MULTIFUNCTIONAL (NOx/CO/O2) SOLID-STATE SENSORS FOR
COAL COMBUSTION CONTROL

Technical Progress Report

Start Date: September 30, 2003
End Date: October 1, 2004

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March 21, 2005

DOE Award Number – DE-FG26-02NT41533

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ABSTRACT

Sensing properties of a La$_2$CuO$_4$- and WO$_3$-based potentiometric NO$_x$ sensor were investigated both in N$_2$ and in a simulated exhaust gas. We performed temperature programmed reaction (TPR) and desorption (TPD) experiments to determine the reaction and adsorption characteristics of O$_2$, NO$_x$, CO, CO$_2$, and their mixtures on the electrodes, and related the results to sensor performance.

The relative responses of the La$_2$CuO$_4$-based sensor under varied concentrations of NO, NO$_2$, CO, CO$_2$ and O$_2$ were studied. The results showed a very high sensitivity to CO and NO$_2$ at 450 °C in 3 % O$_2$, whereas the response to O$_2$ and CO$_2$ gases was negligible. The NO response at 400 – 500 °C agreed with the NO adsorption behavior. The high NO$_2$ sensitivity at 450 °C was probably related to heterogeneous catalytic activity of La$_2$CuO$_4$. The adsorption of NO was not affected by the change of O$_2$ concentration and thus the sensor showed selective detection of NO over O$_2$. However, the NO sensitivity was strongly influenced by the existence of CO, H$_2$O, NO$_2$, and CO$_2$, as the adsorption behavior of NO was influenced by these gases.

The WO$_3$-based sensor was able to selectively detect NO in the presence of CO$_2$ in 3 % O$_2$ and at 650 °C. The NO sensitivity, however, was affected by the variation of the NO$_2$, CO, and H$_2$O concentration. No gas-solid reactions were observed using TPR in the NO-containing gas mixture, indicating that the NO response was not obtained by the conventionally accepted mixed-potential mechanism. At the same condition the sensor had high sensitivity to ~ 10 ppm NO$_2$ and selectivity in the presence of CO, CO$_2$, and H$_2$O, showing it to be applicable to the monitoring of NO$_2$. Significantly different sensing properties of NO in simulated exhaust gas suggested the occurrence of gas composition change by the gas-phase and gas-solid reactions, and strong adsorption of water on the electrodes. The NO$_2$ sensitivity in simulated exhaust gas was modified by O$_2$ and H$_2$O, but not by CO and CO$_2$.

A positive voltage response was obtained for NO$_2$ but negative for NO at 650 °C with the n-type semiconducting WO$_3$-based sensor. In contrast the opposite response direction for NO$_x$ was observed at 450 °C with the La$_2$CuO$_4$ (p-type semiconductor).
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1. INTRODUCTION

There is a tremendous environmental and regulatory need for the monitoring and control of NO\textsubscript{x} emissions from coal, natural gas and oil combustion sources [1 – 4]. Solid oxide electrochemical O\textsubscript{2} sensors are inexpensive and have been well demonstrated in harsh high-temperature combustion exhaust environment. If modified to selectively measure NO\textsubscript{x} and CO concentrations this type of sensor can be used to further improve combustion control, resulting in improved fuel utilization and reduced emissions.

We have developed solid-state sensor technology that can provide an inexpensive, rugged, small, solid-state device capable of measuring the concentration of multiple species (such as NO, NO\textsubscript{2} and CO) in coal, natural gas and oil combustion exhaust [5]. Our sensor technology is similar to that used in conventional automotive O\textsubscript{2} sensors and thus can be used directly in high temperature exhaust. However, both the sensing and reference electrode are in the same gas stream, significantly reducing fabrication costs. These small (<1 cm\textsuperscript{2}) simple potentiometric (voltage output) sensors are sensitive to each of these gasses and can be readily combined on a single chip to provide a multifunctional (NO\textsubscript{x}, CO, O\textsubscript{2}) sensor (Fig. 1). This technology is the basis for a low cost, simplified way to meet emissions monitoring regulations as well as to improve combustion control, thus, improving fuel utilization and reducing emissions from coal, natural gas and oil combustion sources.

![Fig. 1. Multifunctional NO\textsubscript{x}, CO, O\textsubscript{2} sensor.](image_url)
The key scientific issue that must be addressed for this type of sensor to effectively measure NO\textsubscript{x} and CO concentrations in coal, natural gas and oil combustion exhaust gas streams is the selectivity of the electrode(s) for discrimination between gaseous NO\textsubscript{x} and CO vs. O\textsubscript{2}. Specifically, the sensors must exhibit a highly selective response to ppm levels of NO\textsubscript{x} and CO in the presence of percent levels of O\textsubscript{2}. Not only must the sensor exhibit a selectivity factor of, for example, 1000:1 NO/O\textsubscript{2}, based on the typical concentration differences between NO and O\textsubscript{2}, but the sensor must be insensitive to large changes in the O\textsubscript{2} concentration associated with variations in combustion conditions.

We have developed an innovative scientific approach "Differential Electrode Equilibria" (described below), and demonstrated that this approach provides the necessary selectivity to measure for example, ppm levels of NO with high sensitivity in lean-burn (13 – 17 % O\textsubscript{2}) exhaust gas unaffected by variations in O\textsubscript{2} concentration. Since we have already demonstrated this works for NO, the objectives of our proposed research are to: advance the fundamental understanding of this approach, apply it to the development of selective NO\textsubscript{2}, CO and O\textsubscript{2} electrode elements; fabricate and test a multifunctional (NO\textsubscript{x}, CO, O\textsubscript{2}) sensor; and develop a miniature low-cost multifunctional (NO\textsubscript{x}, CO, O\textsubscript{2}) sensor prototype for evaluation by commercial/industrial companies. In achieving these objectives we will both advance the science of solid-state electrochemical sensors, including the education and training of students, and bring closer to commercialization a device that will result in both improved fuel utilization and reduced emissions from coal, natural gas and oil combustion.

**Differential Electrode Equilibria**

A difference in electrochemical potential between two electrodes exposed to the same environment will occur if one or both of the electrodes does not achieve thermodynamic equilibrium. In a potentiometric sensor this non-Nernstian response produces a voltage that depends on the concentration of one or more of the species present.

Semiconducting resistive sensors have been investigated for many years for detection of gases [6]. Sensor characteristics depend on the microstructure of the material and
geometrical configuration of the sensor element. However, most of these sensors lack the ability to selectively detect the individual gases. For instance, it is difficult to monitor NO under varying O2 concentration in combustion exhaust using only a resistive sensor.

Traditional potentiometric sensors operate on the principle that a voltage arises at the surface between two similar electrodes, fabricated on two opposite faces of an electrolyte material, when exposed to different environments [7]. The voltage is proportional to the log of the pO2 difference.

In contrast, our sensors operate with two dissimilar electrodes exposed to the same environment. The differential electrode equilibria created between the gas molecules and the dissimilar sensor electrode surfaces give rise to a potential gradient between the electrodes, resulting in a voltage response [8]. Semiconducting oxide electrodes combined with platinum reference electrodes on YSZ substrates are sensitive and selective to NO with negligible response to O2 or CO.

The composition and microstructure of the sensing electrode are the key parameters that influence the sensing mechanism, and hence key sensor performance parameters: sensitivity, selectivity and response time. During the previous reporting period we investigated the effect of microstructure and the fundamental heterogeneous gas-solid interactions of La2CuO4. We demonstrated that the microstructure of electrodes has a dramatic effect on both sensitivity and response time of potentiometric NO sensors. We also used the TPD technique to determine the adsorption characteristics of O2, NO, CO, CO2, and their mixtures, on the La2CuO4 electrode material and related the results to sensor performance.

Various potentiometric gas sensors based on semiconducting metal oxides have shown good sensitivity with stable response. Di Bartolomeo et al. reported that potentiometric planar sensors built using WO3, LaFeO3, La0.8Sr0.2FeO3, and ZnO, where both electrodes were on the same face, showed fast and stable response to NO2 and CO [9, 10]. Gas sensing properties of potentiometric tubular sensors based on semiconducting metal oxides such as WO3, SnO2, ZnO, CdO, MoO3, In2O3, etc., were also investigated [11, 12]. Among the above oxides, WO3 is of particular interest because it has been known to be sensitive to
NO$_x$ without significant sensor signal drift. According to earlier studies, the potentiometric response to NO$_x$ using a WO$_3$ electrode was fast and stable, and a linear relationship was obtained in a plot of the sensor emf vs. the logarithm of NO$_x$ concentration [12, 13]. However, only limited information is currently available about the sensing properties of a WO$_3$-based potentiometric sensor. Therefore studies of its selectivity, stability, and reproducibility are required. In the previous report a potentiometric La$_2$CuO$_4$ sensor showed adequate and stable response to NO$_x$. The critical requirement for NO$_x$ detection in combustion exhausts containing hydrocarbons, CO$_2$, H$_2$O, O$_2$, CO, and NO$_x$ is the selectivity of the electrode. In this report, sensing properties and selectivities for the detection of low concentration NO$_x$ (10 – 650 ppm) in N$_2$ and in a simulated exhaust gas by using asymmetrical potentiometric sensors based on La$_2$CuO$_4$ and WO$_3$ electrode are described. Additionally sensing mechanisms are discussed using temperature programmed reaction (TPR) and desorption (TPD) results.
2. EXECUTIVE SUMMARY

During this reporting period we investigated the selectivity of NO\textsubscript{x} over O\textsubscript{2}, CO, CO\textsubscript{2}, and H\textsubscript{2}O, as enhanced selectivity is a critical requirement for the applications in combustion exhausts. In the potentiometric sensor a potential difference arises between the two electrodes, due to dissimilarity in electrochemical reactions, catalytic activities, and adsorption of gases of either side. Along with the selectivity studies, the characteristics of the gas-phase and gas-solid reactions, and adsorption of O\textsubscript{2}, NO\textsubscript{x}, CO, CO\textsubscript{2}, and their mixtures was studied by using the temperature programmed reaction (TPR) and desorption (TPD) techniques, and the results interpreted considering the sensing behavior.

The cross-sensitivities of the La\textsubscript{2}CuO\textsubscript{4}-based sensor for NO, NO\textsubscript{2}, and CO were high, but for CO\textsubscript{2} and O\textsubscript{2} were negligible. The WO\textsubscript{3}-based sensor responded highly to ~ 10 ppm NO\textsubscript{2} and selectively in the existence of CO, CO\textsubscript{2}, and H\textsubscript{2}O, showing it to be applicable to the monitoring of NO\textsubscript{2}. No gas-solid reactions were observed in the NO-containing gas mixture during TPR experiments, indicating that the NO response was not obtained by the so-called mixed-potential mechanism.

The p-type La\textsubscript{2}CuO\textsubscript{4}–based sensor operated at 450 °C with reasonably high NO sensitivity and fast response. An abrupt decrease in sensitivity occurred above 500 °C and at 350 °C the response was saturated, in good agreement with the TPD results. This indicates that NO sensing by La\textsubscript{2}CuO\textsubscript{4} is likely due to the chemisorption of NO and the resulting change in Fermi level of the oxide.

The n-type semiconducting WO\textsubscript{3}-based sensor showed optimal NO\textsubscript{2} sensing behavior at 650 °C and the response decreased with temperature. This temperature effect can be explained using the NO\textsubscript{2} TPR results. Since a dissymmetry of the catalytic activity for NO\textsubscript{2} reduction between the two electrodes is temperature dependent and the difference decreases with temperature, the NO\textsubscript{2} response decreases with increasing temperature.
3. EXPERIMENTAL

3-1. Potentiometric NO\textsubscript{x} Sensor

As described in the previous report and shown in Fig. 2, an asymmetrical planar sensor was built using an 8-mole % Y\textsubscript{2}O\textsubscript{3}-doped ZrO\textsubscript{2} plate (Marketech International Inc., YSZ-8Y, 20 × 10 × 0.1 mm) as a solid electrolyte, and a metal oxide (WO\textsubscript{3} or La\textsubscript{2}CuO\textsubscript{4}) and a Pt layer as electrodes.

![Schematic diagram of a potentiometric sensor. (a) Top view, (b) Side view.](image)

Tungsten oxide (WO\textsubscript{3}, 99.8 % purity, Alfa Aesar) powder was purchased and La\textsubscript{2}CuO\textsubscript{4} was prepared by the auto-ignition method (The details were given in the previous report). For the preparation of a sensing electrode, the powder was dispersed in ethanol with polyethylene glycol 400 (PEG-400, Avocado Research Chemicals Ltd.), and subsequently ball-milled for 24 hr. The mixed slurry was then heated at 60 °C for 10 hr to completely remove the ethanol. One face of the YSZ-8Y substrate was screen-printed with the WO\textsubscript{3} (or La\textsubscript{2}CuO\textsubscript{4}) slurry and the other with platinum paste (Heraeus, Conductor paste CL11-5349). Platinum wires (dia. = 0.127 mm) were connected to both electrodes. After securing the end of Pt wires with high temperature adhesive (Aremco Products Inc., Ceramabond 571-VFG-P), the sensor electrodes were sintered at 800 °C for 10 hr with heating and cooling rate = 1 °C/min. Micrographs of the sintered sensing electrodes were obtained using a scanning electron microscope (SEM, JEOL JSM 6400 SEM).
3-2. Measurements of NO\textsubscript{x} Sensing Properties

An apparatus for the sensor measurements was constructed using a gas-tight quartz tube. The sensor was installed in the tube, where both electrodes were exposed to the same gas atmosphere, and then connected to a Keithley 2000 multimeter for the measurements of electromotive force (emf) \{(-) Pt/YSZ-8Y/WO\textsubscript{3} (or La\textsubscript{2}CuO\textsubscript{4}) (+)\}. A Eurotherm 2408 temperature controller was used to operate a home-made furnace. The flow rate of the gases was controlled using mass flow controllers (MFCs, MKS Instruments Inc.). The total gas flow rate was fixed at 300 cc/min. Gaseous water was produced using a water bubbler. LabView software controlled the overall experiments through GPIB and RS 232 communication ports.

The sensor was allowed to equilibrate with an initial gas environment of 3 % O\textsubscript{2} in N\textsubscript{2} or simulated exhaust gas (16 % CO\textsubscript{2}, 100 ppm CO, 3 % O\textsubscript{2}, and 3 % H\textsubscript{2}O). The sensor emf was measured with increasing and then decreasing concentration steps of NO\textsubscript{x}. The retention time at every step was 200 – 300 sec. First, the emf changes were recorded as a function of temperature, 300 – 800 °C, while varying the concentration of NO\textsubscript{x}, 0 – 650 ppm. Second, the selectivities to NO\textsubscript{x} over CO, CO\textsubscript{2}, O\textsubscript{2}, and H\textsubscript{2}O were investigated both in 3 % O\textsubscript{2} with N\textsubscript{2} balance and in the simulated exhaust environment.

3-3. TPR/TPD Experiments

Gas reactions catalyzed by the WO\textsubscript{3} powder (W), the WO\textsubscript{3} film on the YSZ-8Y (W+Y), the Pt on the YSZ-8Y (Pt+Y), the YSZ substrate alone (Y), and the La\textsubscript{2}CuO\textsubscript{4} powder were analyzed using the temperature-programmed reaction (TPR) technique. Additionally, the TPR experiments were performed using a blank reactor (B) to determine the uncatalyzed reaction. Initially, 500 – 2000 ppm of the reactant gases or the gas mixtures flowed at 30 cc/min through the reactor at 50 °C. When the gas flow was stabilized, the temperature was increased from 50 to 800 °C at 30 °C/min while measuring the concentration of effluent gases with a quadrupole mass spectrometer (QMS). We scanned carbon fragment (m/e =
12), nitrogen fragment (m/e = 14), CO (m/e = 28), NO (m/e = 30), O₂ (m/e = 32), CO₂ (m/e = 44), N₂O (m/e = 44) and NO₂ (m/e = 46) during the TPR measurements.

The temperature-programmed desorption (TPD) experiments were performed to investigate the adsorption characteristics of exhaust gases such as NO, CO, O₂, CO₂, and their mixtures on 0.033 g La₂CuO₄ powder (total BET surface area ≈ 0.066 m²). The TPD experiments started with the adsorption of a particular gas (or gas mixture) at 300 °C for 30 min. The reactor was then cooled down to 30 °C at 5 °C/min and then purged at 30 °C with Helium containing 1 % Argon for internal calibration. The temperature was then increased from 50 to 800 °C under flowing 30 cc/min Helium and the desorption products measured with the QMS.
4. RESULTS AND DISCUSSION

4-1. \textit{La}_2\textit{CuO}_4\textit{-based Sensor}

4-1-1. Sensing properties of \textit{La}_2\textit{CuO}_4\textit{-based sensor}

The sensor emf (mV) obtained with variation of NO concentration is plotted against time (sec) in Fig. 3 (a). The NO concentration at each step is labeled in the figure.

![Figure 3. Sensor response to NO concentration (0 – 650 ppm) at 450 ºC in 3 % O\textsubscript{2} with N\textsubscript{2} balance. (a) Typical plot of sensor EMF (mV) vs. NO concentration step, (b) Reproducibility of sensor EMF vs. NO concentration (ppm) for different measurements under same conditions.](image)

The response time ($t_R$), time required to reach 90 % of the steady-state emf value, was less than 30 sec, irrespective of gas concentrations at 450 ºC. As shown in Fig. 3 (b), the measurement of NO showed good reproducibility between different measurements repeated over a 300 hr period under the same conditions.

The relative response with varying NO, NO\textsubscript{2}, CO, CO\textsubscript{2} and O\textsubscript{2} concentrations are plotted in Fig. 4. Results show a high sensitivity to NO, CO, and NO\textsubscript{2} at 450 ºC, whereas the cross-sensitivity to O\textsubscript{2} and CO\textsubscript{2} was negligible.
Fig. 4. La$_2$CuO$_4$ sensor response to NO, NO$_2$, CO, and CO$_2$ in 3 % O$_2$, and O$_2$ in N$_2$, at 450 °C.

4-1-2. Temperature dependence of La$_2$CuO$_4$-based sensor

The temperature dependence of the NO response was investigated at 350 < $T$ < 550 °C (Fig. 5 (a)).

Fig. 5. Variation of the NO$_x$ and CO sensitivity as a function of temperature in 3 % O$_2$. (a) NO, (b) NO$_2$, and (c) CO.
Above 500 ºC values of the emf were very small, less than 5 mV for 650 ppm NO, and at 350 ºC and below the response was saturated. This temperature dependence can be explained by the TPD (Fig. 6 (a)) and TPR results. From TPR results no reaction for either direct decomposition of NO to N₂ and O₂, or oxidation of NO to NO₂ was observed up to 800 ºC. Thus any catalytic mechanism (e.g. mixed potential) can be ruled out. Therefore, the mechanism is due to adsorption of the gas and the resulting change in Fermi level of the oxide. Nitric oxide was physically and chemically adsorbed onto the oxide surface at T < 400 ºC, thus saturating the surface and sensor response at low temperature.

Fig. 6. TPD of (a) NO (1 %) and (b) CO (500 ppm) + O₂ (1 %) over the La₂CuO₄ powder.
The plot of the sensor emf (mV) vs. logarithm of CO concentration (ppm) is linear at $300 < T < 550 \, ^\circ C$ (Fig. 5 (c)). The sensor was very sensitive to CO at $T < 450 \, ^\circ C$. CO TPD results show broad desorption of CO$_2$ and CO at $200 < T < 450 \, ^\circ C$ in Fig. 6 (b), indicating that the high CO response is likely due to CO adsorption and its related surface oxidation.

Temperature dependence of the NO$_2$ sensitivity was also studied. As presented in Fig. 5 (b), the NO$_2$ response was also strongly temperature-dependent with an abrupt decrease above 500 $^\circ C$. The TPR results (Fig. 7 (a)) show that above 250 $^\circ C$ NO$_2$ is reduced to NO and that by 600 $^\circ C$ it is completely reduced. Thus the NO$_2$ response at this temperature range involves heterogeneous catalysis in sensitivity. The NO$_2$ TPD also shows signs of surface reaction (Fig. 7 (b)). Nitrogen dioxide began desorption at 225 $^\circ C$, and the peak was followed by a similar desorption peak for NO, shifted 25 $^\circ C$ higher and the second NO desorption peak lined up with the desorption peak for chemisorbed oxygen. At temperatures above 600 $^\circ C$, lattice oxygen from the sample was emitted. Thus a series of complex reaction steps occurred on the surface of La$_2$CuO$_4$ over the temperature range where it is most sensitive to NO$_2$.

![Fig. 7. TPR/TPD of NO$_2$ over the La$_2$CuO$_4$ powder. (a) TPR, (b) TPD of NO$_2$ (500 ppm).](image-url)
4-1-3. Selectivity to NO

The response of the sensor with variation of NO concentration was studied in the presence of other gases. The NO sensitivity was not affected by the change of O$_2$ concentration (Fig. 8 (a)). In the NO+O$_2$ TPD experiments the NO adsorption was found to not be affected by O$_2$, showing NO desorption peaks very similar to those obtained in the NO TPD (Fig. 6 (a)).

![Graphs showing sensor EMF vs NO concentration under different conditions: (a) 3 - 30 % O$_2$, (b) 0 - 3 % H$_2$O, (c) 0 - 200 ppm CO, (d) 0 - 400 ppm NO$_2$.]

Fig. 8. Effect of O$_2$, H$_2$O, CO, NO$_2$, and CO$_2$ on the NO response at 450 °C and in N$_2$. (a) O$_2$ effect (3 – 30 %), (b) H$_2$O effect (0 – 3 %), (c) CO effect (0 – 200 ppm), (d) NO$_2$ effect (0 – 400 ppm), (e) CO$_2$ effect (0 – 16 %). Measured in 3 % O$_2$ for (b) – (e).
Fig. 8. (cont.) Effect of O\textsubscript{2}, H\textsubscript{2}O, CO, NO\textsubscript{2}, and CO\textsubscript{2} on the NO response at 450 °C and in N\textsubscript{2}. (a) O\textsubscript{2} effect (3 – 30 %), (b) H\textsubscript{2}O effect (0 – 3 %), (c) CO effect (0 – 200 ppm), (d) NO\textsubscript{2} effect (0 – 400 ppm), (e) CO\textsubscript{2} effect (0 – 16 %). Measured in 3 % O\textsubscript{2} for (b) – (e).

By addition of 3 % H\textsubscript{2}O the sensor emf was reduced ~ 2 mV but the slope remained about the same (Fig. 8 (b)). The formation of a hydroxylated surface by water may influence the NO sensing behavior.

CO decreased the slope gradually and increased the emf values (Fig. 8 (c)). This is surprising since the response of the sensor to both NO and CO is positive. Thus one would expect an additive response. We find in Fig. 9 (a) that the presence of CO enhances NO adsorption so that NO continues to desorb up to 800 °C (Compare Fig. 9 (a) to Fig. 6). Thus, the decrease in sensitivity with CO addition can be described in terms of the surface saturation that was exhibited for the NO response alone below 400 °C (Fig. 5 (a)). The intense CO\textsubscript{2} desorption peak at 200 – 500 °C in the NO+CO+O\textsubscript{2} TPD, probably formed by the surface reactions of CO with adsorbed oxygen or lattice oxygen. High CO oxidation catalytic activity was observed during the NO+CO+O\textsubscript{2} TPR above 200 °C (Fig. 9 (b)).
Fig. 9. TPD/TPR of NO+CO+O₂ over the La₂CuO₄ powder. (a) TPD of NO (500 ppm) + CO (500 ppm) + O₂ (1 %), (b) TPR.

Fig. 8 (d) showed that the NO sensitivity was strongly affected by NO₂, where the baseline shift occurred with the NO₂ concentration change. The slope remained positive even with the large changes in the emf values.

The effect of CO₂ is presented in Fig. 8 (e). High concentration of CO₂ reversed the NO sensitivity. This can be explained from the results of the NO+CO₂ TPD (Fig. 10). When NO and CO₂ were coadsorbed the CO₂ displaced the NO, shifting the NO desorption peaks to less than 200 ºC.

Fig. 10. TPD of NO (500 ppm) + CO₂ (1000 ppm) over the La₂CuO₄ powder.
4-2. **WO$_3$-based Sensor**

4-2-1. **Characterization of WO$_3$ electrodes**

Fig. 11 shows a scanning electron micrograph of a WO$_3$ and a Pt layer on the YSZ-8Y substrate prepared by sintering at 800 °C for 10 hr. The WO$_3$ thick film exhibited a very porous microstructure with 0.5 – 3 µm grains and 10 – 30 µm thickness. The porous Pt layer was deposited uniformly, showing a thickness ~ 9 µm.

![Scanning electron micrograph of Pt and WO$_3$ layers](image)

Fig. 11. Scanning electron micrograph of the Pt (a) and WO$_3$ (b) electrode.

4-2-2. **Sensing properties**

The sensor emf is plotted against time with NO concentration steps (50 – 650 ppm) and NO$_2$ steps (10 – 200 ppm) at 650 °C in 3 % O$_2$ (Fig. 12). A positive response was obtained for NO$_2$ and negative for NO. The direction of response of n-type semiconducting WO$_3$ is opposite to that of p-type La$_2$CuO$_4$. It agrees with the previous results, where the potentiometric sensor measurements were performed with different cell configurations [12, 13].
Fig. 12. Typical plot of sensor emf (mV) vs. time (sec) as a function of NO (50 – 650 ppm) and NO2 (10 – 200 ppm) concentration steps at 650 °C in 3 % O2 and balance N2.

Values of the emf measured for NO2 were much higher than those formerly reported at 650 °C and in air. For example, value of the emf measured for 200 ppm NO2 was ≈ 90 mV in the present experiments which is more than two times higher than in previous results [12, 13].

The response time (tR) was dependent on the gas concentration, showing shorter tR at higher concentration for both gases. The tR was ≈ 20 sec for 400 – 650 ppm NO, and ≈ 50 sec for 50 – 100 ppm NO. The sensor response to 10 – 200 ppm NO2 was faster than to NO with tR less than 15 sec and attained a steady-state value within 60 sec at 650 °C even in the low concentration region, 10 – 20 ppm.

Measured emf values while increasing the NOx concentration were slightly different from those in the regime of decreasing concentration at 650 °C. The difference of the emf values was ~ 3 mV at NO2 < 20 ppm but less than 1 mV at NO2 > 100 ppm, and less than 1 mV at 50 < NO < 400 ppm. The difference decreased with increasing temperature and became negligible at T > 700 °C for both NO and NO2, indicating that the kinetics of adsorption and desorption might be dissimilar at lower temperature. An average of the emf values measured with increasing and decreasing concentration was used for further analysis.
The measurements were repeated several times over 200 hr. Values of the emf obtained with the conditions described above were repeatable with less than 10 % difference. No systematic trend with the time sequence of the measurements was observed. However, the measurements were slightly affected by reducing (or oxidizing) gases exposure in the previous run and might cause the data scattering. Either changes in oxygen non-stoichiometry at the interfacial region caused by reducing or oxidizing gases or irreversible reactions of a gas with the surface layer most likely occurred.

Three different sensors of the same design were built and their sensing properties were compared with one another. The emf values measured for NOx agreed within 15 % difference on average, under the same conditions. Properties of each sensor were expected to be slightly different because parameters affecting the sensitivity, such as porosity and thickness of electrode, might vary with fabrication process [14]. The differences are indicative of the importance of accurate control of fabrication conditions.

4-2-3. Temperature dependence of WO3-based sensor

The temperature dependence of the NOx emf response was investigated at 550 < T < 800 °C (Fig. 13).

Fig. 13. Variation of the NOx sensitivity as a function of temperature in 3 % O2. (a) NO at 600 – 750 °C, (b) NO2 at 550 – 800 °C.
A plot of the sensor emf (mV) vs. logarithm of NO concentration (ppm) is linear at $600 < T < 750 \, ^\circ\text{C}$ and $50 < NO < 650$ ppm (Fig. 13 (a)). The slope decreased gradually with increasing temperature from 600 to 700 °C and decreased abruptly at 750 °C. The general tendency of the temperature dependence was in agreement with previous results obtained by using a half-open YSZ tube [12].

The temperature dependence of NO$_2$ sensitivity was also studied. As presented in Fig. 13 (b), a linear relationship was observed at $550 < T < 800 \, ^\circ\text{C}$ and $10 < NO_2 < 200$ ppm. The slope increased slightly with temperature at $550 < T < 700 \, ^\circ\text{C}$ and a sudden decrease occurred at $T > 750 \, ^\circ\text{C}$, which was somewhat different from the previous observation showing an abrupt decrease in the slope at 700 °C [12].

As found for the WO$_3$-based sensor (Fig. 13), the sensor response decreases with increasing operating temperature [15, 16]. This is due in part to the amount of adsorbed gas on the surface of the semiconductor which decreases with temperature, as the rate of gas desorption is faster than that of adsorption [5]. In addition, a dissymmetry of the catalytic activity between the two electrodes could also explain it. TPR experiments of the catalytic activity of a Pt electrode for the reduction of NO$_2$ was found to be higher than that of WO$_3$ (Fig. 14). With increasing temperature the difference in the activity became smaller, reducing the sensor response.

![Fig. 14. TPR of NO$_2$ over WO$_3$ on YSZ (W+Y), Pt on YSZ (Pt+Y), YSZ (Y), and blank (B).](image)
4-2-4. Selectivity to NO

The effect of H$_2$O, NO$_2$, CO, CO$_2$, and O$_2$ on the NO sensitivity was investigated at 650 °C. Fig. 15 shows plots of the sensor response to NO in the existence of other gases.

Fig. 15. Effect of CO$_2$, O$_2$, NO$_2$, CO, and H$_2$O on the NO response at 650 °C and in N$_2$ balance. (a) CO$_2$ effect (0 – 20 %), (b) O$_2$ effect (3 – 30 %), (c) NO$_2$ effect (0 – 200 ppm), (d) CO effect (0 – 400 ppm), (e) H$_2$O effect (0 – 3 %). Measured in 3 % O$_2$ for (a) and (c) – (e).
The WO3-based sensor was able to selectively detect NO in the presence of CO2 (Fig. 15 (a)). Values of the sensor emf with three different concentrations of CO2 were very close to each other, exhibiting a maximum difference of emf values less than 1.5 mV. The sensor was also selective to NO without any interference by changing O2 concentration, 3 – 30 % (Fig. 15 (b)).

The influence of NO2 on the NO sensitivity is shown in Fig. 15 (c). When NO2 was added to the NO step, values of the emf increased significantly but the sign of the slope was not changed. The slope increased considerably by the addition of 20 ppm NO2. The gas-phase oxidation of NO, eqn. (1), is thermodynamically favorable in the present condition and thus in equilibrium most of the NO should be converted to NO2.

\[
\text{NO} + \frac{1}{2}\text{O}_2 \rightarrow \text{NO}_2 \quad (1)
\]

However, no conversion of NO to NO2 was observed in the TPR experiments (Fig. 16), because of unfavorable NO oxidation kinetics. As discussed previously for the La2CuO4-based sensor, the mixed potential theory cannot explain the occurrence of the NO sensitivity of the WO3-based sensor.

Fig. 16. TPR of NO+O2 (1000 ppm) over WO3 on YSZ (W+Y) and Pt on YSZ (Pt+Y).

Fig. 15 (d) shows the effect of CO on the NO sensor response. Values of the emf increased without significant change of slope. In the TPR experiments (Fig. 17) WO3 and
Pt electrodes exhibited different catalytic activities for the oxidation of CO at 650 °C, either non-electrochemically (eqn. (2)) or electrochemically (eqn. (3)).

\[
CO + \frac{1}{2}O_2 \rightarrow CO_2 \quad (2)
\]

\[
CO + O^{2-}_{\text{lattice}} \rightarrow CO_2 + 2e^- \quad (3)
\]

This difference might give rise to the CO response. However, neither CO$_2$ formation from the reaction of NO with CO, eqn. (4), nor the oxidation of NO, eqn. (1), was observed in the present system.

\[
CO + NO \rightarrow CO_2 + \frac{1}{2}N_2 \quad (4)
\]

Fig. 17. TPR of NO+CO+O$_2$ (1000 ppm) over WO$_3$ on YSZ (W+Y) and Pt on YSZ (Pt+Y).

Water is known to be strongly adsorbed on the surface of metal oxides, giving a so-called hydroxylated surface, where the OH$^-$ anions are bonded to the metal cations, and the H$^+$ ion to the oxide anions [5]. As shown in Fig. 15 (e), the slope decreased slightly by addition of 3 % H$_2$O. A linear relationship was still shown even in the presence of H$_2$O.
4-2-5. Selectivity to NO$_2$

The influence of CO$_2$ (0 – 20 %) and H$_2$O (0 – 3 %) on the NO$_2$ response at 650 ºC is presented in Fig. 18 (a) and (b), respectively. The difference in emf values with and without CO$_2$ and H$_2$O was less than 1 mV in the whole NO$_2$ concentration range.

![Graphs](image)

Fig. 18. Effect of CO$_2$, H$_2$O, and CO on the NO$_2$ response at 650 ºC in 3 % O$_2$. (a) CO$_2$ effect (0 – 20 %), (b) H$_2$O effect (0 – 3 %), (c) CO effect (0 – 300 ppm).

As shown in Fig. 18 (c), the addition of 100 and 300 ppm CO did not influence the NO$_2$ sensitivity. Values of the emf obtained with 300 ppm CO were ~ 3 mV smaller than those without CO, but the difference was still within the general range of reproducibility. As
commented previously, the selective detection of NO against NO$_2$ and CO was not accomplished, but interestingly the NO$_2$ response was not influenced by CO. In the NO$_2$+CO+O$_2$ TPR experiments (Fig. 19) the NO$_2$ reduction reactions, eqn. (5) and (6), were found to be dominant at 650 °C over the CO oxidation reactions, eqn. (2) and (3), and that was likely why the influence of CO was not significant.

\[
\text{NO}_2 \rightarrow \text{NO} + \frac{1}{2}\text{O}_2 
\]

(5)

\[
\text{NO}_2 + 2\text{e}^- \rightarrow \text{NO} + \text{O}^2_- \text{(lattice)}
\]

(6)

![Fig. 19. TPR of NO$_2$+CO+O$_2$ (1000 ppm) over WO$_3$ on YSZ (W+Y), Pt on YSZ (Pt+Y), YSZ (Y), and blank (B).](image)

The present sensor made of YSZ-8Y with a Pt and a WO$_3$ electrode is very promising for the monitoring of NO$_2$, as it selectively detected NO$_2$ with very high sensitivity down to low concentrations NO$_2$ (~ 10 ppm).

4-2-6. Sensing properties of WO$_3$ based sensor in simulated exhaust

Comparison of the NO$_x$ response between the sensor in 3 % O$_2$ and the sensor in simulated exhaust condition (3 % O$_2$, 3 % H$_2$O, 16 % CO$_2$, and 100 ppm CO) is given at 650 °C and $10 < \text{NO}_x < 650$ ppm (Fig. 20).
Fig. 20. Comparison of the NOx sensitivity at 650 ºC between in 3 % O2 and in a simulated exhaust gas (3 % O2, 3 % H2O, 16 % CO2, and 100 ppm CO). (a) NO, (b) NO2.

The exhaust condition included most gases generally formed during the combustion process, except hydrocarbons. Values of the emf measured for NO were significantly different for each condition and the slope of the plot was much greater in the exhaust gas than in 3 % O2 (Fig. 20 (a)). This higher sensitivity for NO in combustion gas than in 3 % O2/N2 mixture indicates a complex equilibrium occurs on the electrode surface when all gas species are present. In contrast, Fig. 20 (b) shows that in the exhaust both values of the emf and the slope for the NO2 step decreased compared to those in 3 % O2.

The influence of each of the individual gases on the NOx response was investigated and the results are shown in Fig. 21 and 22. For example, to study the effect of O2, measurements were performed by varying O2 concentration (0.5 – 20 %) while maintaining constant concentrations of the other gases (3 % H2O, 16 % CO2, and 100 ppm CO). Similarly, the effect of H2O (0 – 3 %), CO2 (0 – 16 %), and CO (0 – 200 ppm) was studied.
4-2-7. Selectivity to NO in simulated exhaust

As presented in Fig. 21 (a) ~ (d), the NO sensing behavior was strongly affected by H₂O, O₂, and CO, but not by CO₂.

![Graphs showing the effect of H₂O, O₂, CO, and CO₂ on the NO response.](image)

Fig. 21. Effect of H₂O, O₂, CO, and CO₂ on the NO response at 650 ºC and in a simulated exhaust gas (3 % O₂, 3 % H₂O, 16 % CO₂, and 100 ppm CO). (a) H₂O effect (0 – 3 %), (b) O₂ effect (3 – 20 %), (c) CO effect (0 – 200 ppm), (d) CO₂ effect (0 – 16 %).

The effect of H₂O in the combustion gas mixture was especially remarkable (Fig. 21 (a)). 3 % H₂O increased the emf by more than 40 mV at the same NO concentration. Further, the
NO sensitivity increased in the combustion mixture, whereas it decreased in the simple N₂-based gas mixtures. As shown in Fig. 15 (e) the effect of 3 % H₂O on the NO response in 3 % O₂ was much smaller than in the gas mixture, indicating water vapor itself did not greatly affect sensitivity. Therefore, the large change in response by H₂O is probably due to the water vapor on the surface of the electrode enhancing the kinetics of NO₂ production (eqn. (1) and (7)) [5, 17] or the formation of complex NO–H₂O surface species.

\[
\text{NO} + \text{H}_2\text{O} \rightarrow \text{NO}_2 + \text{H}_2
\]  

Fig. 21 (b) shows the effect of O₂ on NO sensitivity. Increasing the concentration of O₂ caused both values of the sensor emf and the slope to decrease in contrast to the N₂ mixture where it was independent (Fig. 15 (b)). The influence of CO was also significant (Fig. 21 (c)). The slope of the NO step was enhanced by the addition of 50 – 200 ppm CO. Values of the emf increased with CO in the exhaust gas, which is opposite to the results obtained in 3 % O₂, where the emf value decreased with CO (Fig. 15 (d)). As the cross-sensitivity of O₂ is negligible in an N₂ environment and the cross-sensitivity of CO is much smaller than that of NO, the sensing behaviors with O₂ and CO are influenced by the complex equilibrium in the combustion gas mixture.

The NO response was not influenced by inert CO₂ gas (0 – 16 %) (Fig. 21 (d)).

4-2-8. Selectivity to NO₂ in simulated exhaust

The plots showing the effect of O₂ and H₂O at 650 °C on the NO₂ response are given in Fig. 22. Values of the emf for NO₂ were reduced with increasing O₂ concentration (Fig. 22 (a)). In the range of 3 – 20 % O₂ no clear change of the slopes was observed, but a small increase of the slope with 0.5 % O₂ was seen when compared to the response in 3 – 20 % O₂. The same explanation used in the previous section might be applicable. The addition of 3 % H₂O decreased the slope with reduced values of the emf (Fig. 22 (b)). Interestingly, the plot obtained without 3 % H₂O in simulated exhaust was very similar to that in 3 % O₂ (Fig. 20 (b)), showing H₂O played an important role in the NO₂ sensitivity. Both CO (0 – 200 ppm) and CO₂ (0 – 16 %) did not have a significant effect on the sensing of NO₂ (Fig. 22 (c) and (d)).
Fig. 22. Effect of O₂, H₂O, CO, and CO₂ on the NO₂ response at 650 ºC and in a simulated exhaust gas. (a) O₂ effect (0.5 – 20 %), (b) H₂O effect (0 – 3 %), (c) CO effect (0 – 200 ppm), (d) CO₂ effect (0 – 16 %).
5. CONCLUSION

The NO$_x$ sensing properties were studied using a potentiometric sensor (Pt/YSZ/WO$_3$ or La$_2$CuO$_4$) with $0 < NO_x < 650$ ppm. For the WO$_3$-based sensor (n-type semiconductor) a positive response was shown for NO$_2$ but negative for NO at 650 °C. In contrast for the p-type semiconducting La$_2$CuO$_4$-based one the opposite direction of the response for NO$_x$ was observed at 450 °C. A linear relationship was obtained in the plot of the emf vs. the logarithm of NO$_x$ concentration for both.

With the WO$_3$-based sensor, H$_2$O and CO had an effect on the NO sensitivity but not on NO$_2$ sensitivity in 3 % O$_2$ environment, showing it can be used to detect ~10 ppm NO$_2$ selectively. Values of the emf measured with NO in simulated exhaust gas were considerably different from those in 3 % O$_2$. This difference indicated a possible gas composition change at 650 °C and the formation of a hydroxylated surface by water. The NO$_2$ sensitivity also changed in simulated exhaust gas, but not as much.

The results obtained with the La$_2$CuO$_4$-based sensor seemed to indicate that the temperature was the only significant factor in the sensor response for NO in 3 % O$_2$, as the experiments above 400 °C showed good response time and the major tradeoff became sacrificing signal strength for stability. When comparisons were made to the NO TPD results, we found that the temperature dependence was consistent with our proposed “Differential Electrode Equilibria” mechanism. The NO$_2$ response was also strongly temperature-dependent with an abrupt decrease above 500 °C.
6. REFERENCES


