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

Final Technical Progress Report

Start Date: September 30, 2002

End Date: March 29, 2005

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May 29, 2005

DOE Award Number – DE-FG26-02NT41533

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ABSTRACT

We have made great progress in both developing solid state sensors for coal combustion control and understanding the mechanism by which they operate. We have fabricated and tested numerous sensors and identified the role electrode microstructure plays in sensor response. We have developed both p-type (La_2CuO_4) and n-type (WO_3) semiconducting NO_x sensing electrodes. We have demonstrated their respective sensing behavior (sensitivities and cross-sensitivities), related this behavior to their gas adsorption/desorption behavior and catalytic activity, and in so doing verified that our proposed Differential Electrode Equilibria is a more comprehensive sensing mechanism. These investigations and their results are summarized below.

The composition and microstructure of the sensing electrode is the key parameters that influence the sensing performance. We investigated the effect of electrode microstructure on the NO_x sensitivity and response time using a La_2CuO_4 -based potentiometric sensor. Temperature dependence, cross-sensitivity and selectivities of a La_2CuO_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.

In order to optimize the sensor electrode microstructure, powders were prepared using four different powder synthesis routes, resulting in different particle size distributions and BET surface areas. Different sintering conditions were also applied. The microstructure of electrodes, synthesized with the same composition, has a dramatic effect on both sensitivity and response time of potentiometric NO sensors, showing that large surface areas generate a porous morphology with smaller grain size, and that smaller grain size results in a sharper response and faster response time.

The relative responses of the La_2CuO_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 NO, 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_2CuO_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_2O , 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 at 650 °C. The NO sensitivity, however, was affected by the variation of the NO_2 , CO, and H_2O 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_2O , showing it to be applicable to the monitoring of NO_2 . A lot 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_2O , 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_2CuO_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_x emissions from coal [1 – 4]. Solid oxide electrochemical O_2 sensors are inexpensive and have been well demonstrated in harsh high-temperature combustion exhaust environment. If modified to selectively measure NO_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, and small solid-state device capable of measuring the concentration of multiple species (such as NO, NO_2 , and CO) in coal, natural gas and oil combustion exhaust [5]. Our sensor technology is similar to that used in conventional automotive O_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 ($<1 \text{ cm}^2$) 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_x , CO, O_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 combustion.

Fig. 1. Multifunctional NO_x , CO, O_2 sensor.

The key scientific issue that must be addressed for this type of sensor to effectively measure NO_x and CO concentrations in coal combustion exhaust gas streams is the selectivity of the electrode(s) for discrimination between gaseous NO_x and CO vs. O_2 . Specifically, the sensors must exhibit a highly selective response to ppm levels of NO_x and CO in the presence of percent levels of O_2 . Not only must the sensor exhibit a selectivity factor of, for example, 1000:1 NO/O_2 , based on the typical concentration differences between NO and O_2 , but the sensor must be insensitive to large changes in the O_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_2) exhaust gas unaffected by variations in O_2 concentration. The objectives of our proposed research are to: advance the fundamental understanding of this approach, apply it to the development of selective NO_2 , CO, and O_2 electrode elements, fabricate and test a multifunctional (NO_x , CO, O_2) sensor. 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 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, hence key sensor performance parameters: sensitivity, selectivity, and response time. We investigated the effect of electrode microstructure on the NO sensitivity and response time of La₂CuO₄-based potentiometric sensor.

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, La_{0.8}Sr_{0.2}FeO₃, 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 WO₃ 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, information about its selectivity, stability, and reproducibility are not currently available. A potentiometric La₂CuO₄ sensor showed adequate and stable response to NO_x.

The critical requirement for NO_x detection in combustion exhausts containing hydrocarbons, CO₂, H₂O, O₂, 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 N₂ and in a simulated exhaust gas by using asymmetrical potentiometric sensors based on La₂CuO₄ and WO₃ electrode are described. Additionally, sensing mechanisms are discussed using temperature programmed reaction (TPR) and desorption (TPD) results.

2. EXECUTIVE SUMMARY

We have made great progress in both developing solid state sensors for coal combustion control and understanding the mechanism by which they operate. We have fabricated and tested numerous sensors and identified the role electrode microstructure plays in sensor response. We have developed both p-type (La_2CuO_4) and n-type (WO_3) semiconducting NO_x sensing electrodes. We have demonstrated their respective sensing behavior (sensitivities and cross-sensitivities), related this behavior to their gas adsorption/desorption behavior and catalytic activity, and in so doing verified that our proposed Differential Electrode Equilibria is a more comprehensive sensing mechanism. These investigations and their results are summarized below.

Various electrode microstructures were obtained using four different synthesis routes and the effect of particle sizes and surface areas on the sensor response were studied. We demonstrate that large surface areas generate a porous morphology with smaller grain size, and that smaller grain size results in a sharper response and faster response time.

We investigated the selectivity of NO_x over O_2 , CO , CO_2 , and H_2O , 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_2 , NO_x , CO , CO_2 , and their mixtures was studied by using temperature programmed reaction (TPR) and desorption (TPD) techniques, and the results interpreted considering the sensing behavior.

The sensitivities of the La_2CuO_4 -based sensor for NO_x and CO were high, but for CO_2 and O_2 , they were negligible. The WO_3 -based sensor responded highly to ~ 10 ppm NO_2 and selectively in the existence of CO , CO_2 , and H_2O , showing it to be applicable to the monitoring of NO_2 . No reactions were observed in the NO mixtures during TPR, indicating that the NO response was not obtained by the so-called mixed-potential mechanism.

The p-type La_2CuO_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 agreement with the TPD results. This indicates that NO sensing by La_2CuO_4 is likely due to the chemisorption of NO and the resulting change in Fermi level of the oxide.

The n-type semiconducting WO_3 -based sensor showed optimal NO_2 sensing behavior at 650 °C and the response decreased with increasing temperature. This temperature effect can be explained using the NO_2 TPR results. Since a dissymmetry of the catalytic activity for NO_2 reduction between the two electrodes is temperature dependent and the difference decreases with temperature, the NO_2 response decreases with increasing temperature.

3. EXPERIMENTAL

3-1. La_2CuO_4 Synthesis

To synthesize powders of different particle size distribution and surface area, the electrode material was prepared through three different powder preparation techniques: autoignition [14], Pechini [15] and coprecipitation [16], which lead to sensor electrodes of the same composition but with different microstructures and surface areas.

In the autoignition process, nitrate salts of constituent elements were dissolved and citric acid added in appropriate proportion and subsequently heated with thorough mixing forming a gel, which was burnt to ash. The nature of burning depends on the citrate-nitrate ratio and is the key parameter in determining the powder morphology. Depending on citrate-nitrate molar ratio γ , the nitrate and citrate ions in the gel will undergo a redox reaction under stoichiometric condition at $\gamma = 0.277$. Excess citric acid in the gel ($\gamma > 0.277$) presents a fuel-rich condition, while lower concentrations produce a fuel-lean condition. Such conditions are expected to produce perovskite powders with different properties and varying particle characteristics. Therefore, two different ratios were adopted to produce powders which are named as auto-ignition fuel-lean ($\gamma = 0.098$) and auto-ignition fuel-rich ($\gamma = 0.50$), respectively.

In the coprecipitation process, aqueous 1:1 metal stoichiometric solutions of the metal nitrates were prepared in distilled H_2O . The metals were precipitated as hydroxides by slowly adding 10% excess of a basic solution of tetra-methyl ammonium hydroxide in 25% methanol. The precursor metal-hydroxide powders were recovered, rinsed, and air dried at 110°C overnight.

In the Pechini process, a solution was formed from citric acid, ethylene glycol and cation nitrate salts. The solution was heated forming a gel which was subsequently burnt.

X-Ray powder diffraction (XRD) was utilized to characterize the synthesized sample. A Philips APD 3720 automated diffractometer (Cu $\text{K}\alpha$ radiation, $\lambda = 1.54178 \text{ \AA}$) was used to confirm the phase homogeneity of the $\text{La}_2\text{CuO}_{4\pm\delta}$. High resolution Field Effect Scanning

Electron Micrograph (FESEM) and the BET surface area measurements were performed on the powders prepared through the different techniques.

3-2. Potentiometric NO_x Sensor

As described in the previous reports and shown in Fig. 2, an asymmetrical planar sensor was built using an 8-mole % Y₂O₃-doped ZrO₂ plate (Marketch International Inc., YSZ-8Y, 20 × 10 × 0.1 mm) as a solid electrolyte, and a metal oxide (La₂CuO₄ or WO₃) and a Pt layer as electrodes.

Fig. 2. Schematic diagram of a potentiometric sensor. (a) Top view, (b) Side view.

Tungsten oxide (WO₃, 99.8% purity, Alfa Aesar) powder was purchased and La₂CuO₄ was synthesized (The details were given in the previous section). 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 La₂CuO₄ (or WO₃) 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).

3-3. Measurements of NO_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/WO₃ (or La₂CuO₄) (+)). 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% O₂ in N₂ or simulated exhaust gas (16% CO₂, 100 ppm CO, 3% O₂, and 3% H₂O). The sensor emf was measured with increasing and then decreasing concentration steps of NO_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_x, 0 – 650 ppm. Second, the selectivities to NO_x over CO, CO₂, O₂, and H₂O were investigated both in 3% O₂ with N₂ balance and in the simulated exhaust environment.

3-4. TPR/TPD Experiments

Gas reactions catalyzed by the WO₃ powder (W), the WO₃ film on the YSZ-8Y (W+Y), the Pt on the YSZ-8Y (Pt+Y), the YSZ substrate alone (Y), and the La₂CuO₄ 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. La₂CuO₄-based Sensor

4-1-1. Powder and Electrode Characterization

X-ray diffraction patterns (Fig. 3(a)) of powders prepared by the different synthesis techniques showed that the minimum calcination temperature for complete phase formation is 600 °C (10 hr) for the autoignition powders while at least 650 °C (10 hr) was necessary for the coprecipitated and Pechini processed powders, and even at 650 °C the Pechini powders were not phase pure. BET surface area analysis (Fig. 3(b)) shows the highest surface area was obtained with the autoignition fuel-rich process.

Fig. 3. Characterization of electrode powders prepared through different synthesis routes.

High resolution Field Effect Scanning Electron Micrograph (FESEM) pictures of powders prepared through the different techniques are presented in Fig. 4. The average particle size ranges between 50 – 200 nm, depending on the synthesis technique, which were estimated from the micrographs and presented later in Table 1. Typical agglomerated structures of the respective powders are shown in the low magnification figures inside a box within individual pictures. The morphologies of the agglomerated systems, after calcination, are dependent on the method of powder synthesis. In powders prepared through autoignition rich-combustion, the submicron particles join together to form a net-like structure. In coprecipitation, net-like agglomerates are also formed, but from larger particles. In autoignition lean-burn, the nature of agglomeration is different from the net-like structure of the Rich-burn process. Whereas in the Pechini process, the agglomerated microstructure is entirely different – forming solid lumps of particles joined strongly together. Typical agglomerate sizes are also presented in Table 1. During sintering, the agglomerated structures result in different microstructure development, resulting in different morphologies of the sintered electrodes.

Fig. 4. Field Emission Scanning Micrograph of calcined powders.

Average particle size was determined from analysis of FESEM micrographs of the calcined powders. Among the more open net-morphology agglomerates, the lowest particle sizes were obtained from the powders prepared through the autoignition fuel-rich technique. The lower particle size of the autoignition powders must be due to an inherent characteristic of the synthesis process.

The Pechini prepared powders appear to have the smallest particle size; however, the higher packing density of these agglomerates makes quantitative assessment of particle size by this approach more difficult. Moreover, the BET results indicate that the Pechini

processed powders should have the larger particle size. These results are summarized in Table 1.

Preparation Routes	Calcination Condition	Agglomerate Size (μm)	Average Particle Size (nm)	Morphology (appearance)	BET Surface Area (m^2/g)
Autoignition rich	600 °C / 10 hr	24 ± 8	75 ± 25	Flakes	16.7
Autoignition lean	600 °C / 10 hr	19 ± 5	85 ± 50	More spherical	7.57
Coprecipitation	650 °C / 10 hr	35 ± 5	140 ± 50	Net-like	9.15
Pechini	650 °C / 10 hr	17 ± 2	62 ± 12	Spherical	3.7

Table 1. Characteristics of powders prepared through different processing techniques.

The electrode microstructures obtained from powders prepared through these techniques, were studied to identify the morphology of the sensing surface. SEM micrographs of sensor surfaces, for samples fired at the same sintering temperature of 800 °C, are compared in Fig. 5. Powders prepared through the fuel-rich autoignition process show the finest microstructure (Fig. 5(a)) with an average particle size of $\sim 0.15 \mu\text{m}$ and a flakey microstructure, while the fuel-lean conditions produced a comparatively coarser microstructure (Fig. 5(b)) with an average particle size of $\sim 0.29 \mu\text{m}$. The coprecipitation (Fig. 5(c)) and Pechini (Fig. 5(d)) processed powders similarly resulted in $\sim 0.29 \mu\text{m}$ grains, but with some differences in microstructure.

(a) Autoignition Rich, 800 °C / 10 hr

(b) Autoignition Lean, 800 °C / 10 hr

(c) Coprecipitation, 800 °C / 10 hr

(d) Pechini, 800 °C / 10 hr

Fig. 5. Morphology of sintered sensing electrodes from powders fabricated through different techniques.

The effect of sintering temperature was studied with the coprecipitated powders. SEM micrographs of coprecipitated powders sintered at four different temperatures are presented in Fig. 6. The figure shows a limited increase in grain size between 700 °C and 800 °C, whereas there is dramatic increase in grain size beyond 800 °C. At 1050 °C, the grains are very large, more joined together, and have a large reduction in contact angle between grains.

Fig. 6. Variation of microstructure of coprecipitated sensing electrode material sintered at various temperatures: (a) 700 °C/10 hr, (b) 800 °C/10 hr, (c) 900 °C/10 hr, and (d) 1050 °C/10 hr.

Similar variations with sintering temperature were observed for powders produced through the other three different synthesis routes. Some of the microstructures are presented in Fig. 7, showing variation of morphology with sintering temperature and time.

Fig. 7. Variation of microstructure of electrode material sintered at various temperatures and processes. Autoignition Fuel-lean (a) 700 °C / 10 hr and (b) 900 °C / 10 hr; Autoignition Fuel-rich (c) 700 °C / 10 hr and (d) 800 °C / 18 hr; Pechini (e) 700 °C / 10 hr and (f) 800 °C / 18 hr.

Powders prepared through other techniques also have a limited grain growth up to 800 °C as can be observed by comparing Fig. 7(c) (700 °C / 10 hr) and Fig. 5(a) (800 °C / 10 hr) for autoignition rich powders, and relatively large grain growth at 900 °C and above. The effect of sintering time is less of an issue, although there is some grain growth between 10 hr and 18 hr of sintering at 800 °C as presented in Fig. 5(a) (800 °C/10 hr) and Fig. 7(d) (800 °C / 18 hr) for autoignition rich powders, and Fig. 5(d) (800 °C / 10 hr) and Fig. 7(f) (800 °C / 18 hr) for Pechini powders. Based on all these observations, the temperature of sintering was selected to be 800 °C for 10 hr, yielding small sized uniform distribution of grains and pores.

4-1-2. Effect of microstructure on the Sensing Properties

The sensor response for samples prepared through these preparation techniques are compared in Fig. 8 at 450 and 500 °C. The autoignition powders showed the sharpest response at lower temperature of operation.

Fig. 8. Response for NO sensors fabricated through Pechini, Autoignition Lean, Autoignition Rich, and Coprecipitation processes, at (a) 450 °C and (b) 500 °C in simulated exhaust.

This may be due to the flaky grains having higher available surface area (Fig. 5(a)) for the gas species. Samples prepared from Pechini powders showed the highest sensitivity (~ 20 mV at 650 ppm of NO), whereas coprecipitated powders showed the lowest sensitivity (~ 13 mV at 650 ppm of NO) at 450 °C. However, at 500 °C, coprecipitation and autoignition lean exhibited the greatest sensitivity.

The temperature dependence of sensor response for the samples prepared from the different powders is shown in Fig. 9.

Fig. 9. Sensor response at varying measurement temperatures for powders prepared through different processes (all sintered at 800 °C/10 hr). (a) Autoignition Rich, (b) Autoignition Lean, (c) Coprecipitation, and (d) Pechini.

Among these, sensors prepared from Pechini processed powders have the strongest temperature dependence. The results also show that the sensitivity increases at lower operating temperatures. The lower limit of operating temperature is limited by the response stability and autoignition rich prepared electrodes were the only ones that had reasonable stability down to 400 °C. Response stability is our qualitative assessment of the rise and fall of sensor voltage with each concentration step. Deviation from a rapid vertical rise (or fall) followed by a 90° transition and flat plateau is an indicator of a less than stable response. An example of this is the overshoots of the 400 °C data in Fig. 5(a).

At lower measurement temperature, the sensitivity at lower gas concentration also increases. The range of maximum sensitivity for detection of NO gas concentration is also dependent on the powder synthesis route. The autoignition rich samples are highly sensitive between 0 – 50 ppm, whereas samples prepared from the Pechini process are more sensitive at higher ppm ranges. Correlating these results with microstructures (Fig. 5) of corresponding samples, it may be concluded that higher resolution at lower ppm can be achieved with finer microstructural features.

The mean values of response for the four (up and down) measurements, calculated from Fig. 9 at each NO gas concentration, are plotted in Fig. 10(a) and (b).

Fig. 10. Sensitivity and response time of sensors fabricated from powders prepared through different techniques (all sintered at 800 °C / 10 hr). (a) Sensitivity at 450 °C, (b) Sensitivity at 500 °C, (c) Response time at 450 °C, and (d) Response time at 500 °C.

The standard deviations are presented as error bars. At 450 °C, autoignition lean and Pechini prepared electrodes exhibit higher voltage responses. The dependence of voltage response on NO concentration (sensitivity) is non-linear for autoignition lean and coprecipitation prepared electrodes. At 500 °C, the autoignition lean and coprecipitation samples are most sensitive and the sensitivity is more linear.

The response time was taken to be the time to reach 90% of the stable value. At 450 °C, response times range from 10 to 80 sec and is faster at higher NO concentrations. For autoignition rich, response time is nearly constant. At 500 °C, average response time is decreased to 10 – 40 sec and the response time dependence on NO concentration is relatively small. The autoignition rich exhibits the fastest and most stable response at both 450 °C and 500 °C.

Synthesis Technique	Powder Surface Area ^a (m ² /g)	Electrode Grain Size ^b (μm)	Sensitivity (mV/decade)		Response Time ^c (sec)	
			450°C	500°C	450°C	500°C
Autoign. Rich	16.7	0.146 ± 0.055	9.59	2.88	13.2 ± 2.2	16.8 ± 5.8
Pechini	3.7	0.292 ± 0.110	10.99	4.49	47.4 ± 19.1	23.0 ± 8.2
Autoign. Lean	7.6	0.292 ± 0.100	6.81	9.70	28.0 ± 15.0	25.0 ± 6.8
Coprecipitation	9.2	0.285 ± 0.111	5.71	7.99	36.0 ± 20.0	29.8 ± 1.4

Table 2. Correlation between synthesis techniques and response of fabricated sensors.

(^a B.E.T. surface areas measured on as-calcined powders, ^b Grain size measurements of sintered electrodes from SEM micrographs, and ^c Average value of response times for five different ppm ranges, based on 90% criteria.)

A comparison of the response time and overall sensitivity as a function of powder surface area and electrode grain size, due to the different powder preparation techniques, is presented in Table 2. The overall sensitivity is defined by the slopes of the curves in Fig. 10 (a) and (b) over the total gas concentration range investigated, even though they deviate from linearity. At 450 °C, Pechini powders have the highest sensitivity and coprecipitation powders have the least. At 500 °C, autoignition lean powders have the highest sensitivity and autoignition rich powders have the least. These results show that microstructure plays a role in sensitivity; however, no direct correlation can be made between microstructure and

sensitivity. Further analysis of sensitivity over specific concentration regions and temperatures may elucidate a relationship.

It is apparent, however, that the highest surface area powders, from autoignition rich processing, resulted in the finest grain size and that these electrodes resulted in the fastest response time at both 450 and 500 °C. All three of the other techniques resulted in significantly lower surface area powders and almost identical larger grain sizes in the sintered electrode microstructure. Furthermore, all three had essentially the same response time (within the statistical significance of the data). Hence, it may be concluded that starting powders with large surface areas generate a porous morphology with smaller grain size, and that smaller grain size results in a sharper response and faster response time.

La_2CuO_4 prepared by the autoignition rich method was selected for further studies and detailed sensing properties of this sample will be presented and discussed.

4-1-3. Sensing properties of La_2CuO_4 -based sensor

The sensor emf (mV) obtained with variation of NO concentration is plotted against time (sec) in Fig. 11(a). The NO concentration at each step is labeled in the figure.

Fig. 11. Sensor response to NO concentration (0 – 650 ppm) at 450 °C in 3% O_2 with N_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.

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 °C. As shown in Fig. 11(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, NO₂, CO, CO₂ and O₂ concentrations are plotted in Fig. 12. Results show a high sensitivity to NO, CO, and NO₂ at 450 °C, whereas the cross-sensitivity to O₂ and CO₂ was negligible.

Fig. 12. La₂CuO₄ sensor response to NO, NO₂, CO, and CO₂ in 3% O₂, and O₂ in N₂ at 450 °C.

4-1-4. Temperature dependence of La₂CuO₄-based sensor

The temperature dependence of the NO response was investigated at 350 < T < 550 °C (Fig. 13(a)). Above 500 °C values of the emf were very small, less than 5 mV for 650 ppm NO and at 350 °C and below, the response was saturated.

Fig. 13. Variation of the NO_x and CO sensitivity as a function of temperature in 3% O₂. (a) NO, (b) NO₂, and (c) CO.

This temperature dependence can be explained by the TPD (Fig. 14(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 °C, 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 $T < 400$ °C, thus saturating the surface and sensor response at low temperature.

Fig. 14. 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 $300 < T < 550$ °C (Fig. 13(c)). The sensor was very sensitive to CO at $T < 450$ °C. CO TPD results show broad desorption of CO₂ and CO at $200 < T < 450$ °C in Fig. 14(b), indicating that the high CO response is likely due to CO adsorption and its related surface reduction.

Temperature dependence of the NO₂ sensitivity was also studied. As presented in Fig. 13(b), the NO₂ response was also strongly temperature-dependent with an abrupt decrease above 500 °C. The TPR results (Fig. 15(a)) show that above 250 °C, NO₂ is reduced to NO and by 600 °C, it is completely reduced. Thus the NO₂ response at this temperature range involves heterogeneous catalysis in sensitivity. The NO₂ TPD also shows signs of surface reaction (Fig. 15(b)). Nitrogen dioxide began desorption at 225 °C, and the peak was followed by a similar desorption peak for NO, shifted 25 °C higher and the second NO desorption peak lined up with the desorption peak for chemisorbed oxygen. At temperatures above 600 °C, lattice oxygen from the sample was emitted. Thus a series of complex reaction steps occurred on the surface of La₂CuO₄ over the temperature range where it is most sensitive to NO₂.

Fig. 15. TPR/TPD of NO₂ over the La₂CuO₄ powder. (a) TPR, (b) TPD of NO₂ (500 ppm).

4-1-5. 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 O₂ concentration (Fig. 16(a)). In the NO+O₂ TPD experiments, the NO adsorption was found to not be affected by O₂, showing NO desorption peaks very similar to those obtained in the NO TPD (Fig. 14(a)).

Fig. 16. Effect of O₂, H₂O, CO, NO₂, and CO₂ on the NO response at 450 °C and in N₂. (a) O₂ effect (3 – 30%), (b) H₂O effect (0 – 3%), (c) CO effect (0 – 200 ppm), (d) NO₂ effect (0 – 400 ppm), (e) CO₂ effect (0 – 16%). Measured in 3% O₂ for (b) – (e).

Fig. 16. (cont.) Effect of O₂, H₂O, CO, NO₂, and CO₂ on the NO response at 450 °C and in N₂. (a) O₂ effect (3 – 30%), (b) H₂O effect (0 – 3%), (c) CO effect (0 – 200 ppm), (d) NO₂ effect (0 – 400 ppm), (e) CO₂ effect (0 – 16%). Measured in 3% O₂ for (b) – (e).

By addition of 3% H₂O the sensor emf was reduced ~ 2 mV, but the slope remained about the same (Fig. 16(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. 16(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. 17(a), that the presence of CO enhances NO adsorption so that NO continues to desorb up to 800 °C (Compare Fig. 17(a) to Fig. 14). 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. 13(a)). The intense CO₂ desorption peak at 200 – 500 °C in the NO+CO+O₂ 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+O₂ TPR above 200 °C (Fig. 17(b)).

Fig. 17. TPD/TPR of NO+CO+O₂ over the La₂CuO₄ powder. (a) TPD of NO (500 ppm) + CO (500 ppm) + O₂ (1%), (b) TPR.

Fig. 16(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. 16(e). High concentration of CO₂ reversed the NO sensitivity. This can be explained from the results of the NO+CO₂ TPD (Fig. 18). When NO and CO₂ were coadsorbed, the CO₂ displaced the NO, shifting the NO desorption peaks to less than 200 °C.

Fig. 18. TPD of NO (500 ppm) + CO₂ (1000 ppm) over the La₂CuO₄ powder.

4-2. WO₃-based Sensor

4-2-1. Characterization of WO₃ electrodes

Fig. 19 shows a scanning electron micrograph of a WO₃ and a Pt layer on the YSZ-8Y substrate prepared by sintering at 800 °C for 10 hr. The WO₃ 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.

Fig. 19. Scanning electron micrograph of the Pt (a) and WO₃ (b) electrode.

4-2-2. Sensing properties

The sensor emf is plotted against time with NO concentration steps (50 – 650 ppm) and NO₂ steps (10 – 200 ppm) at 650 °C in 3% O₂ (Fig. 20). A positive response was obtained for NO₂ and negative for NO. The direction of response of n-type WO₃ is opposite to that of p-type La₂CuO₄. This agrees with previous results, where the potentiometric sensor measurements were performed with different cell configurations [12, 13].

Fig. 20. 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 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 (t_R) was dependent on the gas concentration, showing shorter t_R at higher concentration for both gases. The t_R 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 t_R 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 NO_x 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) gas exposure in the previous run and might have caused the data scattering. Either changes in oxygen non-stoichiometry at the interfacial region caused by reducing or oxidizing gas 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 NO_x agreed within 15% difference on average under the same conditions. Properties of each sensor were expected to be slightly different due to parameters affecting the sensitivity, such as porosity and thickness of electrode, might vary with fabrication process [17]. The differences are indicative of the importance of accurate control of fabrication conditions.

4-2-3. Temperature dependence of WO_3 -based sensor

The temperature dependence of the NO_x emf response was investigated at $550 < T < 800$ °C (Fig. 21).

Fig. 21. Variation of the NO_x sensitivity as a function of temperature in 3% O_2 . (a) NO at 600 – 750 °C, (b) NO_2 at 550 – 800 °C.

A plot of the sensor emf (mV) vs. logarithm of NO concentration (ppm) is linear at $600 < T < 750$ °C and $50 < NO < 650$ ppm (Fig. 21 (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 NO₂ sensitivity was also studied. As presented in Fig. 21(b), a linear relationship was observed at $550 < T < 800$ °C and $10 < NO_2 < 200$ ppm. The slope increased slightly with temperature at $550 < T < 700$ °C and a sudden decrease occurred at $T > 750$ °C, which was somewhat different from the previous observation showing an abrupt decrease in the slope at 700 °C [12].

As found for the WO₃-based sensor (Fig. 21), the sensor response decreases with increasing operating temperature [18, 19]. 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 NO₂ was found to be higher than that of WO₃ (Fig. 22). With increasing temperature, the difference in the activity became smaller, reducing the sensor response.

Fig. 14. TPR of NO₂ over WO₃ on YSZ (W+Y), Pt on YSZ (Pt+Y), YSZ (Y), and blank (B).

4-2-4. Selectivity to NO

The effect of H_2O , NO_2 , CO , CO_2 , and O_2 on the NO sensitivity was investigated at 650 °C. Fig. 23 shows plots of the sensor response to NO in the existence of other gases.

Fig. 23. Effect of CO_2 , O_2 , NO_2 , CO , and H_2O 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_2O 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. 23(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. 23(b)).

The influence of NO₂ on the NO sensitivity is shown in Fig. 23(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.

However, no conversion of NO to NO₂ was observed in the TPR experiments (Fig. 24), due to 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. 24. TPR of NO+O₂ (1000 ppm) over WO₃ on YSZ (W+Y) and Pt on YSZ (Pt+Y).

Fig. 23(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. 25) 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)).

This difference might give rise to the CO response. However, neither CO₂ formation from the reaction of NO with CO, eqn. (4), nor the oxidation of NO, eqn. (1), was observed in the present system.

Fig. 25. TPR of NO+CO+O₂ (1000 ppm) over WO₃ 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% H₂O. A linear relationship was still shown even in the presence of H₂O.

4-2-5. Selectivity to NO₂

The influence of CO₂ (0 – 20%) and H₂O (0 – 3%) on the NO₂ response at 650 °C is presented in Fig. 26(a) and (b), respectively. The difference in emf values, with and without CO₂ and H₂O, was less than 1 mV in the whole NO₂ concentration range.

Fig. 26. Effect of CO₂, H₂O, and CO on the NO₂ response at 650 °C in 3% O₂. (a) CO₂ effect (0 – 20%), (b) H₂O effect (0 – 3%), (c) CO effect (0 – 300 ppm).

As shown in Fig. 26(c), the addition of 100 and 300 ppm CO did not influence the NO₂ 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 NO₂ and CO was not obtained, but interestingly the NO₂ response was not strongly influenced by CO. In the NO₂+CO+O₂ TPR experiments (Fig. 27), the NO₂ concentration obtained with Pt+Y was not affected by CO and slightly decreased with W+Y at 650 °C, resulting in small decrease in the emf values. Reduction reactions, eqn. (5) or (6), were likely dominant at 650 °C over the CO-involving reactions.

Fig. 27. TPR of NO₂+CO+O₂ (1000 ppm) over WO₃ on YSZ (W+Y), Pt on YSZ (Pt+Y), YSZ (Y), and blank (B).

The present sensor made of YSZ-8Y with a Pt and a WO₃ electrode is very promising for the monitoring of NO₂, as it selectively detected NO₂ against CO, CO₂, and H₂O with very high sensitivity down to low concentrations NO₂ (~ 10 ppm).

4-2-6. Sensing properties of WO₃ based sensor in simulated exhaust

Comparison of the NO_x response between the sensor in 3% O₂ and the sensor in simulated exhaust condition (3% O₂, 3% H₂O, 16% CO₂, and 100 ppm CO) is given at 650 °C and 10 < NO_x < 650 ppm (Fig. 28).

Fig. 28. Comparison of the NO_x sensitivity at 650 °C 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. 28(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. 28(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 NO_x response was investigated and the results are shown in Fig. 29 and Fig. 30. 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. 29(a) ~ (d), the NO sensing behavior was strongly affected by H_2O , O_2 , and CO, but not by CO_2 .

Fig. 29. Effect of H_2O , O_2 , CO, and CO_2 on the NO response at 650 °C and in a simulated exhaust gas (3% O_2 , 3% H_2O , 16% CO_2 , and 100 ppm CO). (a) H_2O effect (0 – 3%), (b) O_2 effect (3 – 20%), (c) CO effect (0 – 200 ppm), (d) CO_2 effect (0 – 16%).

The effect of H_2O in the combustion gas mixture was especially remarkable (Fig. 29(a)). 3% H_2O 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 N_2 based gas mixtures. As shown in Fig. 23(e) the effect of 3% H_2O 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, 20] or the formation of complex NO–H₂O surface species.

Fig. 29(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. 23(b)). The influence of CO was also significant (Fig. 29(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. 23(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. 29(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. 30. Values of the emf for NO₂ were reduced with increasing O₂ concentration (Fig. 30(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. 30(b)). Interestingly, the plot obtained without 3% H₂O in simulated exhaust was very similar to that in 3% O₂ (Fig. 28(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. 30(c) and (d)).

Fig. 30. Effect of O₂, H₂O, CO, and CO₂ on the NO₂ response at 650 °C 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

We have made great progress in both developing solid state sensors for coal combustion control and understanding the mechanism by which they operate. We have fabricated and tested numerous sensors and identified the role electrode microstructure plays in sensor response. We have developed both p-type (La_2CuO_4) and n-type (WO_3) semiconducting NO_x sensing electrodes. We have demonstrated their respective sensing behavior (sensitivities and cross-sensitivities), related this behavior to their gas adsorption/desorption behavior and catalytic activity, and in so doing verified that our proposed Differential Electrode Equilibria is a more comprehensive sensing mechanism. These investigations and their results are summarized below.

La_2CuO_4 powders, prepared through different synthesis routes, have different specific surface areas which lead to different morphologies of the sintered sensing electrode element. This variation in morphology has a large effect on sensor response and modifies the sensitivity and range of detection of NO gas. With sintered electrode elements having finer grain distribution, higher resolution at low gas concentrations and faster response times were obtained. The temperature dependence of stability, sensitivity and response time was determined. It was shown that stability improves with increase in operating temperature and stable response was not observed at temperatures below 400 °C. Faster response time was observed at higher operating temperature as the system comes to equilibria much quicker. However, it was observed that sensitivity decreases significantly at temperature above 550 °C. Therefore, depending on the morphology of the electrode, the sensor may be operated at sufficiently high temperature (450 – 500 °C), for significant stability and fast response time, without sacrificing much sensitivity.

The NO_x sensors based on La_2CuO_4 were tested in the simulated exhaust gas environment containing N_2 , CO_2 , H_2O , O_2 , CO , and NO_x . The sensor showed high selectivity toward NO_x , and NO sensitivity (voltage response) increased with decreasing temperature, from 600 °C to 400 °C. However, at the lower temperatures, sensing response was limited by slow unstable heterogeneous kinetics, thus limiting sensor operation to >

400 °C. NO does not fully desorb from the surface of metal oxide until > 400 °C. Therefore, the instability of sensor response at low temperature can be explained using the TPD results by saturation of the metal oxide surface with NO. That is, at < 400 °C the rate of NO adsorption is greater than the rate of NO desorption. The sensing mechanism is dominated by adsorbed NO species that are not in full equilibrium with the gas phase composition, most likely by a semiconducting response (change in Fermi level) rather than heterogeneous kinetics (Mixed Potential). At > 400 °C, the rate of NO desorption is greater than the rate of NO adsorption. Any surface NO species are now directly proportional to the gas-phase composition. The lack of any NO₂ from co-adsorbed NO and O₂ would tend to indicate that the sensor voltage is not due to the conventional Mixed Potential theory.

For the WO₃-based sensor (n-type semiconductor) a positive response was shown for NO₂, but negative for NO at 650 °C. In contrast, for the p-type semiconducting La₂CuO₄-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 WO₃-based sensor, H₂O and CO had an effect on the NO sensitivity but not on NO₂ sensitivity in 3% O₂ environment, showing it can be used to detect ~ 10 ppm NO₂ selectively. Values of the emf measured with NO, in simulated exhaust gas, were considerably different from those in 3% O₂. This difference indicated a possible gas composition change at 650 °C and the formation of a hydroxylated surface by water. The NO₂ sensitivity also changed in simulated exhaust gas, but not as much.

6. REFERENCES

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