C. Development of NO_X Sensors for Heavy Vehicle Applications

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Objectives

- Develop NO_X sensors for remediation and monitoring of diesel engines.
- Develop sensors that have an operating temperature of 500–700°C and are able to measure NO_X concentrations from ~10–1500 ppm at oxygen levels from 5 to 20 vol %.
- Ensure that sensors are selective for either NO or NO_2, or able to measure "total NO_X" ([NO] + [NO_2]) since "NO_X" refers to mixtures of NO and NO_2.

Approach

- Fabricate prototype sensing elements by screen printing electrode layers onto oxygen-ion conducting [typically yttria stabilized zirconia (YSZ)] substrates.
- Operated elements either in a "non-Nernstian" mode (where the output is a voltage) or under direct current electrical bias.
- Characterize sensor in bench setting and in NG engine exhaust for NO_X sensor response, sensitivity to varying [O_2], and recovery/response kinetics.
- Develop breadboard based sensor for exhaust gas sensing.

Accomplishments

- Developed sensing elements displaying near "total NO_X" behavior and stable in simulated long-term service.
- Developed sensing elements that are capable of repeatedly detecting [NO_X] in the range of ~10 ppm and can operate at temperatures as high as 750°C with ±1 ppm sensitivity.
- Developed novel techniques for applying electrical stimulus to combat drift of the sensor background output.

Future Direction

- Evaluate the stability and performance of these sensing elements in real exhaust streams to quantify and correct for drift.
- Characterize the cross-sensitivity to other species (e.g., CO) that may be present in real exhaust streams.
- Clarify both the sensing mechanism and the cause(s) for sensor drift.

Introduction

The primary pollutants (excluding the greenhouse gas CO_2) from the combustion of low-sulfur fuels are CO, hydrocarbons (HC), and oxides of nitrogen ("NO_x," a mixture of NO and NO_2). 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 $[O_2]$ in the exhaust, losing its effectiveness for NO_x removal at high partial pressures of O_2. 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 O_2-rich (typically 5–20 vol % O_2).

In this current absence of a "lean-NO_x" catalyst, three technologies are 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).

In this project we are developing NO_x sensing elements that can be used in diesel engine exhausts. The *minimum* requirement for this application is an operating temperature of 500–700ºC and the ability to measure 1–1500 ppm NO_x. It should be emphasized that "NO_x" refers to mixtures of NO and NO_2; therefore, full NO_x characterization of the exhaust may require two of the following three concentrations to be measured: [NO], $[NO_2]$, $[NO_x]$ (= [NO] + $[NO_2]$). This project is a cooperative research and development agreement with Ford Motor Company.

Approach

The approach selected is to build a sensing platform on yttria-stabilized zirconia (YSZ). YSZ, an oxygen-ion conducting material, is currently widely used in $[O_2]$ sensors for gasoline engines. This approach is not original, because two NO_x sensors based on YSZ are near commercialization and have been proven by the engine manufacturers association not to be adequate to measure NO_x less than 50 ppm. In addition, both are relatively complex with multicavity constructions. This construction is required because in the first design[2] preliminary O_2 removal from the sampled exhaust is required before the NO_x is measured amperometrically. In the second design[3] the sampled exhaust passes over a conversion electrode in order to convert the NO_x into NO_2 before measurement in the sensing cavity.

The lion's share of work to date has focused on the sensing *element* portion of the sensor. This is the portion of the sensor that responds to the presence of NO_x. The reason for adopting this approach is that the working characteristics of the sensing element will dictate many aspects of sensor design (operating temperature, need for catalytic overlayers, etc.).

To fabricate sensing elements, electrodes are screen-printed and fired onto YSZ substrates (Figure 1). These elements are then tested for NO_x response using a furnace to simulate elevated temperature service and a commercial gas mixing unit to deliver blends of N_2, O_2, NO_x (either NO or NO_2), and other species as required.

Results

Much of the work on this project has been devoted to all-oxide "total NO_x" sensing elements. These sensing elements, a sample of which is depicted in Figure 1, consist of compositionally identical oxide electrodes on a YSZ substrate. These sensing elements are attractive because the use of a single electrode material will reduce production cost, and more importantly, their "total NO_x" (similar response to NO and NO_2) sensing behavior

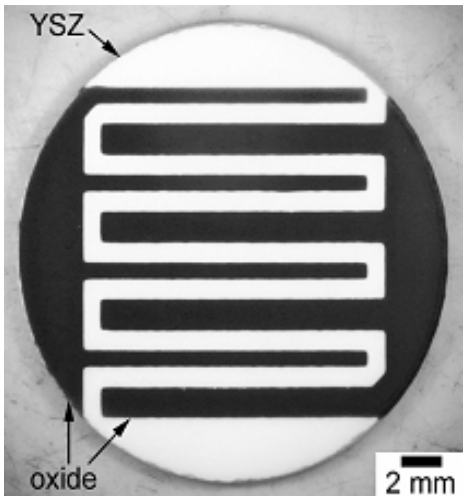

Figure 1. Prototype sensing element.

would enable measurement of [NO_x], regardless of the [NO]:[NO_2] ratio in the exhaust gas. This obviates the necessity to perform any NO_x conversion of the type described in Ref. 3.

Several electrode compositions have been evaluated in order to develop a composition with large NO_x response magnitudes. The best of these, when operated at 600ºC and 7 vol % O_2, had responses to 77 ppm NO and NO_2 of –37%* and –40%, respectively. However, long-term (>200-h) lab-scale testing of this composition revealed that it was unstable in exhaust conditions, and thus the development of new compositions, stable in exhaust conditions, has been carried out.

The NO_x sensing performance of two promising new compositions is shown in Figure 2. It can be seen that the NO_x responses are similar in magnitude over the concentration range 20–190 ppm, and efforts are ongoing to narrow the response between [NO] and [NO_2].

Figure 3 shows X-ray diffraction patterns from extensively tested sensing elements made with old electrode composition and the new composition. The new composition is clearly more stable as shown by the lack of decomposition products.

The data in Figure 2 were collected at 600ºC. It may be desirable to operate the sensing element at higher temperatures, both in order to improve the response/recovery time and prevent condensation on the sensing element. The higher temperature NO

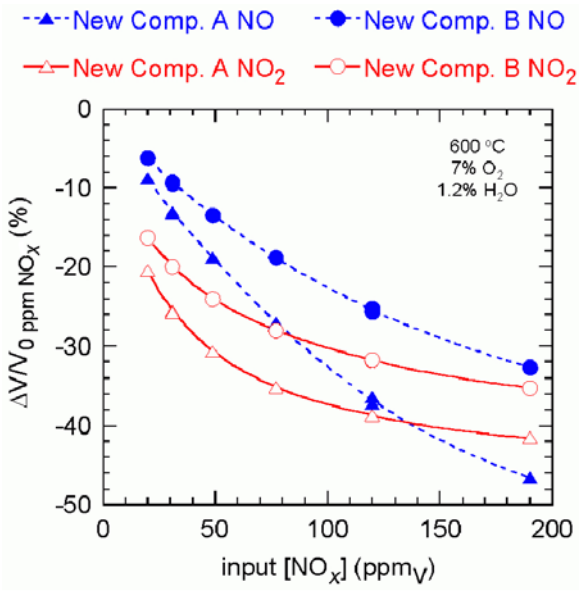

Figure 2. NO_x responses of two new electrode compositions.

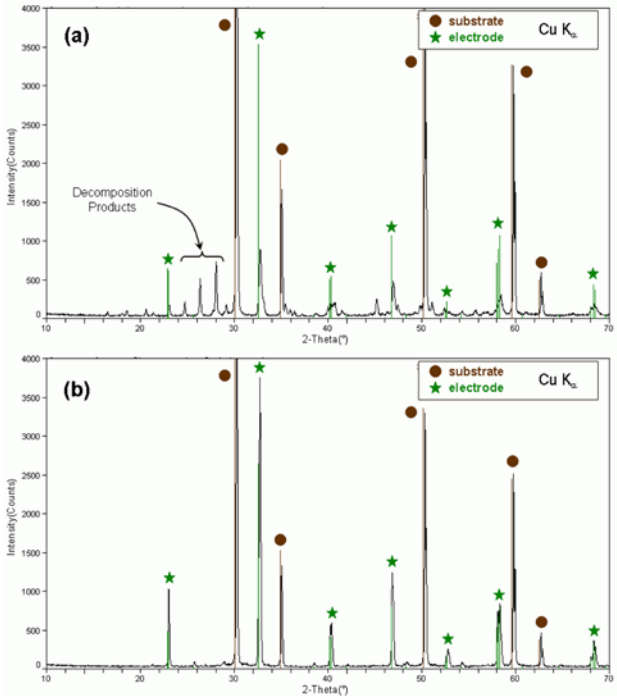

Figure 3. X-ray diffraction patterns of used elements made with (a) original and (b) new compositions.

sensing performance of these sensing elements is illustrated in Figure 4, which shows sensing element performance at 750ºC. Two aspects of the sensing performance in Figure 4 differ from that observed in Figure 2. First, the magnitude of the changes due to

*This is the change in measured voltage when NO_x is present.

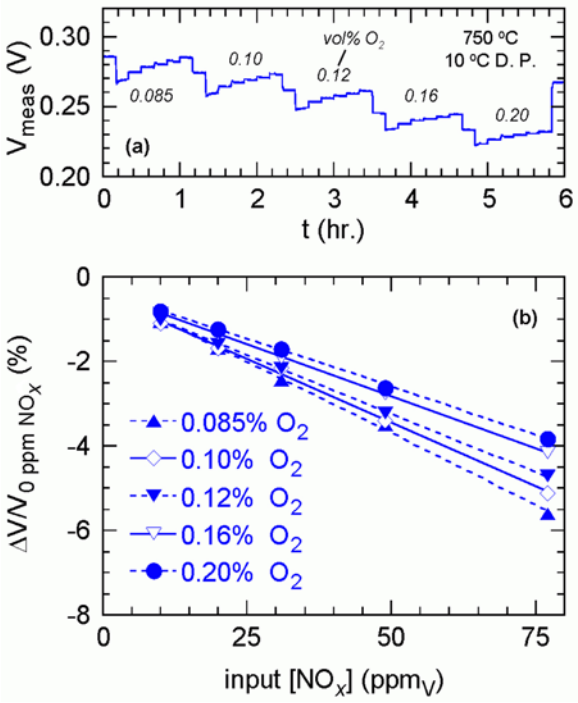

Figure 4. Sensing performance at 750°C. In (a) [NO] is stepped through the sequence 0, 77, 49. 31, 20, 10, 0 ppm at the indicated [O_2]. Computed changes in voltage are shown in (b).

NO are much smaller. Second, the dependence of the response on [NO] is linear. Note also that the response decreases with increasing [O_2]. This means that operation at these temperatures will most likely require lowering of the [O_2] in the sampled exhaust (by means of a pumping cell).

These sensing elements are electrochemical in nature, and electrochemical sensing elements are prone to drift. Drift is frequently observed because electrochemical sensors usually rely on charge transfer at interfaces, and these interfaces will age with use of the sensor.

Sample drift behavior observed with these sensing elements is illustrated in Figure 5. Shown there are the element responses to identical programmed changes in [NO] and [O_2] after 0, 10, and 70 h of continuous operation. The background resistance of the element is monotonically increasing, but the responses to the gas concentration changes are repeatable.

To combat this drift, we have been investigating alternate methods of applying an electrical stimulus to the sensing element. One such example is shown in Figure 6.

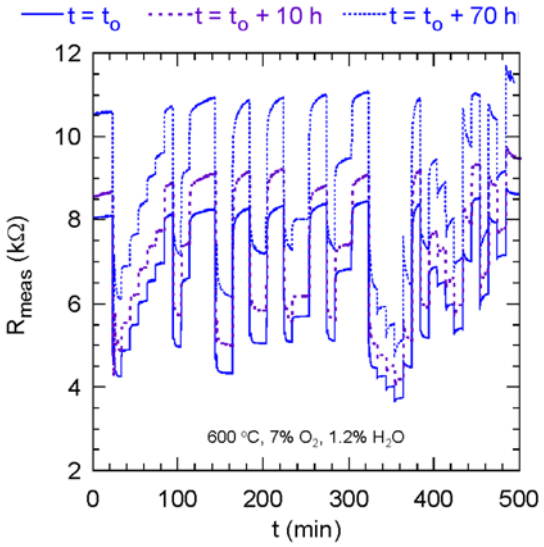

Figure 5. Response to identical changes in [NO] and [O_2] after 0, 10, and 70 h of continuous operation.

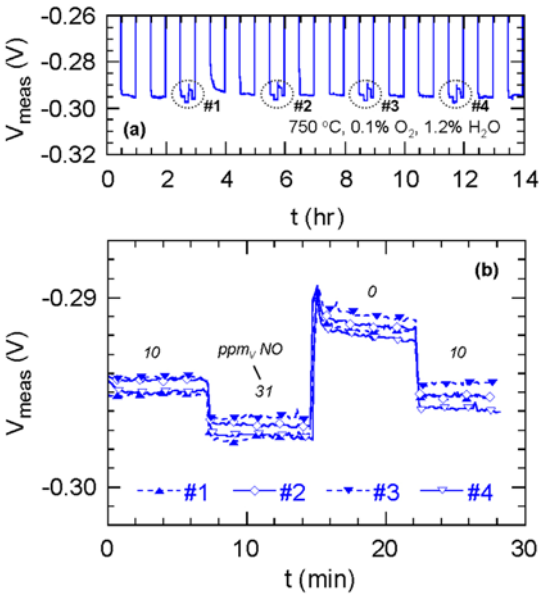

Figure 6. Element performance with alternating application of positive and negative electrical stimulus.

The electrical stimulus was alternated between positive and negative values (only the negative values are shown in Figure 6). During every third negative excursion, the [NO] concentration was varied systematically as indicated in Figure 6. Operated in this manner, the sensing element is capable of repeatedly detecting [NO] changes on the order of 10 ppm over more than 10 h of continuous

operation. These are thought to be the demands that monitoring of a lean NO_x trap would place on a NO_x sensor.

Conclusions

Sensing elements capable of "total NO_x" sensing behavior are under development. During the course of this project the following accomplishments have been achieved:

- Sensing elements displaying near "total NO_x" behavior and stable in simulated long-term service have been developed.
- NO sensing elements have been demonstrated.
- Sensing elements are capable of repeatedly detecting [NO_x] in the range of ~10 ppm and can operate at temperatures as high as 750°C with ±1 ppm sensitivity.
- Sensing elements stable for more than 1000 h in oxygen and steam containing environments have been developed.

The challenges ahead are fourfold: (1) the stability and sensitivity of these elements must be examined in real exhaust streams, (2) the cross-sensitivity to other species that may be present in the exhaust must be characterized, (3) techniques for combating drift must be introduced and optimized, and (4) the sensing mechanism of these elements needs to be elucidated.

This last item is important as ease of fabrication and cost may dictate changes in materials or geometry during the incorporation of these elements into sensors suitable for any engine application. Understanding of the sensing mechanism will be critical in predicting how such changes might affect the sensor performance.

References

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Patents

F. C. Montgomery, D. L. West, T. R. Armstrong, and L. C. Maxey, "NO_x Sensing Devices Having Conductive Oxide Electrodes," *ORNL Docket 1348C*.

Presentations and Publications

1. D. L. West, F. C. Montgomery, and T. R. Armstrong, "Total NO_x sensing elements with compositionally identical oxide electrodes," accepted by *Journal of the Electrochemical Society*, September 2005.
2. D. L. West, F. C. Montgomery, and T. R. Armstrong, "NO-selective NO_x sensing elements for combustion exhausts," accepted by *Sensors and Actuators B*, February 2005.
3. D. L. West,* F. C. Montgomery, and T. R. Armstrong, "All-oxide "total NO_x" sensing elements," *207th Meeting of the Electrochemical Society*, 2005.
4. D. L. West, F. C. Montgomery, and T. R. Armstrong, "DC electrical-biased, all-oxide NO_x sensing elements for use at 873 K," *29th International Cocoa Beach Conference on Advanced Ceramics and Composites*, 2005.
5. 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*, 2004.