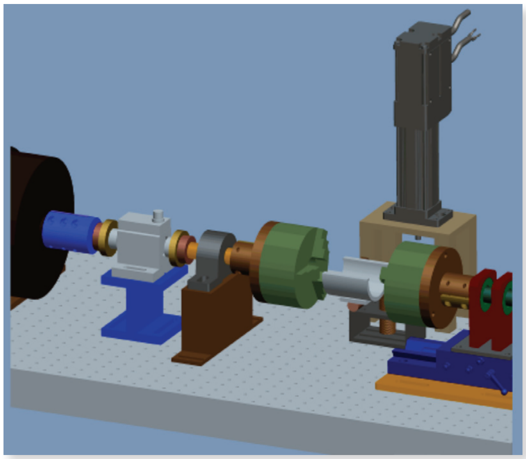
A three phase approach is being undertaken: phase I, selection and bench testing of candidate surface engineering treatments and coatings; phase II, design and use of a simulator to impart variable loads, as would be seen by a connecting rod bearing; and phase III, presentation of a design concept for a full-scale prototype Ti connecting rod with engineered bearing surfaces.

Phase I was completed in FY 2010 with the selection, testing, and evaluation of 20 different combinations of bulk materials, surface treatments, and hard or soft coatings. Some were commercial treatments or coatings, but others were experimental and not yet commercialized. Friction and wear tests were performed following an American Society for Testing and Materials standard (G133) whose prior development was supported by the DOE Office of Energy Efficiency and Renewable Energy, Vehicle Technologies Program. The suite of tests, which is described in detail in a paper accepted for the 2011 International Conference on Wear of Materials, was performed using engine-conditioned diesel oil to better replicate the conditions in engines. Criteria for passing these tests was based on a friction coefficient of less than 0.15 and acceptable wear rates of both the slider (bearing steel) and the treated Ti coupon. Friction data are shown in the top figure at right. Copper based traditional bearing bronze was used as a reference material. The most promising treatments, down-selected for further investigation in phase II, were a diamond film, titanium nitride coating, chromium nitride coating, heat treated nickel titanium alloy, oxygen-diffusion-treated Ti, and nitrided Ti.



Average friction coefficient for various surface engineering treatments showing the pass/fail limit established for the project.

In preparation for phase II in FY 2011, a computer-controlled apparatus that simulates the variations in loading condition, like those for a bearing in a connecting rod, was designed. A schematic diagram of the apparatus is shown at right.



Schematic diagram of the variable-loading bearing materials system being built at Oak Ridge National Laboratory for use in phase II of this effort.

Status

Phase 1 work, which involved friction and wear screening studies of 20 variants of commercial and precommercial surface engineering processes for Ti alloys, has been completed. We have completed the design and begun the construction of a unique computer controlled variable-load bearing material testing system. This will be used in phase II to simulate the friction and wear conditions in plain shell-type bearings like those used in diesel engine connecting rods.

Benefits

- Enables the use of Ti based alloys in engine components involving rubbing contact.
- Provides friction and wear data to engine designers to aid their selection of materials and surface treatments.
- Contributes to the advancement and understanding of the application of duplex surface engineering approaches to enable expanded use of difficult-to-lubricate and normally high-wearing lightweight materials.

Thermoelectric Materials: Theory and Structure

Background

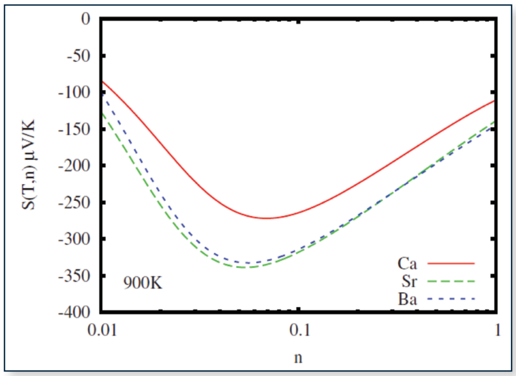
Advanced thermoelectric materials with improved performance can be used for recovering waste heat in engine exhaust and reducing fuel consumption. However, identifying and optimizing such materials have been barriers to their broader application. Theoretical methods based on first principles calculations and transport theory have been developed at ORNL. These have been applied to determine the potential performance of materials under consideration and to pinpoint the chemical composition ranges where high thermoelectric performance can be found. Such studies have been used to map out the doping level dependence of the thermopower in both oxide and nonoxide thermoelectric materials. For example, the temperature and doping-level dependence of the thermopower in La_3Te_4 were calculated to determine whether this high performance high temperature material could be modified for use at the lower temperatures needed for vehicular applications. In this case, the answer was no, with the result that much experimental effort was saved. More recently this approach has been applied to oxides, skutterudite phases, PbTe, PbSe, and other promising thermoelectric materials.

Technology

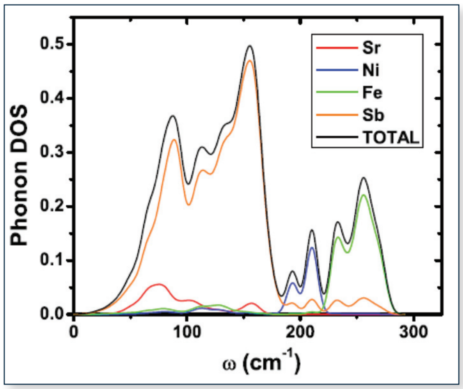
These studies are made possible by state-of-the-art density functional codes including in-house linearized augmented plane wave codes; new density functionals that yield greatly improved electronic structures over older more standard versions; and a transport code, called BoltzTraP, that was codeveloped by ORNL and the University of Aarhus. These codes, run on ORNL computer facilities, allow studies of complex next generation thermoelectric materials.

Status

Work on PbTe showed that this material can have very high thermoelectric performance without doping with the highly toxic element thallium. This finding is important because previously the highest performance PbTe was doped with a substantial amount of thallium. It was found that thallium was needed only because it can be incorporated at suitable levels. Following the ORNL calculations, groups at the University of Illinois and the California Institute of Technology have reported that indeed PbTe heavily codoped with nontoxic elements such as sodium and potassium has similar performance to thallium doped material at temperatures relevant for vehicular waste heat recovery. Further work showed that at least for p-type compositions, which constitute half of the material in a thermoelectric generator, it may be possible to replace the costly element tellurium with less costly selenium while at the same time improving high temperature performance. Work on skutterudite materials showed that high performance could be achieved using alkaline-earth-filled compositions based on iron and nickel in addition to the more common rare-earth-filled cobalt based material (see below). This is of importance because it may offer a way to improve performance and also because it allows the elimination of rare earth elements and replaces cobalt with less costly nickel. The development of these methods and ways of applying them to new classes of thermoelectric materials is ongoing. In the long run, this approach offers the potential for greatly shortening the materials development cycle for thermoelectrics and providing high performance compositions for waste heat recovery.



Calculated 900 K thermopower of n-type alkaline earth filled Fe-Ni skutterudites as a function of doping. The p-type (not shown) is similarly favorable.



Vibrational density of states for skutterudite $SrFe_3NiSb_{12}$ showing the effect of alkaline earth filling.

Benefits

- First principles studies provide understanding of the mechanisms for high thermoelectric performance and the compositions in which it can be realized.
- Doping and composition dependent studies help guide experimental work optimizing advanced thermoelectrics to realize their full potential performance.
- Theoretical modeling points out substitutions to eliminate toxic or costly elements while maintaining materials performance.

Ultrahigh-Resolution Electron Microscopy for Catalyst Characterization

Background

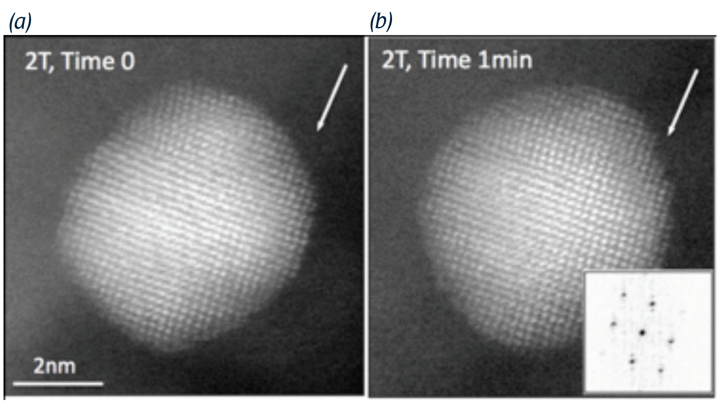
Ultrahigh-resolution electron microscopy is making important contributions to understanding atomic-level mechanisms that control the behavior and performance of catalytic materials. Fundamental imaging studies of the distribution of catalytic species down to the level of single atoms on oxide substrates (e.g., platinum on a variety of aluminas) are being coupled with concurrent computational and modeling studies and with research on the same materials using several indirect spectroscopic methods such as nuclear magnetic resonance. ORNL is partnering with other national laboratory collaborators (e.g., Pacific Northwest National Laboratory), and university/industry partners (e.g., Michigan/Ford) to use these capabilities for studies of catalytic materials and reactions leading to improved automotive catalysts.

Technology

Our work is furthering catalyst studies with our partners through the development of innovative new capabilities for treating catalytic materials in situ at elevated temperatures and under reactive gas conditions, allowing atomic-level imaging in the aberration-corrected electronic microscope that elucidates mechanisms of catalyst behavior. Working with industry partner Protochips Co. (Raleigh, North Carolina), which provides unique microelectromechanical systems based heater devices (called Aduro) that are adaptable to electron microscope holders, we have fabricated a holder using an Aduro device in a second generation Gen2 design environmental cell, or "E-cell," for reaction studies and another holder that allows a second tilting action (double-tilt) to allow precise orientations of crystalline samples along with heating capabilities.

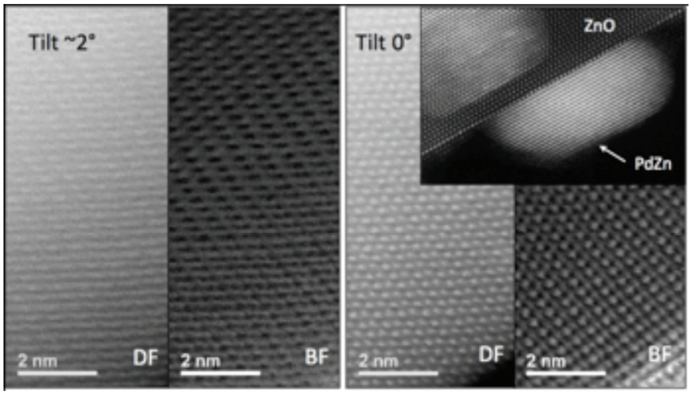
Status

The Gen 2 E-cell has shown the ability to image catalyst crystal structure at gas pressures up to 20 Torr and at temperatures of 700°C (1,000°C achievable). A gold nanoparticle on an iron oxide support material is imaged at 2 Torr and 500°C in the cell images shown below. These dark-field images recorded at a direct magnification of 10 Mx show the development of surface facets (arrowed) with time at temperature and the 2.04 Å lattice structure of the gold perfectly resolved.



Gold nanoparticle on iron oxide support imaged at 500°C with 2 Torr reducing gas pressure in Gen 2 E-cell: (a) initial condition; (b) after 1 minute at elevated temperature. Note formation of atomic ledges with time at temperature. Original magnification of 10 Mx shows stability of E-cell holder.

The figure shown below compares dark-field–bright-field image pairs before and after using the double-tilt capability to achieve a perfect orientation on a ZnO single-crystal catalyst support. A small mis-tilt of as little as 2 degrees distorts the crystal structure image, whereas the near-perfect alignment allows clear resolution of atomic columns. The importance of this capability is clear in the inset image, which shows PdZn nanoparticles epitactically aligned on a similar ZnO single-crystal support, allowing information about the nanoparticle-support interface to be elucidated



Dark-field (DF)–bright-field (BF) image pairs before (left) and after (right) correcting for ~2° mis-tilt of ZnO single-crystal catalyst support. Inset shows PdZn nanoparticles in epitactical orientation on similar ZnO single crystal.

Benefits

- Sub-Ångström resolution microscopy provides unique information leading to fundamental understanding of how catalysts behave at the atomic level.
- Future work using E-cell technology to understand catalyst reactions such as oxidation-reduction cycles that control the behavior of "intelligent catalysts" for NO_X reduction applications.
- Attraction of top catalyst researchers in the country eager to collaborate with the U.S. Department of Energy.

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