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CRADA Final Report
for
CRADA number ORNL 99-0566

**DEVELOPMENT OF NOX SENSORS FOR
HEAVY VEHICLE APPLICATIONS**

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Prepared by the
Oak Ridge National Laboratory
Oak Ridge, Tennessee 37831
managed by
UT-Battelle, LLC
for the
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Under Contract DE-AC05-00OR22725

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Abstract

A DOE CRADA was initiated in February 2000 between Ford Motor Company and the U. S. Department of Energy's Oak Ridge National Laboratory (ORNL). The overall objective of the research agreement was to characterize the performance of emission sensors and identify potential areas of improvement and to develop improved insulating materials with a lower capacitance to minimize radio frequency (RF) interference.

A bench-scale device was developed at ORNL to evaluate sensor performance. The test stand was designed to enable control of the gas composition, flow rate, and temperature. An air-actuated three-way valve was used to control the injection of the test gas in order to elucidate the transient behavior of the sensor. The major finding from our studies was that transient test results showed that response time of the sensor to NO was highly dependent on the temperature. The time constant decreased with increasing gas temperature and achieved a constant value of 610 ms for temperatures greater than or equal to 350°C. The steady-state valves O₂ and NO_x pumping currents were measured under steady-state conditions using a picoammeter. The measured pumping currents were extremely low and required an electrically quiet environment for accurate readings.

ORNL developed also modified the existing insulator material to decrease its dielectric constant in order to reduce radio frequency interference from the internal heater. This was accomplished by adding low dielectric constant sintering aids to alumina.

Objectives

The purpose of this project is to develop a zirconia-based NO_x sensor for improved engine and exhaust diagnostics in class 1-8 truck engines. The overall objective of this study is to characterize the performance of emission sensors and identify potential areas of improvement and to develop new materials for the dielectric body and electrodes of the sensing element. One aspect of this project was to benchmark the NGK NO_x sensor under development.

Benefits to DOE

Sensors that can quantitatively measure NO_x emissions in real time are potentially an enabling technology for the clean diesel engines of the future. Closed loop engine control systems that monitor emissions and continuously adjust engine and emission-control parameters such as fuel injection behavior, valve timing, EGR and air-handling control are envisioned for near-zero emission heavy vehicles for the future. However, the closed loop control systems are dependent upon rapid, reliable and accurate sensors. The electrochemical sensors under development by the automotive industry are very complex; no US supplier has commercial prototypes at present. This project supports DOE by developing technology sensor technology to control pollutant emissions and greenhouse gases.

Technical Discussion

Urea selective catalytic reduction (SCR) and NO_x adsorbers systems used being investigated to reduce NO_x emissions from diesel engines. Optimization of these devices on an automotive platform will likely require feedback control. The availability of emission sensors is limited, in fact the only currently available NO_x sensors are those manufactured by NGK. Before any NO_x sensor can be integrated into an emission controls package, its performance must be accurately assessed to determine its range of operation and response.

The NGK NO_x sensor design consists of two cells with diffusion barriers. Exhaust enters the first cell where it is thermally decomposed into NO and elemental oxygen. The oxygen present in the exhaust is pumped out of the first cell to levels approaching 10 ppm. The current generated by pumping out the oxygen from cell 1 is transformed into a voltage by the controller to become the O₂ signal output for the device. The NO present in cell 1 moves through a diffusion barrier to cell 2. In cell 2 the NO is decomposed into elemental nitrogen and oxygen on a rhodium electrode. The current generated by pumping O₂ out of cell 2 is used to provide the NO_x output signal of the device.

A bench-scale rig was developed in order to measure the transient response of selected NO_x (or oxygen) emission sensors. The performance of the rig was modeled assuming well-stirred tank conditions and verified using fast NO analyzer. Steady state measurements of NO and NO₂ were initially performed to confirm the baseline performance of the sensors. Transient measurements were made using of NO and O₂ test gases in order to determine sensor response. In order to elucidate the sensor behavior more fully, the O₂ and NO_x pumping currents were to be measured under both steady

state and transient conditions. Analysis of the pumping currents during transient testing may provide insights into computational techniques to improve sensor response.

Two NGK NOx sensors were sent to ORNL for evaluation by Ford Motor Company. The sensors were placed in the bench rig and evaluated under steady-state and transient conditions. The steady-state results are shown in Fig. 1 and confirmed the baseline performance for this device. Transient tests were performed on the sensor at several different gas temperatures. The sensor response as a function of was determined. The τ (33-66) time constant decreased with increasing gas temperature and was constant (around 610 ms) for temperatures greater than or equal to 350°C.

The O₂ and NOx pumping currents of the sensor were measured under steady-state conditions by splicing a picoammeter into the sensor wiring. The pumping current for the oxygen increased linearly with increasing oxygen concentration and ranged from a few μ A to 2 mA. The NOx current also increased linearly with NO concentration, but the current was very low ranging from 200 nA to around 8 μ A. These low currents indicate that the sensor may be susceptible to electromagnetic interference and, therefore, the package needs to be improved.

Figure 1. NGK sensor response to NO and NO₂ under steady state conditions.

An improved dielectric was developed during this project that had a lower dielectric constant than the current material. The new material was improved by adding a unique sintering aid that aided densification and provided a grain boundary phase that lowered the dielectric constant. This new material reduces the radio frequency interference from

the internal heater. However, the improvement does not eliminate the need to signal enhancement.

Inventions

No inventions were made during the course of this project.

Commercialization Possibilities

This effort is ongoing and several technical barriers, such as improved electronics for signal enhancement and new electrode materials, remain to be overcome before the sensors will be commercialized. The CRADA with Ford Motor Company and collaboration with Visteon Automotive Systems provides a clear path to commercialization.

Plans for Future Collaboration

ORNL and Ford anticipate future collaboration for the development of NOx and ammonia sensors. ORNL plans to assist Ford in developing signal enhancing electronics for the NOx sensor as well as to evaluate new simplistic designs that avoid the use of pumping cells.

Conclusions

A bench-scale rig was developed at ORNL to evaluate NOx sensor performance. The response of the rig was determined and the gas flow behavior was characterized. A commercially available NOx sensor was placed in the rig and evaluated under steady state and transient modes of operation. The time constants for the sensor were found to decrease with increasing temperature up to 350°C. This will be an important consideration when integrating these devices into an after treatment system since the range of temperature in a diesel engine exhaust can vary between 150°C and 500°C.

The pumping currents of the NGK sensor were measured under steady state conditions. The currents were found to be extremely low and therefore susceptible to electromagnetic interference. Transient analysis of these currents may indicate that computational techniques could be used to improve the sensor response.

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