Development and Application of Gas Sensing Technologies to Enable Boiler Balancing

DE-FC26-03NT41615

Prabir Dutta, The Ohio State University Research Foundation
1960 Kenny Road
Columbus, Ohio 43210

Final Technical Progress Report

July 2, 2003 to December 31,2008

Submitted: May 4, 2009

Revised: May 26, 2009

DISCLAIMER

TABLE OF CONTENTS

Summary : Identifying gas species and their quantification is important for optimization of many industrial applications involving high temperatures, including combustion processes. CISM (Center for Industrial Sensors and Measurements) at the Ohio State University has developed CO, O_2, NO_x, and CO_2 sensors based on TiO_2 semiconducting oxides, zirconia and lithium phosphate based electrochemical sensors and sensor arrays for high-temperature emission control. The underlying theme in our sensor development has been the use of materials science and chemistry to promote high-temperature performance with selectivity. A review article presenting key results of our studies on CO, NO_x, CO_2 and O_2 sensors is described in : Akbar, Sheikh A.; Dutta, Prabir K.. Development and Application of Gas Sensing Technologies for Combustion Processes, *PowerPlant Chemistry,* 9 (1) 2006, 28-33

Below we provide more details of these specific developments.

1.Combined NO_x/O_2 sensor : Simultaneous measurement of total NO_x and O_2 using two electrochemical methods are demonstrated in this study using metal/metal oxide internal oxygen reference electrode-based sensors at high temperatures. The Pd/PdO-containing reference chamber was sealed within a stabilized zirconia superstructure by a high pressure/temperature plastic deformation bonding method exploiting grain boundary sliding between the ceramic components. Amperometric and potentiometric NOx sensing devices were assembled on the outside of the sensor. Pt-loaded zeolite Y was used to obtain total NOx capability..Both the amperometric and potentiometric type sensors showed total NO_x response, with the potentiometric device showing better NOx/O_2 signal stability and lower NOx/O_2 cross-interference. Since these sensors do not require plumbing for reference air, there is more flexibility in the placement of such sensors in a combustion stream.

The results of these studies are documented in the following manuscript:

Yang, J, et al. "Compact electrochemical bifunctional NOx/O_2 sensor with metal/metal oxide internal reference electrode for high temperature applications." *SENSORS AND ACTUATORS B-CHEMICAL*, v. 131 issue 2, 2008, p. 448-454.

2.NO_x sensor: Potentiometric sensors provide a promising approach for NO_x detection in harsh environments, but typically suffer from interferences with other gases. Potentiometric sensors use two electrodes, and both chemical and electrochemical reactivity at each electrode are critical to sensor performance. We have examined Pt electrode covered with Pt containing zeolite Y (PtY) and WO_3 as the two electrode materials. Temperature programmed desorption of NO from NO_x /O_2 -exposed PtY and WO_3 was studied. In addition, the ability of PtY and WO_3 to equilibrate a mixture of NO and O_2 was examined over the temperature range of 200–600 °C. Significant reactivity differences were found between PtY and WO_3, with the latter being largely inactive toward NO_x equilibration. With gases passing through a PtY filter, it was possible to remove interferences from 2000 ppm CO, 800 ppm propane, 10 ppm NH_3, as well as minimize effects of 1–13% O_2, CO_2, and H_2O. By maintaining a temperature difference between the filter (typically at 400 °C) and the sensor at 600 °C, total NO_x concentration ($NO + NO_2$) was measured. By connecting three sensors in series, the sensitivity was also significantly improved.

The electrical signal from yttria-stabilized zirconia (YSZ) electrolyte-based potentiometric gas sensors is dependent on the electrochemical reactivity of the gases around the triple-phase boundary points. However, chemical reactions taking place at these triple-points can influence the performance of gas sensors, typically resulting in reduction of the electrochemical signal. We have focused on a NOx sensor using Pt-zeolite Y as the reference electrode and WO_3 as the sensing electrode. Significant improvement of NOx sensitivity measured at 600°C was noted if the sensor assembly was heated to 950°C as compared to 700°C. From temperature-programmed desorption (TPD), diffuse reflectance FT-IR (DRIFTS), and chemical reactivity measurements, NOx interaction with YSZ was found to be strong, forming surface nitrates on YSZ and exhibiting high activities toward NOx equilibration. On the contrary, NOx adsorption on heat-treated WO_3-YSZ mixtures was found to be weak and the surface was barely active toward NOx equilibration ($2NO + O_2 \rightarrow 2NO_2$) even at 600°C. From powder diffraction and Raman experiments, it was discovered that WO_3 reacts with YSZ upon thermal treatment, resulting in the formation of polytungstates and monoclinic ZrO_2. These interfacial species suppress the chemical reactions around the triple-phase boundary because of their lower NOx catalytic activities, thereby enhancing the electrochemical sensor signal.

We have also designed an amperometic total-NOx sensor that integrates a Pt-loaded zeolite Y (PtY) catalyst for NOx equilibration with electrochemical oxidation of NO on an yttria-stabilized zirconia (YSZ) electrolyte. PtY is found to be an effective catalyst for equilibrating mixtures of NO, O_2 and NO_2 at temperatures in excess of 400°C. By applying a low anodic potential of 80 mV, the NO in the NO_2 equilibrated mixture can be oxidized at a Pt working electrode on the YSZ electrolyte at 500°C. The current thus generated provides a measure of the total NOx in the gas stream and is the basis of the sensing measurements in this study. The PtY can be held separate from the YSZ or coated onto the YSZ as a film, the latter being more appropriate for the practical embodiment of this design. We demonstrate that this sensor exhibits total-NOx detection capability, a low NOx detection limit (<1 ppm), high NOx selectivity relative to CO and oxygen, and linear dependence on NOx concentration.

The results of these studies are documented in the following manuscripts:

Yang, J; Dutta, P. "Influence of solid-state reactions at the electrode-electrolyte interface on high-temperature potentiometric NOx-gas sensors." *JOURNAL OF PHYSICAL CHEMISTRY C*, v. 111 issue 23, 2007, p. 8307-8313.
Yang, J; Dutta, P. "High temperature amperometric total NOx sensors with platinum-loaded zeolite Y electrodes." *SENSORS AND ACTUATORS B-CHEMICAL*, v. 123 issue 2, 2007, p. 929-936.
Jiun-Chan Yang, Prabir K. Dutta. Promoting selectivity and sensitivity for a high temperature YSZ-based electrochemical total NO_x sensor by using a Pt-loaded zeolite Y filter, Sensors and Actuators, 125(1), 2007, p. 30-39

3.O_2 sensor : Potentiometric internal reference oxygen sensors were created by embedding a metal/metal oxide mixture within a yttria-stabilized zirconia oxygen-conducting ceramic superstructure. Three metal/metal oxide systems based on Pd, Ni, and Ru were examined. A static internal reference oxygen pressure is produced inside the reference chamber of the sensor at the target application temperature. The meta/metal oxide-containing reference chamber is sealed within the stabilized zirconia ceramic superstructure by a high pressure (3-6 MPa) and high temperature (1200-1300°C) bonding method that initiates grain boundary sliding between the ceramic components. The bonding method creates ceramic joints that are pore-free and indistinguishable from the bulk ceramic. The Pd/PdO-based oxygen sensor presented in this study is capable of long-term operation and resistant to the strains of thermal cycling. The current temperature limit of the device is limited at 800°C. As the sensor does not require reference gas plumbing there is flexibility in placement of sensors in a combustion stream. Furthermore, the sensor assembly process readily lends itself to miniaturization.

A comparative study of gas sensing response and electrical properties of three electrodes for potentiometric YSZ-based oxygen sensor was also examined. Platinum (Pt), lanthanum strontium iron cobalt oxide ($La_{0.6}Sr_{0.4}Fe_{0.8}Co_{0.2}O_3$: LSFCO) and chromium oxide (Cr_2O_3) were used as the sensing electrodes. The microstructural features, electrochemical impedance for the charge transfer processes and oxygen sensing characteristics were studied at different temperatures and correlated. Impedance measurements indicate that the LSFCO electrode exhibits lower resistance and higher capacitance by almost two to three orders of magnitude for the chemical exchange and ion transfer processes compared to the other two electrodes. The relaxation time constants of all three electrodes are comparable to each other and found to be in the range of fraction of a second. But, the measured response times for oxygen sensors using these electrodes showed values of the order of minutes at temperatures of 500°C and below. So, the controlling factor for oxygen response at temperatures below 500°C seems to be adsorption and/or surface diffusion of oxygen rather than the charge transfer process for a given morphology of the electrode.

The results of this study are documented in the following manuscripts:

Spirig, J, et al. "High temperature zirconia oxygen sensor with sealed metal/metal oxide internal reference." *SENSORS AND ACTUATORS B-CHEMICAL*, v. 124 issue 1, 2007, p. 192-201.
Ramamoorthy, R; Akbar, S; Dutta, P. "Dependence of potentiometric oxygen sensing characteristics on the nature of electrodes." *SENSORS AND ACTUATORS B-CHEMICAL*, v. 113 issue 1, 2006, p. 162-168.

4. CO Sensor: High-temperature gas sensors based on semiconducting metal oxides show potential for optimization of combustion processes, resulting in efficient energy use and minimization of emissions. Such metal oxides can function as gas sensors because of the reaction of the sensing gas (e.g., CO) with ionosorbed oxygen species on the oxide surface with the resulting increase in conductivity. A limitation of metal oxide sensors is their difficult of distinguishing between different gases. Designing selectivity into sensors necessitates a better understanding, of the chemistry of gas-solid interactions at high temperatures. In this paper, we have used in situ infrared spectroscopy to monitor the dehydration of a hydrated anatase surface up to 600°C and also to examine the hydration/dehydration of anatase held at 400°C. When the O-H stretching region (3000-3800 cm^{-1}) was primarily focused on, it was found that water loss from the titania surface proceeded at lower temperatures (< 200°C) through desorption, whereas at higher temperatures, water dissociation to terminal (similar to 3710 cm^{-1}) and bridged (similar to 3660 cm^{-1}) hydroxyl groups was noted. With a further increase in temperature to 600°C, the bridged hydroxyl groups disappeared faster than the terminal ones. The electrical resistance of anatase at 600°C was measured in the presence of moist gas streams and resulted in an increase in conductivity in the presence of water. In situ vibrational spectroscopy indicated a temporal correlation between the appearance of the bridging hydroxyl group and the change in electrical resistance. Several possible mechanisms are discussed. The chemical reaction of water with anatase at high temperatures necessitates that water be removed from the gas stream to avoid interference. A strategy involving the use of a hydrophobic microporous filter that can reject water and let gases such as CO pass unimpeded is examined. Successful use of such a concept has been demonstrated with a silicalite filter using moist CO gas streams.

The hypothesis that chemical reactivity of the surface for CO oxidation of a titania sensor impregnated with gold or copper oxide is related to the sensing behavior was tested. Results show that the mechanism of the oxidation reaction is more important to the sensing characteristics than the extent of reaction.

Sputtered films of titania were explored for sensing of carbon monoxide (CO) at 550°C. Film thickness was varied from 24 to 1000 nm by varying the sputtering time. The films were amorphous as prepared and converted to rutile upon thermal treatment. Highest sensor sensitivity, as measured by the resistance change of the film upon exposure to CO was noted for the 240 nm film, and characterization focused on this film. Microstructure studies using electron microscopy show that the film was dense, with grain sizes of rutile of 20 nm. Atomic force microscopy showed considerable surface roughness. The 240 nm sputtered films exhibited higher sensitivity (factor of 3) as compared to optimized porous films made with commercially available anatase particles.

The results of these studies can be found in the following manuscripts:

Trimboli, J; Mottern, M; Verweij, H; Dutta, P. "Interaction of water with titania: Implications for high-temperature gas sensing." *JOURNAL OF PHYSICAL CHEMISTRY B*, v. 110 issue 11, 2006, p. 5647-5654.
Dutta, P; Frank, M; Hunter, G; George, M. "Reactively sputtered titania films as high temperature carbon monoxide sensors." *SENSORS AND ACTUATORS B-CHEMICAL*, v. 106 issue 2, 2005, p. 810-815.

Dutta, P; De Lucia, M. "Letter to the editor." *SENSORS AND ACTUATORS B-CHEMICAL*, v. 115 issue 1, 2006, p. 1-3.

5. CO_2 Sensor: An electrochemical CO_2 gas sensor using Li_2CO_3 and Li_2TiO_3+TiO_2 as sensing and reference electrodes, respectively, and Li_3PO_4 as the electrolyte was examine. The sensor response to CO_2 gas showed a systematic deviation from the prediction of the Nernst equation at low p_{CO2}. Based on the electromotive force (emf) measurement, the transference numbers of Li_3PO_4, a lithium-ion conductor, were estimated for different p_{CO2} values, and the conduction domain boundary for Li_3PO_4 separating n-type electronic conduction from ionic conduction was constructed. The conduction domain predicts that change in the Li activity in the sensing side of the cell drives the Li_3PO_4 electrolyte to a mixed (n-type electronic and ionic) conduction region at low p_{CO2}. Hebb-Wagner dc polarization measurements also indicate n-type electronic conduction in Li_3PO_4 with a mixture of Li_2CO_3 and gold as a reversible electrode. The transference numbers obtained from both the emf measurement and the Hebb-Wagner polarization measurements demonstrate that the origin of the non-Nernstian behavior of the CO_2 sensor is due to the lithium mass transport from the Li_2CO_3-sensing electrode to the Li_3PO_4 electrolyte, resulting in nonstoichiometry of Li_3PO_4 at temperatures above 500°C.

The results of these studies can be found in the following manuscripts:

Chonghoon Lee, Prabir K. Dutta,b Ramasamy Ramamoorthy, and Sheikh A. Akbar. Mixed ionic and electronic conduction in Li3PO4 electrolyte for a CO2 gas sensor *Journal of The Electrochemical Society*, 2005, Vol. 153, No. 1, pp. H4–H14

6. Sensor Arrays : A sensor array comprising of three chemical gas sensors was evaluated to predict the concentrations of O_2, CO, and CO_2 in a gas stream with the sensors at 600°C. The data analysis involved a non-linear multivariate regression method (kernel ridge regression, KRR) along with a searching algorithm to predict gas concentrations. The sensors in the array included a resistance-based 2% CuO/10% La_2O_3/TiO_2 sensor, and two potentiometric sensors, including a yttria stabilized zirconia (YSZ) sensor with a metal/metal oxide internal reference electrode, and a lithium phosphate-based sensor. In addition, the possibility of using the KRR algorithm to predict gas concentrations beyond the training data was explored.

The results of these studies can be found in the following manuscripts:

Zhang, P, et al. "High temperature sensor array for simultaneous determination of O-2, CO, and CO2 with kernel ridge regression data analysis." *SENSORS AND ACTUATORS B-CHEMICAL*, v. 123 issue 2, 2007, p. 950-963.

7. Applications in Real World Scenario: Studies were carried out for in situ measurement of CO, NO_x and CO_2 concentrations in exhaust emitted from an automotive diesel engine. These data were obtained with a series of ternperature-controlled sensor probes and compared to exhaust concentrations measured simultaneously with an exhaust motor analyzer. The CO_2 sensor is a Nernstian type with a Li_2CO_3, Au sensing electrode, a Li3PO4 electrolyte and a $Li_2TiO_3 + TiO_2$/Au reference electrode. The total NOx sensor measures the difference between potential responses of two porous Pt electrodes on an ion-conducting stabilized cubic zirconia support. The potential difference results because one Pt electrode is covered with a catalyst to achieve a locally equilibrated NO mixture, whereas the other electrode exposed to the sensing gas mixture, pre-equilibrated at a different temperature. The CO sensor is a resistive type and responds to selective sorption of reducing species. All sensor types have simple planar configurations but require accurate temperature control to deal with significant fluctuations in the engine exhaust stream. A constant sensor temperature of 400°C is achieved with a ceramic heater strip and tight control using a direct digital PID algorithm. The NO_x sensor requires a second temperature con- trolled pre-conditioning filter. This filter is integrated in the probe and controlled with a thermo-coax heating wire and another PID implementation. Generally, the sensors responses in the engine agree with the laboratory tests, but calibration errors resulted due to lack of thermal homogeneity of the sensor. In addition, some drift is observed due to particulate contamination from the exhaust stream. The CO_2 sensor appeared to be the most robust, though the probe signal may have been influenced by the evacuation effect at high gas velocities present in the car exhaust.

The results of these studies can be found in the following manuscripts:

Figueroa, O, et al. "Temperature-controlled CO, CO2 and NOx sensing in a diesel engine exhaust stream." *SENSORS AND ACTUATORS B-CHEMICAL*, v. 107 issue 2, 2005, p. 839-848.