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Washington, DC 20585-0121**

**FY 2004**

**Progress Report for Automotive Propulsion  
Materials Program**

**Energy Efficiency and Renewable Energy  
Office of FreedomCAR and Vehicle Technologies**

**Edward Wall                      Program Manager**

**February 2005**



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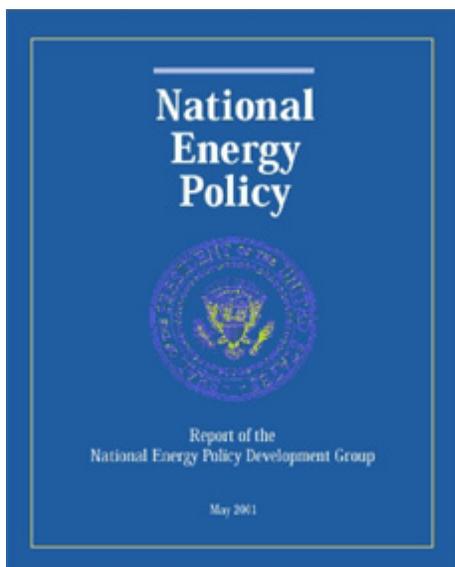


## 1. INTRODUCTION

### **Automotive Propulsion Materials R&D: Enabling Technologies to Meet FreedomCAR Program Goals**

The Department of Energy's (DOE's) Office of FreedomCAR and Vehicle Technologies (OFCVT) is pleased to introduce the FY 2004 *Annual Progress Report for the Automotive Propulsion Materials Research and Development Program*. Together with DOE national laboratories and in partnership with private industry and universities across the United States, the program continues to engage in research and development (R&D) that provides enabling materials technology for fuel-efficient and environmentally friendly light-duty vehicles.

This introduction summarizes the objectives, progress, and highlights of the program in FY 2004. It also describes the technical barriers remaining and the future direction of the program. The FY 2004 annual progress reports on *Combustion and Emission Control for Advanced CIDI Engines* and *Power Electronics* provide additional information on OFCVT's R&D activities that support the development of propulsion materials technology.



**Report of the National Energy Policy  
Development Group**

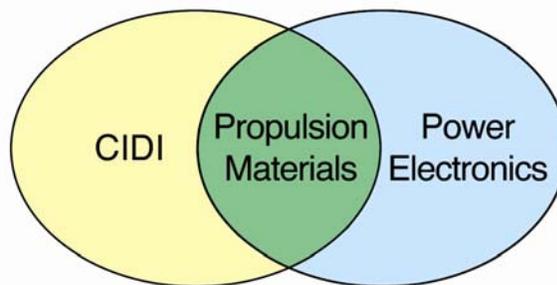
In May of 2001, the President's National Energy Policy Development Group published the National Energy Policy (NEP). This comprehensive energy policy specifically addresses the development of energy-efficient vehicle technologies, including hybrid systems, advanced emission control technologies, fuel cells, and hydrogen-based systems. The NEP is a strong indicator of the continuing federal support for advanced automotive technologies and the materials work that supports them.

The Automotive Propulsion Materials (APM) R&D Program has supported the FreedomCAR Program since its inception. FreedomCAR is not an automobile or prototype but rather a new approach to developing the technologies for vehicles of the future. In research areas where industry views the risks as too high and uncertain, the FreedomCAR Program conducts long-term research, development, and demonstration activities that bring the technology to a stage of maturity such that industry can undertake the final commercialization stages.

The APM Program is a partner with the OFCVT programs for Power Electronics and Electric Machines and for Combustion and Emissions Control for Advanced CIDI Engines. Projects within the APM Program address materials concerns that directly impact the critical technical barriers in each of these programs—barriers such as thermal management, emissions reduction, and reduced manufacturing costs. The program engages only the barriers that involve fundamental, high-risk materials issues.

## Enabling Technologies

The APM Program focuses on enabling materials technologies that are critical in removing barriers to the power electronics and compression-ignition, direct-injection (CIDI) engine and emissions control research programs. The program supports these two core technology areas by providing materials expertise, testing capabilities, and technical solutions for materials problems. The component development, materials processing, and characterization that the program provides are enablers of the successful development of efficient electric drive systems and emissions-compliant CIDI engines.



**The Propulsion Materials Program focuses on two applications.**

Thermal management is a crosscutting engineering issue that affects both the power electronics and CIDI programs. The components necessary for high-fuel-economy, low-emission hybrid electric and fuel cell vehicles require that power electronics be smaller and lighter and operate at higher temperatures than those for conventional vehicles. These requirements are being addressed by developing electronic materials (i.e., materials for low-cost dc bus capacitors) that operate at higher temperatures and by improving the capability to dissipate heat generated in electronic devices. The APM Program has been addressing electric drive system heat dissipation issues through the development of advanced carbon foam technology.

Current CIDI engines must strike a delicate balance between high efficiency and low tailpipe emissions. CIDI engine and aftertreatment system development will greatly benefit from the Program's efforts to develop improved engine components and subsystems. The APM Program featured a project to develop technology to produce very small (~50 micron) orifices for fuel injectors used in high-pressure common rail systems. The smaller orifices can enable better control of fuel atomization that will increase efficiency and reduce emissions. An exploratory study was initiated in FY 2004 at Pacific Northwest National Laboratory (PNNL) to determine the frictional behavior of metals—like those used in fuel injectors—in the hydrogen environment of a hydrogen internal combustion engine or fuel cell. The friction and wear characteristics of metallic materials depend largely on surface oxide films. However, a hydrogen environment is chemically reducing, so the loss of the surface oxide by wear will result in bare surface contact and an increase in friction and wear. The Program is also working to reduce emissions through the development of advanced particulate filters.

A new project was also initiated to develop a low-cost, higher-temperature polymer electrolyte membrane (PEM) capable of operating at 120°C without significant degradation due to CO poisoning. This is a collaborative project between Oak Ridge National Laboratory (ORNL), The University of Tennessee, and The University of Southern Mississippi. Funding for this project will be provided for one year only; if successful, the project will be transferred to the Office of Hydrogen, Fuel Cells, and Infrastructure or to private industry.

## Collaboration and Cooperation

As with other programs under FreedomCAR, collaboration and cooperation across organizations is a critical part of the APM Program. Throughout the FreedomCAR Program, scientists at the national laboratories are collaborating with manufacturers to identify and refine the materials characteristics necessary for meeting system performance requirements. Researchers at Lawrence Livermore National Laboratory (LLNL) are

working with Ford Motor Company and ORNL to develop low-cost, rapid-response nitrogen oxides (NO<sub>x</sub>) sensors that can be used in feedback control loops to monitor and minimize NO<sub>x</sub> emissions from diesel engines. There is also cooperation among national laboratories to take advantage of the expertise of each facility. ORNL and Argonne National Laboratory, for example, are collaborating in the development of higher-strength NdFeB permanent magnets that will enable significant reductions in the size, weight, and cost of electric motors used in hybrid vehicles. In another project, ORNL is characterizing ~5-micron-thick polymer films that are being developed by Sandia National Laboratories (SNL). SNL is funded by the Power Electronics Program to develop smaller, higher-temperature dc bus capacitors. SNL is using the information provided by ORNL to optimize the properties of the films in order to minimize manufacturing defects during capacitor winding. These electric drive system projects in turn are regularly reviewed by the EE Technical Team of the U.S. Council for Automotive Research to get feedback on research direction and progress.

**Contractor-industry collaboration**

Technology	Industrial partner
Capacitors	✓ TPL, Inc.
	✓ Brady Corporation
	✓ Steiner Film, Inc.
	✓ AVX, Inc.
	✓ Custom Electronics
Magnets	✓ IAP, Inc.
	✓ Magnaquench, UG, Inc.
	✓ Ability Engineering Technology
	✓ Electron Energy Corporation
	✓ Bronson and Bratton, Inc.
Carbon foam heat sinks	✓ Ford Scientific Research Laboratory
	✓ DaimlerChrysler
	✓ General Motors Corporation
	✓ Delphi
	✓ Visteon
Fuel injectors	✓ Siemens, USA
	✓ Siemens, AG
	✓ Navistar/International Harvester
	✓ Imagineering Finishing Technologies
NO <sub>x</sub> sensors	✓ Ford
	✓ Cummins Engine Company
	✓ Detroit Diesel
	✓ Honeywell
	✓ DuPont
Particulate traps	✓ Ford-Jaguar
	✓ GE Locomotive
	✓ Ahlstrom Paper
	✓ Tennaco Automotive
	✓ Arvin Meritor

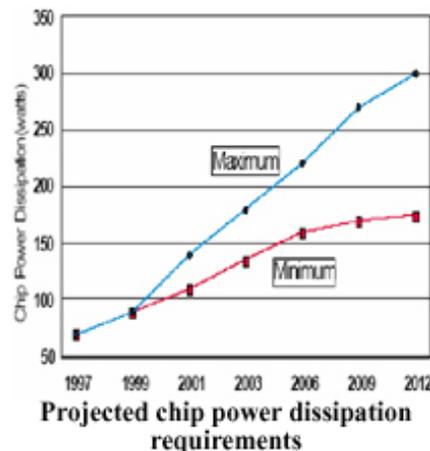
In addition to participation by national laboratories and large industries, the FY 2004 APM Program included important R&D conducted by a small business. Industrial Ceramic Solutions, LLC (ICS), located in Oak Ridge, Tennessee, is developing a ceramic filter to reduce particulate emissions from diesel engines. As in the collaborative efforts of national laboratories with industry, researchers at ICS are working closely with representatives from DaimlerChrysler, Ford, General Motors, and ORNL to develop a filter that will meet the emissions targets of the program.

**Accomplishments**

FY 2004 featured significant advancements in both materials program areas. The following section highlights some of these noteworthy accomplishments.

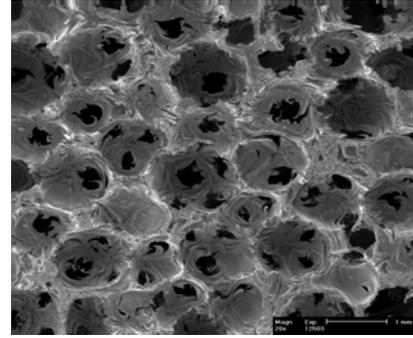
**Power Electronics**

High-power electronic components such as power modules and computer chips being developed for hybrid electric and fuel cell vehicles have ever-growing power requirements (see the graph). Dissipation of the heat generated by these devices in hybrid electric vehicles often requires an additional cooling loop and water-cooled heat sink to prevent overheating and failure of the devices. The increasing power requirements of electronic devices require that more-sophisticated heat sinks be developed to keep the temperature of the electronics below about 120°C. High-thermal-conductivity,



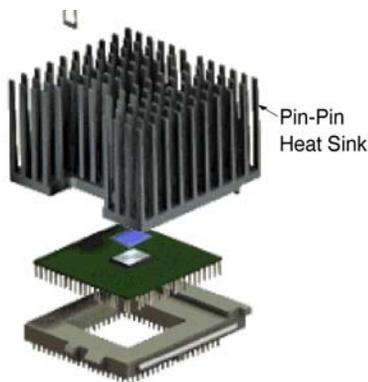
high-surface-area carbon foam is an innovative new material that offers great potential for advanced heat sinks and heat spreaders.

Porous carbon foam developed at ORNL has an extremely high specific conductivity and an interconnected internal structure that potentially will allow reduction of the thermal resistance of heat transfer devices. Measured cooling rates from a prototype air-water radiator made of carbon foam fins confirm that it can reduce the air-side thermal resistance. During FY 2003/2004, a thermal engineering model to represent heat transfer from porous carbon foam was developed for use in design processes for heat exchangers with finned tubes. Characteristic parameters for carbon foam geometries—exposed surface absolute roughness, exposed surface area factor, effective thermal conductivity, surface-area-to-volume ratio and permeability—are calculated with a simple geometric model of a unit cube with a spherical void surrounded by carbon-foam ligaments. The air-side thermal resistance is calculated with an engineering model derived from conventional correlations that are extended to represent the effects of the rough, porous foam.

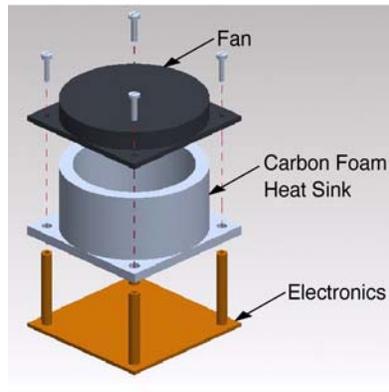


**Graphite foam material developed at ORNL**

During FY 2004, the use of a similar engineering model developed at the University of Western Ontario and tested at ORNL led to the consideration of an alternative design in which all of the cooling air is forced through a thin cylinder of foam (see heat sink designs). Calculations predict that this simple configuration should dissipate approximately 2× the heat dissipated by conventional heat sinks and aluminum foam devices of similar design. Prototype devices will be built and tested in FY 2005 to verify the designs. Subsequently, it appears that the continued use of models to investigate and develop new carbon foam configurations will be valuable in meeting the increased demand for higher, more efficient heat dissipation.



**Conventional heat sink for computer CPU**



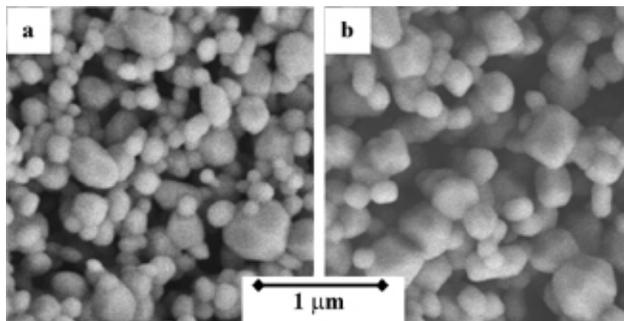
**Alternative configuration for carbon foam CPU heat sink**

**Advanced Combustion Engine and Emissions R&D**

In addition to particulate emissions, NO<sub>x</sub> gaseous pollutants in tailpipe emissions are becoming increasingly regulated. Reduction of NO<sub>x</sub> emissions is an important issue for both CIDI and lean-burn gasoline engines. Several technologies are being developed to reduce NO<sub>x</sub>

emissions, including the lean NO<sub>x</sub> trap and urea injection systems. Regardless of the method used, accurate and durable NO<sub>x</sub> sensors will be needed for on-board diagnostics to monitor NO<sub>x</sub> exhaust levels and for feedback engine control systems to minimize NO<sub>x</sub> emissions. Electrochemical solid state NO<sub>x</sub> sensors based on oxide ceramics are being developed at LLNL in collaboration with ORNL and Ford. Prototype sensors have shown initially promising sensing characteristics, and ongoing work is being performed to demonstrate the viability of the sensor concept.

Work conducted at LLNL during FY 2004 concentrated on evaluating and characterizing the aging process for the sensors. The sensors use yttria-stabilized zirconia, an oxygen-ion-conducting ceramic, for the electrolyte and porous metal oxides for the electrodes. Scanning electron microscopy (SEM), X-ray



Typical electrode microstructures (a) before and (b) after aging.

diffraction (XRD), and X-ray photoelectron spectroscopy (XPS) have been used to evaluate the changes occurring within the electrode materials, and at the electrode/electrolyte interfaces, after extended operation. SEM and XRD indicate coarsening of the electrode microstructure driven by the electrochemical process. This is shown in the figure at left, where there is clearly a larger average particle size after aging. XPS shows changes in the surface stoichiometry of the electrode material. These changes in the electrodes can cause drifting of the sensor response during the first 50–100 hours of operation, implying a minimum

“burn-in” that must be achieved before the sensors can provide stable results. Ongoing work is directed toward developing a better understanding of this aging process, longer-term aging effects, and sensing mechanisms.

### High-Temperature Polymer Electrolyte Membrane

Robust, highly conductive, and inexpensive, PEMs allow practical and reliable fuel cell operation at elevated temperatures. The performance of fuel cells is currently limited at temperatures higher than 90°C because of CO and peroxide formation. The use of polymeric membranes able to operate at 120°C would deter CO adsorption, but polymeric membranes are expensive, exhibit limited thermal stability, and are not well suited for high-humidity operation above 100°C. The current benchmark PEM material, Nafion<sup>®</sup>, is a perfluorinated copolymer with sulfonation to promote water retention and proton conduction, but its conductivity performance drops with increasing temperature and decreasing relative humidity. Furthermore, as a proprietary, fluorinated material, it is relatively expensive. The production of hydrocarbon-based polymers for PEM materials is critical to the development of marketable high-performance membranes.

ORNL and University of Tennessee collaborators have synthesized two new classes of materials for potential PEM applications. Poly(phenylene sulfonate) has been synthesized into a thin-film configuration that demonstrates outstanding thermal stability and resistance to inexpensive conventional processing techniques, such as hot-pressing. A fluorinated, sulfonated copolymer of methyl styrene and cyclohexadiene has also been developed that exhibits high thermal stability and improved workability. The application of these materials can prepare the way for energy-efficient fuel cell vehicles by providing thermal and chemical stability under system operating conditions, improved humidity performance through use of functional modifiers, and low-cost processing of non-fluorinated polymers into thin-film configurations.



Thin-film membrane samples of crosslinked, sulfonated poly(phenylene sulfonate) (left) and a fluorinated copolymer of methyl styrene and sulfonated cyclohexadiene (right).

### Future Direction

The APM Program will continue to work closely with FreedomCAR partners and industry to understand requirements related to propulsion materials. Building upon the recent advances in materials technologies, many of this year’s projects will be moved out of the laboratory and over to industry for testing. For example, ICS will work with identified strategic manufacturing partners in the automotive industry to move the durability and soot-holding capacity performance of the diesel

particulate filter cartridge into compliance with the system requirements of automotive original equipment manufacturers. LLNL, Ford, and ORNL have formed a partnership to develop and prototype a NO<sub>x</sub> sensor and control system to control the operation of NO<sub>x</sub> traps and engine emissions. Other projects will continue to refine manufacturing requirements and necessary characteristics to meet the challenges of the FreedomCAR program.

As advanced automotive technology developments uncover new challenges, the APM Program will continue to provide breakthrough technology solutions through collaboration with industry, FreedomCAR partners, national laboratories, and small businesses.

### **Project Abstracts**

The remainder of this report communicates the progress achieved during FY 2004 under the APM Program. It consists of nine abstracts of national laboratory projects—four that address power electronics, four that address combustion and emission technologies, and one that addresses advanced PEMs. The abstracts provide an overview of the critical work being conducted to improve these systems, reduce overall cost, and maintain component performance. In addition, they provide insight into the challenges and opportunities associated with advanced materials for high-efficiency automobiles.

Rogelio Sullivan

A handwritten signature in cursive script that reads "Rogelio Sullivan".

Team Leader, Materials Technologies  
Office of FreedomCAR and Vehicle Technologies  
Energy Efficiency and Renewable Energy

## 2. Power Electronics

### A. Low-Cost, High-Energy-Product Permanent Magnets

*Y. S. Cha and John R. Hull*

*Energy Technology Division, Bldg. 335*

*Argonne National Laboratory, Argonne, IL 60439*

*(630) 252-5899; fax: (630) 252-5568; e-mail: yscha@anl.gov*

*DOE Materials Technologies Team Leader: Rogelio Sullivan*

*(202) 586-8042; fax: (202) 586-1600; e-mail: rogelio.sullivan@ee.doe.gov*

*ORNL Technical Advisor: David Stinton*

*(865) 574-4556; fax: (865) 241-0411; e-mail: stintondp@ornl.gov*

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*Contractor: Argonne National Laboratory, Argonne, Illinois*

*Prime Contract No.: W-31-109-Eng-38*

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#### Objective

- Develop a low-cost process to fabricate anisotropic NdFeB permanent magnets (PMs) with an increase of up to 25% in energy product to enable significant size and weight reductions in traction motors for hybrid vehicles.

#### Approach

- Use high fields of superconducting solenoids to improve magnetic grain alignment while pressing compacts for sintering, thus producing higher-performance magnets.
- Develop an automated press system, including the superconducting magnet, for the fabrication of NdFeB PMs.
- Fabricate near-final-shape PMs for cost reduction.
- Characterize, compare, and correlate engineering and microscopic magnetic properties of magnets processed under varying conditions.
- Conduct economic analysis of the automated superconducting PM fabrication system and compare with the conventional system.

#### Accomplishments

- Modified the hydraulic system for more precise indication and control of initial pressure during compact pressing.
- Procured and installed a new glove box for better oxygen control and operation during pre- and post-compact pressing and alignment.
- Fabricated near-final-shape powdered compacts under various alignment fields (1 to 8 Tesla) for L/D ratios of less than 0.25.
- Completed the conceptual design of a semi-automated superconducting PM fabrication system.
- Completed the economic study (comparison of superconducting and conventional systems).

## Future Direction

- Continue to work with industrial partners on sintering and annealing the compacts and on measuring the magnetic properties of the PMs.
  - Improve the success rate of making compacts with L/D ratios of less than 0.25. The approach includes considering (1) a vacuum powder-filling system and (2) compact ejection under pressure; both may help to alleviate the cracking problems.
  - Finalize the conceptual design of the superconducting fabrication system, including powder-filling and compact ejection systems.
  - Fabricate compacts with shapes other than a circular disk.
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## Introduction

The strength of sintered NdFeB magnets greatly depends on the method by which the compact is magnetically aligned and pressed. Large blocks can be made by cold-isostatic pressing that are within 5% of their theoretical maximum; but these must be sliced, diced, and ground to final shape, making the magnets very expensive. Magnets that are axial-die-pressed and sintered to near-final shape are the least expensive to make, but they have magnetic properties farthest from their theoretical maximums. The current industry goal is to fabricate higher-energy-product magnets by near-net-shape processing to avoid expensive machining operations. The major objectives of this project are to increase the energy product of the sintered PMs by 10 to 15% (to within ~10% of the theoretical maximum) and to develop low-cost methods of production for high-energy-product, near-final-shape PMs. The higher-performance magnets will replace ones made by traditional powder metallurgy processing and will enable significant size and weight reductions in traction motors for hybrid vehicles.

## Approach

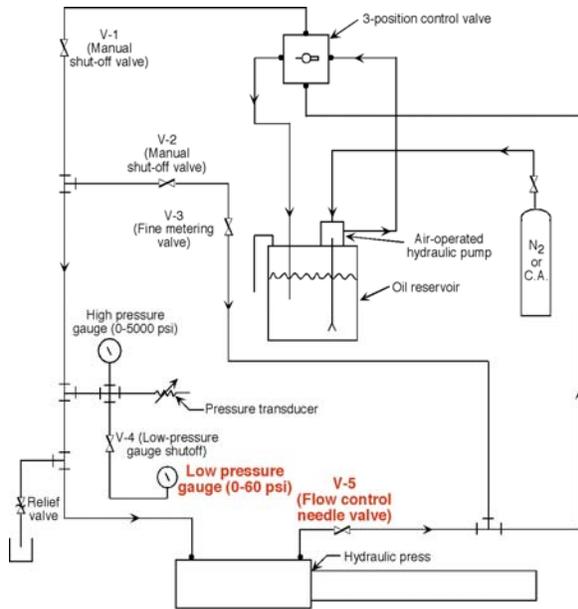
Our approach is to align the NdFeB powder in a superconducting magnet, which can generate magnetic fields much higher than those generated by the electromagnets presently used in industry. Alignment of the powder in these higher magnetic fields improves the properties of the PMs. To develop a low-cost mass-production method for high-energy-product PMs, we plan to design, fabricate, and demonstrate a semi-automated axial-die-press system for making near-final-shape NdFeB PMs.

Previously, a 9-T superconducting solenoid was procured and made operational. Production-grade magnet powder was obtained from Magnequench UG. The 3- to 5-micron single-crystal grains of powder were aligned and compacted at Argonne National Laboratory (ANL). Then the anisotropic compacts, with their grains mechanically locked in place, were returned to Magnequench UG for sintering, annealing, machining, and measuring engineering magnetic properties. Finally, selected PMs were sent to Oak Ridge National Laboratory (ORNL) for measurement of microscopic properties and texture (the alignment of the crystals' easy magnetic axes).

Previously, we demonstrated that significant improvement of energy product (10–15%) can be achieved by using higher alignment fields (>2 T).<sup>1</sup> Industry considers an improvement in energy product of as little as 3–5% compared with current PMs to be significant. The progress achieved so far is based on a batch process at ANL. Major issues remaining for acceptance of the technology by industry are (1) to demonstrate that PMs can be made at a much faster rate than in the batch process, (2) to demonstrate that near-final-shape PMs can be processed, resulting in greater cost reduction, and (3) to demonstrate that the superconducting magnet and its associated press systems are economically feasible by conducting an economic analysis.

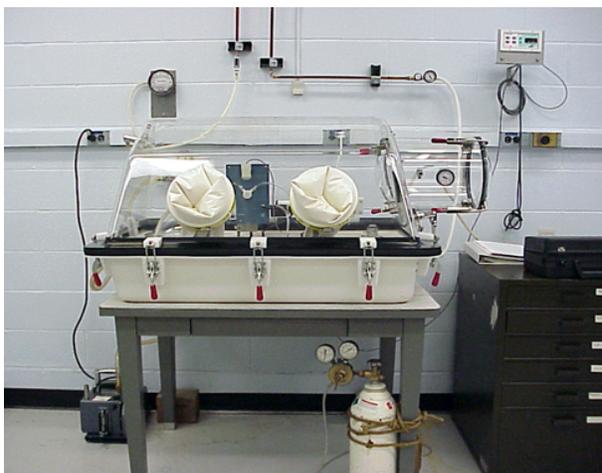
## Results

In FY 2004, we modified the hydraulic loop for better indication and control of the pressure during the initial stage of the compact pressing operation. As shown in Figure 1, we installed a low-pressure gauge upstream of and a needle control valve downstream of the press tube. These modifications allowed better pressure control and resulted in smooth



**Figure 1.** Schematic diagram of the modified hydraulic system. The low-pressure gauge and the needle control valve are installed for better pressure indication and control.

(less pressure fluctuation) operation during the early stage of the pressing. We believe that it is very important to remove the trapped air from the powder; otherwise, the compact is likely to crack when it is ejected from the die. Sufficient time and a passage-way must be provided to allow air to escape from the die before the powder is completely pressed into the final compact. We also procured a new glove box, shown in Figure 2, for better control of oxygen during pre- and post-compact-press operation. The new glove box can provide an environment with less



**Figure 2.** New glove box for better oxygen control during pre- and post-compact-press operation.

than 300 parts per million of oxygen, which is needed to avoid oxidation of the powder and degradation of the magnetic properties of the PM. This is particularly important for the laboratory environment at ANL because the compacts will be stored in the glove box for an undetermined period before shipping to Magnaquench for sintering.

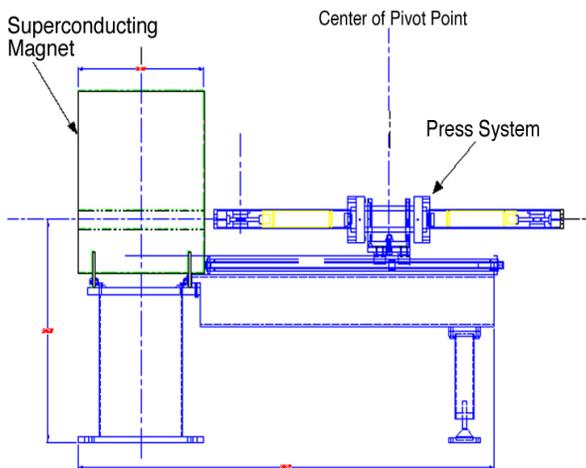
The most effective use of the high alignment fields that can be provided by superconducting solenoids is in making near-final-shape magnets. Their finite and usually short length in the direction of magnetization makes alignment of the powder grains especially difficult. When subjected to a uniform alignment field, the powder in the die cavity develops a highly non-uniform self-field. Because grains align along the total field lines, unidirectional alignment can be achieved only by increasing the strength of the applied alignment field until the effects of the self-field become negligible. Because the self-field distortion becomes greater for shorter magnets, conventional 2-T electromagnets cannot adequately provide alignment. We fabricated, with limited success, a number of near-final-shape compacts with L/D ratios smaller than 0.25 in various alignment fields from 1 to 8 T. Figure 3 shows such a compact with L/D = 0.21. These compacts are quite fragile because they are very thin (only 3.3 mm thick) and must be handled with extreme care. The success rate is low (~25%). We still do not know exactly what causes the compact to fail (crack) after ejection from the die, although we suspect the main culprit is trapped air. We need to improve the success rate in the future. Two dozen compacts were sent to Electron Energy Corporation



**Figure 3.** Near-final-shape compact with an L/D ratio of 0.21 (L = 15.9 mm).

for sintering and annealing. (Magnequench UG recently moved its factory to China and can no longer heat-treat the compacts).

We completed a conceptual design of a semi-automated superconducting PM fabrication system. As shown in Figure 4, the system includes mainly a dual-ended, four-position, horizontal press system and an actively shielded, helium-cooled, superconducting magnet with a horizontal room-temperature bore. The horizontal press can be slid into and out of the bore of the superconducting magnet. The four arms of the press, 90° apart, rotate around a pivot point. The four positions represent the pressing, ejection, cleaning, and filling stations. It is estimated that the system can produce eight compacts per minute.



**Figure 4.** Schematic diagram of the conceptual design of a superconducting magnet and a four-position press system.

The superconducting magnet is similar to the one currently in use at ANL. In designing the superconducting PM fabrication system, we collaborated with Ability Engineering Technology, Inc., a local design engineering firm. After the conceptual design was completed, vendors were contacted and quotations were received. The cost information was sent to Data Decisions and employed in the economic study.

We contracted Data Decisions to conduct an economic study of the superconducting PM manufacturing system, which was recommended after the 2003 DOE review meeting. The main objective is to compare the cost of manufacturing PMs using the

superconducting technology and the cost with conventional technology using electromagnets. The economic study is near completion, and we expect a final report will be issued by the end of FY 2004.

## Conclusions

Previously, we demonstrated that significant improvement of energy product (10–15%) can be achieved by using higher alignment fields (>2 T). Industry considers an improvement of 3–5% in the energy product of current PMs to be significant. Major issues remaining for acceptance of the technology by industry are (1) to demonstrate that PMs can be made at a much faster rate than in the batch process and (2) to demonstrate that near-final-shape PMs can be processed, resulting in greater cost reduction. In FY 2004, we modified the hydraulic loop to provide better indication and control of the pressure during early stages of compact pressing. We procured a new glove box to provide better oxygen control during the pre- and post-compact-pressing operation. We fabricated a number of near-final-shape compacts with L/D ratios of less than 0.25 with an alignment field ranging from 1 to 8 T. However, the success rate is low (~25%). We completed the conceptual design of a superconducting PM manufacturing system and received quotations from vendors for major components (the superconducting magnet and the semi-automated hydraulic press system). An economic study was carried out to compare the cost of manufacturing PMs using the superconducting magnet and using the conventional electromagnet.

In FY 2005, we plan to continue to collaborate with our industrial partners (Magnequench UG and Electron Energy Corp.) for compact sintering and annealing and for measuring magnetic properties of the sintered magnets. We want to improve the success rate of making near-final-shape compacts by considering (1) compact ejection under pressure and (2) powder-filling under vacuum; both may help to alleviate the cracking problem. We would like to finalize the conceptual design of the semi-automated superconducting PM manufacturing system, including the powder-filling and compact-ejection systems. Another task would be to fabricate PMs with shapes other than a circular cylinder or disk, such as the rectangular-shaped PM used in the motor of a hybrid car. Our long-term and final goal is to demonstrate the technical and economic feasibilities of

this new technology by designing, fabricating, and operating an automated superconducting magnet and press system in continuous-mode operation.

### **References**

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### **Publications/Presentations**

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the Annual Review of Advanced Power Electronics and Electrical Machines, DOE FreedomCAR and Vehicle Technologies Program, June 7–9, 2004, Knoxville, TN.

R. E. Wolf, "Low-Cost High-Energy-Product Permanent Magnets, An Economic Study," presented at the Annual Review of Advanced Power Electronics and Electrical Machines, DOE FreedomCAR and Vehicle Technologies Program, June 7–9, 2004, Knoxville, TN.

R. E. Wolf, *An Economic Study of the Manufacture of High Energy Permanent Magnets for Traction Motors in Hybrid Electric Vehicles*, report submitted by Data Decisions to Argonne National Laboratory, July 2004.



## B. Characterization of Rare Earth Permanent Magnets for Automotive Applications

*Edgar Lara-Curzio, Andrew Payzant, and Chris Cofer*

*Building 4515, MS-6069*

*Oak Ridge National Laboratory*

*(865) 574-1749; fax: (865) 574-6098; e-mail: laracurzioe@ornl.gov*

*DOE Materials Technologies Team Leader: Rogelio Sullivan*

*(202) 586-3976; fax: (202) 586-9811; e-mail: rogelio.sullivan@ee.doe.gov*

*ORNL Technical Advisor: David Stinton*

*(865) 574-4556; fax: (865) 241-0411; e-mail: stintondp@ornl.gov*

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*Contractor: Oak Ridge National Laboratory*

*Prime Contract No.: DE-AC05-00OR22725*

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### Objective

- Determine the effect of thermal cycling on the magnetic and mechanical properties of sintered and bonded rare earth permanent magnets (PMs).

### Approach

- Develop a test facility with an environmental chamber capable of cycling temperature between  $-40$  and  $300^{\circ}\text{C}$ .
- Instrument environmental chamber to determine in real time the magnetic strength of test specimens as a function of temperature and thermal cycling.
- Evaluate the residual mechanical properties of sintered and bonded rare earth PMs after thermal cycling.

### Accomplishments

- Developed a test facility capable of cycling temperature between  $-40$  and  $300^{\circ}\text{C}$ . The test facility is instrumented to determine, in real time, the magnetic strength of sintered and bonded rare earth PMs.

### Future Direction

- Utilize test facility to evaluate bonded and sintered NdFeB magnets.
- 

## Introduction

Achieving FreedomCAR and Fuel Partnership goals will require the development of new technologies for electric machinery. The new technologies must be compatible with high-volume manufacturing; must ensure high reliability, efficiency, and ruggedness; and must simultaneously reduce cost, weight, and volume. Key components for hybrid

vehicles include motors, sensors, and control systems.<sup>1</sup>

PM motors have the highest power density; but they don't have a sufficient constant power speed range; and their cost is too high because of the cost of magnet materials, magnet manufacturing, and

rotor fabrication. Sintered and polymer-bonded particulate magnets are being developed with the objectives of increasing their useful operating temperature to 150°C and decreasing the cost to about 25% of the current price of approximately \$90/kg. Furthermore, these magnets should be rugged and reliable enough to operate in harsh environments, including extreme temperatures, humidity, and thermal cycling for 150,000 miles or 15 years. The objective of this project is to determine the resistance of sintered and bonded rare earth PMs to thermal cycling between -40 and 150°C.

### Approach and Results

A test facility was designed and fabricated to evaluate the resistance of sintered and bonded rare earth PMs to thermal cycling. The test facility consists of a chamber, shown in Figures 1 and 2, capable of cycling temperature between -40 and 300°C. Cooling is achieved using liquid nitrogen,

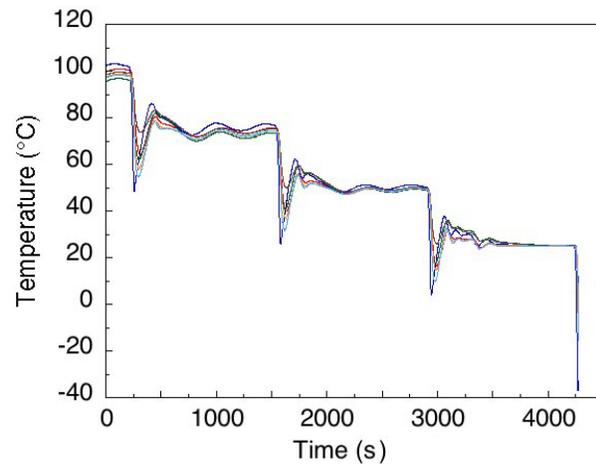


**Figure 1.** Environmental chamber for thermal cycling.



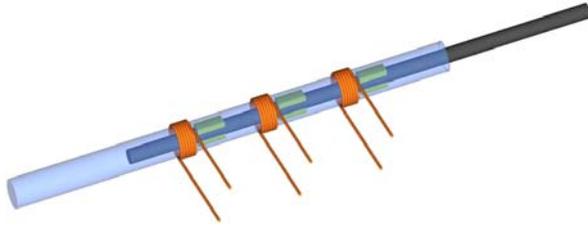
**Figure 2.** Detail of environmental chamber showing pneumatic actuator and frame with sixteen 6.5-mm diameter rods.

compressed air, and a solenoid valve, while heating is achieved using compressed air and two cartridge heaters. The interior of the chamber, which has dimensions of 61×30×30 cm, is lined with one layer of insulating material. Temperature measurements obtained with type K thermocouples placed at various locations inside the chamber demonstrated that it is possible to attain a very uniform temperature distribution inside the chamber. Figure 3 shows the temperature history recorded by seven thermocouples during heating/cooling. Results from these tests also provided information on the time required to achieve thermal equilibrium.



**Figure 3.** Temperature history recorded with seven thermocouples located at different locations within the environmental chamber. These results demonstrate that it is possible to achieve nearly isothermal conditions within the chamber.

A computer-based system was assembled for controlling the operation of the test facility and for data acquisition. The system consists of a personal computer, a high-speed A/D data acquisition system, customized software using the commercially available package LabView, and a digital temperature controller. Inside the box, an array of sixteen 6.5-mm-diam rods is attached to a frame, which in turn is connected to a pneumatic actuator. The PMs under evaluation, which are shaped in the form of prismatic beams, are placed at various locations along the rods. The reciprocating motion induced by the pneumatic actuator will slide the PMs through coils, which are placed around plastic tubes that are concentric to the rods (Figure 4). The motion of the magnets through the coils will induce a voltage in



**Figure 4.** Schematic of test configuration illustrating the relative location of the coils with respect to the supporting rods and the permanent magnet test specimens.

the coils. According to Faraday’s law,<sup>2</sup> the voltage induced in the coil will be proportional to the change in the magnetic flux through the coil ( $\Phi$ ), according to

$$V = -\frac{d\Phi}{dt} \quad , \quad (1)$$

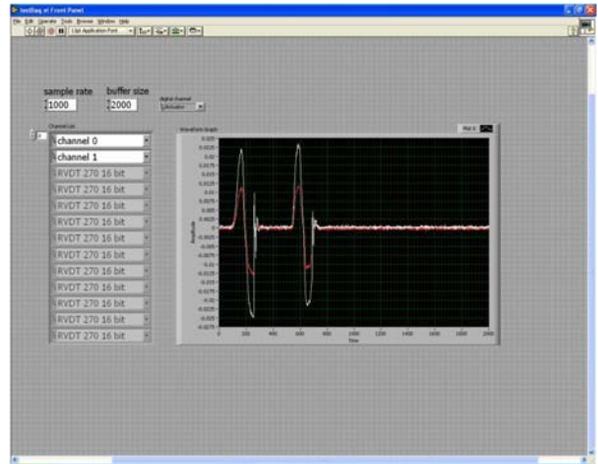
where the magnetic flux through the coil is given by

$$\Phi(t) = B(t) N A \quad . \quad (2)$$

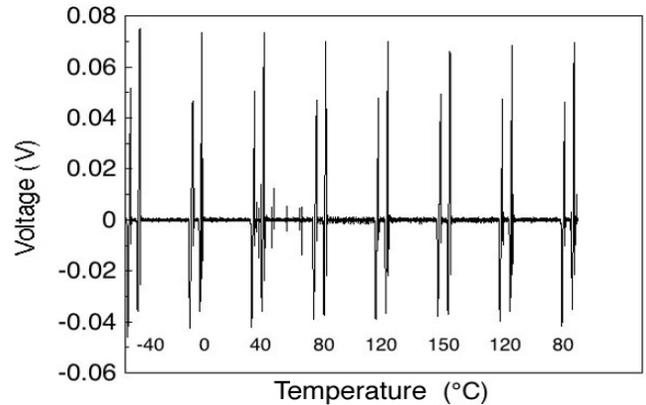
$B(t)$  is the magnetic field of the magnet,  $N$  is the number of turns in the coil, and  $A$  is the cross-sectional area of the coil.

The voltage induced across the terminals of the coil is recorded as a function of temperature and number of thermal cycles. Figure 5 shows voltage traces resulting from the displacement of a bonded permanent NdFeB magnet sample through the coils; Figure 6 illustrates the effect of temperature on the magnitude of the voltage and therefore on the magnitude of the magnetic field of the test specimen.

After a prescribed number of thermal cycles, test specimens are removed from the chamber and evaluated in a 4-point bending to assess the effect of thermal cycling on their mechanical strength. During FY 2005, the effect of thermal cycling on the magnetic and mechanical properties of bonded NdFeB magnets, received from IAP (Columbus, OH) will be evaluated.



**Figure 5.** Voltage trace associated with the motion of magnet through coil.



**Figure 6.** Voltage traces associated with the motion of magnet through coil as a function of temperature. Changes in voltage are proportional to changes in magnetic strength.

### Summary

A test facility was designed and fabricated to evaluate the effect of thermal cycling on the magnetic and mechanical properties of sintered and bonded PMs. The test facility is capable of operating between  $-40$  and  $300^{\circ}\text{C}$  and of providing real-time measurement of the magnetic strength of test specimens. The effect of thermal cycling on the mechanical strength of sintered and bonded PMs is determined by 4-point bending after subjecting test specimens to a prescribed number of thermal cycles.

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## C. Carbon Foam for Cooling Power Electronics

*Nidia C. Gallego*

*Oak Ridge National Laboratory*

*P.O. Box 2008, MS 6087, Bldg. 4508*

*Oak Ridge, TN 37831-6087*

*(865) 241-9459; fax: (865) 576-8424; e-mail: gallegonc@ornl.gov*

*Albert Shih, Steve White*

*S. M. Wu Manufacturing Research Center*

*University of Michigan*

*DOE Materials Technologies Team Leader: Rogelio Sullivan*

*(202) 586-8042; fax: (202) 586-1600; e-mail: rogelio.sullivan@ee.doe.gov*

*ORNL Technical Advisor: David P. Stinton*

*(865) 574-4556; fax: (865) 241-0411; e-mail: stintondp@ornl.gov*

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*Contractor: Oak Ridge National Laboratory, Oak Ridge, Tennessee*

*Prime Contract No.: DE-AC05-00OR22725*

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### Objectives

- Collaborate with automotive partner to develop carbon foam heat exchanger and heat sink designs that dissipate more than 30 W/cm<sup>2</sup> using standard cooling fluids.
- Develop and demonstrate designs for reducing weight and enhancing heat transfer in power electronic thermal management systems using high-thermal-conductivity carbon foam.
- Determine the foam structure or morphology that results in optimum heat transfer for various thermal management applications.

### Approach

- Study fundamental mechanisms of heat transfer in carbon foam and develop an engineering model that allows comparison of conventional and carbon foam heat exchangers.
- Redesign and build a test apparatus for measuring the heat transfer coefficients and pressure drops of heat sinks made of carbon foam.

### Accomplishments

- Formed a team consisting of Oak Ridge National Laboratory (ORNL), the University of Michigan, and Ford Motor Co. to develop a carbon foam-based heat sink for cooling the power electronics of Ford's H2RV (hydrogen hybrid research vehicle).
- Produced designs that showed potential for foam liquid-cooled heat exchangers in automotive applications, as well as the need for a more precise test rig.
- Produced foams with a variety of pore structures.
- Designed and built an improved heat sink test rig.

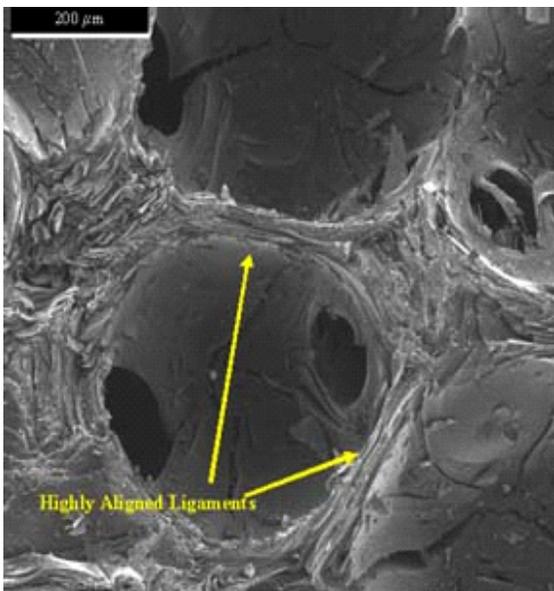
## Future Direction

- Characterize the different bonding techniques and their influence on overall performance of foam-based heat exchangers.
- Evaluate alternative cooling systems (such as passive evaporative coolers) for thermal management of power electronics.
- Modify designs of foam-based heat exchangers based on new foam properties.

## Introduction

In recent decades, performance improvements in electronic components, such as higher-power computer chips and power converters, have led to significantly increased heat generation at small size scales and require more efficient strategies for microscale heat dissipation. A range of techniques such as micro-channels, heat pipes, and other novel designs to improve the efficiency of heat transfer from devices have been explored with limited success. These devices must incorporate very effective heat spreaders into the design of the heat sink to prevent localized hot spots and ensure that the temperature of the silicon (Si)-based electronic components does not exceed 125°C.

The high-conductivity carbon foam developed at ORNL is an open-cell structure with highly aligned graphitic ligaments (see Figure 1); studies have shown the typical interlayer spacing ( $d_{002}$ ) to be 0.3356 nm, very near that of perfect graphite



**Figure 1.** Graphite foam material developed at ORNL.

(0.3354 nm). As a result of its near-perfect structure, thermal conductivities along the ligament are calculated to be approximately 1700 W/m•K, with bulk conductivities  $\geq 180$  W/m•K. Furthermore, the material exhibits low density (0.25-0.6 g/cm<sup>3</sup>) such that the specific thermal conductivity is approximately four to five times greater than that of copper. This high conductivity, combined with the very large surface area, results in overall heat transfer coefficients for foam-based heat exchangers that are up to two orders of magnitude greater than those of conventional heat exchangers. As a result, foam-based heat exchangers or heat sinks can be dramatically smaller and lighter than conventional ones.

This year we have teamed with Ford to evaluate the application of carbon foam for cooling of the power inverter of Ford's H2RV; both forced-air and circulating-water systems were evaluated. Simultaneously, effort was directed toward further understanding of the relationship between processing and foam structure in order to obtain foams with a more open structure that allows access to the internal surface area of the foam, therefore maximizing its performance in thermal management applications. Also, the test rig used to quantify pressure drop and heat transfer coefficients was redesigned.

## Results

### Design of Cooling System for Ford's H2RV

Hybrid and fuel cell vehicles using electric wheel motors require high-power electronics for motor control. These electronics create a considerable amount of heat and require a heat exchanger and separate radiator. Ford's H2RV currently has three cooling systems: one for the combustion engine, one for the power electronics, and one for the transmission. This project explored the use of high-thermal-conductivity carbon foam as a heat exchanger in the cooling systems of hybrid vehicle power electronics. The current aluminum pin-type heat exchanger used

is being redesigned using carbon foam to increase the heat transferred from the electronics while maintaining or reducing the pressure drop of the coolant. A corrugated foam geometry was used in the design because the corrugations force the fluid to flow through instead of around the pores. Table 1 lists the engineering specifications for Ford’s H2RV cooling system.

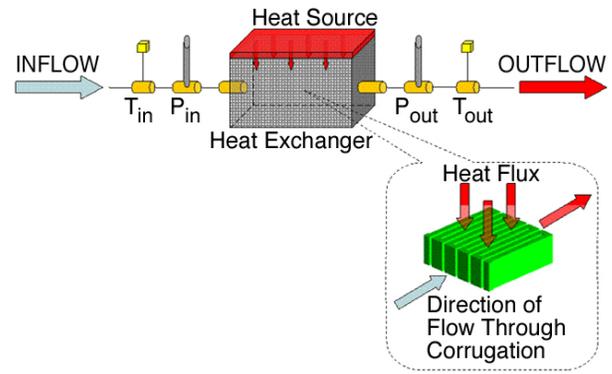
**Table 1.** List of engineering specifications for heat sink for power electronics of H2RV

Engineering specifications	
1	Dissipate 650 W of power
2	Maintain a chip operating temperature at or below 125°C
3	Operate in the temperature range -40 to 125 °C
4	Maximum coolant pressure drop of 0.5 psi
5	Fluid inlet temperature 60–65 °C
6	Insulate the 300 V necessary to power the circuits
7	Hold circuit board (~110 × 60 × 1 mm)
8	Fit in a similar-size case as Ford’s current design
9	Work for the life of the vehicle (~10 years or 200,000 cycles)

Two approaches were evaluated: (1) liquid-cooled heat exchanger and (2) forced-air heat exchanger.

**Liquid-cooled heat exchanger**

Testing the corrugated foam geometry with a liquid-cooled heat exchanger shows that it performs in the operating temperature range with heat transfer of approximately 15–20 W/cm<sup>2</sup>. For Ford’s application, it would need to dissipate an amount of heat near 30 W/cm<sup>2</sup>. This means that engineering specifications 1 and 2 from Table 1 were not met. Knowing the foam and fluid could operate over this temperature range validated specifications 3 and 5. Specifications 6, 7, and 8 were met using the foam as a replacement for the pin-fin aluminum heat exchanger; and no life-cycle estimate was done to validate specification 9. The test setup is shown in Figure 2. This design potentially allows the existing pin-fin heat exchanger to be replaced with a corrugated foam



**Figure 2.** Experimental test setup.

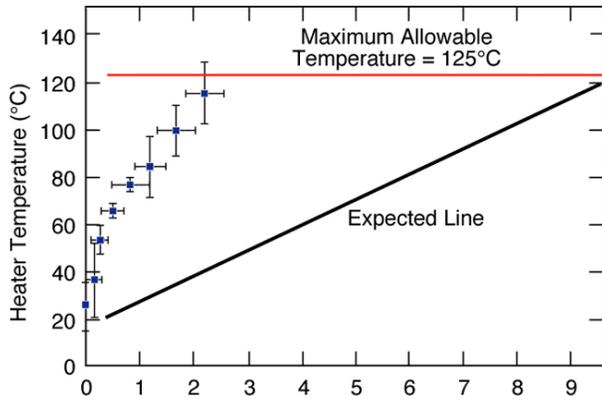
geometry, reducing the number of cooling systems in the hybrid car from 3 to 2. Calculations showed an average heat transfer coefficient of 1064 W/m<sup>2</sup>K, suggesting that the design could be improved considerably through flow rate control and foam porosity, based on comparisons with carbon foam characterization studies at ORNL.

To characterize the pressure drop imposed by the liquid-cooled carbon foam heat exchanger, the pressure drop across the housing was recorded (1) when no foam was present, (2) when corrugated foam was present, and (3) when blind-hole foam was present (holes drilled parallel to the flow in a solid block). All three data sets were within 10% of each other, with no distinct separation, implying that the housing is the dominant source of pressure drop. This can be attributed to the change in cross-sectional area from inlet to housing and from housing to outlet. While we cannot verify the expected pressure drop of the system to be less than 0.5 psi (engineering specification 4), we can conclude that the drop is relatively small.

**Forced-air heat exchanger**

Table 1 lists the engineering specifications for the forced-air packaging system design. Two specifications, 1 and 2, were not met. To validate the operating temperature range (no. 3), the thermal properties of each material were used to ensure that they could withstand extreme temperatures. Since the design was air cooled, the pressure drop (no. 4) and inlet coolant temperature (no. 5) were not needed. Specification 6 was validated through an electrical resistivity analysis. Specifications 7 and 8 were validated by choosing dimensions that were similar. There was no life-cycle estimate to validate specification 9. The prototype maintains the chip tempera-

ture at below 125°C at a maximum power density of  $2.4 \pm 0.4 \text{ W/cm}^2$ . The carbon foam has a maximum heat transfer coefficient of  $320 \pm 100 \text{ W/m}^2\cdot\text{K}$ . These results were obtained with a flow rate of  $12.1 \pm 0.5 \text{ cfm}$  and are shown in Figure 3.

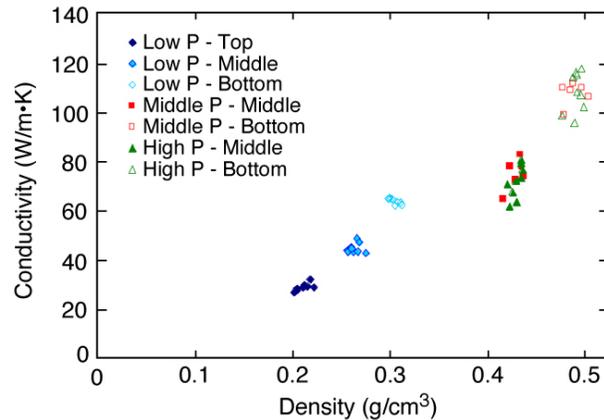


**Figure 3.** Heater temperature vs. power density shows the prototype did not deliver the expected performance (points correspond to experimental data).

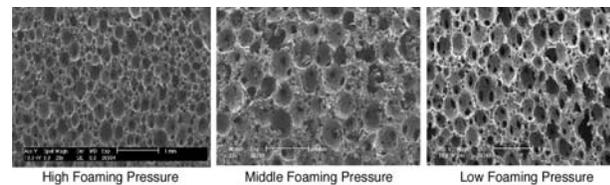
Both design teams found the convective coefficient of the foam to be lower than expected, possibly because of the lack of a bonding agent between the foam and the heat sink, lack of data on the heating element, and the inability to control water and air flow rates over a large range. More precise test set-ups and heater designs should be used in future testing.

### Processing Foams with Varied Pore Structures

Based upon B.E. Thompson’s modeling work<sup>1</sup>, which shows the importance of controlling pore density and maintaining an open structure to maximize the benefits of the foam’s porous surface in thermal management applications, we have directed our materials development efforts toward understanding the relationship between graphite foam structure and both roughness and area-recruitment phenomena. We have produced foam samples at different pressures (this being the processing variable that most affects pore size) to obtain foams of various pore structures. The density, thermal diffusivity, and compressive strength of the samples were measured. Figure 4 show the variations in thermal conductivity and density for samples produced at low, middle and high foaming pressures; Figure 5 shows



**Figure 4.** Thermal conductivity versus density for carbon foams produced at varying foaming pressures.



**Figure 5.** Pore structure of foams produced at varying foaming pressures.

scanning electron microscope images of the varied pore structures produced.

### Redesigned Heat-Sink Test Rig

Accurate measurements of pressure drop and heat transfer coefficients are necessary in order to properly design carbon-foam-based heat exchangers. We identified several limitations of our previous test rig that may have caused inaccurate measurements. A new design was developed and a new test rig built. Samples produced at various foaming pressures will be tested in this rig to measure pressure drop and heat transfer coefficients.

### Conclusions

Liquid-cooled heat exchangers show potential for use in automotive applications. The setup at the University of Michigan showed the need for more accurate pressure and temperature measurement. The further redesign of the test setup will provide a more accurate description of the foam’s capabilities in these applications.

The foam structure of carbon foam can be modified by varying the processing conditions. The improved access to the foam internal surface area will

greatly influence the performance of foam-based heat exchangers.

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N.C. Gallego, A. Shih, D. P. Stinton, E. Jih, "Graphite Foam for Cooling of Automotive Power Electronics," presented at the Carbon 2004 Conference, Providence, RI, July 11–16, 2004.

DOE Office of FreedomCAR and Vehicle Technologies Program Power Electronics Review Meeting, National Transportation Research Center, Knoxville, TN, June 7–9, 2004.



## D. Mechanical Characterization of Electronic Materials and Electronic Devices

*A. A. Wereszczak, T. P. Kirkland, and H. -T. Lin*

*Ceramic Science and Technology Group*

*Oak Ridge National Laboratory*

*P.O. Box 2008, MS 6068, Bldg. 4515*

*Oak Ridge, TN 37831-6068*

*(865) 576-1169; fax: (865) 574-6098; e-mail: wereszczakaa@ornl.gov*

*DOE Materials Technologies Team Leader: Rogelio Sullivan*

*(202) 586-8042; fax: (202) 586-1600; e-mail: rogelio.sullivan@ee.doe.gov*

*ORNL Technical Advisor: David Stinton*

*(865) 574-4556; fax: (865) 241-0411; e-mail: stintondp@ornl.gov*

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*Contractor: Oak Ridge National Laboratory, Oak Ridge, Tennessee*

*Prime Contract No.: DE-AC05-00OR22725*

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### Objectives

- Mechanically characterize hydroxylated polystyrene (PVOH) dielectric films being developed by Sandia National Laboratories (SNL) for fabrication into higher-temperature, more compact dc bus capacitors.
- Interpret and quantify the mechanical performance of PVOH films and their derivatives and rank them based on their potential for manufacturing scale-up.

### Approach

- Conduct tensile testing on SNL-supplied PVOH films and measure their ultimate strengths and elastic moduli.
- Using ultimate strength and elastic modulus, predict the minimum allowable radius of curvature that each film can withstand during processing into dc bus capacitors without breaking.

### Accomplishments

- Determined the average ultimate strength and elastic modulus of nine PVOH film sets comprising three different elastomer additives, anneal temperatures, and elastomer content.
- Identified one PVOH film (30% 4010 elastomer annealed at 225°C) as having the best combination of average tensile strength and minimum scatter in strength. It is predicted that this film can withstand being subjected to a radius of curvature of  $\sim 290 \mu\text{m}$  (0.011") without breaking.

### Future Direction

- Measure the tensile strength distribution of additional derivatives of PVOH films as a function of temperature.
- Measure and interpret the tear resistance of PVOH films.

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### Introduction

A primary focus of the Power Electronics effort in the Automotive Propulsion Materials Program is to develop polymer capacitor technology that will replace current electrolytic, dc bus capacitors for

power electronic modules in hybrid electric vehicles. The ultimate objective is to make the power modules more compact while maintaining tight voltage and temperature requirements and long service life without compromise caused by mechanical breakdown of the dielectric film.

Toward that end, we collaborated with SNL in this project to mechanically evaluate a suite of SNL-manufactured PVOH dielectric polymers that have the potential to satisfy the objectives. The present effort has two objectives:

- Measure baseline mechanical properties of that suite of PVOH compositions and interpret their results so as to suggest which are most suitable for manufacturing scale-up
- Quantify the mechanical performance of those manufactured films so manufacturers and end-users of these dielectric films may use them without mechanical breakdown.

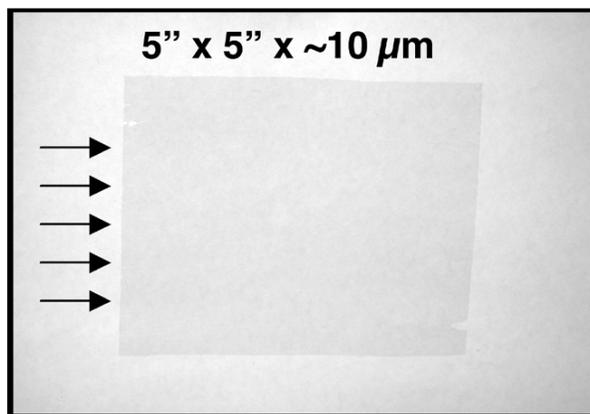
### Results

SNL provided three sets of PVOH-elastomer film sets for testing of tensile strength ( $S_{ten}$ ) and elastic modulus ( $E$ ). The tests examined two elastomers (designated as 4010 and 5015) having equal additive contents (16%). The effect of the additive content was also examined in the PVOH/4010 and a third set of films with 30% additive. The effect of annealing temperature (190, 225, and 250°C) on each of the three sets also was examined. The nine film combinations are listed in Table 1.

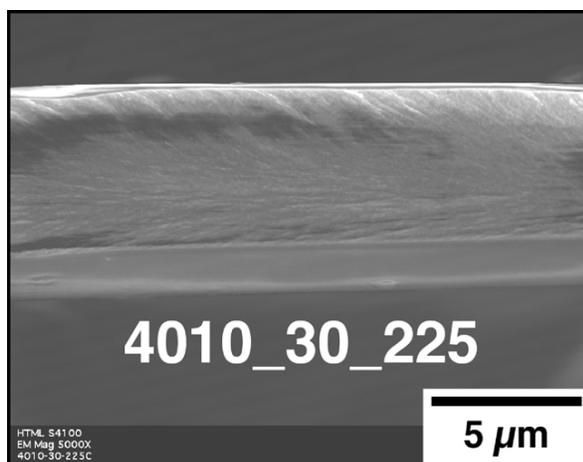
**Table 1.** Film test matrix

Dielectric film	Elastomer content	Anneal (°C)
PVOH/4010	16%	190
	16%	225
	16%	250
PVOH/4010	30%	190
	30%	225
	30%	250
PVOH/5015	16%	190
	16%	225
	16%	250

Sheets of film of the nominal size 125 mm × 125 mm × 10 μm (see Figure 1) were received and cut into 12.5-mm or 19-mm widths. Different widths were examined to see if specimen size had an effect on strength (it was found that it did not). An example of the cut cross-section of one of the PVOH films is shown in Figure 2. Specimens were “end-tabbed” with tape, producing a 25-mm gage length. The specimens were then mounted into pneumatically activated, face-loading flat grips



**Figure 1.** Example of as-received PVOH film.



**Figure 2.** Example of PVOH film cross-section.

housed in an electromechanical universal test machine (see Figure 3). Tests adhered to ASTM D882<sup>1</sup> and were conducted in displacement control at a crosshead speed of 0.5 mm/min until specimen fracture was produced.

Tensile load and crosshead displacement were measured and used to calculate true tensile stress and strain, respectively. Examples of true stress-strain curves for the PVOH film with 30% 4010 elastomer additive annealed at 225°C is shown in Figure 4; this film had the greatest average strength and least amount of scatter of the nine films, as shown in Figure 5 and listed in Table 2. Generally, the 5015/16% elastomer systems were weaker than their 4010/16% and 4010/30% counterparts; the 250°C anneal produced more scatter in strength than the 190 and 225°C anneals; and the 225°C anneal produced higher strengths than the 190°C anneal.

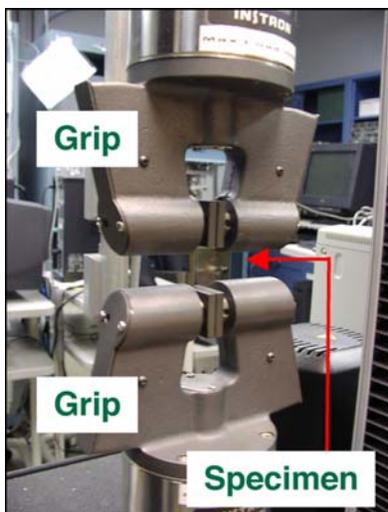


Figure 3. Film tensile test setup.

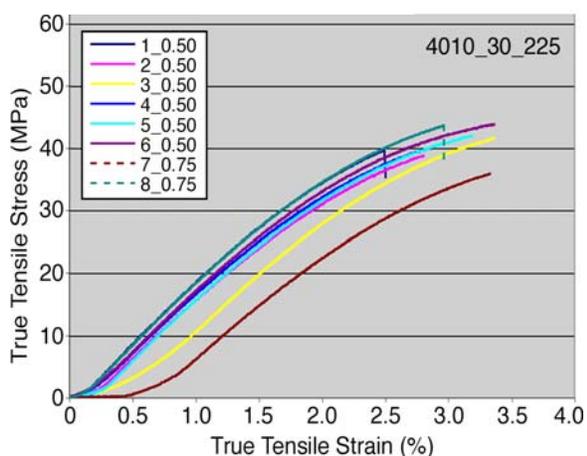


Figure 4. True tensile stress as a function of true tensile strain for all the test specimens from the PVOH-30% 4010 film annealed at 225°C.

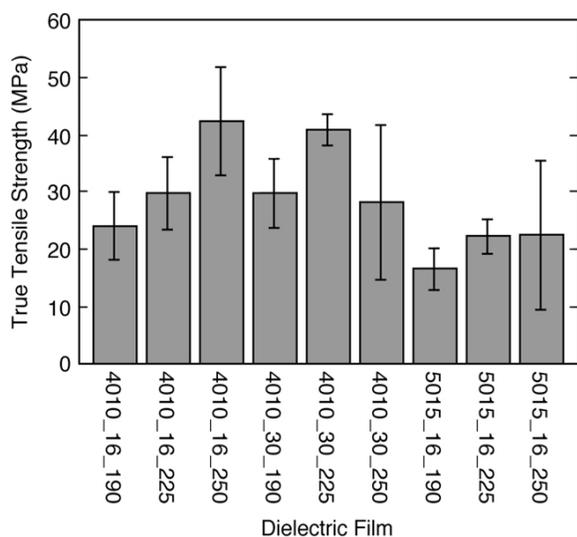


Figure 5. Comparison of average tensile strength.

Table 2. Film test matrix

Dielectric film	Ave $S_{tens}$ (MPa)	Ave E (GPa)
4010_16_190	$23.9 \pm 6.0$	$1.37 \pm 0.15$
4010_16_225	$29.6 \pm 6.3$	$2.02 \pm 0.15$
4010_16_250	$42.2 \pm 9.4$	$2.31 \pm 0.32$
4010_30_190	$29.6 \pm 6.0$	$1.74 \pm 0.08$
4010_30_225	$40.7 \pm 2.7$	$1.97 \pm 0.12$
4010_30_250	$28.0 \pm 13.5$	$1.85 \pm 0.26$
5015_16_190	$16.4 \pm 3.6$	$1.38 \pm 0.27$
5015_16_225	$22.1 \pm 3.0$	$1.80 \pm 0.43$
5015_16_250	$22.3 \pm 13.0$	$1.38 \pm 0.19$

These films are subjected to winding during their processing or during the capacitor manufacturing (Figure 6), so the (minimum) radius,  $R$ , of curvature was determined for each film that would produce a stress equal to the measured strength according to ref. 2:

$$R = \frac{Et}{2S_{tens}}$$

where  $t$  is the film thickness. A smaller radius of curvature is promoted with a less stiff film, a thinner film or a film with greater tensile strength. Based on this expression, then PVOH film with 4010/30% elastomer annealed at 225°C would survive being wound around the smallest radius (i.e., smallest mandrel). See Figure 7 and Table 3.

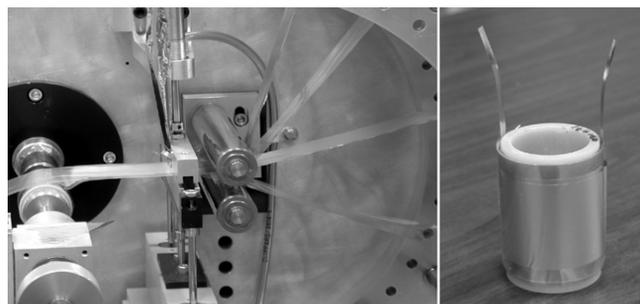
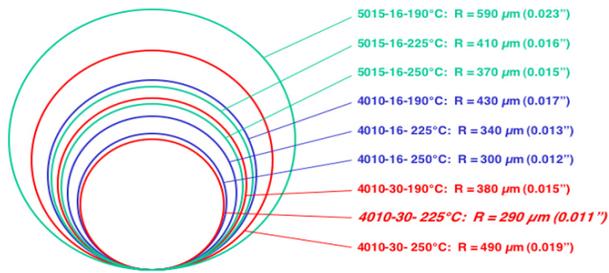


Figure 6. Dielectric films are subjected to winding during their fabrication and capacitor manufacturing. Images supplied by SNL.



**Figure 7.** The PVOH-30% 4010 film annealed at 225°C can be subjected to the smallest radius of curvature without fracturing.

**Table 3.** Minimum average radius of curvature

Dielectric film	Radius of curvature (mm)
4010_16_190	0.43
4010_16_225	0.34
4010_16_250	0.30
4010_30_190	0.38
4010_30_225	0.29
4010_30_250	0.49
5015_16_190	0.59
5015_16_225	0.41
5015_16_250	0.37

## Conclusions

The PVOH-4010/30% film annealed at 225°C had the best combination of high average strength and minimum strength scatter of all nine films tested. The 5015/16% elastomer systems were weaker than their 4010/16% and 4010/30% counterparts. The 250°C anneal produced more scatter in strength than the 190 and 225°C anneals and higher strengths than the 190°C anneal. There was no obvious effect of specimen size on ultimate tensile strength.

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## 3. CIDI ENGINES

### A. Round Pleated Ceramic Fiber Diesel Particulate Filter Cartridge

*Richard Nixdorf*

*Industrial Ceramic Solutions, LLC*

*1010 Commerce Park Drive, Suite I*

*Oak Ridge, TN 37830*

*(865) 482-7552; fax: (865) 482-7505; e-mail: nixdorfr@indceramicsolns.com*

*DOE Materials Technologies Team Leader: Rogelio Sullivan*

*(202) 586-8042; fax: (202) 586-1600; e-mail: rogelio.sullivan@ee.doe.gov*

*ORNL Technical Advisor: David Stinton*

*(865) 574-4556; fax: (865) 241-0411; e-mail: stintondp@ornl.gov*

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*Contractor: Industrial Ceramic Solutions, Oak Ridge, Tennessee*

*Prime Contract No.: 4000000723*

*Subcontractors: Springboard Technology, Pittsfield, MA*

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#### Objectives

- Design a round pleated ceramic fiber diesel particulate filter (DPF) cartridge suitable for the exhaust flow of a 7.3-L Ford F250 truck.
- Develop a ceramic injection molding or casting process capable of producing the structural frame for the pleated filter media.
- Develop, fabricate, and road test the round pleated ceramic fiber filter cartridge, which reduces engine back-pressure and filter thermal mass compared with conventional particulate filters.
- Conduct an independent laboratory stationary diesel test cell evaluation on the round pleated cartridge to validate particulate removal efficiency.

#### Approach

- Contract with a skilled design engineer to calculate dimensions and produce drawings of the round pleated cartridge.
- Subcontract structural frame development for the pleated cartridge to a ceramic injection molding company.
- Fabricate and road test the round cartridge system on a 7.3-L diesel vehicle to optimize shape and size and verify durability.

#### Accomplishments

- Produced several sets of engineering drawings, along with a computer model to accurately calculate available filtration surface resulting from any dimensional design changes.
- Developed an injection molding material and application technique for the ceramic structural frame on the filter media.
- Road-tested several flat pleated filter cartridge systems to investigate various structural support designs for the pleated filter on a 7.3-L Ford F250 truck.

- Designed a specifically sized round pleated filter cartridge for testing by a major vehicle manufacturer.

### Future Direction

- Enlist exhaust system, catalyst, engine, and vehicle manufacturers in a joint product development effort to move toward commercialization of the ceramic fiber pleated particulate filter in 2005.
- Work with multiple ceramic subcontractors to reduce the cost of the fabricated ceramic components.
- Conduct joint development with a ceramic fiber media company to improve the soot and ash capacity of the round pleated filter.
- Partner with a volume filter cartridge manufacturer to provide large quantities of the pleated filter cartridges necessary to the diesel industry over the next 10 years.

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## Introduction

Diesel emissions regulations in the United States, Europe, and Japan have become a reality for all diesel engine manufacturers. Diesel engine and vehicle suppliers worldwide are working on particulate control devices. Catalyst-regenerated systems, which require high exhaust temperatures, seem to be working reasonably well on heavy duty diesel trucks (>10-L engine sizes). These engines account for about 10% of the diesel engine market in the world. Smaller vehicles with lower exhaust temperatures—such as medium-duty trucks, buses, delivery vans, pickup trucks, passenger cars, future diesel sport utility vehicles, and off-road vehicles—will need an auxiliary-heated particulate filter to operate under all engine conditions. This creates an opportunity in 90% of the diesel engine market for the pleated ceramic fiber Industrial Ceramic Solutions (ICS) DPF cartridge because of its lower backpressure and reduced thermal mass. A number of actively heated DPFs are under development, but none have the proven record of performance, maintenance, and price required for commercial diesel vehicles. ICS's completion of the FY 2004 DOE Propulsion Materials Program vehicle road test will place the ICS round pleated ceramic fiber filter cartridge high on the list of potential actively heated DPF systems.

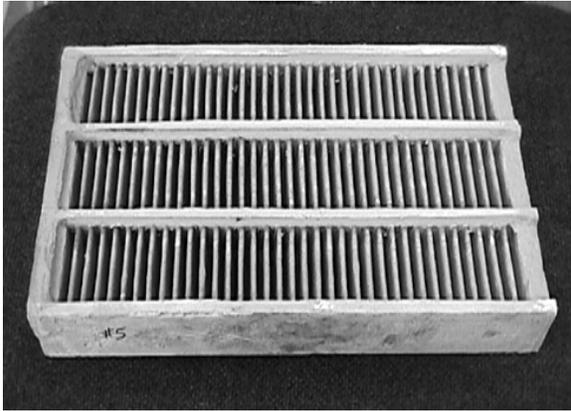
In FY 2003, a second product alternative to control diesel particulates across all market applications emerged—the ceramic fiber pleated filter cartridge itself. All approaches to particulate matter (PM) control must use some form of a ceramic filter. To date, that filter choice has been an extruded honeycomb “wall-flow” product. Experiments conducted by ICS and others under the FY 2003 program demonstrated that the pleated ceramic DPF results in much lower

exhaust backpressure on the diesel engine, which will improve engine performance and reduce the fuel penalty imposed by the PM control device. The pleated ceramic fiber DPF, which weighs significantly less than the extruded wall-flow filter, is lower in thermal mass, so it achieves soot combustion temperatures more quickly and adds less weight. The transition from the flat pleated filter to the round pleated filter cartridge is necessary because of the demands of exhaust manufacturers for a round DPF shape to fit their current canning processes. ICS is in discussions with several diesel engine and exhaust system manufacturers to test the pleated ceramic fiber filter cartridge in their existing regeneration technologies.

## Approach

ICS's FY 2003 work developed the flat pleated ceramic fiber filter cartridge. Many experiments were conducted to determine the optimum geometry of the filter and the best means to fabricate this geometry in the laboratory. A pleating process, using a ceramic binder, was developed. A number of structural designs to enclose and support the pleated fiber media in the exhaust were investigated. That product is shown in Figure 1. During FY 2004, ICS designed a round pleated filter cartridge based upon the diesel engine testing data from its rectangular pleated filter cartridge. Extensive road testing on the Ford F250 diesel truck has shown that the 8 ft<sup>2</sup> of media in the rectangular pleated filters is approximately 20% less than that required for optimum filter operation.

ICS approached the project with an initial round pleated filter that is approximately 7 in. in diameter and 12 in. long. This will yield 10 ft<sup>2</sup> of effective filter media surface area to accommodate a full



**Figure 1.** ICS flat pleated filter cartridge.

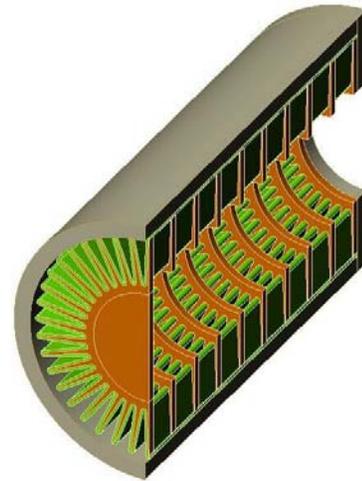
spectrum of diesel exhaust flow rates on the truck. ICS employed a mechanical engineer to design and model the optimum pleat geometry and cartridge size to accommodate the Ford truck's exhaust flow. ICS worked with an experienced ceramic injection molding company to develop structural support for the pleated filter media. We have contracted with this company to provide the injection molding tooling for the round pleated filter structural frame. The efforts of the filter cartridge design engineer and the injection molding company are being coordinated to arrive at a robust round filter cartridge structure for the first attempt at a diesel exhaust prototype test cartridge.

The injection molding tooling will produce a cartridge for road testing on the ICS 7.3-L diesel Ford truck. Cartridges and exhaust can assemblies will be manufactured for the Ford truck testing. ICS will contract with an independent diesel engine testing laboratory, such as Oak Ridge National Laboratory, to evaluate the mechanical behavior, durability, and filtration efficiency. Then the round pleated filter assembly will be installed on the ICS Ford test vehicle. Road testing will be performed at a full range of engine operating conditions.

Issues with the filter design and performance will be identified and resolved. Several iterations of design adjustments may be necessary to arrive at the optimum prototype configuration. These will be confirmed using the Ford truck testing. When a robust and durable cartridge is available, these cartridges will be provided to selected U.S. diesel manufacturers for in-house testing and evaluation.

## Results

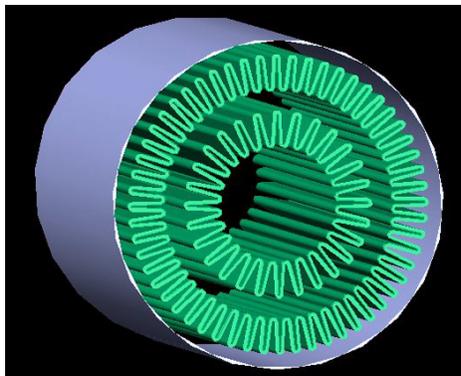
The first engineering design of the round pleated filter, including the ceramic support structure, was a 7-in.-diam by 12-in.-long filter cartridge, as shown in Figure 2. A laboratory replica of this prototype was fabricated to investigate feasibility. Figure 3 shows the laboratory model. The filter media surface available in this design was approximately 8 ft<sup>2</sup>. Discussions and bench testing with commercial vehicle manufacturers pointed to a need for more filter surface. Therefore, a second concept was designed by the ICS engineers to provide slightly more than 10 ft<sup>2</sup> of surface area. This 6-in.-diam by 12-in.-long cartridge design, shown in Figure 4, will be the design that ICS pursues for future prototype vehicle testing.



**Figure 2.** Initial engineering design of the round pleated filter.



**Figure 3.** Laboratory model of the initial prototype design.



**Figure 4.** Cartridge design with improved surface area.

The injection molding development for the ceramic support structure was accomplished on a flat pleated filter to minimize injection-molding tooling cost for the initial materials and injection molding parameter investigations. The ceramic frame material selected for this development was silicon carbide, as this seems to be the material preferred by diesel manufacturers. The final product from that preliminary injection molding work is shown in Figure 5. ICS is currently working with the injection molding company to design the tooling for the round pleated filter cartridge.



**Figure 5.** Injection-molded structure on a pleated filter.

ICS has fabricated a can assembly to test the pleated filters on the Ford F250 truck. The exhaust is directed through the bed of the truck to facilitate easy installation and removal of filter cartridges for evaluation. That test apparatus is shown in Figure 6. ICS can test both round and flat pleated filters in this test device. It has been valuable in investigating the durability of support structures and soot loading capacity of the pleated filter cartridges.



**Figure 6.** Ford truck filter cartridge test apparatus.

## **Conclusions**

The pleated ceramic fiber filter cartridge has demonstrated lower backpressure and thermal mass properties that can make it a valuable addition to all types of PM control systems. ICS is negotiating with a major international filter manufacturer to license the use of the technology to supply the large volumes of filter cartridges that will be necessary to supply the worldwide diesel industry. Completion of the successful road testing of the Ford diesel truck will allow ICS to begin supplying test cartridge samples to diesel engine and vehicle manufacturers in 2005. Support by the diesel engine manufacturers and the vehicle original equipment manufacturers is expected to lead to fleet testing and eventual commercial use. The round pleated ceramic fiber filter cartridge DPF can solve many problems that exist for companies seeking diesel particulate control solutions for 2007 and beyond.

## **Publications/Presentations**

“Microwave-Regenerated Particulate Filter,” presented at the American Filtration Society Diesel and Gasoline Engine Emission Solutions Conference, Ann Arbor, MI, October 2003.

## **Patents Issued**

“Manufacturing Process for Whisker-Free Silicon Carbide Fibers,” June 2004.

## B. Fabrication of Small Fuel Injector Orifices

*John B. Woodford, George R. Fenske*

*Argonne National Laboratory*

*9700 South Cass Avenue*

*Argonne, IL 60439*

*(630)252-0910; fax (630)252-4798; e-mail gfenske@anl.gov*

*DOE Technology Development Manager: Rogelio Sullivan*

*(202) 586-4082; fax: (202) 586-1600; e-mail: rogelio.sullivan@ee.doe.gov*

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*Contractor: Argonne National Laboratory, Argonne, Illinois*

*Prime Contract No.: W-31-109-Eng-38*

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### Objectives

- Develop a methodology for reducing the diameter of fuel injector orifices to 50  $\mu\text{m}$  by applying material to the internal diameter (ID) of the orifice. Smaller orifices should improve fuel distribution, improve efficiency, and reduce emissions.
- Characterize the spray and combustion properties of the fuel injector system coated with electroless nickel (EN).
- Transfer the developed technology to DOE industrial partners.

### Approach

- Transfer EN plating deposition technology for reducing the orifice diameter to a commercial plating company.
- Evaluate the potential of EN plating for improving surface finish and reducing deposit formation on injector nozzles.

### Accomplishments

- Worked with a commercial plating company to successfully reduce the orifice diameter of diesel engine fuel injectors from 180 to 80  $\mu\text{m}$  with EN plating.
- Characterized the relative vulnerability of injectors plated with different alloys to deposit formation.
- Collaborated with Pennsylvania State University (Penn State) on deposit formation testing using Penn State's micro-oxidation test method, and with the U.S. Environmental Protection Agency (EPA) National Vehicle and Fuel Emissions Laboratory (NVFEL) on plating injectors for EPA's Clean Diesel program.
- Initiated contact with Siemens AG through International Harvester/Navistar regarding possible transfer of the plating technology.

### Future Direction

- Characterize spray characteristics of coated injectors in collaboration with Argonne National Laboratory–Energy Systems (ANL–ES).
  - Provide coated injector tips to NVFEL personnel for spray characterization and combustion tests.
  - Refine test method for measuring deposit formation on coated surfaces.
-

## **Introduction**

In 2007, EPA regulations mandate a reduction in diesel engine emissions to 0.01 g of particulate matter (PM) per engine horsepower per hour, and 0.2 g nitrogen oxides (NO<sub>x</sub>) per engine horsepower per hour. Further reductions are expected for 2010. To achieve these levels, a great deal of research is being performed on engine design changes and aftertreatment devices. One design change under consideration is the reduction of the fuel injector orifice diameter.

Pickett and coworkers<sup>1,2</sup> have demonstrated elimination of soot in a test cylinder by reducing the injector orifice diameter to 50 μm, even with high levels of exhaust gas recirculation (EGR) and concomitant reduction in NO<sub>x</sub> emissions. NVFEL researchers have observed reduced PM emissions from a light-duty diesel engine equipped with 75-μm-diam injector orifices. These reductions arise from increases in fuel atomization efficiency, leading to more complete combustion.<sup>3</sup> Although it is currently possible to economically mass-produce injectors with 100-μm-diam orifices using electrical discharge machining (EDM), further reductions in hole size are accompanied by unacceptable fabrication error rates.

While reducing orifice diameter has the potential to reduce PM emissions, the reduction leads to a number of potential difficulties. Smaller orifices are more susceptible to partial or complete blockage by coking deposits. In addition, in its as-made state, the interiors of EDM-fabricated orifices are extremely rough and must be smoothed with an abrasive slurry. The average R<sub>A</sub> of these internal surfaces is about 0.5 μm, with sharp peaks and valleys. This roughness actually promotes coking deposit formation, starting in the deeper valleys. In addition, the rough orifice wall creates a highly turbulent layer adjacent to it during injection, reducing the volume of fuel delivered. The effect of this reduction increases markedly as the orifice diameter decreases.

We have demonstrated the potential of EN plating as a method for production of small-orifice injectors. It also offers a route to minimizing deposit formation by tailoring surface chemistry, and we have previously shown that EN-plated orifice interior surfaces are smoother than the underlying substrate.

## **Approach**

As described in previous reports, we are using EN plating to reduce orifice diameter. EN plating is a method of depositing nickel/phosphorus or nickel/boron alloys onto metallic surfaces from aqueous solution, and we have deposited other metals using the same principle.

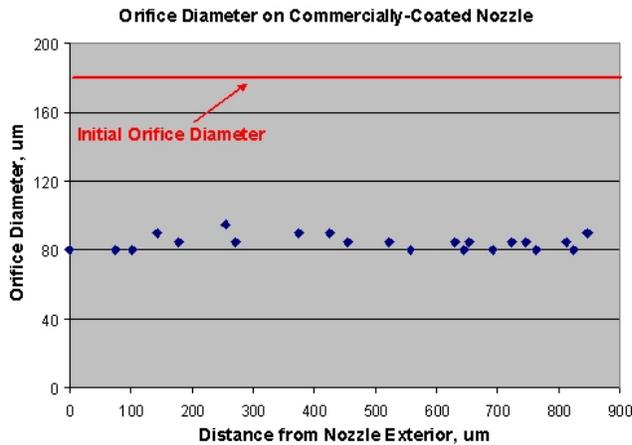
Having previously shown that EN plating can be used on a bench scale to reduce orifice diameter from 200 to 50 μm and to reduce the R<sub>A</sub> of plated surfaces, we plan to scale up the technique. We will also continue to evaluate the ability of EN plating to mitigate deposit formation.

## **Results**

In last year's peer review of this project, many of the reviewers strongly urged us to characterize the spray properties of plated nozzles. To that end, we have begun a collaboration with EPA–NVFEL, under which we will coat nozzles for EPA's Clean Diesel program and EPA will provide us with the results of spray and single-cylinder engine tests on the nozzles. If these initial tests go well, EPA–NVFEL plans to do light-duty engine tests on plated nozzles as well. We are also working with ANL–ES personnel on plating nozzles for optical spray characterization. In addition, SNL researchers have expressed an interest in testing some of our plated nozzles.

We are working with Imagineering, Inc., a commercial plating company, to scale up nozzle plating. It has provided us with a number of plated nozzles for evaluation in the key areas of coverage, uniformity, surface finish, and adhesion.

- Coverage has been excellent (Figures 1 and 2); even the first set of injectors Imagineering sent had plating along the entire length of the orifices.
- Uniformity is likewise as good as we saw in bench-scale tests, with one exception related to surface finish (see below).
- The company is still having minor problems with surface finish, which also negatively impacts uniformity. Areas of thinner coating are caused by the presence of hydrogen bubbles on the surface during the plating process. Greater agitation of the bath during the course of plating is expected to resolve this issue. The variability in orifice diameter seen in Figure 1 is likewise



**Figure 1.** Orifice diameter as a function of position in a nozzle plated by Imagineering.



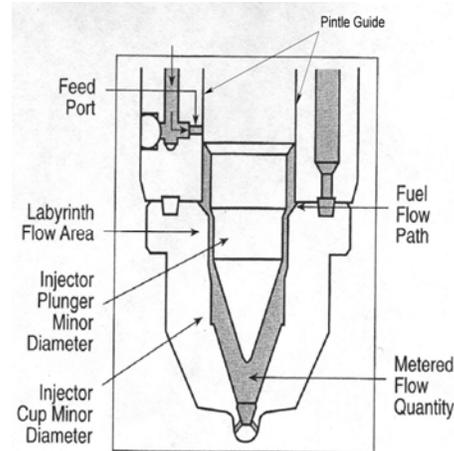
**Figure 2.** Optical micrograph of a cross-section of the plated nozzle in the orifice region.

due to the presence of bubbles in the orifice during plating.

While adhesion was poor in the first set of injectors plated, Imagineering rapidly resolved that issue, and all of the plated injectors we have received since then have had excellent adhesion. We evaluate adhesion by indenting the plated surfaces under load and examining the indentation. If adhesion is poor, there is substantial loss of coating around the indentation. If adhesion is good, the coating remains adherent around the indentation. Imagineering personnel estimate that plating the nozzles should add \$0.25 or less to the cost.

Because of the superior adhesion it has achieved, Imagineering will coat the nozzles for

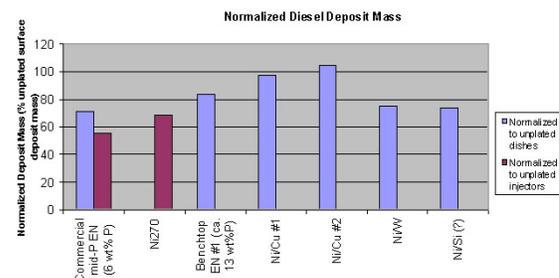
evaluation by NVFEL and ANL-ES as soon as it has resolved the surface finish issue. For the nozzles to be suitable for testing, there must be no coating in the pintle guide area (cf. Figure 3).



**Figure 3.** Plan sketch of nozzle, indicating the pintle guide area.

We have shown the feasibility of using commercially available masking compounds to keep that area from being coated. Imagineering has the capability to keep the critical area free of EN and will do so when all other coating parameters are acceptable.

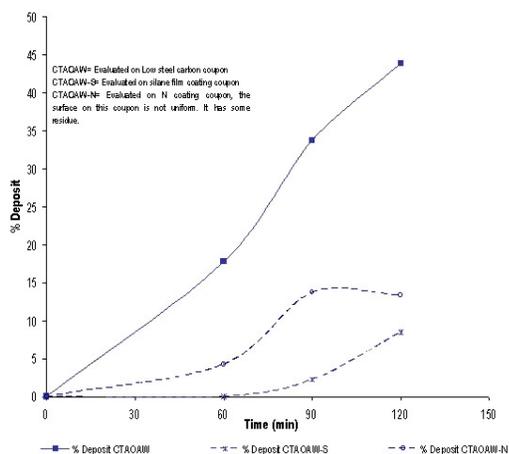
As reported last year, we tested deposit formation by dropping diesel fuel onto plated and unplated surfaces at approximately 240° C and measuring the mass gain. These initial tests showed EN plating to be less prone to coking than the base metal of the nozzle. We have expanded upon that work, using the same test method to determine the coking potential of several different alloys. Figure 4 is a plot of deposit mass on different alloys expressed as a fraction of the deposit mass on an unplated surface. It appears that the commercial plat-



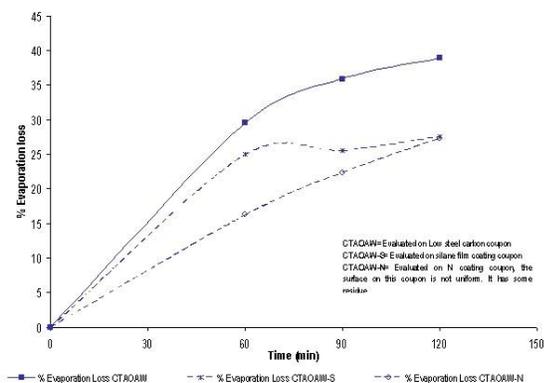
**Figure 4.** Deposit mass on different alloys, normalized to deposit mass on unplated surfaces in the same test run.

ing bath we have been using is still as good as or better than any of the alloy coatings we have tested. A review of the literature on metal-based catalysts for reactions of organic molecules has suggested a number of other candidate metals for examination.

Because our test method was not in general use, we provided plated sample dishes to Professor Joseph Perez at Penn State. He performed Penn State micro-oxidation tests on the plated dishes and confirmed our results. These tests entail heating dishes with fixed initial volumes of fuel or lubricant to 200°C and flowing air over them for varying lengths of time. Figure 5 is a plot of deposit mass vs. time at temperature, showing the results for EN plating, for unplated dishes, and for a silicon-based coating that was tested at the same time. Figure 6 is a plot of



**Figure 5.** Plot of Pennsylvania State micro-oxidation deposit mass as a function of time for unplated, EN-plated, and Si-coated samples.



**Figure 6.** Plot of Pennsylvania State micro-oxidation mass loss as a function of time for unplated, EN-plated, and Si-coated samples.

mass loss vs. time at temperature for the same three samples. High mass loss is an indication of oxidative fragmentation of the test fluid; when long-chain organic molecules partially oxidize, they can break apart in the vicinity of more reactive hydrogens and carbons, such as those around carbon-carbon double bonds. The fragmented molecules are both volatile and reactive. Some evaporate quickly, as shown by the mass loss; the rest condense into deposit precursors, as shown by the increase in deposit mass. Professor Perez has also provided invaluable insights into the nature of the deposit formation reactions.

We are investigating methods of measuring or estimating the cavitation erosion resistance of EN-plated surfaces. There is a wide range of opinion in the literature regarding the relationship between basic material properties such as hardness and cavitation erosion resistance; however, it appears that erosion resistance for widely dissimilar materials (e.g., brittle ceramic coatings vs. ductile metals) can be predicted from different properties. In the case of EN plating, it should be possible to estimate erosion resistance from hardness. Now that we have been able to obtain highly adherent coatings from Imagi-neering, we plan to consider the possible effect of thermal fatigue on coating durability.

To address the issue of engine tests in heavy-duty diesel engines, we initiated contact with Siemens AG research personnel. They expressed an interest in the technology but cautioned that reducing orifice diameter will require extensive changes in heavy-duty engine design. They were also concerned about the long-term durability of the coatings, as well as their propensity for deposit formation.

## Conclusions

This year's work has shown that scaling up the technique is technically and economically feasible. We have seen that there is still strong interest on the part of fuel system original equipment manufacturers (OEMs), and we are already working to address their primary concerns about the technology. The next step is spray visualization; positive results from those tests will lead to engine tests, where success should increase OEM interest and drive application and use of the technology in light-duty engines.

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1. L. M. Pickett and D. L. Siebers, "Orifice Diameter Effects on Diesel Fuel Jet Flame Structure," American Society of Mechanical Engineers, Internal Combustion Engine Division, ICE **37**(1) 65–76, *Proceedings of the 2001 Fall Technical Conference of the ASME Internal Combustion Engine Division*, 2001, Ed.: V. W. Wong.
2. L. M. Pickett, D. L. Siebers, A. F. Morales, J. Hachman, and A. K. Sinensky, "An Investigation of Diesel Soot Formation Processes Using High Aspect Ratio Micro-Orifices," presented at HARMST 2003 High-Aspect Ratio Micro-Structure Technology Workshop, Monterey CA, 2003.
3. J. B. Heywood, *Internal Combustion Engine Fundamentals*, McGraw-Hill, 1988.

**Publications and Presentations**

J. Woodford and G. Fenske, *Use of Autocatalytically-Deposited Coatings to Fabricate Small-Orifice Fuel Injectors*, Argonne National Laboratory, in press.

J. Woodford and G. Fenske, *Fuel Deposit Formation on Electroless Nickel Coatings*, Argonne National Laboratory, in press

Poster, DOE Advanced Combustion Engine R&D Merit Review, May 18–20, 2004, Argonne National Laboratory

**Patents**

J. Woodford, J. Perez, A. Erdemir, and G. Fenski, "Use of Catalytic Metal Coatings to Mitigate Deposit Formation on Engine Components," invention disclosure ANL-IN-04-063.



## C. Electrochemical NO<sub>x</sub> Sensor for Monitoring Diesel Emissions

*L. Peter Martin and Robert S. Glass*

*Lawrence Livermore National Laboratory*

*P.O. Box 808, MS L-353*

*Livermore, CA 94551-0808*

*(925) 423-9831; fax: (925) 423-7040; e-mail: martin89@llnl.gov*

*DOE Materials Technologies Team Leader: Rogelio Sullivan*

*(202) 586-78042; fax: (202) 586-1600; e-mail: rogelio.sullivan@ee.doe.gov*

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*Contractor: Lawrence Livermore National Laboratory, Livermore, California*

*Prime Contract No.: W-7405-Eng-48*

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### Objectives

- Develop a compact, rapid-response electrochemical nitric oxide (NO) or total nitrogen oxides (NO<sub>x</sub>) sensor for compression-ignition, direct-injection (CIDI) engine exhaust gas monitoring.
- Demonstrate the commercialization potential of a new NO<sub>x</sub> sensor technology.
- Collaborate with Ford Research Laboratory and Oak Ridge National Laboratory (ORNL) to optimize sensor materials, operating parameters, and performance.

### Approach

- Use an ionic (O<sup>2-</sup>) conducting ceramic as a solid electrolyte and a catalytic metal oxide as a working electrode.
- Apply a constant current-bias between the working electrode and a second, "counter" electrode.
- Correlate the NO<sub>x</sub> concentration with the potential developed across the cell in response to the applied current-bias.
- Optimize the sensor performance (sensitivity, response speed, cross sensitivity, and stability) by identifying and resolving materials-related and design issues.

### Accomplishments

- Performed more extensive testing of a tin-doped indium oxide (ITO) sensor reported last year.
- Identified new electrode material with better NO selectivity and higher operating temperature.
- Expanded collaboration with Ford Research Lab and with ORNL.

### Future Direction

- Continue to explore materials issues related to sensitivity and stability.
  - Investigate sensing mechanism using electrochemical and analytical techniques.
  - Evaluate microstructural evolution during sensor aging.
  - Evaluate cross-sensitivity to important redox species.
  - Demonstrate the commercialization potential of the current-biased sensor technology.
  - Transfer technology to a commercial entity.
-

## **Introduction**

New emissions regulations will increase the need for compact, inexpensive sensors for monitoring and control of automotive exhaust gas pollutants. Species of interest include hydrocarbons, carbon monoxide, and NO<sub>x</sub>. The most promising NO sensors for exhaust gas monitoring are based on ionically conducting solid state electrochemical devices.<sup>1,2</sup> These devices typically consist of a solid ceramic electrolyte onto which two or more metal or metal-oxide electrodes are deposited, and they can be operated in either potentiometric or amperometric modes. Significant progress has been made toward the development of deployable sensors using yttria-stabilized zirconia (YSZ) as the electrolyte and catalytically active metal oxides as the sensing electrodes.<sup>3</sup> However, improvement is still needed in sensitivity, response time, reliability, and cross-sensitivity. The current work is directed toward the development of fast, high-sensitivity electrochemical NO<sub>x</sub> sensors for automotive diesel engine applications.

NO<sub>x</sub> sensing technology providing fast response time and high sensitivity to NO at 600–750°C has been developed. The sensor is based on a novel current-biased mode of operation in which a fixed current is applied between the sensing and counter electrodes and the resultant potential is measured. Target operating parameters have been determined for the proposed sensor based on discussion with industry collaborators at Ford Research Lab.

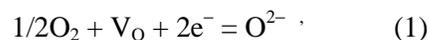
## **Approach**

The proposed approach is to develop a sensor using catalytic metal oxide electrodes on a solid ionic conductor electrolyte. Similar technology has been widely investigated for various gas sensing applications and has been successfully developed for use in exhaust gas oxygen sensors. The current effort approaches the problem by the application of novel materials and fabrication processes designed to optimize electrode microstructures. In addition, a novel mode of operation has been identified that yields enhanced NO response sensitivity and speed.

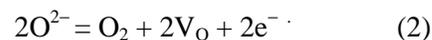
Sensors are prepared by spray deposition or spin coating of metal oxide working electrodes onto dense YSZ electrolyte substrates, followed by sintering at 900–1100°C. Working electrodes are composed of nanocrystalline metal oxides. Initial suc-

cess was encountered using n-type semi-conducting oxides, such as ITO or ZnO. More recently, it has been demonstrated that promising performance can be achieved using various perovskite-type oxides. Counter electrodes are generally made from platinum, although they can also be fabricated from metal oxides. NO<sub>x</sub> sensing experiments were performed in a quartz tube inside a furnace using a standard gas handling apparatus. All tests were performed in the temperature range of 600 to 750°C.

Sensors are typically first characterized through generation of current-voltage (I-V) curves in various atmospheres. The measured current is directly related to the amount of oxygen being “pumped” through the electrolyte by the reaction



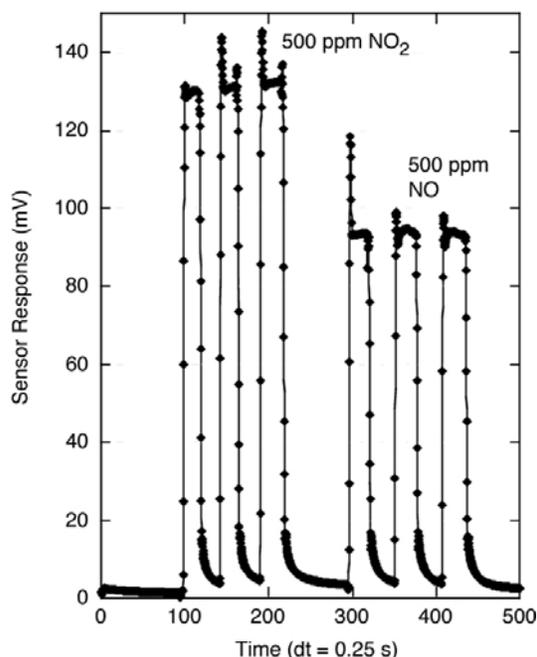
where  $V_O$  represents an oxygen vacancy and  $O^{2-}$  represents an oxide ion in the electrolyte lattice. At the anode, oxygen is liberated:



Because all tests are performed in high O<sub>2</sub> (~10%) and low NO<sub>x</sub> (≤ 500 ppm) concentrations, any changes in the I-V behavior upon changing the NO<sub>x</sub> concentration can be attributed to reactions involving oxidation or reduction of these species. Once the I-V behavior is determined, the operating bias condition can be selected based on the desired NO and NO<sub>2</sub> sensitivities. Sensor testing under a constant current bias is then performed to determine the sensitivity, selectivity, response time, and stability characteristics of the sensor.

## **Results**

Figure 1 shows the response of a biased sensor using an ITO electrode to 500 ppm of both NO and NO<sub>2</sub>. The sampling interval in the figure is 0.25 s, and the test temperature is 650°C. Figure 1 shows a similar response to both NO and NO<sub>2</sub>. These data were reported last year, and they show turn-on and turn-off times ( $\tau_{90}$ ) ~1.25 and 2.5 seconds, respectively, for the NO response. This fast response is attributed to the enhancement of the electrode kinetics caused by the biasing current. In the past year, continued testing has been performed to investigate some of potential cross-sensitivities of the ITO-based sensor.

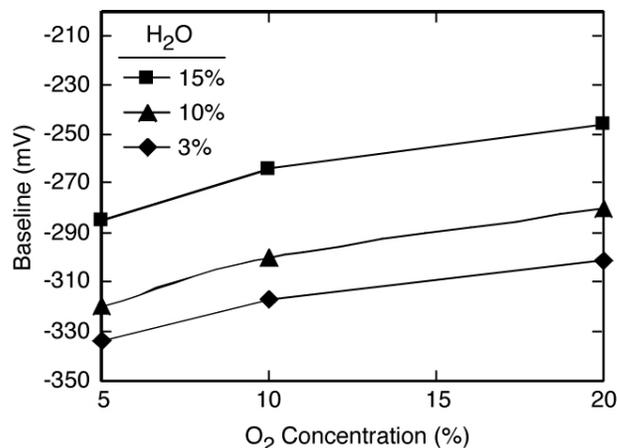


**Figure 1.** Response time vs. time for an ITO-based sensor exposed to 500 ppm NO and NO<sub>2</sub> at 650°C in 10% O<sub>2</sub>.

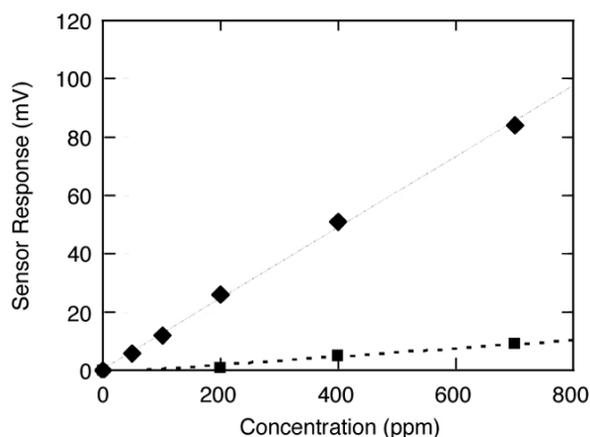
Last year it was reported that the NO<sub>2</sub> and NO responses of the ITO-based sensor are affected by the oxygen concentration very strongly and not at all, respectively. Figure 2 shows the effect of H<sub>2</sub>O and O<sub>2</sub> concentration on the baseline of the sensor. The baseline is defined as the sensor voltage required to maintain the pumping current in Eq. (1) in the absence of NO<sub>x</sub>. The data in Figure 2 show that the baseline is slightly affected by the O<sub>2</sub> concentration and strongly affected by the H<sub>2</sub>O concentration. This behavior could be problematic for a sensor of this composition, since the H<sub>2</sub>O concentration varies widely in CIDI exhaust. Therefore, alternative electrode materials have been investigated.

Figure 3 shows the NO and NO<sub>2</sub> response of a similar sensor using a ZnO sensing electrode and tested at 750°C. Note the very high selectivity for NO versus NO<sub>2</sub>. Such high selectivity enables the sensor to function as an NO sensor or, by the use of an NO<sub>2</sub> decomposition catalyst, as a total NO<sub>x</sub> sensor. The high operating temperature mediates some of the concerns regarding interfering gases, which are easily oxidized to less reactive species above 700°C.

Figure 4 shows the response to 400 ppm NO and NO<sub>2</sub>, and the sensor baseline, as a function of the oxygen concentration. The data show some depend-



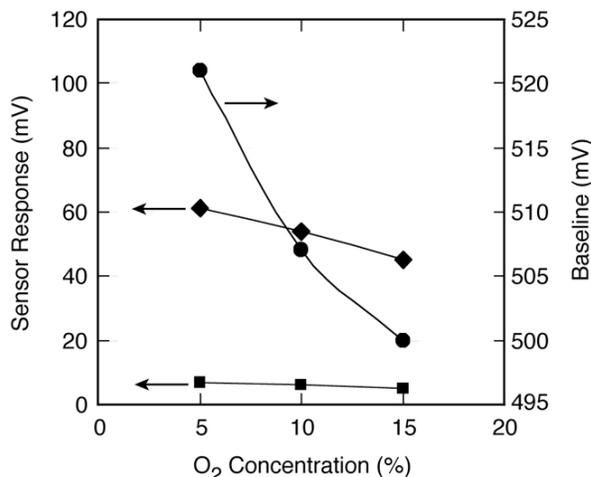
**Figure 2.** Baseline vs. O<sub>2</sub> concentration for the ITO-based sensor in 3 (♦), 10 (▲), and 15% (■) H<sub>2</sub>O.



**Figure 3.** Sensor response vs concentration of NO (♦) and NO<sub>2</sub> (■) for a ZnO-based sensor at 750°C in 10% O<sub>2</sub>.

ence on O<sub>2</sub> concentration, which is to be expected for a sensor of this type. This effect can be corrected for by the incorporation of a second sensor for monitoring O<sub>2</sub> concentration. The effect of H<sub>2</sub>O concentration on this sensor has not been carefully evaluated yet for the ZnO sensor.

Ongoing investigations are being performed to elucidate the sensing mechanism of this type of sensor. It has been observed during testing that there is a tendency for the sensor baseline to drift over time (~1-5 mV/hour). This may be attributable to coarsening of the electrode microstructure during testing or to changes in the stoichiometry at the electrode surface. Future efforts will involve identifying the mechanism for the baseline drift and evaluating means for stabilizing this effect. Possible techniques



**Figure 4.** Sensor baseline (●), and response to 400 ppm NO (◆) and NO<sub>2</sub> (■) vs oxygen concentration for a ZnO-based sensor at 750°C.

for doing so are modifying the electrode microstructure (for example, by incorporation of a more refractory phase), intentionally aging the electrodes, or selecting alternate electrode materials.

## Conclusions

A novel current-biased mode of operation is being investigated for NO<sub>x</sub> sensing in automotive diesel exhaust. Electrode materials have been identified that provide excellent sensitivity and response time for sensing NO at 650–750°C in 10% O<sub>2</sub>. Sensor stability and cross-sensitivity will be further addressed in future efforts. Long-term dynamometer testing is to be performed by Ford, and planning has been initiated for ultimate technology transfer to a commercial entity.

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## Publications/Presentations

L. P. Martin, D. Kubinski, R. Soltis, J. Visser, M. Parsons and R. S. Glass, "A Current-Biased NO<sub>x</sub> Sensor for Automotive Diesel Exhaust," presented at the 204<sup>th</sup> Meeting of The Electrochemical Society, Orlando, FL, October 12–17, 2003.

## Patents Issued

Patent application by L. P. Martin and A.-Q. Pham, "Current-Biased Potentiometric NO<sub>x</sub> Sensor for Vehicle Emissions," LLNL Docket #: IL-11022, submitted April 2003.

## **D. Hydrogen Compatibility of Materials for Automotive Applications**

*Russell H. Jones, James Holbery, and Thomas Gallant*

*Pacific Northwest National Laboratory*

*P.O. Box 999*

*Richland, Washington 99354*

*(509) 376-4276; fax: (509) 376-0418; e-mail: rh.jones@pnl.gov*

*DOE Technology Development Manager: Rogelio Sullivan*

*(202) 586-8042; fax: (202) 586-1600; e-mail: rogelio.sullivan@ee.doe.gov*

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*Contractor: Pacific Northwest National Laboratory, Richland, Washington*  
*Prime Contract No.: DE AC06 76RLO 1830*

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### **Objectives**

- Measure the friction and wear characteristics of injector materials in hydrogen environments.
- Measure the performance of actuators and actuator materials in hydrogen environments.

### **Approach**

- Use atomic force microscopy (AFM) in friction force microscopy (FFM) mode and nanomechanical measuring techniques to evaluate the friction and wear characteristics of injector materials in hydrogen environments.
- Perform in situ voltage/current pulses of fuel injector actuators in high-pressure hydrogen gas simulating engine conditions.

### **Accomplishments**

- Established a testing and research plan in collaboration with Westport Innovations, Inc., and Ford Motor Company.
- Conducted initial AFM and FFM testing of injector materials.
- Acquired actuators and actuator materials for high-pressure hydrogen testing.
- Defined the required apparatus and initiated the design and construction of apparatus for the high-pressure hydrogen testing of fuel injector actuators.

### **Future Direction**

- Complete AFM/FFM tests on several fuel injector materials in ambient and hydrogen environments.
  - Complete in situ actuator tests on two types of actuators in high-pressure hydrogen gas.
  - Develop concepts for an engineering wear simulation test in high-pressure hydrogen.
  - Evaluate durability of other engine materials such as steels and aluminum alloys in hydrogen environments.
-

## **Introduction**

The friction and wear characteristics of metallic materials depend largely on surface oxide films. However, a hydrogen environment is chemically reducing so that the loss of the surface oxide by wear will result in bare surface contact and an increase in friction and wear. An exploratory study will be undertaken to determine the frictional behavior of metals in a hydrogen environment using in situ AFM/FFM. Measurements will be made in a hydrogen environment on metallic materials used by Westport Innovations in its actuators. These materials include AISI H13, M2 and 4140 steels, 400 and 316L series stainless steels, and Aquamet 22.

This study aims to better understand and quantify the mechanisms that determine friction coefficient and surface properties of actuator needles and nozzles within a 100% hydrogen service environment by comparing hydrogen-exposed and as-received actuator materials. Using a combination of AFM in FFM mode and nanomechanical measurement techniques, we will analyze hydrogen effects on needle and nozzle materials to determine sliding contact degradation and extended wear behavior. In addition, we will perform repeated indentations at a single spot to simulate cyclical impact. This work will be coordinated with Westport Innovations, a manufacturer of hydrogen internal combustion injectors. The two sets of tests will be correlated and used to provide guidance on selection of hydrogen injector materials.

Piezoelectric injectors made by KCI and EPCOS use the piezoelectric material PZT, a lead zirconium titanate embedded in epoxy or other polymer materials. Potential degradation mechanisms include changes in the capacitance<sup>1-3</sup> and cracking<sup>4</sup> of the PZT material, separation of the PZT wafers within the stack, loss of electrical contact, or degradation of the epoxy or polymer holding the PZT materials. Any of these processes will result in loss of performance. Tests will be conducted on actuators and the PZT material in a high-pressure hydrogen environment of up to 100°C, typical of that in the engine application. The actuators and materials will be monitored during in situ voltage cycling that matches the actuator conditions.

## **Approach**

Nanomechanical surface properties and the relative friction coefficient of each candidate material will be determined using apparatus in place at

Pacific Northwest National Laboratory (PNNL). Candidate materials to be evaluated are all currently used by Westport Innovations to produce injector needle and nozzles. They include the following: carburized steel, AISI M2 (heat treated, with WCC coating), AISI H13 (gas nitride case-hardened), and 400 stainless steel. These samples will be tested both in the as-received condition and after exposure to 100% hydrogen under the following conditions: 50–100°C, a pressure of 31 MPa, and a test duration of 100 h or greater.

Nanomechanical surface properties will be determined in the ambient environment of each material listed using a Hysitron Picoindenter<sup>®</sup> mounted on a Digital Instrument Nanoscope<sup>®</sup> II AFM. We will perform two series of experiments: surface property characterization, including modulus and hardness, and repeated impact testing by repeating an indentation at the same location to determine material pile-up around the indent as a measure of deformation under a repeat load condition. Subsequently, the surface will be imaged with the AFM to quantify the impact zone.

The relative friction coefficient between an Si<sub>3</sub>N<sub>4</sub> AFM tip and each candidate material will be measured, in both the as-received and hydrogen-exposed conditions, using the AFM in FFM mode. These tests will be run in both an ambient and a 100% hydrogen atmosphere, the first time this is known to have been attempted. Using a multi-pass cantilever tip contact technique, whereby the AFM cantilever tip is in contact and passed across the surface under a constant load dependent upon the cantilever stiffness, the objective will be to determine the duration of surface wear necessary to measurably increase the material pair friction coefficient. We anticipate that each material will act differently, a reflection of their end-of-life wear properties; and we will make an attempt to relate these nano-scale measurements with larger bulk tests through a well-characterized material system, namely 316 stainless steel.

The performance of EPCOS and KCI piezoelectric actuators will be evaluated in a high-pressure hydrogen environment. A high-pressure autoclave with a pressure rating of 60 MPa will be used. The actuators will be electrically energized in situ in a high-pressure hydrogen environment under conditions consistent with injector operation. The voltage will be applied with a KCI power supply/driver unit. The actuators will be held in spe-

cially designed holders that allow the application of a compressive force during the test. The autoclave will have an oxygen monitor to ensure the environment remains at 100 ppm of oxygen or less.

The test conditions that will be used are these:

**EPCOS actuator:** peak voltage, 150 V; frequency, 80 Hz; pulse width, 1.0 ms; rise time, 100–200 microseconds; fall time, 100–200 microseconds; temperature, 50–100°C; hydrogen pressure, 31 MPa (4500 psi); test duration, 100 h or greater.

**KCI actuator:** peak voltage 450 V; frequency, 80 Hz; pulse width, 1.0 ms; rise time, 300–500 microseconds; fall time, 300–500 microseconds; temperature, 50–100°C; hydrogen pressure, 31 MPa (4500 psi); test duration, 100 h or greater.

The output of these tests will include the voltage, current, and capacitance of the actuators as a function of time. Breakdown time and probable breakdown mechanisms will be determined as warranted by the results.

## **Results**

AFM and nanoindentation testing has begun in ambient conditions using a Digital Instrument multi-mode II fixed with a Hysitron Nanoindenter. The Park CP 5 AFM, located in PNNL Building 325, is currently being retrofitted to accept 100% hydrogen in the chamber; this process and safety procedure are scheduled to be complete by December 1, 2004. In preparation, Radiation II training by James Holbery has been completed. Testing using the Park CP5 is to begin in November, starting with ambient condi-

tion friction force microscopic surface measurements on candidate materials.

Actuator testing is due to begin in early December. The actuators are in hand, the power supply is on order, and other autoclave systems such as the oxygen analyzer and valves are in hand and being checked out. The safety issues have been identified, and a safety procedure has been written. A preliminary safety review was completed.

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## 4. OTHER

### A. Polymer Electrolyte Membrane Materials for Fuel Cell Applications at Elevated Temperature

*J. M. Simonson*

*Oak Ridge National Laboratory*

*P.O. Box 2008, MS 6064*

*Oak Ridge, TN 37831-6110*

*(865) 574-4962; fax: (865) 574-4961; e-mail: simonsonjm@ornl.gov*

*J. W. Mays*

*University of Tennessee, Knoxville, and Oak Ridge National Laboratory*

*655 Dabney-Buehler Hall, 1416 Joe Johnson Drive*

*Knoxville, TN 37996*

*(865) 974-0747; e-mail: jimmymays@utk.edu*

*K. A. Mauritz*

*University of Southern Mississippi*

*P.O. Box 10076*

*118 College Drive*

*Hattiesburg, MS 39406-0001*

*(601) 266-559-5865; e-mail: kenneth.mauritz@usm.edu*

*DOE Technology Development Manager: Susan Rogers*

*(202) 586-3976; fax: (202) 586-9811; e-mail: susan.rogers@ee.doe.gov*

*ORNL Technical Advisor: David Stinton*

*(865) 574-4556; fax: (865) 241-0411; e-mail: stintondp@ornl.gov*

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*Contractor: Oak Ridge National Laboratory, Oak Ridge, TN*

*Prime Contract No.: DE-AC0500OR22721*

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#### **Objective**

- Develop a low-cost, high-performance polymer membrane material that operates at temperatures of up to 120°C for transportation fuel cell applications.

#### **Approach**

- Synthesize new membrane materials, based on polyphenylene sulfonate, with potential for high ionic conductance, long-term stability, and low cost.
- Test membrane material performance for electrical conductivity and test in single-cell test stand to assess potential applicability.
- Improve performance characteristics of novel membrane materials through chemical and morphological modification and through the addition of functional inorganic modifiers.

## Accomplishments

- Demonstrated synthesis of polyphenylene sulfonate, including polymerization, aromatization, crosslinking, and sulfonation steps.
- Carried out initial water-swelling tests of novel membrane materials.
- Identified inorganic functional modifiers with potential for membrane improvement.

## Future Direction

- Complete the testing of membrane conductance and single-cell test stand performance with current membrane materials.
- Initiate parametric determinations of membrane performance to assess optimal structural, functional, and modifier characteristics.
- Establish additional capabilities for rapid assessment of novel membrane material performance.
- Partner with the private sector to advance application of novel membrane materials for fuel cell applications to 120°C.

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## Introduction

Robust, highly conductive, and inexpensive polymer electrolyte membranes (PEMs) are needed for practical and reliable fuel cell operation at elevated temperatures. The current class of PEM fuel cells operating at 90°C is plagued by sensitivities to CO and peroxide formation that limit performance and require the use of high-purity fuels. A polymeric membrane able to operate at temperatures of up to 120°C will minimize issues with CO, since adsorption is no longer kinetically favorable. The nature of the polymeric membrane plays a crucial role in determining the performance of the fuel cell. Unfortunately, current membranes based on polymers such as Nafion™ suffer serious disadvantages, including high cost and limited thermal stability at temperatures above 100°C. Our approach combines novel material synthesis, characterization, and testing with the goal of demonstrating capabilities of new classes of PEMs for sustained operation at elevated temperatures. We have synthesized new polymeric membrane materials and are currently performing initial screening studies of their thermal, electrical, and transport properties.

## Approach

Our approach is to apply advanced synthetic techniques to prepare membrane materials with potential for high performance at low cost and to test

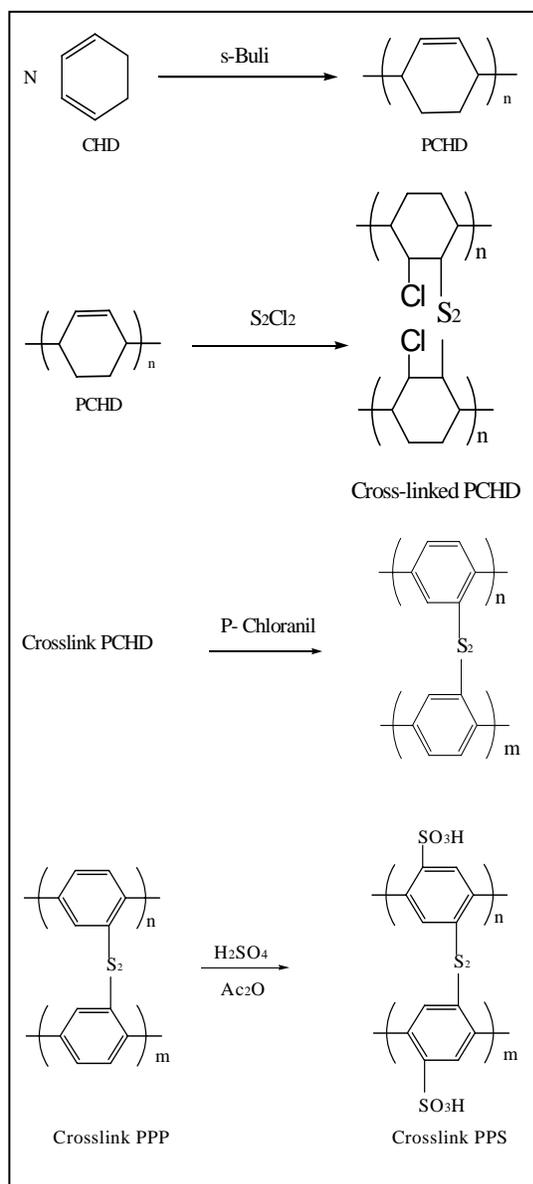
these materials under fuel cell operating conditions. Polyphenylene sulfonate (PPS) has been selected as the initial candidate material for high-performance membrane applications at elevated temperatures (120°C). The material is synthesized using cyclohexadiene monomer starting material. After living-ionic polymerization, the polymer is aromatized for thermal stability and resistance to attack from peroxides, crosslinked to control morphology and provide ion-conduction channel architecture, and sulfonated for ion conductance and water retention.

Membrane materials are tested for thermal stability using thermal [differential scanning calorimetry (DSC)] and thermogravimetric analysis (TGA) techniques. Water-sorption measurements are used to assess the conditions for humidification of the PEM. Agreements are in place to test membrane materials using standard four-point-probe conductance measurements, and to prepare and test membrane-electrode assemblies (MEAs) based on these new materials, at Battelle Memorial Institute. This testing is designed to establish proof-of-principle for the novel membrane materials.

Further improvement in membrane performance, both temperature capability and water retention, is anticipated through the addition of inorganic modifiers such as silica, either in a co-synthesis process or by incorporation as particulate materials.

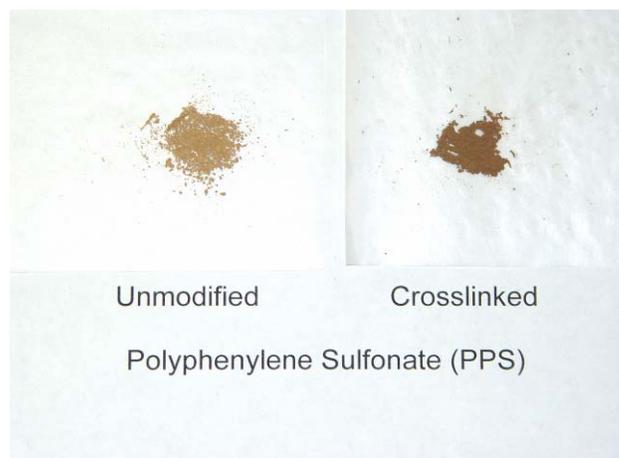
## Results

In FY 2004, we focused on the preparation of new membrane materials, starting from polycyclohexadiene (PCHD). The basis of the synthetic approach is to prepare the polymer in the desired molecular weight. Then the materials can be aromatized, crosslinked, and sulfonated as shown in the schematic in Figure 1.



**Figure 1.** Synthetic preparation of crosslinked polyphenylene sulfonate membrane material from cyclohexadiene starting material.

The form of material obtained from the steps in Figure 1 depends on the details of the synthesis route. The crosslinked polyphenylene is poorly soluble in most solvents tested and not amenable to straightforward solution casting of thin films appropriate for direct use as membranes. We have pursued two approaches to membrane preparation. In the first, PPS is synthesized by straightforward batch processing with subsequent purification of the material. This approach gives granular samples, as shown in Figure 2.

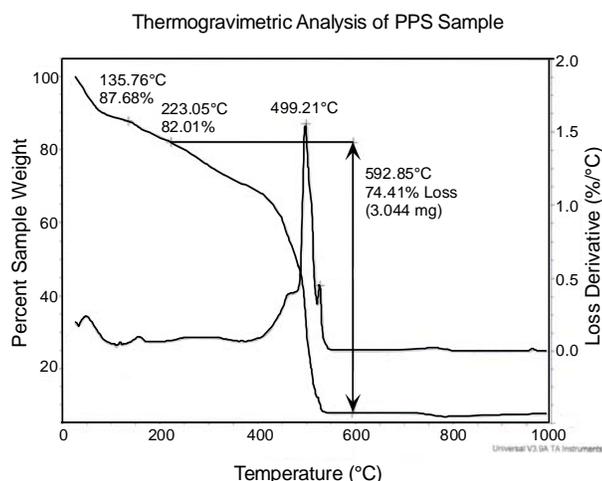


**Figure 2.** Polyphenylene sulfonate granular samples.

While it has proved difficult to form reproducible membranes from this granular material, given its high thermal stability and high glass-transition temperature, further efforts to prepare these membranes are in progress. Alternatively, we are investigating the preparation of membranes from solvent deposition of PCHD thin films (step 1 of Figure 1), with subsequent crosslinking, aromatization and sulfonation. These efforts are currently in progress in parallel with membrane fabrication from granular materials.

Thermal stability of the membrane is a key issue in sustained performance at the target temperature of  $120^\circ\text{C}$ . PPS has been tested for thermal stability by DSC and TGA, and results from these tests are shown in Figure 3.

The primary decomposition temperature for the material is near  $500^\circ\text{C}$ , as indicated by the strong peak in the derivative plot shown in Figure 3. Hot-



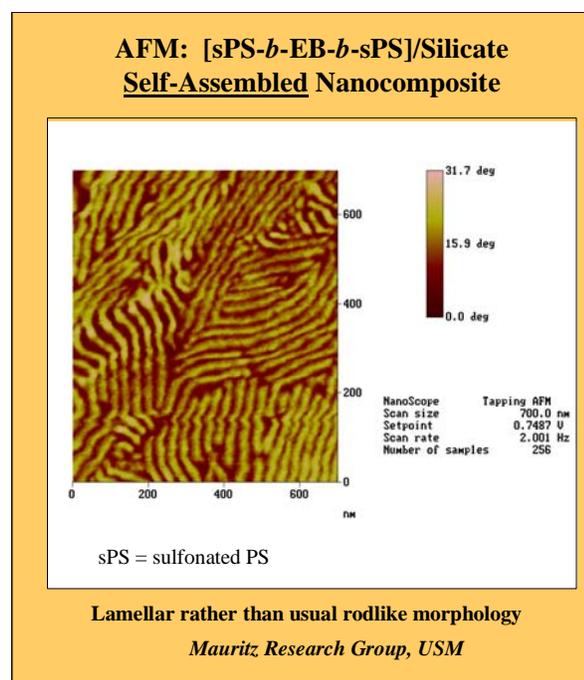
**Figure 3.** Thermogravimetric analysis of membrane material, indicating primary thermal decomposition near 500°C.

pressing the granular material results in thermal traces that show essentially no features in DSC to temperatures above 200°C. Thus it appears that the pressing process, or alternatively, initial heat treatment of the membrane material, “burns out” residual solvent and/or volatile components of the membrane and the stability of the material is subsequently improved through the intended working temperature range. Further testing, including analysis of thermal decomposition products by gas chromatography or mass spectrometry, is needed to confirm the stability of the material after initial heat treatment.

Capabilities for rapid screening (i.e., four-probe conductance measurements) and fuel cell test environments are being assembled at Oak Ridge National Laboratory for membrane and MEA tests. Until these facilities are available, to demonstrate proof-of-principle of the new membrane materials, agreements are in place with Battelle Memorial Institute in Columbus, Ohio, for testing in membrane and MEA configurations.

It is anticipated that membranes based on PPS material can be further improved through a parametric investigation of the effects on performance of molecular weight (chain length) and the extent of aromatization, crosslinking, and sulfonation. In addition, it is anticipated that addition of inorganic functional modifiers (e.g., silica) to the membrane

will help improve performance at relatively low humidity. A target has been established for operation at 20% relative humidity at 120°C, and efforts under contract at the University of Southern Mississippi are aimed toward improving performance through addition of candidate modifiers. As shown in Figure 4, in addition to improvements expected from potential preferential adsorption of water on nanoparticle sites within the membrane, addition of these modifiers can also affect the polymer structure. We are working toward establishing a network structure that will promote the formation of ion-conducting channels at the nanoscale, while minimizing gas flow through the membrane.



**Figure 4.** Lamellar structure in polymer matrix created through silica addition.

## Conclusions

We have demonstrated that PPS, a candidate material for PEM transportation applications at 120°C, can be readily synthesized from PCHD starting material; and we have demonstrated straightforward chemistry for aromatization, crosslinking, and sulfonation. Particularly if the precursor cyclohexadiene monomer becomes a readily-available commodity chemical, as is currently under market investigation, this new polymer electrolyte has the

potential to provide a very cost-effective route to high-temperature membrane applications. Thermal stability testing has shown that the primary decomposition temperature of PPS is near 500°C. Thus in addition to its potential for low cost, the thermal stability of the polymer electrolyte is promising for applications even above the current target temperature of 120°C.

Collaborative agreements are in place for near-term testing of novel membrane materials, and for the addition of functional inorganic modifiers to further improve membrane performance under conditions of elevated temperature and low relative humidity. In-house capabilities for expanded testing of PEM systems are being established and tested.

Proof-of-principle of PPS as a membrane material for high-temperature applications is expected in FY 2004. Major issues remaining for deployment of fuel cells based on this material are optimization of membrane performance through variation of major synthetic variables (molecular weight; degree of aromatization, crosslinking and sulfonation), demonstration of acceptable ion conductance and membrane durability in test-stand environments, investigation of the potential for addition of inorganic functional modifiers for improved perform-

ance at low humidity levels, and estimation of material cost based on optimized membrane configuration. Initial contacts with potential industrial collaborators indicate significant interest in the possibilities of this new material for PEM applications, and these contacts will be pursued further as the technical status of the project matures.

In FY 2005, we plan to continue synthesis and parametric testing of a range of PPS membrane materials and MEAs to assess the effects of changing material properties and treatment protocols on cell performance. Benchmarking test results and estimated costs against commercially available materials will provide the basis for selection of optimized synthesis, modification, and processing procedures. Our long-term goal is to define conditions needed for membrane performance in order to permit industrial scale-up of membrane production.

### **Publications/Presentations**

J. M. Simonson, J. W. Mays, and K. A. Mauritz, "Cost Effective Proton Exchange Membrane Materials for High-Temperature Fuel Cell Applications," poster presentation at the Hydrogen and Fuel Cell Program Review, Philadelphia, PA.



## APPENDIX A: ACRONYMS AND ABBREVIATIONS

AFM	atomic force microscopy
ANL	Argonne National Laboratory
ANL-ES	ANL-Energy Systems
APM	Automotive Propulsion Materials
ASTM	American Society for Testing and Materials
CIDI	compression-ignition direct-injection
CO	carbon monoxide
DOE	U.S. Department of Energy
DPF	diesel particulate filter
DSC	differential scanning calorimetry
EDM	electrodischarge machining
EDX	energy-dispersive X-ray spectroscopy
EE	Electrical and Electronics
EGR	exhaust gas recirculation
EN	electroless nickel
EPA	Environmental Protection Agency
FCVT	FreedomCAR and Vehicle Technologies
ffm	friction force microscopy
FTP	Federal Test Protocol
FY	fiscal year
<i>H</i>	hardness
H <sup>+</sup>	hydrogen ion
H <sub>2</sub>	hydrogen gas
H2RV	hydrogen hubrid research vehicle
I-V	current-voltage
ICS	Industrial Ceramic Solutions
ID	internal diameter
ITO	tin-doped indium oxide
kg	kilogram
LANL	Los Alamos National Laboratory
L/D	length-to-diameter
LLNL	Lawrence Livermore National Laboratory
MEA	membrane electrode assembly

NdFeB	neodymium-iron-boron
ND	neodymium
NEP	National Energy Policy
NIST	National Institute for Standards and Testing
nm	nanometer, $10^{-9}$ meters
NO	nitrogen oxide
NO <sub>x</sub>	oxides of nitrogen
NVFEL	National Vehicle and Fuel Emissions Laboratory
OEM	original equipment manufacturer
OFCVT	Office of FreedomCAR and Vehicle Technologies
ORNL	Oak Ridge National Laboratory
PCHD	polycyclohexadiene
PEM	polymer electrolyte membrane
Pd	palladium
PM	permanent magnet
PNNL	Pacific Northwest National Laboratory
PPS	polyphenylene sulfide
Pt	platinum
PVOH	hydroxylated polystyrene
PZT	lead zirconium titanate
R&D	research and development
S	sulfur
SAE	Society of Automotive Engineers
SEM	scanning electron microscope/scanning electron microscopy
SNL	Sandia National Laboratories
T	Tesla
TGA	thermogravimetric analysis
WC	tungsten carbide
XPS	X-ray photoelectron spectroscopy
XRD	X-ray diffraction
YSZ	yttria-stabilized zirconia