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Ceramic-based chemical sensors, probes and field-tests in automobile engines

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The monitoring and control of combustion-related emissions is a top priority in many industries. The major methods used to detect combustion gases fall short of practical applications for *in-situ* measurements in industrial environments involving high temperature and chemical contaminants. The real challenge is not only to develop highly sensitive and selective sensors, but to maintain long-term stability in such aggressive environments. This article presents an overview of a multidisciplinary research effort in ceramic-based chemical sensors, highlighting opportunities as well as challenges. The group of sensors (CO, NO_x, O_2, and CO_2) selected for this article can, in general, be used to determine the state of combustion in a wide variety of applications. Fabrication of sensor probes and their field-test results in automobile engines are also presented.

1. Introduction

Development of rugged and reliable chemical sensors capable of making measurements in harsh industrial environments is critical in the present era when industry has become far more environmentally conscious [1–7]. Chemical sensors are used in a wide range of industries including steelmaking, heat treating, metal casting, glass, ceramic, pulp and paper, automotive, aerospace, utility and power. Emissions monitoring sensors for these applications include those for CO, NO_x, O_2, CO_2, hydrocarbons (HCs) and volatile organic compounds (VOCs). Chemical sensors are also being used in domestic appliances and air quality monitoring. More recently, chemical sensors are attracting attention for applications such as early detection of smoke/fire as well as hazardous chemical agents to provide safety and security in public places and mass transportation systems. According to a recent market report, US demand alone for chemical sensors (gas sensors and biosensors) is projected to reach $2.7 billion by 2006 [8].

The monitoring and control of combustion-related emissions is a top priority in many industries. Availability of reliable sensors along with predictive emission modeling tools would provide a better control of combustion leading to reduction of toxic emissions and subsequent energy savings. According to a DOE report [9], harsh environment sensors are predicted to save 0.25 quadrillion BTU/year of energy across all energy-consuming industries, identified as Industries of the Future (IOF). The automotive industry is an excellent example, where increased use of sensor and measurement technology has led to improvements in engine performance, higher energy efficiency and reduced pollutant emissions.

The major methods used to detect combustion gases fall short of practical applications for *in-situ* measurements in aggressive industrial environments involving high temperature and chemical contaminants. The chemiluminescent analyzer for NO_x detection has a high detection limit and fast response time but requires many auxiliary components to function, is costly, and complex to maintain. Fourier transform infrared spectroscopy (FTIR) involves using an infrared beam to obtain a characteristic spectrum of a molecule that can be used for quantitative analysis. The response time and detection limits of the method are very good, but size, costly maintenance, and low temperature range are disadvantages. Resonance ionization spectroscopy is used for measuring the density of species in flames. This method can be used at high temperatures and has a fast response time, but it involves a complex laser device and is not very accurate for quantitative analysis. Gas chromatography/mass spectrometry (GC/MS) uses chromatography to separate mixtures and mass spectrometry to identify components. This method has excellent detection limits, but is suitable for low temperature ranges (<573 K), and is costly and complicated to maintain.

The NSF Center for Industrial Sensors and Measurements (CISM) has been developing several ceramic-based sensors, mostly for the monitoring of combustion gases [10–22]. These include CO, CO_2, O_2, NO_x and hydrocarbons. Prototypes of several of the combustion sensors have been tested inside the exhaust manifold of automobile engines [23–25] showing promising potential for commercialization. This article presents the latest results in a select group of CISM-developed sensors along with results of a probe tested in an automobile engine at the Center for Automotive Research (CAR). The select group of sensors (CO, NO_x, O_2, and CO_2) can, in general, be used to determine the state of combustion in a wide variety of applications.

2. CISM-developed sensors

2.1. Selective CO sensor

In combustion applications, there is need for selective CO sensors in the presence of hydrocarbons, nitrogen oxides and varying levels of oxygen. Semiconductive CO sensors based on SnO_2 are commercially available and can be fabricated by the so-called thick-film technology. A paste of sensor material with controlled rheology is screen-printed on an alumina substrate that has pre-printed electrodes, followed by high-temperature annealing. These sensors have a simple structure and the change in the sensor film resistance is monitored as a function of CO gas concentration in the ambient. Although these thick-film sensors are inexpensive, they are prone to interference from other co-existing gases. CISM researchers have designed a new type of selective CO sensor based on *n-p* heterojunctions of anatase (*n*) and rutile (*p*) using TiO_2 as the base material [18]. Combination of anatase and rutile phases in the appropriate proportions leads to a sensor selective to CO as shown in Fig. 1. These types of composite sensors are of potential importance because by varying the mixing ratio of the *n* and *p* phases, one can create a wide range of sensor arrays including the possibility of designing selective CO and/or hydrocarbon sensors.

2.2. Sensor arrays for CO and O_2 detection

One of the challenges in monitoring a dynamic combustion environment with metal oxide sensors is to accurately detect CO in the presence of fluctuating oxygen levels. Recently, CISM researchers have developed a novel method where signals of titania-based sensor arrays were analyzed using kernel ridge regression modeling to determine the concentration of CO and O_2 in gas mixtures at 873 K [26]. To evaluate the kernel ridge regression methodology, an array comprised of a La_2O_3-doped anatase TiO_2 (AL) sensor and a 8%CuO-La_2O_3-doped TiO_2 (ALC) sensor was used. Each sensor in this array was exposed to mixtures of 250–1000 ppm CO at O_2 concentrations of 2, 5, and 10%. Fig. 2 shows the decrease in resistance of the AL sensor with increasing CO and decreasing O_2 (indicative of an *n*-type semiconductor) and the ALC sensor displaying the opposite (*p*-type) behavior at low CO concentrations (150–300 ppm).

To model these different behaviors, a family of exponential functions was chosen. It was then possible to observe the ranges where the sensor array can make the best predictions for unknown concentrations of gases. Once this was accomplished, the array was used to predict O_2 and CO levels based on sensor resistances for

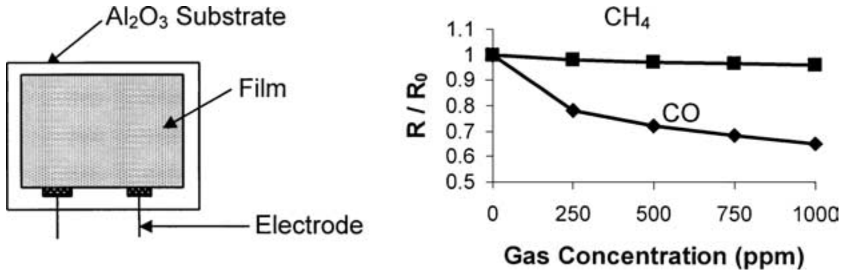

Figure 1 Thick-film sensor configuration and sensing behavior of a 75% rutile and 25% anatase TiO_2 composite sensor at 600°C in 5% O_2. R_o is the resistance in the absence of the sensing gas.

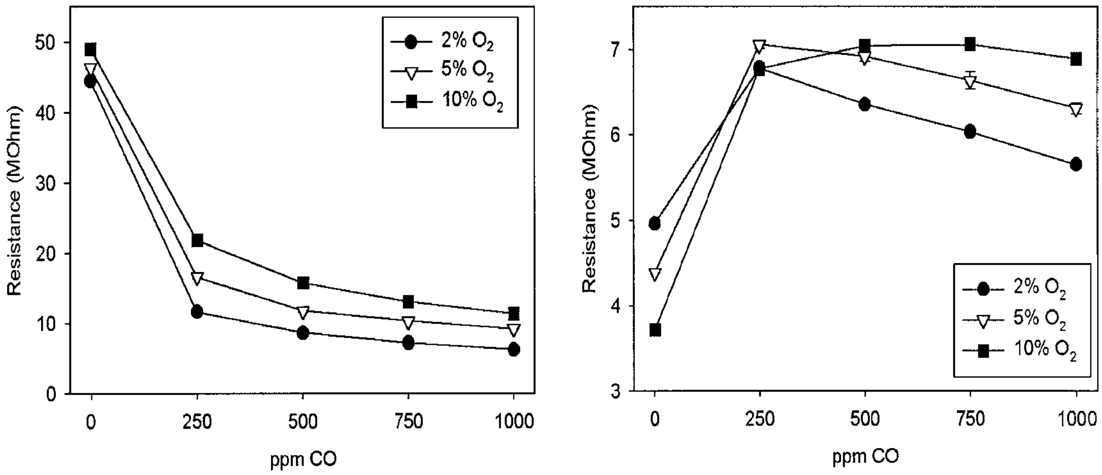

Figure 2 Absolute resistances of AL sensor (a) and 8% CuO-AL sensor (b) to 250–1000 ppm CO and 2–10% O_2.

TABLE I Comparison of actual and predicted values of O_2 and CO in gas mixture testing, with bold type showing regions of particularly good agreement

Actual % O_2	Predicted % O_2	Actual CO (ppm)	Predicted CO (ppm)
3	**2.6**	**250**	**259**
3	1.8	350	229
3	2.9	600	524
3	1.9	800	495
3	2.4	900	702
4	**2.8**	**250**	**216**
4	2.4	350	295
4	2.7	600	404
4	2	800	407
4	2	900	581
8	**8.6**	**250**	**255**
8	11.4	700	1270
8	10.2	900	1005
9	**8.8**	**250**	**242**
9	3.4	700	405
9	16.9	900	1775

a known gaseous environment. It is clear from the data in Table I that this particular pair of sensors is good at predicting low levels of CO at any of the O_2 concentrations tested, as represented in bold type. This is the case because the two sensors chosen were most orthogonal at low levels of CO (150–300 ppm), where their responses are opposite for all O_2 concentrations.

2.3. NO_x sensor in varying oxygen environment

Potentiometric (electrochemical) sensors can be used to detect NO_x by measuring the electrical potential difference between a reference electrode and a sensing electrode on a suitably chosen electrolyte. Such sensors based on yttria-stabilized-zirconia (YSZ) with metal oxide sensing electrodes show promise for NO_x detection [20]. Szabo *et al.* have examined the use of zeolite as a catalytic filter to create asymmetry between two Pt electrodes for NO_x sensors [21, 22]. A total NO_x sensing system was recently developed using a Pt loaded zeolite Y (PtY) catalytic filter. The PtY was prepared by ion-exchanging zeolite NaY in a $[Pt(NH_3)_4]Cl_2$ solution as described elsewhere [27]. Elemental analysis using ICP optical emission spectroscopy determined the Pt content to be 10.9 wt% and Pt particles of sizes 20–80 nm were visible on the surface of the zeolite crystals based on SEM observation.

To demonstrate the concept of a total NO_x sensor, about 70 mg of PtY was heated between 400–700°C to catalytically equilibrate equal concentrations of NO or NO_2 to the same $[NO]/[NO_2]$ ratio. To confirm this, the catalytic conversion of 600 ppm NO or NO_2 in 3% O_2/N_2 was measured by a chemiluminescence (CL) analyzer. In addition, no N_2 or N_2O formation was observed over the range of 400–700°C as verified by mass conservation on the analyzer. The CL analyzer placed after the PtY filter was then replaced with sensor #1 (Fig. 3a) consisting of a Pt air reference and Pt sensing electrode. The sensor was placed in a sealed quartz tube and heated in a furnace to 500°C. When the sensor and filter were at the same temperature, the sensor signal was low because the NO_x gas is at equilibrium on the electrode and this is expected based on the well-known mixed potential behavior [28]. Fig. 4 shows a 4-point calibration curve for 0, 400, 600, and 1000 ppm NO or NO_2 in 3% O_2 passing through the filter at 700°C with the sensor at 500°C. The sensor signals in flowing NO or NO_2 are in the same direction and are nearly identical. CO gas had little effect on the NO_x calibration curves at levels up to 1000 ppm for the 70 mg of PtY filter since it is oxidized to electrochemically inactive CO_2.

Sensor #2 (Fig. 3b) using the PtY filter was designed consisting of a YSZ tube with two Pt sensing electrodes and a Pt air reference. One of the Pt sensing electrodes was covered with a second PtY filter layer that keeps the electrode potential constant (close to the equilibrium potential determined by O_2) by creating an equilibrium NO_x mixture while the other uncovered Pt sensing electrode detects NO_x concentration changes. The sensor #2 response to 560 ppm NO and NO_2 in 3% O_2 with the PtY filter bed at 600°C was measured and compared with the chemiluminescence analyzer signal in Fig. 5. The sign of the sensor signal was changed for a direct

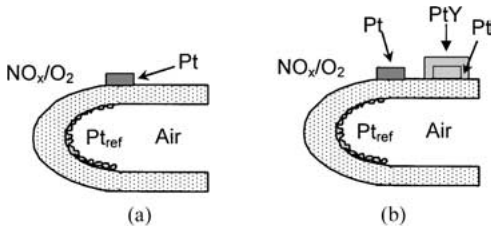

Figure 3 Schematic of sensor #1 (a) and sensor #2 (b).

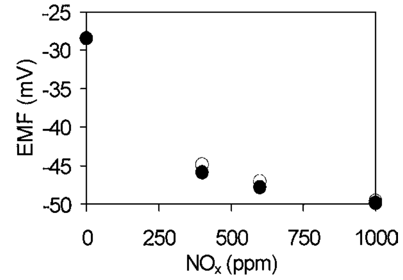

Figure 4 Calibration curves for the air reference YSZ sensor #1 (500°C) and PtY filter (700°C) for NO_x in 3% O_2.

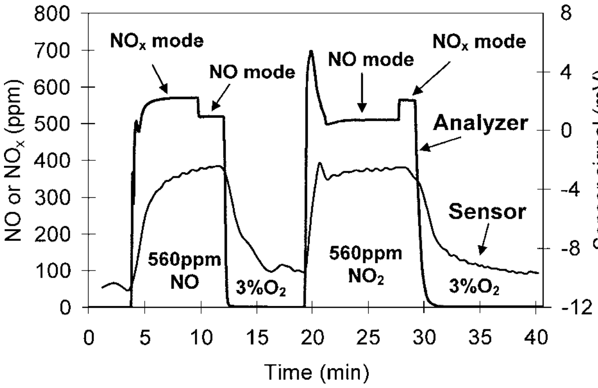

Figure 5 Comparison of the response of the NO_x analyzer to the planar electrode couple on sensor #2 PtY/Pt vs. Pt after the external PtY catalytic filter at 600°C.

comparison with the analyzer signal. Sensor #2 signals to 560 ppm NO and NO_2 have the same sign and approximately same magnitude. This indicates that the Pt/PtY electrode is serving as a pseudo-reference for NO_x and the external PtY filter at 600°C is bringing both NO and NO_2 to equilibrium. As shown by the analyzer readings in the NO_x ($NO + NO_2$) and NO modes, 560 ppm of NO or NO_2 is converted to the same NO/NO_2 ratio. The non-zero baseline is likely caused by slow O_2 kinetics on the electrodes. However, this did not affect the total NO_x sensing properties.

2.4. Oxygen (O_2) sensor with solid reference electrode

Commercially a number of oxygen sensors are in use for monitoring the air-to-fuel ratio in auto exhaust, pollution control, furnace operation, etc. These sensors use air as a reference electrode. In other applications such as kiln monitoring, there is a need for oxygen sensors to measure oxygen at different locations inside the kiln. In these applications, sensors with an air reference is not a suitable technology. An alternative is to use metal/metal oxide mixtures that can provide constant oxygen partial pressure at a fixed temperature [29, 30]. The main advantage of a solid reference over the air is that the metal/metal-oxide mixture inherently produces extremely low O_2 concentrations with respect to the test environment, producing a large oxygen potential difference and consequently a large EMF signal. Another advantage of the metal/metal-oxide reference is that it offers more flexibility in positioning and mobility as compared to the sensors that use an air reference. Sensors using an air reference can only measure oxygen concentrations in an area very near the wall of a combustion chamber, as the length of the zirconia tube limits the location of measurement. Use of the solid reference allows the zirconia tube to be smaller in length, and can be positioned in more remote locations inside the combustion environment. What is potentially more attractive is that such sensors can be miniaturized as planar devices, that can be mass-produced.

We implemented this idea to produce a solid reference oxygen sensor with the electrochemical cell arrangement as shown below [6, 30].

2.5. (Sensing side) Pt electrode |YSZ-tube (one end closed), Al_2O_3 isolation| Ni-NiO solid reference| Pt electrode

A number of oxide mixtures have been examined and a Ni/NiO mixture showed promising results as the solid reference. To avoid Pt—Ni alloy formation, the Pt wire was isolated from the Ni-NiO mixture using an Al_2O_3 tube. A portion of the YSZ tube was filled up first with Al_2O_3 powder covering the Pt contact inside the YSZ tube giving virtual isolation of Ni—Pt contacts. Sensors with this isolation layer showed reproducible response characteristics [19].

An attempt to fabricate a miniature device of the potentiometric planar oxygen sensor was recently undertaken. The sensor design is shown in Fig. 6a. In this design, air tight sealing of the ceramic components is challenging for which many metallic and ceramic sealants are being investigated. In our probe, we attempted to achieve sealing using a gold paste as sealant and firing at 1000°C for one hour. A typical response curve of the planar sensor using the Ni-NiO solid reference tested at 773 K is shown in Fig. 6b. Though the sensitivity is lower than the theoretical Nernstian value, the response is reasonably fast considering the test temperature of 773 K. The lower sensitivity and drift in the sensor signal are believed to be due to lack of proper sealing. If the reference PO_2 chamber containing Ni/NiO mixture is sealed properly from the outside, it is expected that the miniaturized planar O_2 sensor with solid reference would be a viable technology.

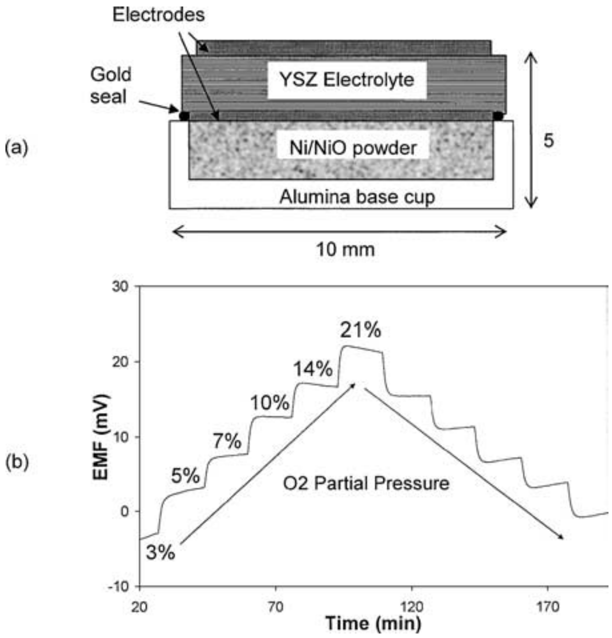

Figure 6 Miniature planar design (a) and response of O_2 sensor (b) using Ni-NiO solid reference.

2.6. Electrochemical CO_2 sensor

Reliable CO_2 gas sensors are needed for monitoring the environment, corrosion rate in chemical processing, carbonation of concrete and in modified atmospheres packaging (MAP) of food [20]. Electrochemical CO_2 sensors (similar to those for NO_x) can be designed by an appropriate choice of an electrolyte, a reference electrode and a sensing electrode. Fig. 7 represents the schematic planar sensor design, where Li_2CO_3 is the sensing electrode and $Li_2TiO_3 + TiO_2$ is the reference electrode. Lithium ion conductor is adopted for a faster response and its anticipated minimal interference from humidity [20]. A carbon dioxide gas

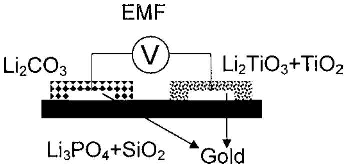

Figure 7 Schematic CO_2 sensor design.

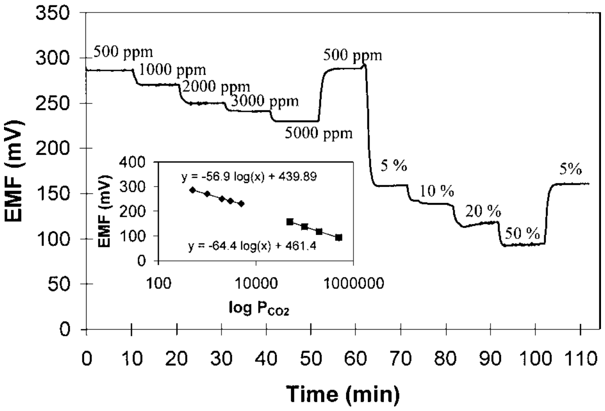

Figure 8 Sensor response to CO_2 concentration changes and its sensitivity slope.

sensor using a lithium ion conductor was first reported by a Japanese group, Imanaka *et al.* [31]. In previous studies ($LiCoO_2 + Co_3O_4$), a composite used as cathode in battery applications, was tested in order to keep the lithium activity constant at the reference electrode. However, it has the general problem of oxygen dependence. Therefore, $Li_2TiO_3 + TiO_2$ was investigated to avoid the oxygen dependence [20]. Fig. 8 shows its response to CO_2 concentration changes from 500 ppm to 50%. As can be seen, it shows very reproducible and stable sensing performance in a wide range of CO_2 concentrations. The sensitivity is, however, lower than the theoretical Nernst slope of −76.7 mV/decade at 500°C. We observed a slope of −64.4 mV/decade for % level CO_2 concentrations and a lower value at low CO_2 concentrations.

Two possible reasons can cause the deviation from the Nernstian behavior: mixed (ionic and electronic) conduction in the electrolyte and a non-reversible electrode. The effect of mixed conduction on the CO_2 sensor was discussed in our recent publication [32]. A reversible electrode is necessary for maintaining thermodynamic equilibrium in an electrochemical sensor. A non-reversible electrode can induce polarization at the interface between the electrolyte and the electrode causing the potential to deviate from the equilibrium value. Fig. 9 shows impedance data using different electrodes for symmetric electrochemical cells with the same electrolyte and geometry. The data clearly indicates that the lithium carbonate electrode shows a much smaller charge transfer resistance (low-frequency arc) than the lithium titanate and gold electrodes. This seems to indicate that while lithium carbonate behaves like a reversible electrode, lithium titanate does not. This non-reversible electrode can cause the sensor to show a deviation from Nerstian behavior. As also shown in the data, the large electrode impedance can affect the bulk conduction due to polarization at the electrode-electrolyte interface.

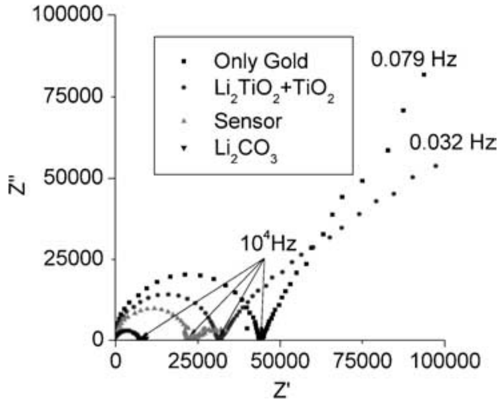

Figure 9 Impedance spectra obtained for lithium phosphate electrolyte with different electrode materials at 500°C.

3. Automotive tests

In laboratory tests, the temperature stability of the sensor is maintained inside a temperature-controlled furnace where the temperature is monitored by a thermocouple placed close to the sensor. Temperature control can be achieved via different types of controllers: ON/OFF, Proportional and PID. The choice of a controller is determined by the amount of error that can be tolerated in a given application. A dynamic environment such as the exhaust stream of an automobile engine encounters large fluctuations in temperature and a PID controller provides the best temperature stability. A PID controller uses specially designed software that adjusts the power delivered to a micro-heater attached to the sensor probe. Prototypes of several of the CISM sensors have been tested inside the exhaust manifold of automobile engines at the Center for Automotive Research (CAR) [23–25]. Here, we report on a recent test of a CO_2 probe.

A probe for testing in an automobile engine was fabricated by integrating the CO_2 sensor on a commercial heater powered by a PID controller (Fig. 10a). For protection, the sensor was housed inside a metallic tube after mounting it on the heater (Fig. 10b). The probe was mounted in the exhaust pipe of a 2.4L-5 cylinder 1997 Fiat diesel engine. The exhaust gases were monitored with a Horiba Motor Exhaust Analyzer MEXA-7500. In this test, the torque (represented in ft-lb) was varied while keeping the engine speed constant. Increasing and decreasing the engine torque changed the concentration of CO_2 in a controlled manner. The comparison of the probe response with that of the Horiba gas analyzer (Fig. 11) confirms reliable sensor performance in the auto-test.

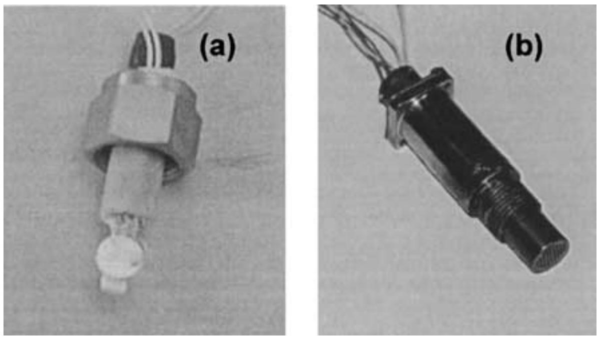

Figure 10 Photograph of the sensor (a) mounted on the PID controlled heater and (b) probe housed inside a protective tube.

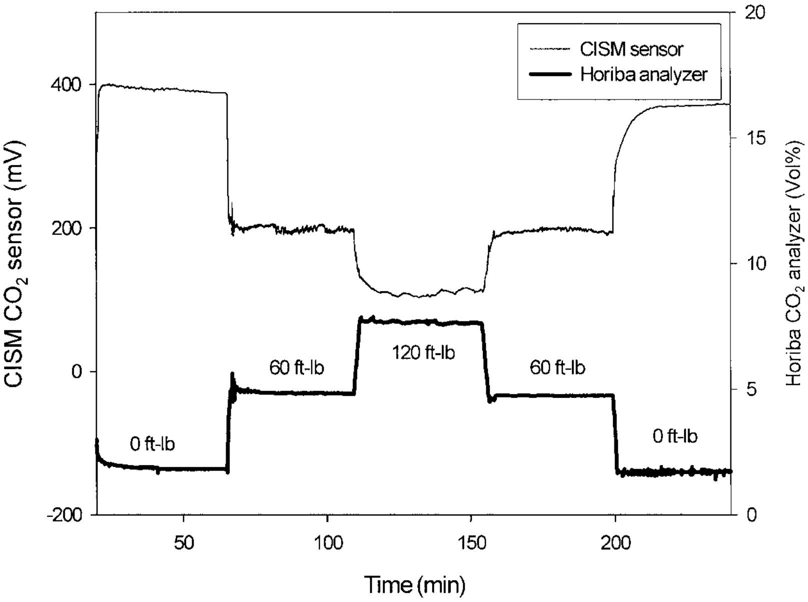

Figure 11 Engine test results of the CO_2 sensor probe compared with the Horiba analyzer data.

4. Future trends

Implementing the appropriate technology to monitor and control combustion processes will rely on the development of robust sensors for the identification of volatile emissions. Selectivity and stability are the major issues limiting widespread applications and further development of ceramic-based sensors. Current efforts to resolve these issues tend to integrate results obtained from both empirical and basic science approaches, and to focus on various stages of sensor development, including the development of new material systems for high temperature applications, sensor fabrication and manufacturing techniques, and neural-network-based smart sensor arrays with signal conditioning and filtration. Also, due to the complexity involved in sensor development, the research is moving towards multidisciplinary collaboration.

4.1. Development of sensor materials

Typical gas sensors often involve a complex mix of different materials including catalysts. However, not much is known about the relation between sensing mechanisms and material characteristics (e.g., crystal structure and microstructure, surfaces and interfaces, defects, etc.) which is necessary to exploit the full potential of existing materials or to find improved sensor systems, as well as to control the stability of fabricated devices. Detailed characterization ranging from electron microscopy to surface analytical techniques is needed for establishing structure-property relationships.

Very little work has been done in the area of modeling and simulation of ceramic gas sensors, particularly modeling of sensor arrays [26, 33, 34]. The difficulty arises since development and integration of modeling at different length scales is necessary to describe the multitude of phenomena occurring in various types of sensors. The fundamental chemical reactions and electron transport through metal oxide surfaces and bulk regions involve events on the atomic scale. Conduction through the poorly sintered microstructure of the ceramic device involves phenomena at the granular or mesoscopic scale while the device electrical properties include behavior at the macroscopic level as well. There is a need to combine successful models developed at these different length scales into an integrated framework that can be used to drive new research and guide experimental efforts for designing sensors and sensor arrays with optimized properties.

Ultra thin or nano-particle films show promise in resistive gas sensor applications because the sensitivity is expected to increase dramatically when the film thickness or particle size becomes comparable to the depletion layer thickness of the material. A challenging issue associated with the development of ultra thin film and nano-structured ceramic sensors is the stability of the nano-scale microstructure against surface grooving, grain growth and coarsening during thermal processing and applications at elevated temperatures. Both experimental and theoretical studies are needed for the kinetics of surface/interface grooving as a function of the ratio of surface/interfacial energy over grain boundary energy, temperature and segregation of impurities.

4.2. Smart sensors and sensor arrays

There is a trend towards the use of more sophisticated design concepts in the development of new sensor systems, notably the so called smart sensor system, which combines sensing elements and signal processing, conversion and output units [35]. This approach aims at simultaneous or sequential acquisition of more than one type of signal, mainly to resolve the problem of selectivity. This may include the use of more than two electrodes (arrays of electrodes) on a single sensor body, employment of sensor arrays made of many sensors or a multi-layer sensor with a filtering membrane, and applications of artificial intelligence for pattern recognition. In applications, the objective of such an approach may be difficult to achieve, as a sensor array functionality relies not only on the right combination or integration of different sensors but also on the stability of individual sensors. Any change or drift in one of the sensors requires a system-wise re-calibration or re-programming of the pattern recognition part. In other words, potential applications of a sensor array system are still going to be determined by the availability of stable and reliable individual sensors.

4.3. Device fabrication and manufacturing

From the device fabrication and manufacturing point of view, semiconductive oxide based sensors are prone to poor reproducibility (unit-to-unit consistency) and high power consumption (particularly for gas sensors to maintain a constant operating temperature). Lack of reproducibility results from poor control over raw materials and processing conditions including forming, firing and electrode attachment. Most of the current commercial sensor devices are produced either by typical ceramic fabrication (sintered body) or thick film processes. Sensors thus produced often have poor unit-to-unit consistency, and therefore require individual inspection and calibration.

Thin film fabrication process and micromachining, which are based on well-defined IC deposition and etching processes, are expected to improve the reproducibility and possibly lower the power usage besides achieving a mass production capability. Alumina fabricated by low temperature co-fire ceramic technology (green tape technology) provides new opportunities for IC packaging as a high-density, high-reliability, low-cost substrate. Thin film metallization can be accomplished by thermal evaporation, sputtering and chemical vapor deposition on a polished alumina substrate. Patterning of the structure can be done using proven photoresist, chemical etching and lift-off techniques. Green tape and laser cutting techniques can be used together to create three-dimensional structures, which are highly desirable for many sensor and device applications.

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