

II.C Critical Enabling Technologies

II.C.1 Development of Metal Substrate for DeNO_x Catalysts and Particulate Traps

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Objectives

- Evaluate materials that would suffice as metallic substrates for catalytic converters. Materials must have a lower cost than the current material used with properties sufficient for off-highway diesel applications.
- Evaluate alternate substrate designs that increase catalyst performance to allow smaller designs with less substrate weight and precious metal content.
- Successfully implement these material and design changes into off-highway production units.

Approach

- Material Identification and Testing: New and existing materials will be identified which meet the current requirements of coating adhesion, strength, and oxidation resistance at the lower temperatures experienced in diesel engines. Material testing will compare these to the current material.
- Alternate Design Testing: Alternate designs will be evaluated that increase catalyst performance with minimal change in backpressure.
- Implementation: Durability testing will be performed to ensure that design and material changes do not lower the useful life of the converter.

Accomplishments

- The long-term cyclic oxidation resistance of the candidate alloys was tested and found to be comparable to the current material up to 900°C.
- Prototype production of converters with candidate materials was completed. In producing prototypes, the coatability of these alloys was confirmed.
- Both new materials were formed into the new design substrate in the annealed condition.
- Small prototypes with the new design were produced.

Future Directions

- Complete testing of full-scale current design prototypes with new materials, including hot shake tests.
- Complete modeling of the new design to determine optimum geometry to maximize activity while minimizing backpressure.
- Produce full-scale prototype of new design substrate with optimized geometry and new material.
- Complete hot shake and engine testing of new design substrate.

Introduction

To meet estimated Tier 2 and Tier 3 Environmental Protection Agency emission limits for off-highway vehicles, it may be necessary to add exhaust aftertreatment devices. Two technologies under consideration are DeNO_x catalysts and particulate traps that utilize a packaged cordierite honeycomb catalyst support. This package performs well in on-highway applications; however, off-highway applications are much harsher. Ceramic material properties are not expected to be adequate for the severe conditions found in off-highway applications, such as high-vibration loads (>10 x gravity). Additionally, the ceramic matrix requires relatively thick walls between cells, causing high flow resistance, which translates to increased engine exhaust backpressure and approximately a 2-3% fuel consumption increase. Because metallic substrates have superior mechanical properties over ceramics in this application, they are a possible solution to both durability and flow resistance issues. Metallic substrates are expected to be a key enabler for durable, commercially viable off-highway exhaust aftertreatment devices.

Approach

The development of the metal catalyst substrate is focused in two areas: materials and design. The materials focus includes investigating metals that are more applicable to the diesel exhaust environment. Current metallic catalyst substrates are made from higher-cost alloys that have properties that are necessary for the automotive market. Since diesel engine applications are less demanding in terms of maximum temperature than the automotive market, the search for a less costly material was a major driver. The material selected must have a few key qualities: good oxidation resistance at diesel exhaust gas temperatures, catalyst coatability and adhesion, and good formability.

On the design side, the investigation is moving to alternative design shapes and packages. Current commercially available catalyst supports have straight channel passages. The current work looks to optimize the flow path, thereby increasing catalyst efficiency and potentially reducing necessary catalyst volume. The approach relies on computation

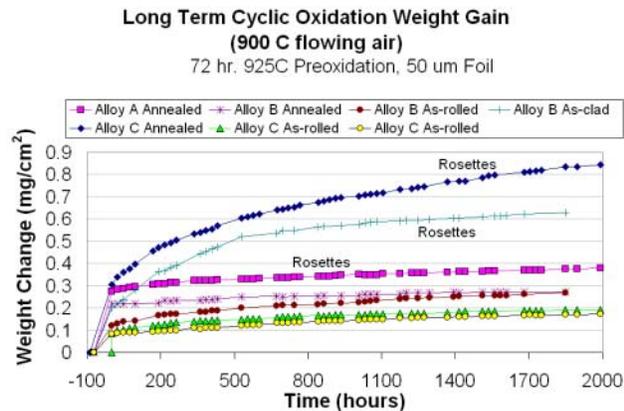


Figure 1. 900°C Flowing Air Cyclic Oxidation Data for Alloys A, B, and C (The material condition and pretreatment are shown in the legend. Each data point represents a cycle from 900°C to room temperature back to 900°C.)

methods to give design direction. The package shape is also critical since off-highway vehicles have severe space limitations on additional equipment. The work will also investigate the applicability of package shapes alternative to cylindrical or rectangular.

Results

The long-term cyclic oxidation testing of the current alloy (Alloy A), Alloy B, and Alloy C was completed (see Figure 1). The alloys were tested with different pre-treatments to create different types of oxide scale to assess their relative oxidation resistance. They were cycled by heating at 900°C followed by a rapid air cool to room temperature five times per week. It appears from these results that the oxide morphology tends to drive the oxidation rate as much as the alloy chemistry. The three samples with the highest oxidation rates (Alloy A annealed, Alloy C annealed, and Alloy B clad) all formed a rosette structure of alumina on the surface (see Figure 2). This structure provides excellent mechanical adhesion of the washcoat, but it apparently is not good at protecting the metal from further oxidation. The oxide structure of the samples with lower oxidation rates was found to have a “nodular” structure of Al, Cr, and Fe oxides (see Figure 2). This structure is a flatter, more protective oxide. Regardless of the oxide structure, it should be noted that all of these samples displayed very low oxidation

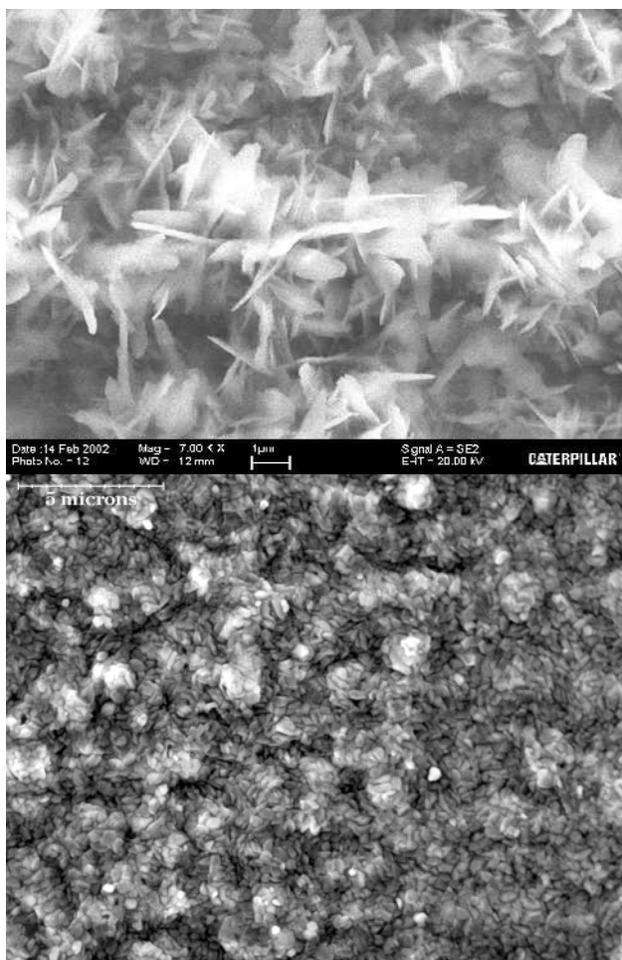


Figure 2. SEM Images of the Alumina Rosette Structure (a) and the Nodular Oxide Structure (b)

rates and are considered acceptable for long-term exposure in diesel engine exhaust.

It was originally assumed that an alumina rosette structure was necessary for optimum washcoat adherence due to good mechanical bonding in addition to any chemical bonding. This was a drawback to these new alloys, as their lower aluminum contents caused more difficulties in forming the rosette structure over the nodular structure. However, based on discussions with suppliers, as well as prototype production with the new materials (see Figure 3), it was determined that the washcoat adherence is very robust. The nodular structure provides sufficient washcoat adherence. Vibration testing of the full-scale prototype samples showed less than 1% weight loss on all samples



Figure 3. Example of 13" Diameter Prototype Substrate with Alloys B and C and a Straight-Channel Design

tested, which is well within the acceptance range for the supplier's test.

For the new substrate design, it was necessary to determine if the different foil materials in various conditions could be easily corrugated with the new, more complex design. Alloy C annealed, with the lowest aluminum content, was easily formed into the new design at production speeds. Alloy B annealed was satisfactorily formed into the new design. However, there were some small crimps and pinholes. Alloy B has an aluminum content only slightly lower than Alloy A. When in the as-rolled condition, both Alloys B and C had extensive splitting of the foil. Therefore, an annealed foil is necessary for the improved design because there is some tensile deformation of the foil during the corrugation.

Conclusions

The two candidate alloys have passed the minimum requirements thus far for oxidation resistance and coating adherence, and are useful for the new design in the annealed conditions. Assuming both alloys pass the durability and emissions testing, we will be able to choose the most cost-effective alloy.

II.C.2 NO_x Sensor for Direct Injection Emission Control

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DOE Technology Development Manager: Roland Gravel

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Objectives

- Develop an electronics control circuit for the NO_x sensor.
- Develop the packaging for the electronic controller.
- Develop the sensing element structure based on integrating zirconia and alumina ceramics and planar element technology.
- Develop the interconnection method to carry power and signal to and from the NO_x measurement device.
- Develop the necessary materials and process refinements in support of the ceramic sense element.

Approach

- Use alumina and zirconia ceramic tapes and thick film screen-printed pastes to form the necessary control and measurement cells. Integrate the heater on the co-fired substrate. Initiate development using simple configuration test samples and coupons. Continue to evolve the design and test samples into a fully functional NO_x measurement sense element.
- Confirm the operation of the sense element using bench and engine testing.
- Use set-based concurrent engineering to develop at least 2 different techniques to interconnect the power and signal wires to the sense element substrate. Use accelerated engine and environmental testing to establish the optimum interconnection approach.
- Use existing sensor packaging technology to house and protect the sense element.

Accomplishments

- Improved sinterability of a highly complex NO_x sense element.
- Developed process for key electrode material.
- Eliminated cross contamination of electrode materials through improved design.
- Implemented and improved an advanced interconnection design.
- Proved operation of the prototype electronic controller.
- Initiated electronics control parameter refinement.

Future Directions

- Evaluate the NO_x sensor subsystem in bench testing and on a running engine.
- Continue sensor technology refinements.

- Complete testing and characterization of the advanced interconnect.
- Investigate enhancements to the controller and associated algorithms.
- Continue process and materials developments.

Introduction

This project continues to develop the remaining technologies needed to deliver a robust NO_x sensor for use in closed-loop control of NO_x emissions in lean-burn engine technologies, particularly compression ignition, direct injection (CIDI) engines. At least two applications for NO_x sensors have been identified: (1) for measuring engine-out NO_x, requiring a high NO_x range of zero to 1500 ppm NO_x, and (2) for aftertreatment control and diagnostics, requiring a low NO_x range of less than about 100 ppm NO_x.

This activity builds on existing and developing Delphi technology in multi-layer and exhaust sensor ceramics, as well as work performed under a separate CRADA with Pacific Northwest National Laboratory (PNNL). Electricore, Inc., a 501c3 advanced technology development consortium, administers this project.

Approach

The Delphi-led team continues to leverage the electrochemical planar sensor technology that has produced stoichiometric planar and wide-range oxygen sensors as the basis for development of a NO_x sensor. Zirconia cell technology with an integrated heater will provide the foundation for the sensor structure. Proven materials and packaging technology will help to ensure a cost-effective approach to the manufacture of this sensor.

The electronics technique and interface are considered to be areas where new strategies need to be employed to produce higher signal-to-noise (S/N) ratios of the NO_x signal with emphasis on signal stability over time for robustness and durability. Both continuous-mode and pulse-mode control techniques are being evaluated.

Packaging the electronics requires careful design and circuit partitioning so that only the necessary signal conditioning electronics are coupled directly in the wiring harness, while the remainder are

situated within the electronic control module (ECM) for durability and cost reasons.

The sense element is based on the amperometric method utilizing integrated alumina and zirconia ceramics. Precious metal electrodes are used to form the integrated heater as well as the cell electrodes and leads. Inside the actual sense cell structure, it is first necessary to separate NO_x from the remaining oxygen constituents of the exhaust, without reducing the NO_x. Once separated, the NO_x is measured using a measurement cell. Development or test coupons have been used to facilitate material selection and refinement as well as cell, diffusion barrier, and chamber development.

The sense element currently requires elaborate interconnections. To facilitate a robust, durable connection, mechanical as well as metallurgical connections are under investigation. Materials and process refinements continue to play an important role in the development of the sensor.

Results

A differential pulse voltammetry (DPV) electronic control strategy was investigated. Significant oxygen cross sensitivity was observed, as shown in Figure 1. Analytical modeling revealed that diffusion of NO_x on the electrode surface is a controlling function. Future work needed to understand the underlying phenomena and their influential factors have been outlined, and it has been

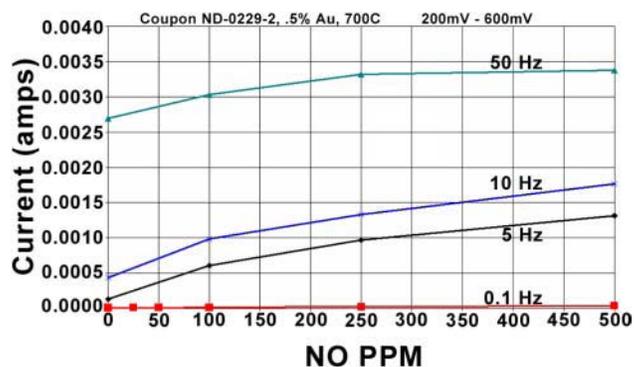


Figure 1. Differential Pulse Voltammetry vs. Frequency



Figure 2. NO_x Sensor Development Controller

decided to focus on continuous-mode control. A prototype electronic controller has been developed based on the continuous-mode control and is pictured in Figure 2. This controller will allow the use of the sensors for initial performance and durability studies.

The NO_x sense element is a device comprised of layers of alumina and zirconia ceramics that are processed to achieve the desired structure. Vias (small holes which are punched through the ceramic tape, later to be filled with precious metal) are used to bring the power and signal from the interior of the element to the exterior. Other features in the device are diffusion ports, chambers, electrodes, leads, contact pads, and air channels. The structure is built layer by layer and then “stacked” in the correct orientation and alignment. The layers are then consolidated using a lamination process, which applies both pressure and heat to mold the layers together. The sensors are each cut from the larger “tile” into individual sense elements prior to sintering.

The ceramic tapes have a significant portion of binders, plasticizers, and organics that require careful removal during the initial stages of sintering. Removal of the organics can cause delamination of the layers and formation of macro and/or micro cracks in the device. In the past, success was achieved through a slow binder removal process in argon to avoid ignition of the organics during the

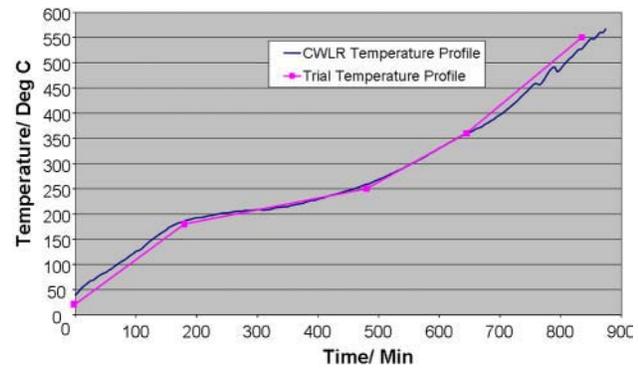


Figure 3. Constant Weight Loss Rate Temperature Profile



Figure 4. NO_x Sensor Packaged Assemblies

removal step. An alternative solution has recently been achieved through the use of a constant weight loss rate of the organics in air, as exemplified in Figure 3. This technique has allowed the successful sintering of the complex-shape NO_x sense elements. The majority of sense elements fabricated are free from defects that would interfere with the performance or structural integrity of the device. Post-sintering techniques and optimization of the chamber-electrode orientations were combined with additional materials development to significantly improve the sensing element.

Once the sense elements are processed and post treated, they are packaged in an exhaust sensor package such as those shown in Figure 4. This involves complex interconnects that require a parallel development activity to ensure robustness and

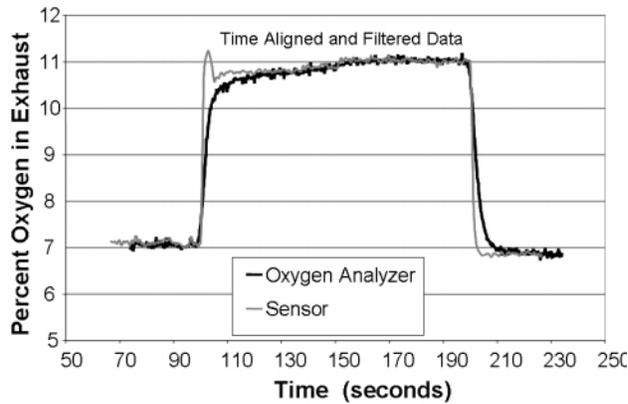


Figure 5. Time-Aligned Oxygen Measurement on the Dyno

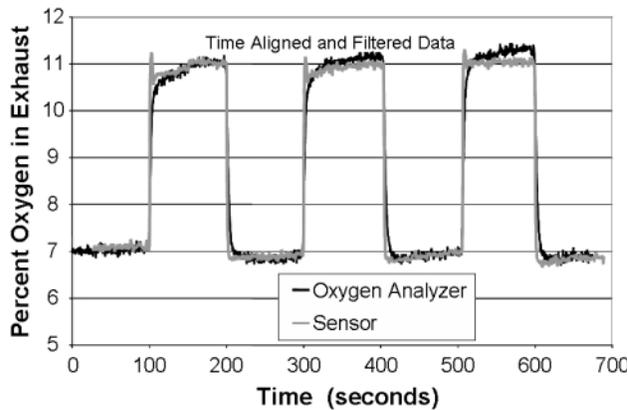


Figure 6. Oxygen Measurement over Several Cycles

enhance the potential for production viability. Mechanical interconnection technology has progressed to the point where it has been chosen as the primary connection technique.

Results of initial testing of the NO_x sensor system on a running diesel engine are shown in Figure 5. This figure compares the sensor oxygen concentration signal at the engine-out location to an oxygen analyzer. It can be seen that the processed oxygen concentration signal from the NO_x sensor correlates well with that from the analyzer. Figure 6

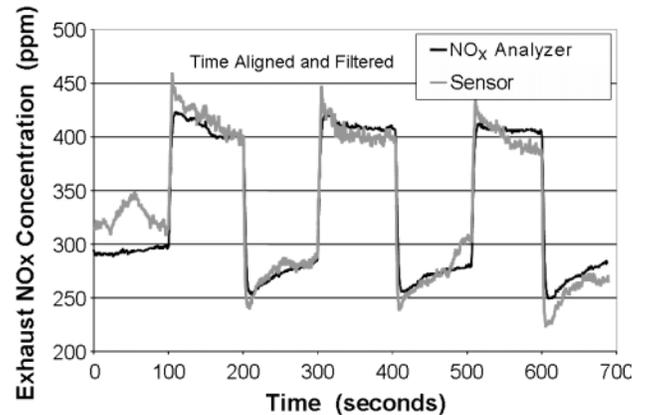


Figure 7. NO_x Measurement on the Dyno

shows six engine exhaust oxygen step changes with similar results from the oxygen concentration signal of the sensor.

Figure 7 shows the NO_x response with time through six step changes. The NO_x levels varied from about 250 ppm to about 450 ppm. In general, the NO_x sensor correlates very well with the NO_x analyzer.

Conclusions

The development needs of the DPV control approach have been identified, and continuous-mode control electronics have been developed and demonstrated.

NO_x sense elements have been fabricated successfully using a constant weight loss rate profile for the debinding stage of sintering.

NO_x sensors have been successfully packaged using a promising robust interconnection technique.

NO_x sensors have been tested on a diesel engine, with both the oxygen and NO_x concentration signals having a reasonable correlation to analyzer data.

II.C.3 Small, Inexpensive Combined NO_x and O₂ Sensor

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Objectives

- Demonstrate miniature, amperometric, inexpensive NO_x sensor body in the form of a multilayer ceramic capacitor.
- Incorporate NO_x sensor body with a similar oxygen sensor body in a zirconia tube as a fully assembled NO_x sensor.
- Demonstrate microprocessor-based measuring electronics.
- Supply sensors and measuring electronics for testing at Rosemount Analytical and other outside institutions.

Approach

- Measure NO_x sensing characteristics of a matrix of sensor bodies manufactured from stabilized zirconia in the form of multilayer capacitors with porous, Rh-based electrodes.
- Determine optimum electrodes, operating temperature range, and long-term stability of NO_x sensor bodies.
- Design and breadboard microprocessor-based measuring electronics and characterize.
- Prepare sensors and measuring electronics and supply these to Rosemount and others for testing.

Accomplishments

- Capacitor-type sensor bodies successfully manufactured with two types of porous Rh-based electrodes.
- Solved, but have not optimized, technical hurdle of rhodium oxidation.
- Large NO_x sensitivity demonstrated with sensor bodies having both types of Rh-based electrodes.
- Operating temperature range and voltage determined.
- Measuring electronics designed, built and tested successfully.

Future Directions

- Optimize Rh-based electrodes.
- Continue characterizations and long-term testing of NO_x sensor body.
- Develop electronic control of pO₂ inside assembled sensor and its temperature.
- Incorporate NO_x and O₂ sensor bodies into fully assembled NO_x sensors.
- Complete testing at outside institutions.

Introduction

The need exists for an inexpensive, reliable, on-board sensor to monitor NO_x emissions of vehicles to meet state and federal regulations. This NO_x -sensor project builds on a recent successful project supported by DOE to develop a miniature, amperometric oxygen sensor manufactured from stabilized zirconia as a multilayer ceramic capacitor with porous Pt electrodes which catalyze oxygen molecules to oxygen ions. The basic concept of the oxygen (and NO_x) sensor is illustrated in Figure 1. Oxygen ions are "pumped" from the (-) to the (+) electrodes across the zirconia ceramic layers under an applied voltage, and this amperometric current provides a measure of the oxygen partial pressure in the surrounding gas. The porosity of the Pt electrodes provides the necessary diffusion limitation, and there is no need for a reference gas. The sensitivity of this oxygen sensor is shown in Figure 2, and the output current is in the milliamp range. The sensor body contains eleven active ceramic layers and is approximately 2 mm x 3 mm x 5 mm. The established manufacturing methods for ceramic capacitors make this a very low-cost sensor body (~ \$1).

It is well known that Rh catalyzes NO_x to nitrogen and oxygen. If porous Rh electrodes are substituted for the porous Pt electrodes above, the resulting sensor will have an amperometric current output due to the oxygen released from the NO_x and will thereby provide a NO_x measurement. A schematic illustration of a combined oxygen and NO_x sensor is shown in Figure 3. The oxygen sensor

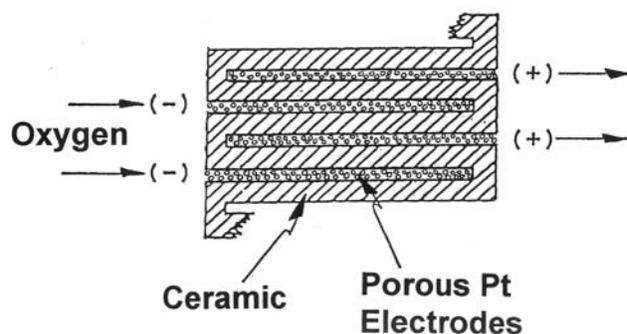


Figure 1. Schematic illustration of the capacitor-type amperometric sensor body showing the porous electrodes. The ceramic layers are stabilized zirconia and the electrodes are Pt in this example.

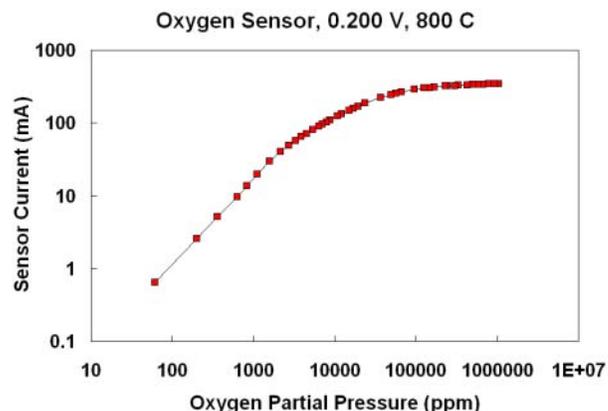


Figure 2. Oxygen sensitivity of the previously developed amperometric oxygen sensor (0.1 VDC applied).

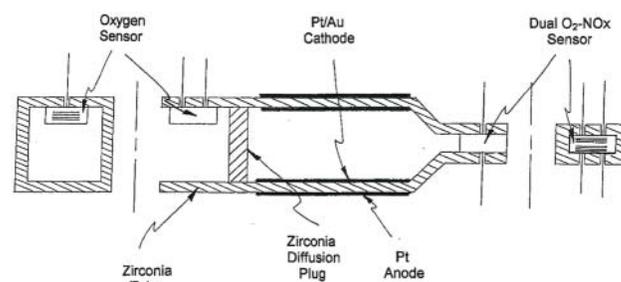


Figure 3. Schematic illustration of the combined sensor for measuring both the oxygen partial pressure and NO_x content of an exhaust gas. The exhaust gas diffuses through the zirconia diffusion plug, and the oxygen level in the inner chamber is pumped to a small, residual level by applying a voltage to the Pt/Au cathode and Pt anode electrodes.

is mounted in the open end of the zirconia tube to measure the oxygen in the exhaust gas, and bonded oxygen and NO_x sensors are mounted in the closed end. Exhaust gas diffuses through a diffusion plug into the inner chamber, where the oxygen in the gas is pumped to a low, residual level by a voltage applied across the Pt anode and the Pt/Au cathode. The oxygen sensor measures only the oxygen content of the gas. The NO_x sensor measures both the oxygen and NO_x contents. The difference in these two measurements is then a measure of the NO_x content of the exhaust gas. It is estimated that this combined sensor would be about 2.5 cm long and 1.3 cm in diameter, and parts cost would be \$5-10.

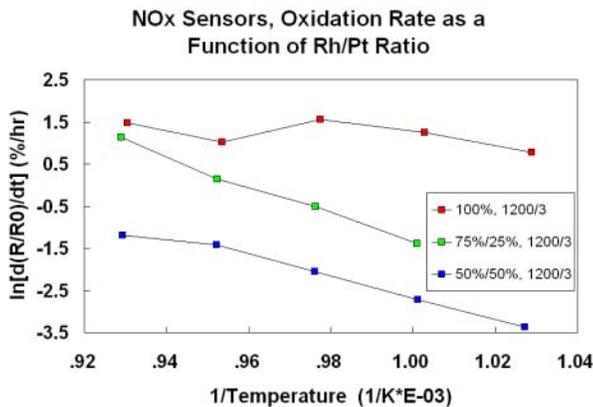


Figure 4. Arrhenius plot of the rate of change of resistance versus temperature for various electrode alloy materials.

Approach and Results

The capacitor manufacturer made zirconia sensor bodies with Rh electrodes and three active ceramic zirconia layers, each 0.008 cm thick. The first step involved measuring the NO_x sensitivity as a function of sintering temperature because, as with the oxygen sensor, the important porosity of the electrodes decreases with increasing sintering temperature. Sintering temperatures in the range 1200-1300°C were used, and the optimum temperature is 1200°C. The basic concept of sensing NO_x was demonstrated in these tests.

However, a fundamental problem arose in that the Rh slowly *oxidizes* in the 600-800°C operating range, and the amperometric current degrades with time. As the oxidation goes to completion, the volume change causes the sensor body to delaminate. Therefore, the emphasis shifted to using Rh-Pt alloys for the electrodes to inhibit electrode oxidation, and the manufacturer made sensor bodies with two alloys, 75%/25% and 50%/50% Rh/Pt electrodes. The alloying significantly decreased the rate of oxidation without affecting the NO_x sensitivity. The rate of oxidation was measured by monitoring the change in resistance of the electrodes as a function of time at various temperatures. Typical results are shown in Figure 4, which is an Arrhenius plot of the change in resistance with time versus temperature. The 50%/50% Rh/Pt electrodes reduce the oxidation rate significantly compared to the pure Rh electrodes.

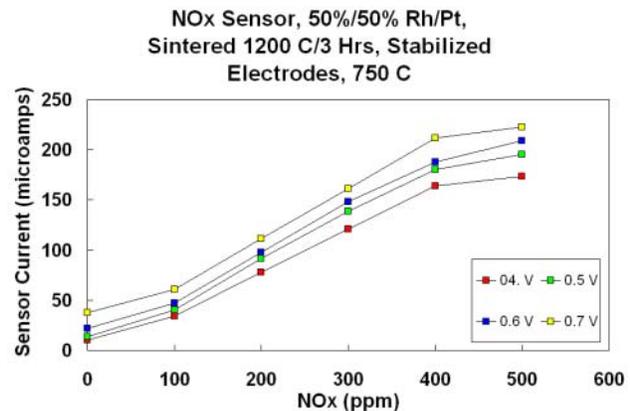


Figure 5. Typical NO_x sensitivity curves for NO_x sensor bodies with three electrodes and 50%/50% Rh/Pt electrodes as a function of applied voltage.

Typical NO_x sensitivity is shown in Figure 5 as a function of the voltage applied to the sensor. In order to keep testing costs down, all these measurements have been made using sensor bodies with only three active layers (refer to Figure 1). The final sensor bodies will have up to 30 electrodes, which will increase the response shown in Figure 5 by a factor of ten.

The basic electronic hardware has been designed, built, and tested successfully. This instrument has three outputs for each of the three sensors shown in Figure 3. Each output holds the voltage constant at the sensor while providing for independent measurement of the current through that sensor.

Conclusions

The basic concept of a miniature, inexpensive, amperometric NO_x sensor *has been demonstrated*, and this is the *key* element in the combined oxygen and NO_x sensor illustrated in Figure 3 (the accompanying oxygen sensor has been developed previously). The prospect of achieving a small, inexpensive NO_x + oxygen sensor that does not require a reference gas is now very promising, and such a sensor would serve an important diagnostic function onboard trucks and other vehicles for emissions control.

The Pt-Rh alloy for the electrodes of the NO_x sensor body has not yet been optimized, but the methods for determining this alloy are straightforward, although time-consuming and expensive.

Patents

1. A patent has issued for the oxygen sensor (US 6,592,731) and for the Combined Oxygen and NOx Sensor (US 6,824,661). Both patents were based on patent disclosures filed with the Patent Office prior to the receipt of the corresponding DOE contract.

II.C.4 Development of an Advanced Automotive NO_x Sensor

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Objectives

- In collaboration with Delphi Corporation, develop an electrochemical NO_x sensor that meets performance targets for sensitivity, range, accuracy and resolution, transient response, cross-sensitivity, lifetime and cost.
- Develop active, selective and stable oxygen roughing pump, oxygen finishing pump, and NO_x sensing electrode compositions and structures.
- Address materials processing issues in producing multistage ceramic sensor structures.

Approach

- Establish rates of electrochemical decomposition for oxygen and NO_x for selected electrode/electrolyte combinations as a function of temperature and partial pressures of oxygen, NO_x and other exhaust gases.
- Explore the suitability of non-noble metal-based compositions for use as the oxygen pump and NO_x sensing electrodes.

Accomplishments

- A ceramic oxygen pumping electrode was developed that is compatible with high sensor processing temperatures, shows very high activity for oxygen pumping, is insensitive to NO_x, and should be less costly than noble metal electrodes.
- Precise control of the oxygen partial pressure in the NO_x sensing stage has been shown to be essential to accurate and stable sensor performance.
- Reactions of carbon monoxide with NO_x over the NO_x sensing electrocatalyst can be suppressed by maintaining the oxygen partial pressure over a critical level.

Future Directions

- Determine how sensor operation is affected by the presence of ammonia in exhaust gases.
- Investigate pulsed detection methods as a means of enhancing sensor sensitivity and accuracy.

Introduction

A reliable NO_x sensor is an important part of advanced diesel exhaust gas treatment systems. The NO_x sensor is necessary to evaluate the efficacy of after-treatment approaches, which include the use of

selective catalytic reduction, NO_x absorbers, and/or plasma-based catalytic reactor systems. Sensors that can accurately assess NO_x slip from NO_x reduction devices are a necessary part of any exhaust treatment strategy. An increase in fuel economy related to the use of a NO_x sensor in a closed loop control mode is

estimated to be between 0.5 and 1%. A particularly challenging requirement for NO_x sensors is that they must continue to function properly even during such operations as trap regeneration, when pulses of reducing gases are introduced.

NO_x sensors were identified in the 2000 DOE Sensor Workshop as a high-priority need for compressed ignition/spark ignition direct injection (CIDI/SIDI) engines (Glass, Milliken, Sullivan and Howden 2000). Performance requirements for a NO_x sensor were recommended: 20-300±5 ppm sensitivity range for diesel fuel; 100-200±20 ppm sensitivity for gasoline; 600-1000°C operating range; 10 year lifetime (150K miles for autos, 500K miles for trucks); 1 second response time; provide separate measurements for NO and NO₂; and be immune to soot, sulfur, and ammonia. The need for improvements with respect to sensor durability, cost, response time, drift, and ammonia interference were noted.

Approach

The purpose of this project is to collaborate with the Delphi Corporation in the development of a reliable NO_x sensor. A multi-stage, amperometric approach is being followed, shown schematically in Figure 1, and consists of an oxygen roughing pump, an oxygen finishing pump, and a NO_x sensing stage, in addition to one or more reference cells. An amperometric design, as opposed to an approach based on mixed potentials, is believed to provide superior sensitivity, selectivity, and durability. Research and development performed at Pacific Northwest National Laboratory (PNNL) focuses on electrochemical response of the oxygen pump and NO_x sensing electrodes under a wide range of exhaust gas conditions, evaluation of alternative metal oxide electrode compositions, investigations of exhaust gas reactions that may affect the accuracy and sensitivity of the sensor, and evaluation of pulsed potential methods as a means of improving sensor response. These activities support Delphi Corporation's efforts to design and develop sensor elements, packages, and associated electronics; building of prototype sensors on a pilot scale; dynamometer and vehicle testing of prototype sensors; and evaluation of degradation processes.

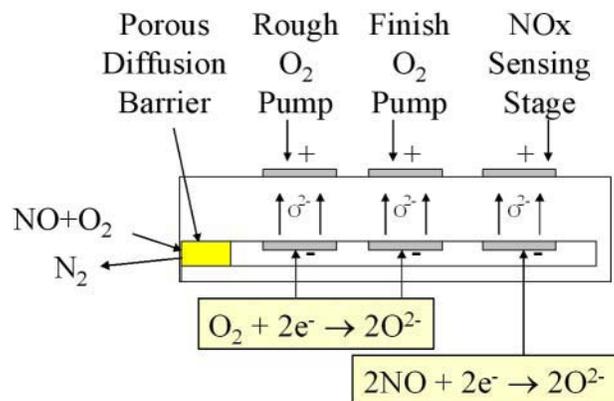


Figure 1. Functional diagram of an amperometric NO_x sensor being developed by the Delphi Corporation.

Results

Alternative ceramic electrode compositions were evaluated for use in oxygen pumping and NO_x sensing cells. One family of ceramic composite compositions is a promising candidate for use as the oxygen roughing pump electrode. The composite is compatible with high processing temperatures used in fabricating the multilayer sensors, provides a good thermal expansion match to other sensor components, shows excellent activity for oxygen pumping, is insensitive to NO_x, and should be less costly than noble metal-based electrode materials. The performance of this electrode is not affected by possible redistribution of gold from the oxygen finishing pump electrode, a dilute Au alloy with Pt. Pumping currents for this ceramic composite versus cell potential for a constant oxygen partial pressure and varied NO_x concentrations are given in Figure 2, which shows virtually no sensitivity to NO_x below an applied potential of 0.4 volts – approximately the operating potential of the roughing pump. Some small response to NO_x was found for higher potentials, but this behavior is unimportant for sensor operation.

Lanthanum strontium chromite compositions were also screened for use as oxygen pumping and NO_x sensing electrodes. The chromites are quite refractory materials with excellent electrical conductivity, and thus would be compatible with many sensor processing and operational requirements. Unlike results for the ceramic

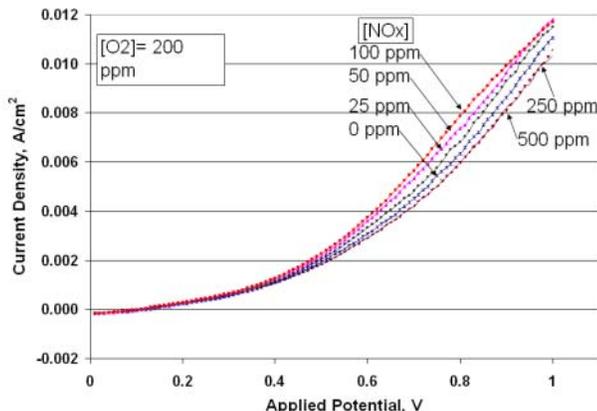
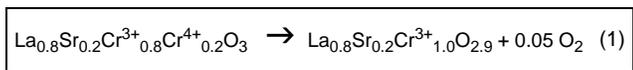


Figure 2. Oxygen pumping current density versus applied potential for an alternative ceramic composite electrode for a constant oxygen partial pressure of 200 ppm and NO_x concentrations ranging from 0 to 500 ppm. The ceramic composite electrode showed no sensitivity to NO_x below ~0.4 volts, approximately the operating potential of an oxygen roughing pump.

composite described above, the chromite electrode showed high sensitivity to NO_x. Further, the NO_x response was sensitive to the partial pressure of oxygen, as is shown in Figure 3. This material quite clearly is not appropriate for use in the oxygen roughing pump, but may be appropriate as the NO_x sensing electrode. Further testing showed the limitations of chromites for that purpose, however.

Lanthanum strontium chromite, and by inference most other metal oxide compositions, can be partially reduced under the conditions of the NO_x sensing stage. The applied electrical potential and low oxygen partial pressure in the NO_x sensing stage combine to create a locally very reducing environment. For the chromites, electrical conductivity is enhanced by partial substitution of Sr²⁺ for La³⁺, which causes an approximately equal quantity of Cr³⁺ to be converted to Cr⁴⁺. These introduced electron holes provide sites for electronic conduction. In a reducing environment, Cr⁴⁺ is converted back to Cr³⁺, as follows:



Oxygen that is produced by partial reduction contributes to an enhanced pumping current, which

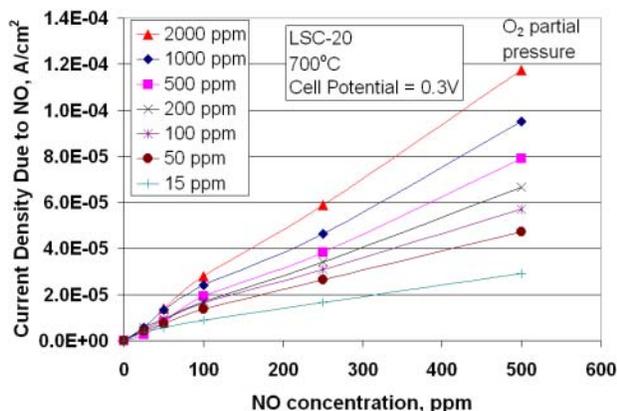
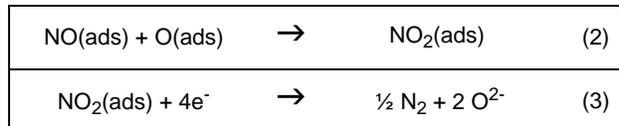


Figure 3. Current density versus NO_x concentration for oxygen concentrations ranging from 15 to 2000 ppm. Unlike the ceramic composite electrode, lanthanum strontium chromite electrodes were sensitive to NO_x. Further, the response depended on the partial pressure of oxygen in the test mixture.

could be mistaken for the presence of NO_x. As shown in Figure 4a, this effect is important for cell potentials greater than ~0.4 volts for chromite electrodes. The transient nature of this enhanced cell current is shown in Figure 4b, which describes changing pumping currents following a potential step. Because the chromites are among the more stable perovskite-based electronic ceramics originally developed for use in solid oxide fuel cells, others are expected to show similar trends. As such, use of metal oxide as the NO_x sensing electrode could complicate signal interpretation.

Response of the NO_x sensing electrode was found to be sensitive to oxygen partial pressure. Incremental current densities due to the presence of NO_x are given as a function of the oxygen partial pressure in Figure 5 for a platinum composite electrode and a constant NO_x concentration of 25 ppm. When the oxygen concentration was held very low, the sensitivity to NO_x was likewise low. An important mechanism for the electrochemical pumping of NO_x appears to involve the oxidation of nitric oxide by adsorbed oxygen, followed by the decomposition of nitrogen dioxide:



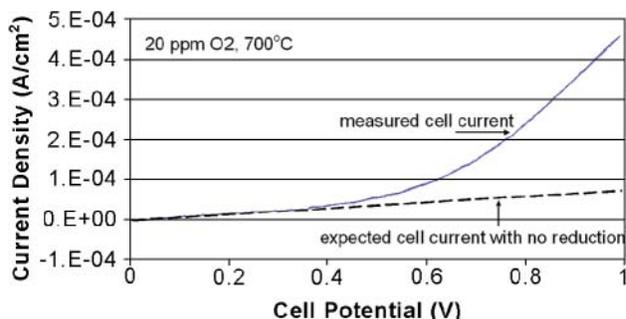


Figure 4a. Current densities arising from the use of a lanthanum strontium chromite electrode versus applied cell potential for low oxygen partial pressures. The partial reduction of the chromite results in higher cell currents than expected.

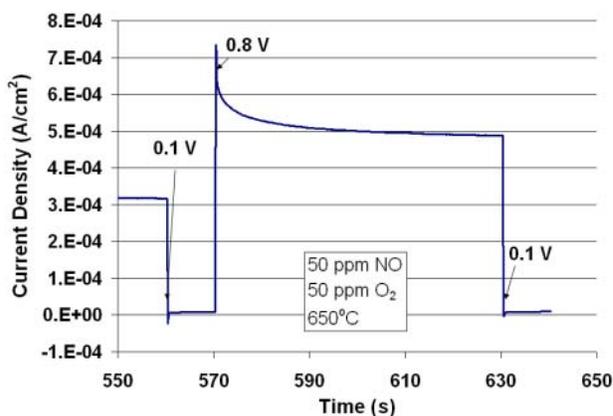
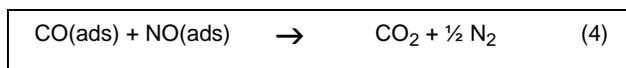


Figure 4b. Application of a voltage step results in a transient cell current for lanthanum strontium chromite electrodes, due to partial reduction of that electronic ceramic.

Mass spectrometer fragmentation patterns for nitrogen and oxygen support the above mechanism. Control of the oxygen partial pressure in the NO_x sensing stage to a constant non-zero level will therefore be necessary to maintain good sensitivity to NO_x.

Carbon monoxide was observed to quantitatively reduce NO_x over a platinum electrocatalyst for very low oxygen partial pressures, as follows:



Because lean diesel exhaust contains low levels of carbon monoxide, nominally 30 ppm, this reaction

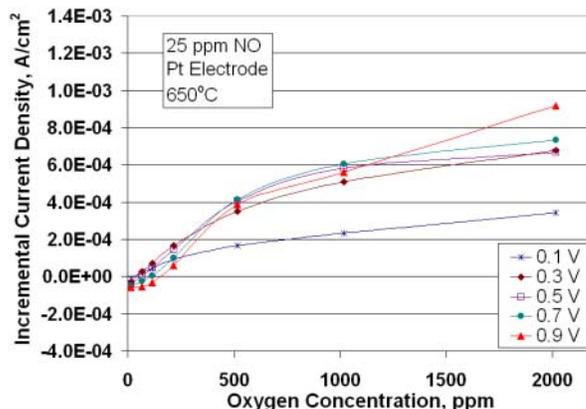


Figure 5. Incremental current density at the Pt electrode due to NO_x versus oxygen partial pressure for a constant NO concentration of 25 ppm. This behavior indicates that control of the oxygen partial pressure to a constant, non-zero value will be necessary to maintain good sensitivity.

could potentially affect the sensitivity of the sensor. Reaction (4) can be suppressed by controlling the oxygen partial pressure to values greater than the critical oxygen decomposition pressure for carbon monoxide. At an oxygen partial pressure of 100 ppm and carbon monoxide concentrations typical of lean diesel exhaust, reactions of nitric oxide and carbon monoxide could largely be suppressed over the platinum electrocatalyst.

Conclusions

A ceramic composite electrode has been identified for possible use as the oxygen roughing pump electrode. The composite is highly conductive, active for oxygen pumping, sufficiently refractory to be compatible with current sensor processing temperatures, and insensitive to the presence of NO_x. Non-noble metal-based, use of the material could help to lower the cost of sensor manufacture. Ceramic electrodes do not appear to be appropriate for use as the NO_x sensing electrode due to the tendency for partial reduction under oxygen partial pressures and applied potentials typical of that cell.

Cell currents due to NO_x were shown to be sensitive to the oxygen partial pressure. A mechanism consistent with observations involves the oxidation of nitric oxide to nitrogen dioxide on the surface of the electrocatalyst, followed by enhanced

electrochemical decomposition of the nitrogen dioxide to produce a cell current. These results suggest that control of oxygen in the NO_x sensing stage to a constant but non-zero value is essential in achieving high sensor sensitivity.

Under certain conditions, carbon monoxide will quantitatively reduce nitric oxide to nitrogen in the NO_x sensing stage, an effect that could significantly lower sensor sensitivity. Through control of the residual oxygen concentration in that portion of the

sensor, reactions of carbon monoxide and NO_x can be suppressed.

References

1. Glass, Robert S., JoAnn Milliken, Ken Howden, and Rogelio Sullivan, "DOE Workshop on Sensor Needs and Requirements for Proton-Exchange Membrane Fuel Cell Systems and Direct-Injection Engines," USDOE Office of Energy Efficiency and Renewable Energy, 2000.

II.C.5 Advanced Portable Particulate Measurement System

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DOE Technology Development Manager: Kevin Stork

Industrial Collaborator:

Sensors Inc., Saline, MI

Objectives

- Evaluate Argonne's portable particulate measuring system for on-vehicle particulate matter (PM) measurements.
- Obtain feedback from an instrument manufacturer for potential improvements.
- Evaluate the instrument measurement sensitivity to the volatile organic fraction of PM.

Approach

- Reconfigure the existing instrument for on-vehicle demonstration on a 1999 Mercedes C-class vehicle.
- Perform measurements using a thermodenuder in the sample line to evaluate the measurement sensitivity to volatile organic fraction of PM.

Accomplishments

- Successfully demonstrated that the present instrument can be used as a portable emissions measurement system (PEMS) for typical vehicle operations on the highway.
- Obtained design goals from the instrument manufacturer for further improvement.

Future Directions

- Redesign and rebuild an improved version of the instrument per manufacturer suggestions.
- Complete the tests evaluating the sensitivity to the volatile organic fraction of PM.
- Explore the possibility to incorporate the capability to measure particle aggregate size and number density.

Introduction

Argonne National Laboratory (with funding from the DOE Office of FreedomCAR and Vehicle Technologies) has developed an instrument for diesel exhaust particulate characterization (Figure 1). This instrument (named TG-1), which is based on a technique called laser-induced incandescence (LII), is portable and facilitates real-time measurements especially during engine transients. Though the measurement of particulate mass concentration (mg/m^3) has been demonstrated so far, measurement of mean particle size and number density is also

possible. Through tests conducted at Argonne, Caterpillar, and Cummins, this instrument was proven to exhibit excellent linearity, insensitivity to vibration, and excellent day-to-day repeatability [Ref. 1,2]. In FY 2004, it was decided to evaluate the instrument for on-vehicle PM measurements.

As diesel engine combustion has been improved to reduce PM emissions, the volatile organic fraction of PM has increased. It was our objective to evaluate the sensitivity of the present instrument to the volatile organic fraction of PM.



Figure 1. The Argonne TG-1 PM Measurement Device

Approach & Results

In FY 2004, Sensors Incorporated, an instrument manufacturer from Saline, Michigan, had shown interest in commercializing the present instrument. After two visits to Argonne, Sensors Inc.'s representative stated that their main interest was in the application of the present instrument to perform on-vehicle measurements, i.e., in adapting the present instrument as a portable emission measurement system (PEMS). Subsequently, the instrument was mounted on a 1999 Mercedes C-class vehicle as shown in Figure 2. The exhaust from the vehicle was partially sampled and diluted with air (in a ratio of 1 to 15) using Matter Engineering's rotating disk dilution system. Subsequently, the sample was passed through the sample cell of the TG-1 instrument, where instantaneous measurements were performed by the instrument. A small sample pump provided the suction necessary to draw in the sample through the system. While the data was collected by the passenger using a laptop computer, the vehicle was operated up to speeds of 60 mph on rural Michigan roads. Some of the photographs of these tests are shown in Figure 3, and Figure 4 shows sample data output.

As the volatile fraction of PM increases, it is possible that the TG-1 can be used to measure total PM. By passing the sample through a denuder, one can strip the volatiles and measure the solid carbon fraction using a TG-1. The difference of these values can give a measure of the volatile organic fraction. This concept is schematically shown in Figure 5. To

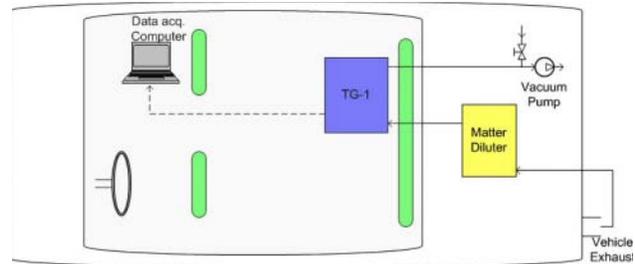


Figure 2. Schematic Layout for On-Vehicle Demonstration of the TG-1



Figure 3. The Instrumented 1999 Mercedes C-Class Vehicle (top) Sensors Inc. Personnel Taking On-Vehicle PM Data (bottom)

evaluate this concept, a thermodenuder from a German company was ordered and received after 3 months (Figure 6). Tests are underway to determine the efficacy of this unit in stripping the volatiles.

Conclusions

Though the use of TG-1 as a PEMS was successfully demonstrated, the following issues were raised by Sensors, Inc.

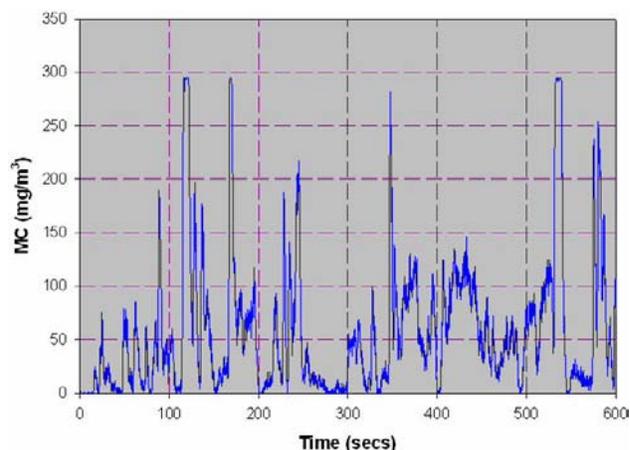


Figure 4. On-Vehicle PM Concentrations Measured Using the TG-1

- Footprint: Desirable to reduce by 50%.
- Weight: Currently at 40 lbs - needs to be reduced by half; in addition, the laser power supply needs to be integrated into the instrument.
- Power requirement: Currently at 1100 watts, which is well above power levels that can be supplied by a typical vehicle; desirable to be reduced to ~250 watts.

Considering the above issues, it was decided to use the recently developed diode pumped solid-state lasers that reduce the footprint, weight and power requirements by an order of magnitude. Additionally, the use of fiber optics for the delivery of both the laser as well the signals was considered. Such an arrangement allows placing the photo sensors away from the heated sample cell, thereby increasing their measurement sensitivity. Efforts are underway to finalize the blueprints of the next-generation version of this instrument.

Special Recognitions & Awards/Patents Issued

1. Portable LII Based Instrument and Method for Particulate Characterization in Combustion Exhaust; US patent No. 6,700,662.

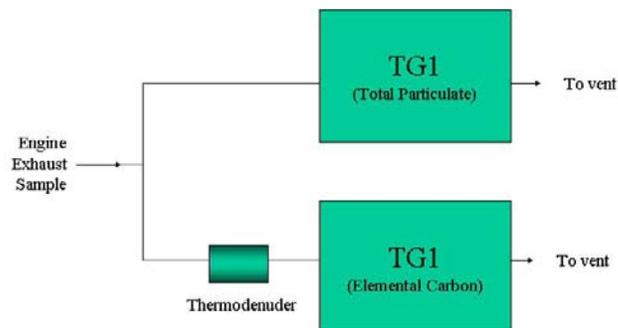


Figure 5. Schematic of the Concept to Measure Volatile Organic Fraction in Real Time



Figure 6. The Thermodenuder Heats the Sample to ~400°C and Absorbs the Volatiles Using Activated Carbon (The solid carbon aerosol is passed through.)

FY 2004 Publications/Presentations

1. Poster presentation at the Annual DOE Advanced Combustion Program Review, Argonne, IL.
2. Poster presentation at the DEER 2005 conference, San Diego, CA.

References

1. Sreenath Gupta, Gregory Hillman, Essam El-Hannouny and Raj R. Sekar, "Transient Particulate Emission Measurements in Diesel Engine Exhausts," SAE 2003-01-3155, Journal of Fuels and Lubricants.
2. Sreenath Gupta, "Transient, Real-time, Particulate Emission Measurements in Diesel Engines," 2003 DEER conference.

II.C.6 High-Energy, Pulsed Laser Diagnostics for the Measurement of Diesel Particulate Matter

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DOE Technology Development Manager: Kevin Stork

Objectives

- Develop real-time, engine-out particulate matter (PM) diagnostics for measuring size, number density, volume fraction, aggregate characterization, volatile fraction, and metallic ash species and concentration.
- Transfer resulting technology to industry.

Approach

- A scanning mobility particle sizer (SMPS) is used as the reference standard for particle size distributions.
- Laser-induced incandescence (LII) is used to measure the soot volume fraction.
- Laser-induced desorption with elastic laser scattering (LIDELS) is used to measure the volatile fraction of the PM.
- Laser-induced breakdown spectroscopy (LIBS) is used to measure metallic ash species and concentration.
- Simultaneous measurements of elastic light scattering (ELS) and LII (ELSLII) are used to obtain the equivalent particle diameter.
- Simultaneous measurements of ELS and LII will be used to obtain the following PM aggregate parameters using the Rayleigh-Debye-Gans polydisperse fractal aggregate (RDG-PFA) approximation:
 - particle volume fraction
 - diameter of primary particles
 - number density of primary particles
 - geometric mean of the number of primary particles per aggregate
 - geometric standard deviation of the number of primary particles per aggregate
 - mass fractal dimension
 - radius of gyration of the aggregated primary particles
- Off-the-shelf components are used to build a measurement system that can be easily duplicated by industry partners.
- Artium Technologies Inc., in Sunnyvale, CA, is commercializing the resulting technology.

Accomplishments

- Time-resolved LII measurements of PM volume fraction have been obtained for engine startup/shutdown, exhaust gas recirculation (EGR) and throttle transients, and these measurements have been compared with SMPS measurements.
- Time-resolved LII measurements obtained for a variety of vehicles during FTP-75 have been compared with tapered element oscillating microbalance (TEOM) and electrical low pressure impactor (ELPI) measurements. LII was shown to be sensitive to better than 0.5 mg/mi.

- Real-time LIDELs measurements of the volatile fraction of diesel PM have been obtained for load and EGR sweeps.
- A collaborative LII investigation of the effects of EGR on PM was conducted with the Combustion Research Group at the National Research Council, Canada.
- Measurements of the calcium in lube-oil ash have been obtained using LIBS.
- A mobile, high-energy laser diagnostics (HELD) system has been built for use in other Sandia engine laboratories and off-site with industrial collaborators. The system was at Ford's Vehicle Emission Research Laboratory for two weeks in February, 2003; Cummins Technical Center for ten weeks in July-September, 2003; and Oak Ridge National Laboratory's National Transportation Research Center for ten weeks in April-June, 2004. All three collaborations resulted in technical papers.
- To demonstrate the ease of use of LII, operator-free measurements were obtained by Cummins for 7.5 weeks of 24/7 operation.
- Artium Technologies' prototype commercial LII instrument was successfully demonstrated on-board a diesel passenger car in November, 2003. The first commercial sales occurred in the spring of 2004.
- Time-resolved (4 Hz data rate) LIDELs measurements of the volatile fraction of diesel PM have been obtained for engine transients.

Future Directions

- Develop experimental capability to measure equivalent particle diameter using ELSLII.
- Extend the LIBS technique to enable time-resolved measurements using inexpensive analog detectors (rather than a spectrometer with an intensified camera).
- Develop experimental and modeling capability for RDG-PFA approximation for aggregate characterization.
- Continue the collaboration with Artium Technologies toward commercialization of HELD instrumentation for PM measurements.

Introduction

LII is a well-established technique for the measurement of PM volume fraction and primary particle size. Light from a high-energy pulsed laser is used to heat the PM to its vaporization point, resulting in thermal radiation that is proportional to the PM volume fraction. Simultaneous measurements of ELS from the particles at several discrete angles relative to the incident laser beam can be used to obtain additional information regarding the characteristics of PM aggregates using the RDG-PFA approximation.

LIDELs is a new technique we have developed for the real-time measurement of the volatile fraction of diesel PM. Laser energy is used to desorb the volatile matter from the diesel PM, and ELS measurements obtained before and after desorption give the volatile fraction. Conventional procedures require collection on filter paper, and subsequent

analysis requires from several hours to several days to obtain a measurement. Our real-time LIDELs procedure uses a single laser to obtain a measurement in approximately one minute. Our time-resolved LIDELs procedure uses two lasers to obtain measurements at 4 Hz.

LIBS is a fairly well-established technique for measuring metallic ash. A focused laser beam is used to ionize the ash, resulting in atomic emissions that identify the species and their concentrations.

The ratio ELS/LII is routinely used in flame studies to measure the equivalent particle diameter of dry soot. Because diesel PM contains considerable volatile material, we are developing a new technique, ELSLII, that measures the elemental carbon diameter.

A single HELD system can perform all of the above tasks. Its main advantages over conventional

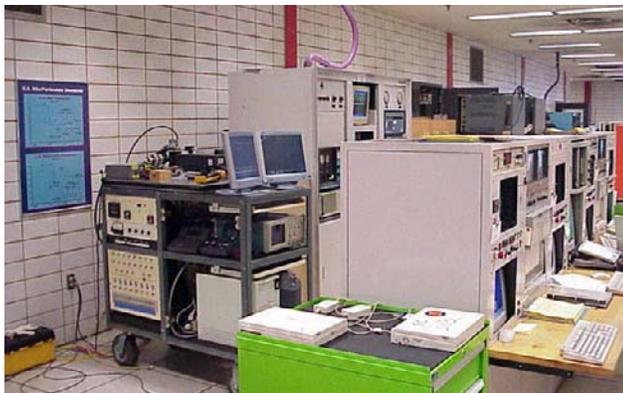


Figure 1. Mobile HELD System at the Cummins Technical Center in Columbus, IN

PM measurement techniques are that it can be applied in any environment (e.g., hot or cold, undiluted or diluted, etc.), it responds in real time and is very sensitive to low PM concentrations (e.g., the lower limit for LII is estimated to be one part per trillion, or about 0.5 mg/mi).

Approach

The complete HELD system has been assembled on a mobile cart of dimensions 2'x4', as shown in Figure 1, at the Cummins Technical Center in Columbus, Indiana. The only external connections required for use are the sample line for the diesel exhaust, a return vent line, and 110-volt power. The optical setups for LII, ELS, LIDELs, and ELSSLII can coexist, whereas LIBS requires the installation of an additional focusing lens. The cabling connections to the data-acquisition oscilloscope are unique for each HELD technique. However, once properly connected, all HELD applications are totally PC controlled, providing essentially "hands-off" operation.

Each time we develop a new HELD technique or make a significant improvement or application of an existing one, we publish the procedures and results in an archived technical article. To further assist the transfer of HELD technologies to outside users, we are pursuing two parallel paths. Because off-the-shelf components are used whenever possible, the expedient approach is to "clone" the system from a shopping list of parts; the PC software and ancillary drawings and schematics are all in the public domain. The alternative is to purchase a commercial unit



Figure 2. 2002 Volkswagen Diesel Jetta with the Artium LII-200™ Instrument in the Trunk

provided by Artium Technologies, Inc., of Sunnyvale, CA. We are working directly with Artium on a no-fee basis to develop commercial products. At this time, Artium is marketing an LII instrument, but neither LIDELs nor LIBS are currently available other than by a development contract.

Results

LII is ideally suited for on-road PM measurements because neither dilution nor an operator is required. Shown in Figure 2 is a 2002 Volkswagen Jetta passenger vehicle with a turbocharged direct injection (TDI) diesel engine. The commercial LII instrument of Artium Technologies, LII 200™, was placed in the trunk along with a small generator and driven around the Livermore Valley for a day. Typical measurements are shown in Figure 3 for a freeway acceleration from a stop. In general, the spikes in PM emissions correspond to gear shifts by the automatic transmission.

The Sandia HELD system was taken to the Cummins Technical Center in the late summer of 2003 (Figure 1). Because Cummins runs the emissions test facility 24/7, the HELD system was configured with the LII output signal connected to the Center's analog data acquisition system. The system ran continuously for 7.5 weeks, logging 1078 individual tests. Among the tests logged were 363 Federal Test Procedure (FTP) steady-state mode tests

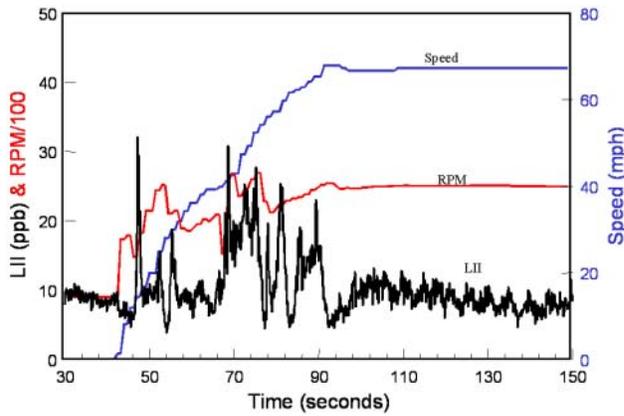


Figure 3. On-road LII Measurements for a Freeway Acceleration from a Stop

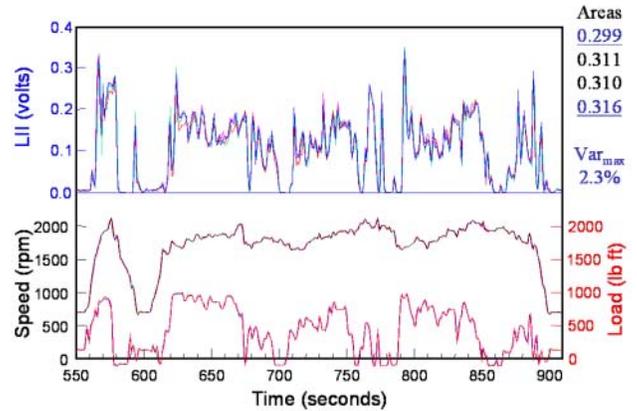


Figure 5. LII Measurements Obtained at Cummins for Four Repeats of a Segment of the Transient Heavy-Duty FTP

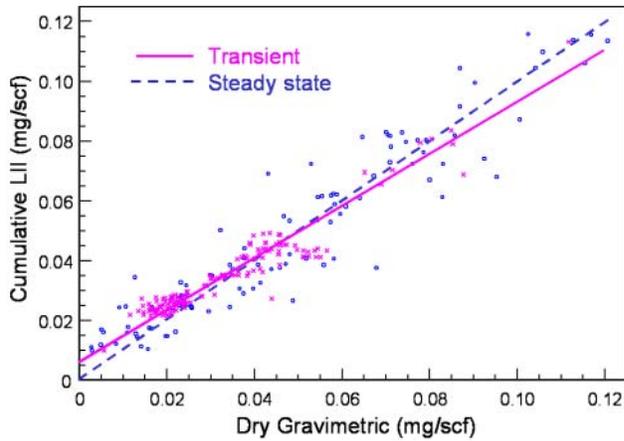


Figure 4. Correlation of LII and Gravimetric Measurements for Both Steady-State and Transient FTPs

and 250 FTP transient tests for which gravimetric measurements of total particulate matter (TPM) were obtained. Of these tests, removal of the filter-based volatile matter using supercritical fluid extraction was performed on 142 and 147 of the tests, respectively. The correlation between the time-integrated LII signals and the dry gravimetric measurements for the steady-state mode tests was used to calibrate the LII measurements in mass units, as shown in Figure 4 (dashed line). This calibration was then used to evaluate the correlation between the LII and dry gravimetric measurements for the transient tests (solid line).

It is our belief that much of the scatter in the data of Figure 4 is due to artifacts in the dry gravimetric measurements. To support this contention, shown in Figure 5 are LII measurements for four repeat tests

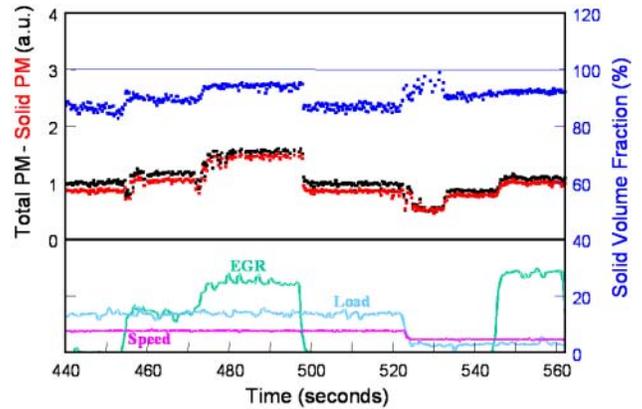


Figure 6. Time-Resolved LIDELs Measurements for Various Engine Transients

for a segment of the transient FTP. The test results are presented in four colors, and from the lower portion of the figure it is evident that the speed and load were precisely repeated. The LII results in the upper portion of the figure show very good reproducibility. The areas under the four LII curves are given to the right and reveal a variance of only 2.3%.

The time-resolved LIDELs technique is still undergoing refinement, but typical measurements for transients in load, EGR rate, and engine speed are presented in Figure 6. Two laser pulses separated by 120 ns are used. The first pulse measures the TPM and deposits the energy that desorbs the volatile material. The second pulse measures the remaining solid PM, i.e., elemental carbon, and the ratio of the two measurements gives the solid volume fraction.

Conclusions

- The LII technique has been demonstrated to run unattended for extended periods of time both at a heavy-duty diesel engine manufacturer's test facility and on-board a light-duty diesel passenger vehicle.
- LII measurements for the steady-state and transient FTP have been shown to correlate well with dry gravimetric measurements.
- Development of the LII technique for PM measurements is completed, and a robust, user-friendly instrument is being marketed by Artium Technologies, Inc.
- Time-resolved measurements of the solid volume fraction by the LIDELS technique have been successfully demonstrated. However, dynamic range, robustness, and cost remain as obstacles to commercialization.

Awards

1. SAE speaker award for Excellence in Oral Presentation at the SAE 2004 World Congress.

FY 2004 Presentations

1. "High-Energy, Pulsed Laser Diagnostics for Real-Time Measurements of Diesel PM Emissions," DOE/AEC Meeting, Livermore, January 27-28, 2004.
2. "Time-Resolved Measurements of Exhaust PM for FTP-75: Comparison of LII, ELPI, and TEOM Techniques," SAE International Congress & Exposition, Detroit, March 8-11, 2004.
3. "On-Board, Time-Resolved Diesel Particulate Measurements by Laser-Induced Incandescence," 14th CRC On-Road Vehicle Emissions Workshop, San Diego, March 29-31, 2004.
4. "Unattended, Around-the-Clock Particulate Measurements Using Laser-Induced Incandescence," 14th CRC On-Road Vehicle Emissions Workshop, San Diego, March 29-31, 2004.
5. "On-Board, Time-Resolved Diesel Particulate Measurements by Laser-Induced Incandescence," SAE Government/Industry Meeting, Washington, DC, May 10-11, 2004.
6. "High-Energy, Pulsed Laser Diagnostics for Real-Time Measurements of Diesel PM Emissions," DOE/AEC Merit Review and Peer Evaluation, Argonne, May 18-20, 2004.
7. "High-Energy, Pulsed Laser Diagnostics for Real-Time Measurements of Diesel PM Emissions," DOE/AEC Meeting, Detroit, June 22-23, 2004.

8. "High-Energy, Pulsed Laser Diagnostics for Real-Time Measurements of Diesel Particulate Matter Emissions," invited Keynote Lecture, 7th International Congress on Optical Particle Characterization (OPC2004), Kyoto, August 1-5, 2004.
9. "Time-Resolved Laser-Induced Incandescence Measurements for the EPA Heavy-Duty Federal Test Procedure," The Sixth International Symposium on Diagnostics and Modeling of Combustion in Internal Combustion Engines (COMODIA 2004), Yokohama, August 2-5, 2004.
10. "High-Energy, Pulsed Laser Diagnostics for Real-Time Measurements of Diesel PM Emissions," IEA Task Leaders Meeting, Helsinki, August 22-25, 2004.
11. "High-Energy Laser Diagnostics (HELD) for the Measurement of Diesel Particulate Matter," 10th Diesel Engine Emissions Reduction Conference (DEER 2004), San Diego, August 29-September 2, 2004.

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1. Michelsen, H. A., Settersten, T. B., and Witze, P. O., "Development of Detection Techniques and Diagnostics for Airborne Carbon Nanoparticles," LDRD Final Report SAND2003-8666, November 2003.
2. Witze, P. O., Payne, G., Bachalo, W. D., and Smallwood, G. J., "Influence of Measurement Location on Transient Laser-Induced Incandescence Measurements of Particulate Matter in Raw Diesel Exhaust," *IEA Annual Report*, Fall 2003.
3. Michelsen, H. A., Witze, P. O., Hochgreb, S., and Kayes, D., "Time-Resolved Laser-Induced Incandescence of Soot: The Influence of Experimental Factors and Microphysical Mechanisms," *IEA Annual Report*, Fall 2003.
4. Witze, P. O., "High-Energy, Pulsed-Laser Diagnostics for the Measurement of Diesel Particulate Matter," *DOE/OFCVT Annual Report*, Fall 2003.
5. Witze, P. O., Chase, R. E., Maricq, M. M., Podsiadlik, D. H., and Xu, N., "Time-Resolved Measurements of Exhaust PM for FTP-75: Comparison of LII, ELPI, and TEOM Techniques," SAE Paper No. 2004-01-0964, March 2004.
6. Witze, P. O., Shimpi, S. A., Durrett, R. P., and Farrell, L. A., "Time-Resolved Laser-Induced Incandescence Measurements for the EPA Heavy-Duty Federal Test Procedure," Proceedings of The Sixth International Symposium on Diagnostics and Modeling of Combustion in Internal Combustion Engines (COMODIA 2004), August 2004.

II.C.7 Particulate Matter Sensor for Diesel Engine Soot Control

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DOE Technology Development Manager: Roland Gravel

Subcontractors:
University of Minnesota, Minneapolis, MN
Honeywell Control Products, Freeport, IL

Objectives

- To develop diesel engine exhaust particulate matter (PM) sensor prototypes that have low cost, high speed, reliability, and are capable of operating directly in the harsh exhaust of a diesel engine.
- Install and test the sensor prototypes and compare test results to results of other reference instrumentation.
- Use test results to improve sensor concepts and develop compatible sensor packages.
- Develop associated sensing electronics and signal processing hardware.
- Demonstrate prototype sensor by 4Q 2004.

Approach

The project has three main steps in order to accomplish the research:

- **PM Sensor Development**—Design and build several prototypes of PM sensors utilizing high-temperature materials for operation directly in the exhaust stream. Develop different readout electronic circuits to monitor the sensor and interface to data acquisition equipment and/or engine controllers.
- **Sensor Testing**—Establish a diesel engine test bed that will include reference particulate measuring instrumentation and potentially other gas sensing instrumentation. Establish a data acquisition system to record the testing results for further data analysis. These tests will be conducted at the University of Minnesota's Center for Diesel Research and will utilize equipment from their Particle Measurement Laboratory. Gas concentration and particle size distribution information will be recorded to compare to sensor test results.
- **Sensor Packaging**—Staff members of Honeywell Labs and Sensing and Controls Division will develop suitable sensor packages for the PM sensors. Packaging materials should provide protection to the sensor as well as the ability to withstand the harsh operational environment. Sensor packages will be exposed to high temperatures and corrosive and potentially condensing environments. Destructive and nondestructive testing of the sensor package will be completed.

Major Accomplishments to Date

- Established test facilities at the University of Minnesota using three commercial diesel engines. The first is a John Deere 4540T engine typical of medium-duty off-road applications, the second is a Caterpillar engine typical of heavy-duty on-road applications, and the third is a Volkswagen TDI (Euro IV) engine typical of passenger car applications.
- Established the feasibility of monitoring particulates directly in the exhaust manifold without pretreatment or dilution and without sensor fouling due to accumulation of particulate matter.

- Demonstrated the feasibility of monitoring particulates from each combustion event in real-time on a cylinder-by-cylinder basis.
- Correlated these cylinder-by-cylinder and cycle-by-cycle variations to engine operating parameters such as fuel injection variability and exhaust gas recirculation (EGR) behavior.
- Completed fabrication of concept prototype devices for testing in end-user facilities.

Future Directions

- Demonstrate prototype sensors and electronics in several end-user facilities. This will constitute the final deliverable on this project.

Introduction

Emission regulations worldwide emphasize reducing fine particulate matter emissions. Recent studies have shown that fine particles are more strongly linked with adverse health effects than are larger particles, and engines are an important source of fine particles.

Particles in the nucleation mode and in the accumulation appear to be formed by different mechanisms. Accumulation-mode particles are primarily carbonaceous and are associated with rich combustion and poor subsequent oxidation during the engine cycle. Most nucleation-mode particles are not even formed until the exhaust dilutes and cools. They consist of a complex, poorly understood mix of sulfuric acid and partially burned fuel and lubricating oil. Formation of these two types of particles likely occurs under different engine operating conditions, with heavy loads favoring carbonaceous accumulation-mode particles and light loads most likely favoring the formation of vapor-phase precursors of nucleation-mode particles. These precursors may not undergo gas-to-particle conversion until the exhaust cools and dilutes in the atmosphere.

In order to meet future emission standards, future diesel engines will have to be fitted with sophisticated combustion control systems and, almost certainly, an aftertreatment system including particle filters or traps. An effective exhaust particulate sensor would not only lead to a reduction of particulate emissions from the engine itself, but would also make traps and other aftertreatment devices more feasible. Particulate traps are now commercially available and are likely to be applied in high volume in the future. They are large, expensive

and impose a significant fuel economy penalty. A particulate sensor would help reduce the amount of particulate matter created through better engine control. It could also be used to monitor particulate loading or breakthrough on downstream traps. Thus, the particulate trap could potentially be made smaller or be regenerated less often.

Approach

Solid particles present in diesel engine exhaust carry a significant electrical charge (Kittelson et al., 1986a; 1986b, Moon, 1984). We examined several types of sensors based on measurement of particle charge such as an ionization sensor, an image charge sensor, and sensors based on alternating current (AC) conductance and capacitance of the exhaust. Our preferred approach is an image charge sensor based on design simplicity, speed, and ruggedness.

The sensor probe is built on a commercial spark plug body as seen in Figure 1. This platform is ideal



Figure 1. Honeywell PM Sensor Probe Based on a “Spark Plug” Configuration

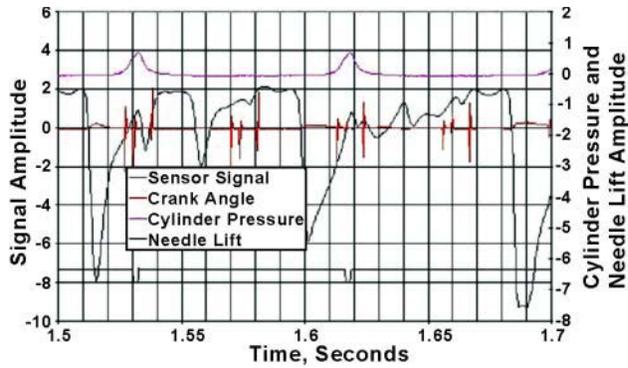


Figure 2. Typical real-time waveforms of sensor signal, cylinder pressure, crank angle, and needle lift. Data was taken on a John Deere 4540T test engine running at 1400 rpm, with no EGR and 90% load.

for placement directly in the exhaust manifold as it withstands high pressures and temperatures and is stable towards vibration, gas composition and sooting found in that environment. Because of the extreme temperature of the probe—measured as high as 700°C—the electronics are remote from the sensor probe.

Results

The John Deere 4045T engine being used has one cylinder (cylinder number 4) that is instrumented with an in-cylinder pressure sensor. This pressure sensor is typically used to frame individual engine cycles for data analysis. Figure 2 shows the basic real-time sensor signal with corresponding traces of cylinder pressure, crank angle and fuel injector needle lift. A high degree of cycle-to-cycle and cylinder-to-cylinder variation is seen in the data. Similar effects, albeit smaller in magnitude on more modern, cleaner-burning engines, have been observed for the Caterpillar engine (showing 6 smoke peaks present for the 6 cylinders) and for the Volkswagen TDI engine. We suspect many of the variations in these more modern engines are due to the static and dynamic behavior of the EGR systems, although the effect is still under investigation.

The peak-to-peak amplitude of the individual smoke pulses and the average sensor output (RMS output) are well-correlated to smoke concentrations as measured with standard reference particulate instrumentation. Figure 3, for example, shows the

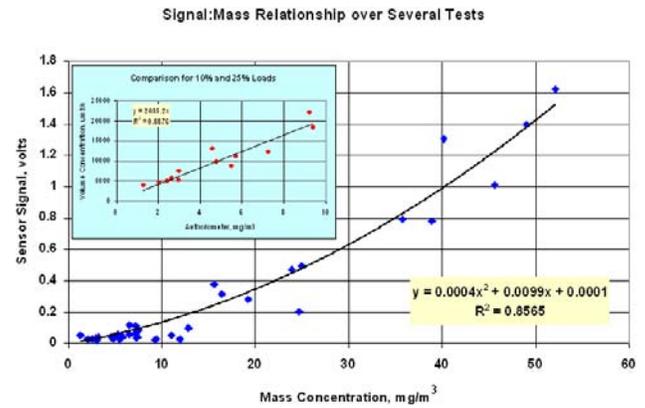


Figure 3. Correlation of Sensor Signal to Black Carbon Concentration as Measured with a Reference Fast-Response Aethelometer

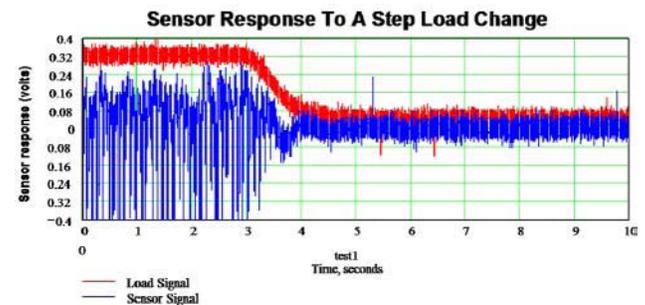


Figure 4. Response of the PM sensor to a step change in engine load. Note the overall effect on peak amplitude as well as changes in individual cylinder behavior.

correlation of sensor output (peak-to-peak) with a reference aethelometer measuring black carbon concentration. The sensor data were averaged over several engine cycles in order to correspond to the 1 second minimum response time of the aethelometer. The sensor output shows minimal correlation to temperature and pressure and has shown no fouling from accumulated particulate matter.

Figures 4 and 5 show the response of the sensor across operating loads—and hence smoke concentrations—of the John Deere test engine. One can see that the PM sensor easily tracks changes in smoke concentration resulting from engine load variations in real-time without sampling lags. This makes the sensor ideal as a feedback control element in engine control and/or EGR control applications.

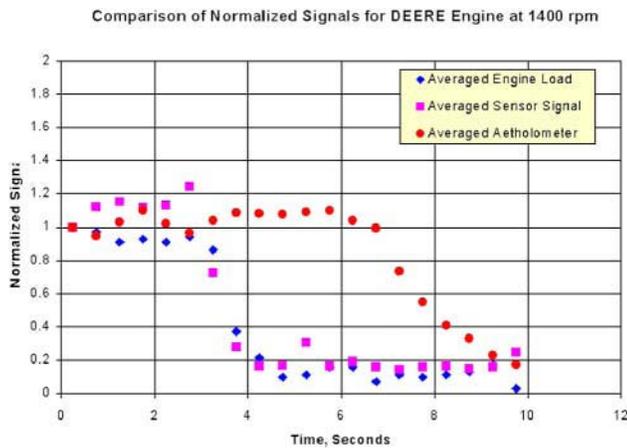


Figure 5. Correlation of the PM sensor signal and aethelometer to a step change in engine load. The time lag in the aethelometer signal corresponds to the residence time in the sampling and dilution tunnels. The PM sensor is running in real-time and shows no such time lag.

Conclusions

Considerable technical progress has been made during FY 2004. Namely, we achieved the following:

- Fabricated and tested several concept prototype sensor probes based on a very simple, manufacturable foundation.

- Developed an adequate test bed and data logging capabilities that allow examination of sensor behavior across multiple engine types and under varying engine conditions.
- Verified that the charge sensor approach gives us a reproducible signal that is well-correlated to exhaust smoke as characterized by several reference methods.
- Verified that the charge sensor responds in real-time (millisecond timescale) to instantaneous smoke concentrations from individual cylinder exhaust events.
- Observed that on our various test engines there is considerable variation in the sensor response from cylinder to cylinder and from cycle to cycle. This variability appears to be real variations in engine behavior and not artifacts of the sensor signal.
- Observed that in many cases, we can correlate this cylinder-to-cylinder or cycle-to-cycle variation to inconsistencies in fuel injection and/or EGR behavior.
- Observed that the sensor probe response does not degrade due to soot build-up or high temperature exposure over several hundred hours of operation.
- Developed prototype hardware and software in order to work with several engine/vehicle end-users to verify our findings in their facilities.