



LAWRENCE
LIVERMORE
NATIONAL
LABORATORY

NO_x Sensor Development

L. Y. Woo, R. S. Glass

October 23, 2013

Disclaimer

This document was prepared as an account of work sponsored by an agency of the United States government. Neither the United States government nor Lawrence Livermore National Security, LLC, nor any of their employees makes any warranty, expressed or implied, or assumes any legal liability or responsibility for the accuracy, completeness, or usefulness of any information, apparatus, product, or process disclosed, or represents that its use would not infringe privately owned rights. Reference herein to any specific commercial product, process, or service by trade name, trademark, manufacturer, or otherwise does not necessarily constitute or imply its endorsement, recommendation, or favoring by the United States government or Lawrence Livermore National Security, LLC. The views and opinions of authors expressed herein do not necessarily state or reflect those of the United States government or Lawrence Livermore National Security, LLC, and shall not be used for advertising or product endorsement purposes.

This work performed under the auspices of the U.S. Department of Energy by Lawrence Livermore National Laboratory under Contract DE-AC52-07NA27344.

Project 18518 – Materials for High-Efficiency Engines

Agreement 8697 – NO_x Sensor Development

Leta Y. Woo and Robert S. Glass

Lawrence Livermore National Laboratory

P.O. Box 808, L-103

Livermore, CA 94551-9900

Phone (925) 423-7140; fax: (925) (422-5844); e-mail: glass3@llnl.gov

DOE Technology Manager: Jerry L. Gibbs

(202) 586-1182; fax: (202) 586-1600; e-mail: jerry.gibbs@ee.doe.gov

Contractor: Lawrence Livermore National Laboratory, Livermore, California

Prime Contract No.: W-7405-Eng-48; LLNL-TR-510234

Objectives

- Develop an inexpensive, rapid-response, high-sensitivity, and selective electrochemical sensor for oxides of nitrogen (NO_x) for compression-ignition, direct-injection (CIDI) OBD II systems.
- Explore and characterize novel, effective sensing methodologies based on impedance measurements and designs and manufacturing methods that are compatible with mass fabrication.
- Transfer the technology to industry for commercialization.

Approach

- Use an ionic (O²⁻) conducting ceramic as a solid electrolyte and metal or metal-oxide electrodes.
- Correlate NO_x concentration with changes in cell impedance.
- Evaluate sensing mechanisms and aging effects on long-term performance using electrochemical techniques.
- Collaborate with Ford Research Center and EmiSense Technologies, LLC to optimize sensor performance and perform dynamometer and on-vehicle testing.

Accomplishments

- Successful technology transfer activities as part of a Cooperative Research and Development Agreement (CRADA) with EmiSense Technologies, LLC, a Salt Lake City, Utah company, which has licensed the Lawrence Livermore National Laboratory (LLNL) NO_x sensor technology. This has resulted in more advanced sensor designs amenable to mass manufacturing. The commercialization goal is for 2016 car models.
- Completed advanced vehicle dynamometer testing at Ford Motor Company of Fiscal Year 2013 sensor prototypes using newly developed prototype electronics for data acquisition. Good performance was obtained in these tests.
- Publications/presentations/patents:

- Du Frane, W. L., L. Y. Woo, R. S. Glass, R. F. Novak, and J. H. Visser, 2013, "Substrate Effects on Electrochemical NO_x Sensor Based on Porous Y₂O₃-Stabilized ZrO₂ (YSZ) and Sr-doped LaMnO₃ (LSM)," *ECS Transactions*, 45 (14), 3–11.
- Woo, L. Y., R. S. Glass, R. F. Novak, and J. H. Visser, "Zirconia-electrolyte-based impedancemetric sensors using Sr-doped LaMnO₃ (LSM) electrodes for measuring NO_x in combustion exhaust streams," *The 10th Pacific Rim Conference on Ceramic and Glass Technology*, in San Diego, California, June 2–7, 2013.
- New patent application (No. 14055562) entitled, "Electrochemical Sensing Using Voltage-Current Time Differential," filed on October 16, 2013.

Future Direction

- Working through the CRADA with EmiSense Technologies, LLC and in collaboration with Ford Motor Company, complete the technology transfer and bring the NO_x sensor technology to the commercialization stage.
-

Introduction

NO_x compounds, specifically NO and NO₂, are pollutants and potent greenhouse gases. Compact and inexpensive NO_x sensors are necessary in the next generation of diesel (i.e., CIDI) automobiles to meet government emission requirements and enable the more rapid introduction of more efficient, higher fuel economy CIDI vehicles (Yamazoe 2005, Moos 2005, and Akbar et al. 2006).

Because the need for a NO_x sensor is recent and the performance requirements are extremely challenging, most are still in the development phase (Menil et al. 2000, Zhuiykov and Miara 2007, and Fergus 2007). Currently, there is only one type of NO_x sensor that is sold commercially and it seems unlikely to be able to meet the more stringent future emission requirements.

Automotive exhaust sensor development has focused on solid-state electrochemical technology, which has proven to be robust for in situ operation in harsh, high-temperature environments (e.g., the oxygen stoichiometric sensor). Solid-state sensors typically rely on yttria-stabilized zirconia (YSZ) as the oxygen-ion conducting electrolyte (which has been extensively explored) and then target different types of metal or metal-oxide electrodes to optimize the response (Moos 2005, Akbar et al. 2006, Menil et al. 2000, Zhuiykov and Miara 2007, and Fergus 2007).

Electrochemical sensors can be operated in different modes, including amperometric (current based) and potentiometric (potential based), both of which are direct current (DC) measurements. Amperometric operation is costly due to the electronics necessary to measure the small sensor signal (nanoampere current at ppm NO_x levels) and cannot be easily improved to meet future technical performance requirements. Potentiometric operation has not demonstrated enough promise in meeting long-term stability requirements, where the voltage signal drift is thought to be due to aging effects associated with electrically driven changes (both morphological and compositional) in the sensor (Song et al. 2006).

Our approach involves impedancemetric operation, which uses alternating current (AC) measurements at a specified frequency. The approach is described in detail in previous reports and several publications (Martin et al. 2007 and Woo et al. 2007, 2008, 2010, 2011). Impedancemetric operation has shown the potential to overcome the drawbacks of other approaches, including higher sensitivity toward NO_x, better long-term stability, potential for subtracting out background interferences, total NO_x measurement, and lower cost materials and operation (Martin et al. 2007, Woo et al. 2007, 2008, 2010, and 2011).

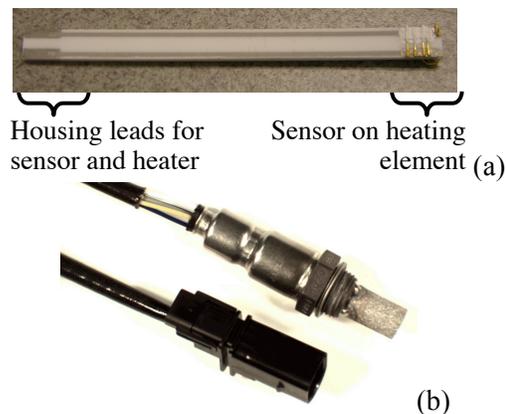


Figure 1. Picture of (a) alumina substrate with imbedded heater, provided by Ford Motor Company, suitable for packaging into (b) protective sensor housing.

Past LLNL research and development efforts have focused on characterizing different sensor materials and understanding complex sensing mechanisms (Martin et al. 2007 and Woo et al. 2007, 2008, 2010, 2011). Continued effort has led to improved prototypes with better performance, including increased sensitivity (to less than 5 ppm) and long-term stability, with more appropriate designs for mass fabrication, including incorporation of an alumina substrate with an imbedded heater and a protective sensor housing (see Figure 1). Using multiple frequency measurements, an algorithm has been developed to subtract out that portion of the response due to interfering species.

Efforts in FY 2013 have focused on working with Ford Motor Company and CRADA partners EmiSense to modify prototypes for

improved performance. Three major accomplishments this year include (1) completing evaluation of strontium-doped lanthanum manganite (LSM) metal oxide electrodes to enable a material down-select to focus on Au-based electrodes; (2) development of new portable electronics for experimental control and data acquisition using low-cost components; (3) further development of a voltage-current time differential measurement strategy that has shown improved results in vehicle dynamometer testing at Ford; and (4) evaluation of processing methods more suitable for mass manufacturing. We have had great success in technology transfer to EmiSense, which licensed the LLNL NO_x sensor technology, and made great progress in commercialization efforts, which are directed toward a 2016 model year goal.

Background

For a two-electrode electrochemical cell, impedancemetric sensing requires that at least one of the electrodes act as the “sensing” electrode with selective response to NO_x over other gas phase components. This contrasts to the case in potentiometric sensing, which relies on differential measurements between the two electrodes. The impedancemetric sensor design is quite flexible and can either contain one sensing electrode and one counter (i.e., non-sensing) electrode or two sensing electrodes. It opens up the opportunity to use a wide variety of materials, both metal and metal oxides.

Both electrode composition and microstructure influence sensitivity, which relies on limiting the oxygen reaction on the electrode so that the NO_x reaction can be resolved (Woo et al. 2007, 2008, 2010, and 2011). In general, for the “sensing” electrode, a dense microstructure is required with appropriate composition to limit the catalytic activity toward oxygen (Woo et al. 2008, 2010, and 2011).

Measured sensor impedance is a complex quantity with both magnitude and phase angle information. The phase angle has been found to provide a more stable response at higher operating frequencies and we prefer it for the sensor signal (Martin et al. 2007 and Woo et al. 2007, 2008, 2010, 2011).

In previous work, impedancemetric sensing using either Au or strontium-doped LSM electrodes (the latter being an electronically conducting metal oxide) was investigated in laboratory and engine testing. Preliminary results indicated that Au electrodes have good stability and the potential for low water cross-sensitivity, but also have a higher thermal expansion coefficient and lower melting temperature than the YSZ electrolyte, which limits processing flexibility. LSM electrodes have high melting temperatures and better thermal expansion match with YSZ, but have shown higher water cross-sensitivity than gold.

Results and Discussion

Metal Oxide Electrodes

To further understand impedancemetric sensing mechanisms and to aid in down selection for either metal-oxide or Au-based electrodes, multiple configurations of the strontium-doped LSM metal oxide electrode prototype sensor were investigated. To conserve space, experimental details of sensor preparation and measurement protocol are omitted, but the interested reader can find these in the Fiscal Year 2012 Annual Report for this project and elsewhere (Woo et al. 2008, 2010, and 2011).

Figure 2a shows a schematic of the previously studied symmetric (i.e., electrode materials the same) in-plane LSM prototype (Du Frane 2013). This design resulted in poor sample-to-sample reproducibility and variability in performance attributable to the formation and growth of random microcracks due to the thermal expansion mismatch between the sensor components (YSZ and LSM) and the substrate (alumina) (Du Frane 2013).

In an attempt to reduce microcracking, an asymmetric (LSM/YSZ/Pt) through-plane geometry (Figure 2b) was evaluated next. Figure 3 shows a comparison of the sensing behavior of the symmetric side-by-side (LSM/YSZ/LSM) and asymmetric through-plane (LSM/YSZ/Pt) configurations (see Figure 2a and 2b) in 10.5% O₂ when 100 ppm NO is added. The asymmetric (LSM/YSZ/Pt) showed lower sensitivity than the symmetric configuration.

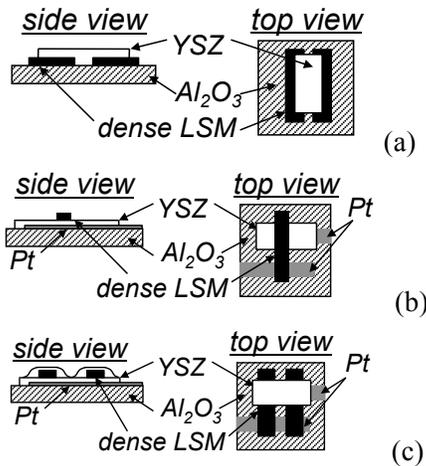


Figure 2. Schematic of NO_x prototype with LSM metal oxide electrode in (a) symmetric side-by-side configuration and (b) alternative asymmetric through-plane configurations with both LSM and Pt electrodes (LSM/YSZ/Pt), and (c) additional LSM electrode.

Figure 2c shows the schematic of a third configuration, which was used to investigate the role of increasing the electrode surface area by adding an additional electrode of dense LSM. Figure 3c shows that this increase in surface area, only the sensitivity further reduced to NO.

In the final design investigated, the bottom platinum electrode was replaced with a piece of LSM, resulting in a symmetric through-plane configuration with two LSM electrodes.

Figure 3d shows an increase in NO sensitivity, similar to the sensitivity of the side-by-side configuration. Based on previous studies, it is anticipated that the through-plane geometry would have better tolerance to microcracks than the side-by-side geometry.

The study of LSM configurations demonstrated that reasonable sensor behavior could be achieved by controlling configuration and materials. This evaluation of alternative LSM configurations allowed for a more complete comparison with the sensing performance of previously studied Au-based designs. Both LSM configurations and Au-based designs had comparable sensitivity to NO_x. Therefore, the down select between the two electrode materials was determined by the potential for more straight-forward mass

manufacturing methods using metal-based pastes and inks, which is an area of expertise for our industrial partner EmiSense.

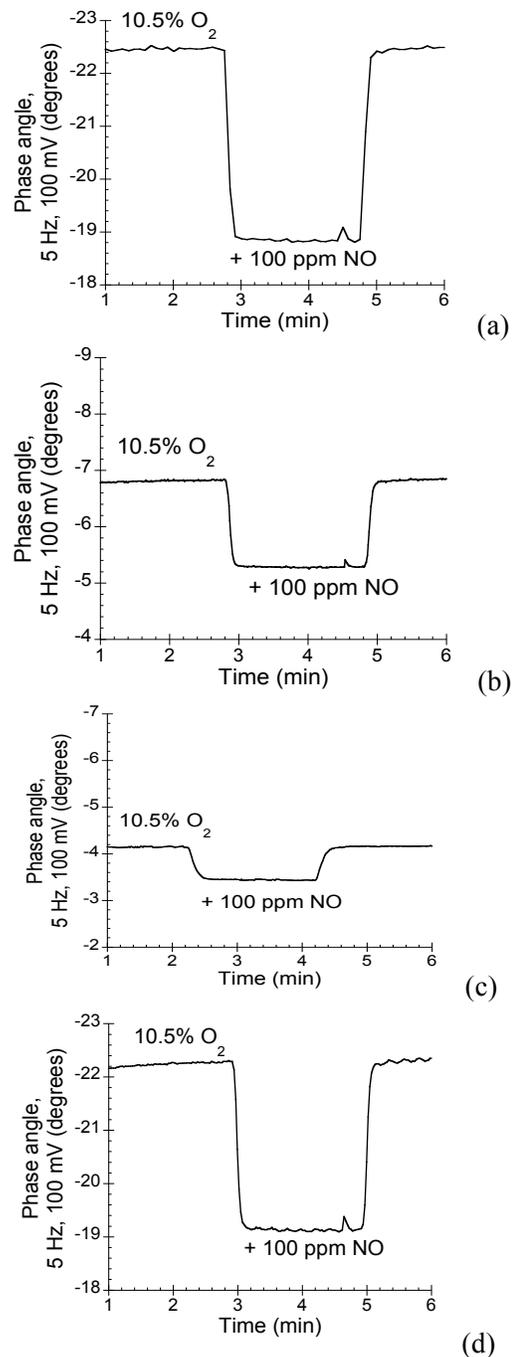


Figure 3. Sensing behavior of (a) symmetric side-by-side, (b) asymmetric through-plane (LSM/YSZ/Pt) with single LSM and (c) additional top LSM electrode, and (d) symmetric through-plane with LSM electrodes (LSM/YSZ/LSM).

Dynamometer Testing with EmiSense Electronics

To aid in development of new electronics for dynamometer testing, the prior studied Au wire-based designs were used. Figure 4 shows a schematic of the sensor using Au wire as the sensing electrode and alumina with an imbedded Pt resistive heater as the substrate ($70 \times 4 \times 1$ mm; see Figure 1a). The substrate has a total of four leads: two leads for the Pt resistive heater located on one side and two leads for the sensor located on the opposite side.

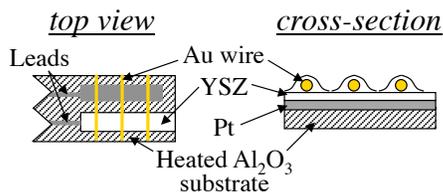


Figure 4. Schematic of Au wire NO_x prototype sensor.

One of the substrate leads contacted the Pt counter electrode. YSZ slurry was then applied on top of the Pt. Au wires were added and additional YSZ slurry was applied on top of the wires with the entire assembly fired at 1000°C to produce the porous YSZ electrolyte. The second substrate lead for the sensor housing contacted the Au wire.

Dynamometer testing of real diesel exhaust was performed at the Ford Research Center using a test vehicle mounted on a chassis. The vehicle exhaust system had a urea-based selective catalytic reduction system for reducing NO_x emissions. The exhaust gas composition was evaluated using both Fourier transform infrared spectroscopy (FTIR) and bench analyzers, including a chemiluminescent NO_x analyzer and a paramagnetic oxygen analyzer. Prototype sensors were packaged by a U.S. supplier into appropriate housings (see Figure 1b) and placed directly into the exhaust manifold at the tailpipe for exposure to real-world diesel exhaust.

In preparation for Fiscal Year 2013 testing in real diesel exhaust, new electronics were developed with LLNL's CRADA partner EmiSense. In our previous work, we focused on frequency-domain impedancemetric modes of

operation using the phase angle as the sensor signal. A surprising discovery occurred during development of inexpensive digital electronics to monitor the voltage-current differential in the time domain, the source and response waves exhibited similar peak-to-peak values, indicating that no phase angle shift or phase angle difference occurred. In contrast, previous impedancemetric modes of operation in the frequency domain using expensive electrochemical equipment indicated phase angle changes. The result was an entirely new mode of time-domain operation, as opposed to frequency-domain operation, using low-cost portable digital electronics to measure the voltage-current time differential as the sensor signal. We have filed a patent application to protect this new intellectual property.

Figure 5 shows measured dynamic data from a portion of the vehicle dynamometer testing using EPA Federal Test Procedure (FTP-75), which was designed to simulate a city driving cycle and was used to measure tailpipe emissions and fuel economy. In Figure 5a, the dynamic NO_x concentration changes are shown as measured by the chemiluminescent NO_x analyzer (blue), the FTIR (red), and the commercial sensor (green), showing some variation between the methods. In Figure 5b, the left y-axis corresponds to the oxygen concentration as measured by the paramagnetic analyzer (blue) and the right y-axis corresponds to the temperature measurement. The oxygen concentration is changing dynamically, along with the NO_x concentration, whereas the overall temperature remained constant during this portion of testing. In Figure 5c, the sensor signal, as measured by the new digital EmiSense electronics, is shown for three different Au-wire-based prototypes. As expected, the Au-wire prototypes responded to changes in both oxygen and NO_x. The rising background observed between 60 and 110s for the sensor prototype is related to other interferences but is not completely understood.

Commercial sensor packages (sensor plus electronics) provide for additional data processing of the raw data, whereas the data shown above for the Au prototype sensor represents the raw sensor signal. Further

development of the LLNL/EmiSense sensor will allow for additional signal processing to remove the obvious oxygen interference. Previously, we have demonstrated algorithms suitable for compensating for interferences, in particular, oxygen (Woo et al. 2011). New algorithms for the digital EmiSense electronics package are being developed.

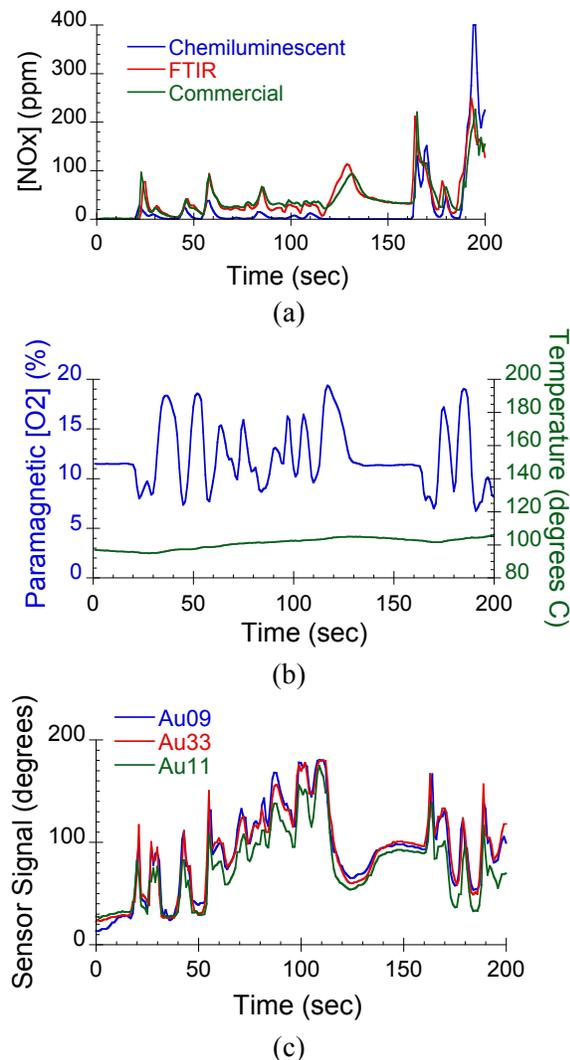


Figure 5. Portion of vehicle dynamometer test: (a) NO_x concentration in ppm as measured by bench chemiluminescent NO_x analyzer (blue), FTIR (red), and commercial NO_x sensor (green); (b) oxygen concentration as measured by bench paramagnetic analyzer (blue, left y-axis) and temperature variation (green, right y-axis); and (c) sensor signal measured using new digital EmiSense electronics for three different Au-wire-based prototype sensors.

Additional Fiscal Year 2013 testing at the Ford Research Center included dynamometer vehicle evaluation in steady-state (non-dynamic) modes for various vehicle speeds. Evaluation also was conducted on an advanced high-flow (40 L/min) test stand with controlled mass flow controllers to alter a range of gas concentrations (O₂, CO₂, H₂O, and NO_x). The test stand also included output from a commercial sensor located near the prototype sensor under evaluation. These data are now being used to further refine strategies for reducing interferences.

Processing Methods for Mass Manufacturing

As a result of extensive testing over several years, a down select was made to focus on Au-based electrodes. In part, this decision was made based on trades offs in sensitivity, selectivity, and, more importantly, on processing ease and capability. A factor in this was the expertise resident at EmiSense for screen printing metal pastes and inks and previous success in development of Au-based pastes suitable for mass manufacturing processes. In contrast, much additional research would have been necessary in order to use metal oxides as electrode materials. In addition to the use of Au-based pastes to replace the Au wire electrode, another processing concern for mass manufacturing was the number of firing steps required. A single high-temperature (greater than 1500°C) co-firing process is desired for sintering with a green (unfired) alumina substrate. As discussed above, previous prototypes with Au-wire electrodes used low-fired (1000°C) porous YSZ electrolyte materials. Therefore, work in Fiscal Year 2013 concentrated on the use of Au paste electrodes and a single sintering step compatible with a green alumina substrate.

Figure 6a shows a schematic of a symmetric side-by-side prototype design used to evaluate two different Au-based pastes, with either a 100% Au composition (ESL 8880-G) or a mixture of Pt and 4% Au (ESL 5801). For a comparison of the effect of firing temperature, the pastes were applied to the substrate, YSZ slurry was then added on top, and the entire

assembly fired at 1000°C. To investigate the influence of high-fired porous YSZ, another symmetric configuration was used that incorporated a slab of porous YSZ (2 × 2 × 5 mm), formed by firing with graphite pore formers at 1550°C (see Figure 6b). In this second sensor, Au-based paste was applied to the fully sintered porous YSZ and the entire assembly was fired at 1000°C. The resulting porous microstructures for the low-fired and high-fired YSZ are shown in Figure 7.

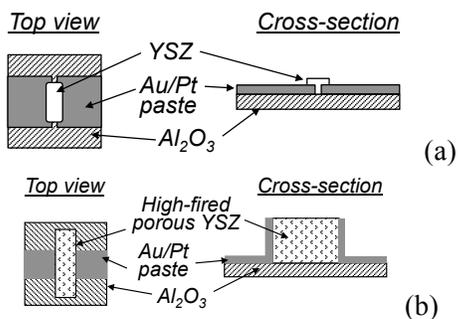


Figure 6. Schematic of NO_x sensor prototypes used to evaluate Au-based pastes with (a) porous YSZ low-fired at 1000°C and (b) porous YSZ high-fired at 1550°C.

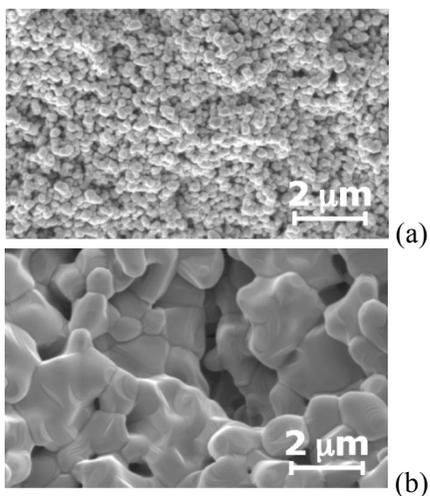


Figure 7. Scanning electron microscopy pictures of (a) porous YSZ low-fired at 1000°C and (b) porous YSZ high-fired at 1550°C.

Figure 8a shows the sensor behavior of the earlier design using an Au-wire electrode in 10.5% O₂ and following the addition of 90 ppm and 10 ppm NO. In Figure 8b, the results for the low-T fired sensor design shown in Figure 6a

are shown using 100% Au paste electrodes, where reduced sensitivity and signal-to-noise are noted. However, when Pt/4% Au paste electrodes are used (Figure 8c), sensor performance improves.

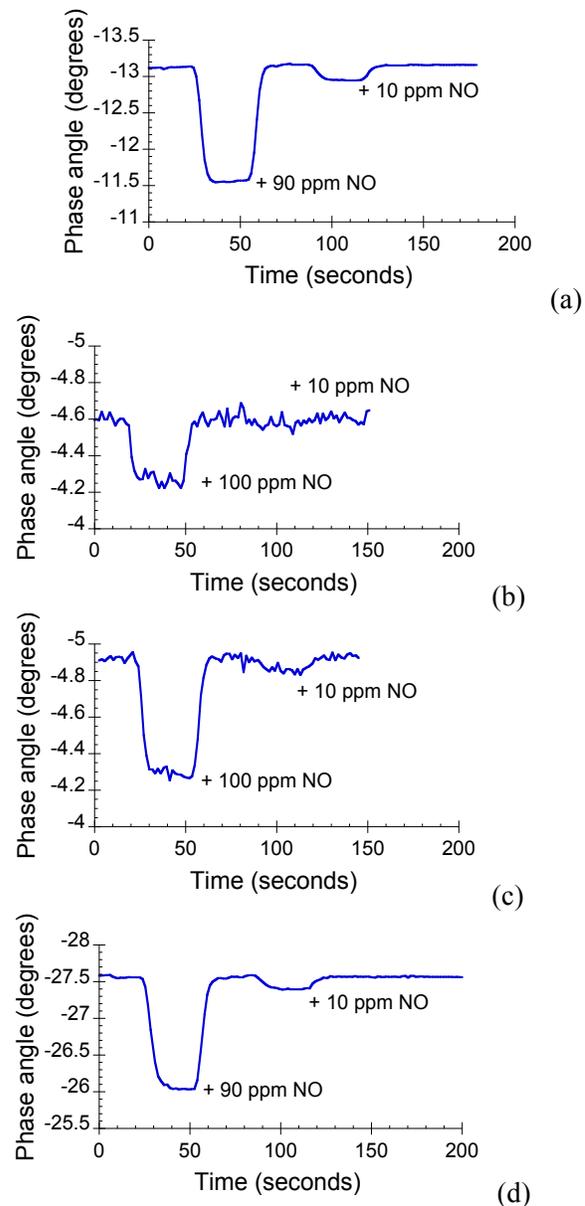


Figure 8. Sensing behavior of (a) Au-wire based design, (b) 100% Au paste with low-fired porous YSZ, (c) Pt/4% Au paste with low-fired porous YSZ, and (d) Pt/4% Au paste with high-fired porous YSZ.

Finally, when Pt/4% Au paste electrodes were used with a fully sintered porous YSZ electrolyte (design shown in Figure 6b), the

sensor performance was found to be very similar in magnitude and signal-to-noise compared with the Au-wire based design (shown in Figure 8a). The results indicated the feasibility for using a traditional screen-printing process for electrode deposition, followed by a single step co-firing manufacturing process.

Conclusions

Work in Fiscal Year 2013 focused on continuing to work with the Ford Motor Company and CRADA partner EmiSense to improve sensor performance and to initiate completion of the technology transfer to industry for commercialization. The three accomplishments this year included (1) down select of materials to focus on Au and Pt-Au electrodes; (2) development of a new portable electronics package for data acquisition fabricated using low-cost components; (3) development of a voltage-current time differential measurement strategy that has shown improved results in vehicle dynamometer testing; and (4) evaluation of processing methods more suitable for mass manufacturing.

To address micro-crack growth and poor sample-to-sample reproducibility for the in-plane geometry, a through-plane geometry was demonstrated. These results for LSM oxide electrodes showed that improved sensor behavior could be achieved by controlling geometry and materials. The completed evaluation of LSM configurations allowed for a better comparison with the sensing performance of Au-based designs and a subsequent electrode materials down select. Because both materials had comparable sensitivity to NO_x , the Au-based materials were chosen based on the potential for more convenient mass manufacturing methods using metal-based pastes and inks, which is an area of particular expertise for EmiSense (the LLNL technology licensee).

A new electronics package for data acquisition was developed by EmiSense. A serendipitous discovery showed that an entirely new measurement strategy in time-domain gave better results than frequency-domain operation, which had been used in all previous studies. As an added bonus, time-domain operation enabled the use of lower cost electronic components.

Attention has been given to replacing early prototype Au-wire electrode sensors with materials more suitable for mass manufacturing. To this end, Au-based and Pt-Au-based pastes were explored. In addition, a final, single-step sensor firing process was sought that used a high-T fired porous YSZ pellet electrolyte. Prior work focused on use of low-fired porous YSZ. The processing steps are intended to be compatible with firing temperatures of the (green body) alumina substrates. From this work, a Pt/4% Au paste composition was found to have better performance than an Au-only paste, and a design incorporating high-fired porous YSZ with the Pt/4% Au paste electrodes was found to have similar performance as earlier Au-wire prototypes with low-fired YSZ. The results indicated the feasibility for using a traditional screen-printing process and single-step co-firing routine for sensor fabrication using either Au or Pt/Au paste electrodes.

A major milestone for this past year was filing of a patent to protect jointly developed (LLNL and CRADA partner EmiSense) intellectual property. The intellectual property development and technology transfer activities this past year are accelerating efforts to bring the LLNL NO_x sensor technology to commercialization. We continue our long-standing collaboration with Ford Motor Company in this effort to test prototype sensors in dynamometers.

References

- Akbar, S., P. Dutta, and C. Lee, 2006, "High-temperature ceramic gas sensors: a review," *Int. J. Appl. Ceram. Technol.*, 3, 302.
- Du Frane, W. L., L. Y. Woo, R. S. Glass, R. F. Novak, and J. H. Visser, 2013, "Substrate Effects on an Electrochemical NO_x Sensor Based on Porous Y_2O_3 -Stabilized ZrO_2 (YSZ) and Sr-doped LaMnO_3 (LSM)," *ECS Transactions*, 45, 3.
- Fergus, J. W., 2007, "Materials for high temperature electrochemical NO_x gas sensors," *Sens. Actuators, B*, 121, 652.
- Martin, L. P., L. Y. Woo, and R. S. Glass, 2007, "Impedancemetric NO_x Sensing Using YSZ

- Electrolyte and YSZ/Cr₂O₃ Composite Electrodes," *J. Electrochem. Soc.*, 154, J97.
- Menil, F., V. Coillard, and C. Lucat, 2000, "Critical review of nitrogen monoxide sensors for exhaust gases of lean burn engines," *Sensors and Actuators B*, 67, 1.
- Moos, R., 2005, "A brief overview on automotive exhaust gas sensors based on electroceramics," *Int. J. Appl. Ceram. Technol.*, 2, 401.
- Song, S.-W., L. P. Martin, R. S. Glass, E. P. Murray, J. H. Visser, R. E. Soltis, R. F. Novak, and D. J. Kubinski, 2006, "Aging Studies of Sr-Doped LaCrO₃/YSZ/Pt Cells for an Electrochemical NO_x Sensor," *J. Electrochem. Soc.*, 153, H171.
- Woo, L. Y., L. P. Martin, R. S. Glass, and R. J. Gorte, 2007, "Impedance characterization of a model Au/yttria-stabilized zirconia/Au electrochemical cell in varying oxygen and NO_x concentrations," *J. Electrochem. Soc.*, 154, J129.
- Woo, L. Y., L. P. Martin, R. S. Glass, W. Wang, S. Jung, R. J. Gorte, E. P. Murray, R. F. Novak, and J. H. Visser, 2008, "Effect of electrode composition and microstructure on impedancemetric nitric oxide sensors based on YSZ electrolyte," *J. Electrochem. Soc.*, 155, J32.
- Woo, L. Y., R. S. Glass, R. F. Novak, and J. H. Visser, 2010, "Effect of electrode material and design on sensitivity and selectivity for high temperature impedancemetric NO_x sensors," *J. Electrochem. Soc.*, 157, J81.
- Woo, L. Y., R. S. Glass, R. F. Novak, and J. H. Visser, 2011, "Diesel engine dynamometer testing of impedancemetric NO_x sensors," *Sensor Actuat. B-Chem.*, 157, 115.
- Yamazoe, N., 2005, "Toward innovations of gas sensor technology," *Sens. Actuators, B*, 108, 2.
- Zhuyikov, S. and N. Miura, 2007, "Development of zirconia-based potentiometric NO_x sensors for automotive and energy industries in the early 21st century: What are the prospects for sensors?" *Sens. Actuators, B*, 121, 639.

Publications/Presentations/Patents

- Du Frane, W. L., L. Y. Woo, R. S. Glass, R. F. Novak, and J. H. Visser, 2013, "Substrate Effects on Electrochemical NO_x Sensor Based on Porous Y₂O₃-Stabilized ZrO₂ (YSZ) and Sr-doped LaMnO₃ (LSM)," *ECS Transactions*, 45 (14), 3–11.
- Woo, L. Y., R. S. Glass, R. F. Novak, and J. H. Visser, 2013, "Zirconia-electrolyte-based impedancemetric sensors using Sr-doped LaMnO₃ (LSM) electrodes for measuring NO_x in combustion exhaust streams," *The 10th Pacific Rim Conference on Ceramic and Glass Technology*, in San Diego, California, June 2–7, 2013.
- New patent application (No. 14055562) entitled, "Electrochemical Sensing Using Voltage-Current Time Differential," filed on October 16, 2013.