

C. Development of NO_x Sensors for Heavy Vehicle Applications

David L. West, Fred C. Montgomery, Timothy R. Armstrong,

Jaco H. Visser* and David J. Kubinski*

Oak Ridge National Laboratory

P. O. Box 2008, Mail Stop 6063

Oak Ridge, TN 37831-6063

(865) 574-5377; fax (865) 574-6918; blaupj@ornl.gov

*Scientific Research Laboratory, Ford Motor Co.

DOE Technology Development Area Specialist: Dr. Sidney Diamond

(202) 586-8032; fax: (202) 586-1600; e-mail: sid.diamond@ee.doe.gov

ORNL Technical Advisor: D. Ray Johnson

(865) 576-6832; fax: (865) 574-6098; e-mail: johnsondr@ornl.gov

Contractor: Oak Ridge National Laboratory, Oak Ridge, TN

Prime DOE Contract Number DE-AC05-00OR22725;

Subcontractor: Ford Motor Company, Detroit, Michigan

Objectives

- Develop nitrogen oxides (NO_x) sensors for remediation and monitoring of diesel engine exhausts.
 - Sensors should have an operating temperature of 500–700°C and be able to measure NO_x concentrations from ~1 to 1500 ppm at oxygen levels from 5 to 20 vol %.
 - Since NO_x is a mixture of NO and NO₂, it would be useful to have sensors selective for either NO or NO₂ or able to measure “total NO_x” ([NO] + [NO₂]).

Approach

- Fabricate prototype sensing elements by screen printing electrode layers onto oxygen-ion-conducting substrates [typically yttria stabilized zirconia (YSZ)].
- Operate elements either in a non-Nernstian mode (where the output is a voltage) or under dc electrical bias.
- Characterize elements for NO_x response, sensitivity to varying O₂, and recovery/response kinetics.

Accomplishments

- Demonstrated NO₂ sensing elements with extremely high sensitivity (50 mV/decade at 700°C, 7 vol % O₂ over the concentration range 20–200 ppm_v NO₂).
- Demonstrated biased NO-selective sensing elements.
- Constructed both types of elements to consist of co-planar electrodes, one oxide electrode and the other a noble metal (usually platinum).

Future Direction

- Determine the effects of H₂O on sensing element performance and stability. (Diesel exhausts are rich in H₂O, typically 4–15 vol %).
- Characterize cross-sensitivity to other species often found in diesel exhausts (CO, hydrocarbons, CO₂).
- Evaluate long-term stability of these sensing elements in atmospheres simulating diesel exhaust.

- Investigate use of low-frequency ac biasing, especially the effect on drift of the baseline sensor response compared with dc-biased elements.

Introduction

The primary pollutants (excluding the greenhouse gas CO₂) from the combustion of low-sulfur fuels are CO, hydrocarbons, and NO_x. Spark-ignited, direct-injection (SIDI) auto and truck engines employ a three-way catalyst (TWC) that can remove all three of these pollutants. However, the TWC is only effective over a narrow range of O₂ in the exhaust, losing its effectiveness for NO_x removal at high partial pressures of O₂. This means that the currently employed TWC is not effective for NO_x remediation of the exhaust from compression-ignited (diesel) engines, as these are O₂-rich (typically 5–20 vol % O₂).

In the current absence of a “lean-NO_x” catalyst, three technologies have been proposed to meet the challenge of NO_x remediation of diesel exhausts: lean-NO_x traps (LNTs), selective catalytic reduction (SCR) with hydrocarbons, and SCR with urea. All of these technologies will require on-board NO_x sensors, to control trap regeneration (LNT) or reagent injection (SCR).

This project is developing NO_x sensing elements that can be used in diesel engine exhausts. The minimum requirement for this application is an operating temperature of 500–700°C and the ability to measure 1–1500 ppm NO_x. It should be emphasized that “NO_x” refers to mixtures of NO and NO₂; therefore, full NO_x characterization of the exhaust may require that two of the following three concentrations be measured: NO, NO₂, or NO_x (= NO + NO₂). This project is a cooperative research and development agreement with Ford Motor Company.

Approach

Some sample geometries for prototype sensing elements are shown in Figure 1. The YSZ substrate is manufactured in-house using Tosoh TZ8YS YSZ powder, and the electrodes (oxide and platinum) are screen-printed and fired. Inks for the platinum electrode are typically obtained commercially; for the oxide electrode, inks are formulated in-house

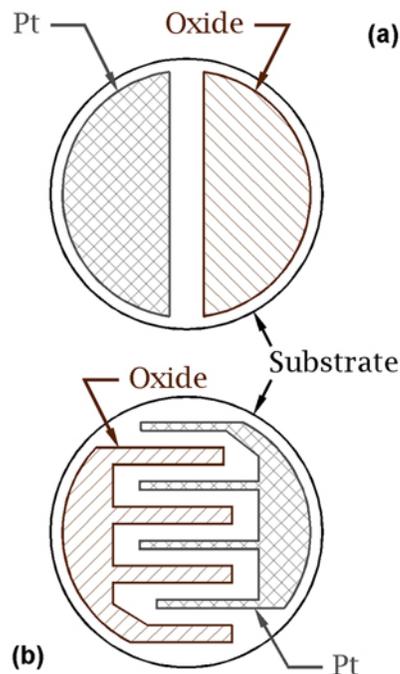


Figure 1. Schematic semicircular (a) and interdigitated (b) sensing element geometries.

using proprietary methods and materials. The precise composition of the oxide electrode is dictated by the target application of the sensing element. For non-Nernstian NO₂ sensing elements, a binary transition metal oxide electrode is sufficient. [The term “non-Nernstian” is used because in the presence of 10–100 ppmv of NO₂, these elements can produce large dc output voltages (on the order of 0.1 V), which far exceed the predictions of the Nernst equation.] For sensing elements that will be biased to yield NO-selective behavior, a more complex oxide electrode is required.

The sensing elements depicted schematically in Figure 1 can be operated in either non-Nernstian or biased mode. In non-Nernstian mode, the voltage between the oxide and platinum electrodes is monitored. In the biased mode, either a constant dc current or voltage is imposed across the electrode pair. The measured voltage (current biased) or current (voltage biased) is then monitored and is useful as a sensing signal for NO_x.

Prototype sensing elements are evaluated both microstructurally and for sensing performance. Isothermal sensing performance is characterized by exposing the sensing elements to varying concentrations of NO_x at a fixed O₂ level or varying O₂ levels at fixed concentrations of NO_x. Because NO_x is a mixture primarily of NO and NO₂, in our characterization we typically expose the sensing element to either NO or NO₂.

Results

Representative electrode and substrate microstructures are shown in Figure 2. The screen-printed and fired (1200°C) ZnO electrode is relatively open and porous compared with the YSZ substrate. The typical electrode thickness after firing is 20–30 μm (determined by non-contact profilometry); this compares well with the predicted thickness given the mesh size and emulsion thickness of the screen used for printing the electrodes.

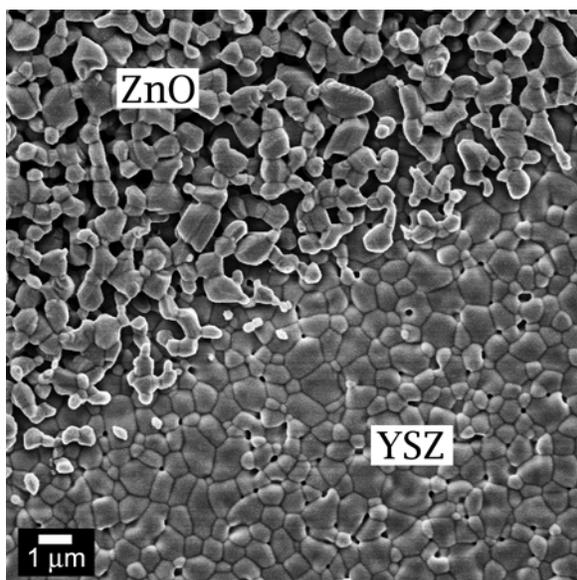


Figure 2. Plan view of a ZnO electrode on a YSZ substrate. Secondary electron image at 5 kV.

As Figure 3 shows, when paired with platinum in the geometry shown in Figure 1a, the binary oxides ZnO, Cr₂O₃, and NiO have yielded excellent non-Nernstian NO₂ sensing elements. For example, a ZnO/Pt sensing element, operating at 700°C in 7 vol % O₂, displayed an NO₂ sensitivity of ~50 mV/decade over the concentration range 20–200

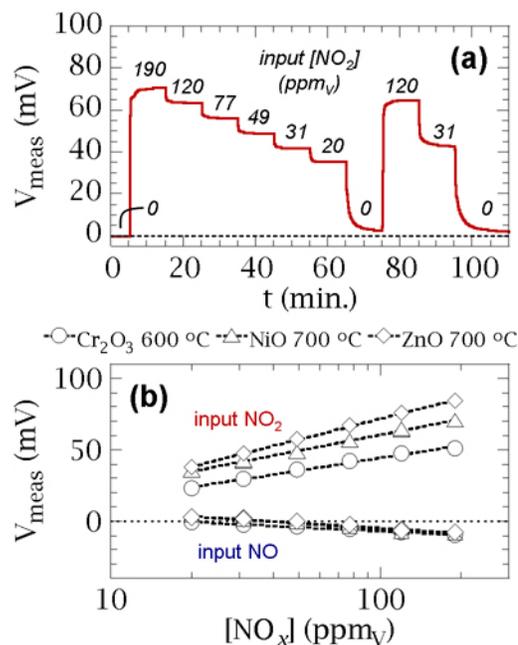
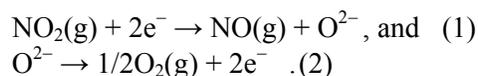


Figure 3. Response trace of an NiO/Pt sensing element as the input NO₂ is varied at 700°C in 7 vol % O₂ (a) and the variation in measured voltage with input NO_x for different binary oxide/Pt sensing elements in 7 vol % O₂ (b).

ppm_v NO₂, with 20 ppm_v NO₂ giving rise to a voltage of approximately 40 mV.

Diesel exhaust varies in O₂, typically ranging from 5 to 20 vol %.¹ Therefore, it is important to characterize the O₂ dependence of the sensing element response. Figure 4 shows that for these non-Nernstian NO₂ sensors, the measured voltage is a function of O₂ only in the presence of NO₂. We currently believe that this is observed because the voltage developed in the presence of NO₂ is related to the different behavior of the oxide and platinum electrodes with respect to the reduction of NO₂ and oxidation of oxygen ions (O²⁻) in the YSZ solid electrolyte:



The simultaneous occurrence of these reactions on both the oxide and platinum electrodes gives rise to a mixed potential on each electrode, the precise value of which will depend on the rate of Eqs. (1) and (2) on each electrode, the absorptive behavior of NO₂ and O₂ on each electrode, and the catalytic behavior of each electrode.² In the absence of NO₂, (Figure 4b), there is no gaseous species readily

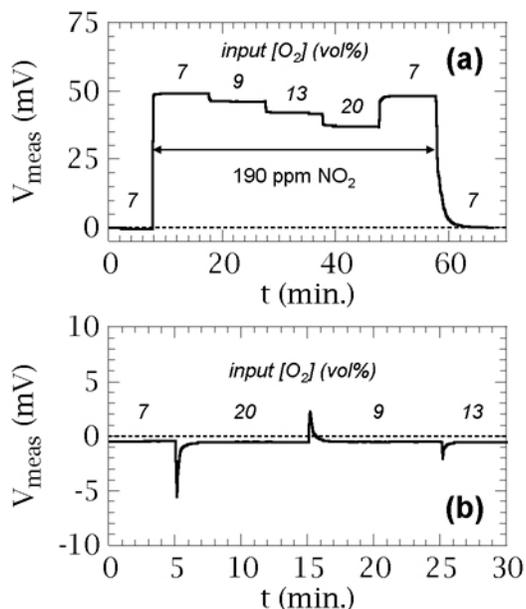


Figure 4. Measured voltage as O_2 is varied between 7 and 20 vol % with 190 ppm_v of NO_2 (a) and 0 ppm_v NO_2 (b) for an NiO/Pt sensing element operated in non-Nernstian mode.

available for reduction, and a mixed potential cannot develop.

The dominant equilibrium NO_x species above 500°C is NO .³ Therefore, although we cannot assume that the NO/NO_2 ratio in diesel exhaust is at equilibrium, it seems likely that NO would be more prevalent in the exhaust at the desired operating temperatures of 500–700°C. Thus sensor design may be simplified if sensing elements sensitive to NO could be developed. This can be done with the application of bias, as described below.

Equations (1) and (2) describe electrochemical reduction of NO_2 and oxidation of O^{2-} , respectively. A similar pair of equations can be written for the electrochemical oxidation of NO (to NO_2) and reduction of O_2 (to O^{2-}). Since these are electrochemical phenomena, it may be possible to adjust the rates of the various reactions by applying electrical bias to the sensing element (as is done in non-Faradaic electrochemical modification of catalytic activity).⁴ To demonstrate this with biased sensing elements, a dc current bias was stepped at discrete levels (e.g., -16, -8, 0, 8, 16 μA for 5 min each), and a brief (2-min) 450-ppm_v pulse of either NO or NO_2 was applied at each bias level. The result is shown in Figure 5, where it can be seen that at negative biases (oxide electrode biased negatively

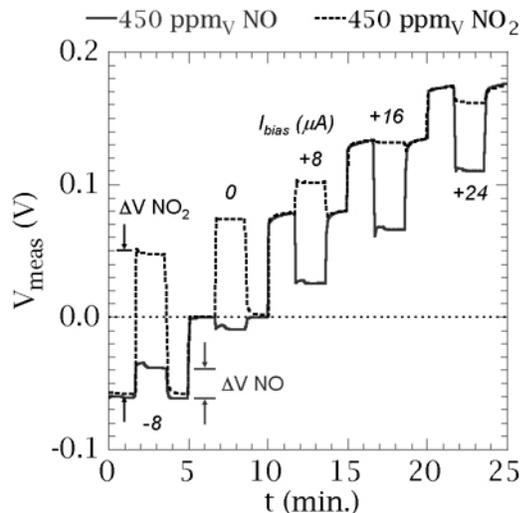


Figure 5. Voltage traces as 2-minute pulses of 450 ppm_v NO_x are applied at different current biases. Data collected at 600°C in 7 vol % O_2 .

with respect to the platinum electrode), the change in voltage induced by NO_2 is much larger than that induced by NO . However, as the bias is increased to positive values, the changes induced by NO are larger relative to those due to NO_2 , and at a certain positive bias ($\sim +16 \mu A$ for the sensing element in Figure 5) the introduction of 450 ppm_v NO gives a large signal while the same amount of NO_2 gives only a small response.

This asymmetry (stronger response to NO than NO_2) was displayed over a wide concentration range (~ 50 – 1500 ppm_v NO_x) as shown in Figure 6. Although the mechanism of the enhanced NO response with bias is still under investigation, it seems clear that the oxide electrode must promote the oxidation of NO in order for the effect to be seen. Under conditions of positive bias, for current to flow through the YSZ electrolyte, oxygen ions must flow through the YSZ to the oxide electrode (the anode), and the external electrical circuit must supply electrons to the platinum electrode (the cathode). Therefore, it would appear that the electrochemical reactions occurring in the presence of NO are the reverse of Eq. (1) (oxidation of NO) at the oxide electrode and the reverse of Eq. (2) (reduction of O_2) at the platinum electrode.

Less clear is the mechanism underlying the weak response to NO_2 seen in Figure 6. One possible explanation is that the oxide electrode strongly promotes the reduction of NO_2 via Eq. (1),

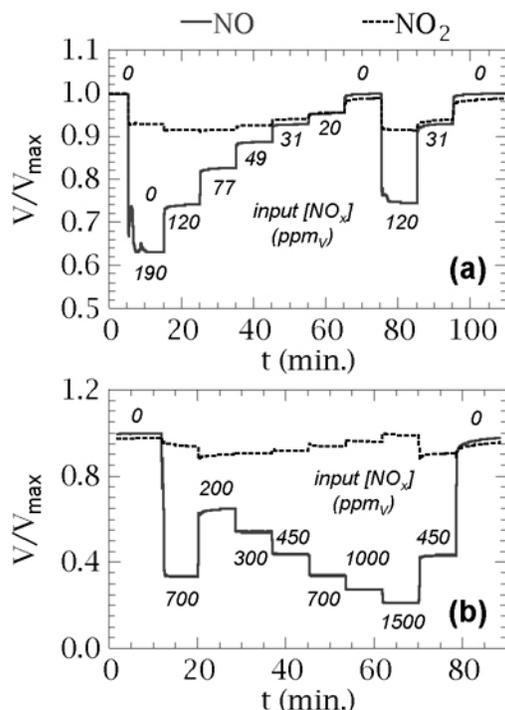


Figure 6. Response (600°C, 7 vol % O₂) of a current-biased sensing element to input NO and NO₂. The concentration variations of the two NO_x species were nominally identical.

and this interferes with the expected anodic reaction [Eq. (2)] at the oxide electrode with positive bias and only NO₂ and O₂ present. Lending credence to this is the observation that at sufficiently large positive biases, as seen in Figure 5, the introduction of either NO or NO₂ decreases the measured voltage.

The O₂ dependence of these biased sensing elements is quite different from the reaction of the non-Nernstian elements discussed earlier. As Figure 7 shows, these elements show an O₂ dependence that is a decreasing function of NO. In the absence of NO, the measured voltage of a current-biased element can vary ~20% as O₂ is varied from 7 to 20 vol % (Figure 7b). However, in the presence of 1500 ppm_v NO, variation of O₂ over this range has little effect (Figure 7a). This behavior points to the presence of NO as having an anomalously strong effect on the electrode/electrolyte interfacial resistance.

An important concern as sensor development progresses is the role of electrode geometry, as rigid space constraints will apply to the final sensor design. As an initial step in addressing these concerns, semicircular and interdigitated sensing

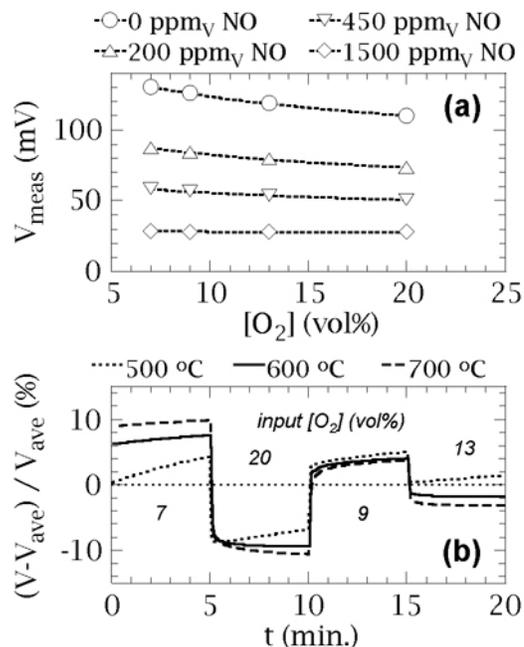


Figure 7. Variation of current-biased sensing element signal (at 600°C) with O₂ with different input NO (a) and response trace measured while varying O₂ with no input NO_x (b).

elements (Figure 1) have been fabricated and characterized. Figure 8 indicates that the geometry variation had little impact on the magnitude and functional form of the NO response. It is also seen in Figure 8 that for these biased sensing elements, an almost linear response is obtained at low input NO, and that the extent of this linear regime increased with the element operating temperature. This is in contrast to the logarithmic behavior exhibited by the non-Nernstian elements in Figure 3. The linear behavior at low NO_x, combined with the observation that the NO-selectivity of the biased elements seemed to decrease with NO_x (Figure 6), indicates that careful sensor design will be necessary to use these biased sensing elements for low NO_x levels. Finally, temperature was much more important than electrode geometry in governing the recovery time from NO exposure, as shown in Figure 9.

Conclusions

Progress in NO_x sensor development has proceeded along two main fronts. In the first approach, non-Nernstian sensing elements using binary oxides and platinum have been developed. These elements respond strongly to NO₂ and produce an output voltage that is proportional to the

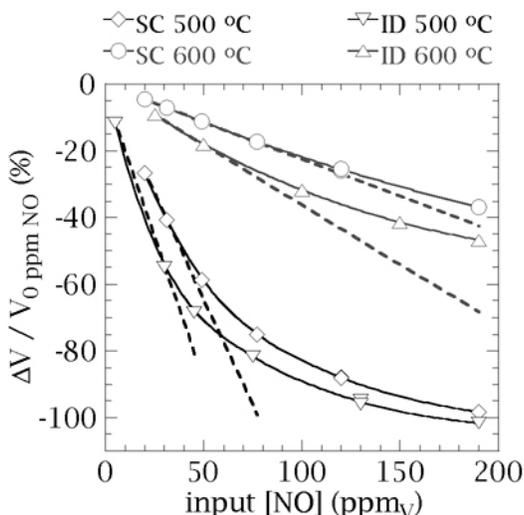


Figure 8. Response to input NO for biased sensing elements with the two different geometries (semicircular (SC) and interdigitated (ID)) of Figure 1. Data collected in 7 vol % O₂.

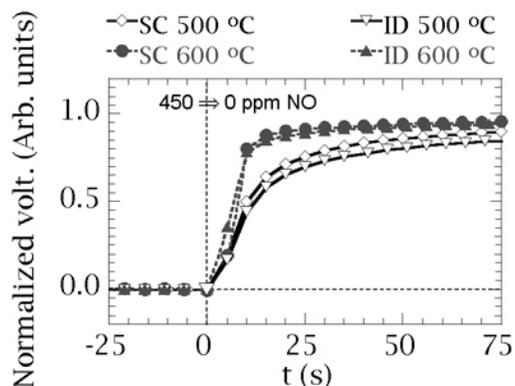


Figure 9. Recovery from NO exposure for biased sensing elements with the two different geometries of Figure 1, semicircular (SC) and interdigitated (ID).

logarithm of NO₂. Use of a more complex oxide electrode and a dc electrical bias enables selective detection of NO, the stable form of NO_x at high temperature. Pending evaluation of selectivity and stability, these two types of sensing elements are candidates for incorporation into NO_x sensors for heavy vehicle applications.

Publications

D. L. West, F. C. Montgomery, and T. R. Armstrong, "Electrically Biased NO_x Sensing Elements with Co-Planar Electrodes," in *205th Meeting of the Electrochemical Society*, San Antonio, TX, May 2004.

D. L. West, F. C. Montgomery, and T. R. Armstrong, "NO-Selective NO_x Sensing Elements for Combustion Exhausts," accepted by *Eurosensors XVIII*, Rome, Italy, September 2004.

D. L. West, F. C. Montgomery, and T. R. Armstrong, "High-T NO_x Sensing Elements Using Conductive Oxides and Pt," *Proceedings of ICEF: Engines for Mobile, Marine, Rail, Power Generation and Stationary Applications*, Long Beach, CA, November 2004.

D. L. West, F. C. Montgomery, and T. R. Armstrong, "Electrode Materials for Mixed-Potential NO_x Sensors," in *Proceedings of the 28th International Cocoa Beach Conference on Advanced Ceramics and Composites*, Cocoa Beach, FL, January 2004.

Patent

D. L. West, F. C. Montgomery, C. Maxey and T. R. Armstrong, "Sensing Devices Having CoPlanar Electrodes," filed with the U.S. Patent Office.

References

1. J. Kaspar, P. Fornasiero, and N. Hickey, "Automotive Catalytic Converters: Current Status and Some Perspectives," *Catalysis Today* **77**, 419–49 (2003).
2. A. A. Arias de Velasco, P. T. Moseley, R. Peat, and J. G. Peláez, "Atmosphere-dependent Potentials at Oxide Interfaces," *Sensors and Actuators B*, **15–16**, 55–62 (1993).
3. K. B. J. Schnelle and C. A. Brown, "NO_x Control," in *Air Pollution Control Technology Handbook*, CRC Press, Boca Raton, 2001.
4. C. G. Vayenas, S. Bebekis, I. V. Yentekakis, and S. Neophytidis, "Non-Faradaic Electrochemical Modification of Catalytic Activity: The Work Function of Metal Electrodes in Solid Electrolyte Cells," *Solid State Ionics* **53–56**, 97–110 (1992).