Final Report

Novel Hydrogen Sulfide Sensors for Portable Monitors

CDC Grant H07471
SBIR Phase II

SUBMITTED BY

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This Phase II was awarded in September 2003 and had an original completion date of 9/15/05, which was extended for 12 months. Dr. Stephen S. Williams was the Principal Investigator and Mr. Clayton J. Kostelecky served as the Project Manager.

1. SPECIFIC AIMS

The primary objective of this SBIR Phase II project was to design, develop, and demonstrate a better sensor technology for detecting the presence of hydrogen sulfide (H_2S), a particularly hazardous gas species. Because of the potential for adverse health effects at very low concentrations, the industrial hygiene community is continually seeking improved performance from H_2S sensors. Specific requirements include reliable and accurate detection in real time, quantitative measurement capabilities, low purchase and life cycle costs, and low power consumption (for portability). Sensors meeting these requirements are in demand for numerous applications within the health and safety field.

Synkera proposed to use its expertise in materials engineering and component fabrication to create a new sensor device to meet these challenges. The original concept was to take advantage of specific benefits associated with metal oxide resistive gas sensors (namely low cost and long lifetime), while working to overcome their widely known disadvantages (primarily poor response and recovery to sulfur-containing species and a lack of reproducibility from sensor to sensor). To accomplish this, an alternative sensor material was used that is highly sensitive to H_2S without substantial response to other chemical species. During the course of Phase II metal oxide sensors were prepared not only in the proposed "chip-style", but also as planar sensors and microsensors (see section 3 for details). In addition, during the project period Synkera began developing low power, solid-state, electrochemical sensors for the detection of various species, one of which was H_2S, so we applied this technology under this program.

The sensors developed by Synkera are applicable to a number of different traditional instrumentation platforms, including fixed and portable systems such as those found throughout today's chemical workplace. In addition, Synkera has developed a "*Smart* H_2S *Card*" for personal monitoring, built around the solid-state electrochemical sensors developed under this program.

2. BACKGROUND & SIGNIFICANCE

2.1 HYDROGEN SULFIDE BACKGROUND

Hydrogen sulfide is a colorless, flammable gas that is highly toxic, even at low concentrations. It reacts with the enzymes in the blood that inhibit cell respiration. At high concentrations, it can literally shut off the lungs, while lower levels can burn the respiratory tract and cause eye irritation. The effects of various concentrations on human health are detailed in Table 1.

Table 1: Effects of Various H_2S Concentrations on Human Health [i].

H_2S Level (ppm)	Resulting Conditions and Heath Effects
0.13	Minimal perceptive odor
0.77	Faint, but readily perceptible, odor
4.6	Easily detected, moderate odor
10	Beginning eye irritation. *This is the OSHA and ACGIH PEL.*
27	Strong, unpleasant odor, but not intolerable.
100	Coughing, eye irritation, loss of sense of smell, altered respiration, drowsiness
200-300	Marked eye inflammation and respiratory tract irritation after 1 hour of exposure
500-700	Loss of consciousness, stopping of respiration, possible death in 30-60 minutes
700-1000	Rapid unconsciousness, cessation of respiration, death
1000-2000	Unconsciousness at once, ceasing of respiration and death within a few minutes. Death may occur even if individual is removed to fresh air at once.

This gas is encountered in a wide range of industries, and a number of standards have been established for occupational exposure. For example, the OSHA Permissible Exposure Limit (PEL) is 10 ppm (8-hour time-weighted average), and the Short Term Exposure Limit (STEL) is 15 ppm (15-minute time-weighted average). Exposures of 300 ppm or greater are considered immediately dangerous to life and health (IDLH) [ii].

The above values clearly indicate the importance of early detection and monitoring of H_2S at low concentrations. Despite monitoring efforts, eighty fatalities related to H_2S exposure were reported in the US between 1984 and 1994, fourteen of which involved attempted rescuers [iii]. Most (77%) were in businesses with more than 11 employees, which were, therefore, subject to routine OSHA inspections. The fatalities were primarily associated with confined space operations (e.g., sewers, animal containment facilities, waste dumps, sludge plants, manure tanks, and cesspools) and the petroleum and natural gas industries. Confined spaces are of particular concern for H_2S exposure, as this gas is 20% heavier than air, and vapors tend to collect in depressions in the ground, requiring the entire area be thoroughly monitored prior to entry. Investigations by OSHA determined that the use of H_2S detection equipment, coupled with better availability of respirators and additional confined space training, could have prevented deaths in the vast majority of these cases.

2.2 HYDROGEN SULFIDE SENSOR TECHNOLOGIES

Sensors currently used for gas monitoring suffer from significant limitations with respect to H_2S detection. For example, traditional liquid electrolyte electrochemical sensors are relatively expensive ($100-300) and typically last only 12-24 months. Furthermore, this life span is often significantly reduced when the sensors are exposed to very high H_2S concentrations, particularly in combination with high humidity [iv]. Such environments can be easily encountered in confined spaces, where monitoring of H_2S is particularly important for worker safety. Plus, these sensors also perform poorly in areas where humidity levels are very low, such as in the Middle East where H_2S sensors are used throughout the petroleum industry.

Conventional resistive metal oxide sensors (e.g., devices based on SnO_2) are relatively inexpensive (less than $50) and longer lasting, making them ideal for workplace applications. However, poor selectivity and stability are common, particularly in the presence of sulfur-containing species. In resolving these issues the gas detection community has shown great interest in products the products Synkera has developed for real-time quantification of H_2S exposures. The two biggest areas of interest have been the use of the solid-state electrochemical sensors for personal monitoring (including the Alert Card concept), and the use of a planar metal oxide sensors for fixed applications in areas with extreme climates such as the Middle East and in the oil fields of Alaska and Northern Canada.

2.3 PERSONAL MONITORS

Personal monitors are commonly used to provide protection against a wide range of industrial gas hazards. Monitors can be either single or multi-gas. Various gases can be monitored, with the most common being flammable, oxygen, carbon monoxide, and hydrogen sulfide. Typically liquid electrolyte electrochemical sensors are used for toxic gases, such as carbon monoxide and hydrogen sulfide. Some of the industries in which personal monitors are used include: mining, refineries/petrochemical, water/waste water treatment, pharmaceutical, utilities, chemical plants, and fire services.

While these personal monitors typically perform adequately, there are a number of potential areas of improvement, areas that are addressed by the sensors developed by Synkera under this program. The solid electrolyte electrochemical sensor is particularly well suited to use in personal monitors. With performance that meets or exceeds the lowest cost liquid electrolyte electrochemical sensors on the market today this sensor has several important advantages that make it attractive to instrument manufacturers. The projected cost of the sensor is approximately ¼ of the cost of traditional sensors ($15 vs. $60) in moderate quantities of 10's of thousands per year. The sensor is only minimally affected by variations in humidity, which is particularly significant as state-of-the-art sensors suffer at both very high and very low humidity levels. Finally, the size of the sensor is very small and the technology used in manufacturing makes surface mounting the sensor possible, allowing the sensor to be incorporated right along with the circuitry to operate the sensor. Taken together, these advances allow the implementation of an affordable and reliable credit card sized personal monitor for hydrogen sulfide.

During the Phase II we have had discussions with instrument companies regarding the use of this sensor in personal monitors and we have sampled sensors to a number of these companies for their evaluation. In addition, we have developed the conceptual design for an "Alert Card". The Alert Card concept is to mount the sensor on with the necessary circuitry on a PCB and package it together with the appropriate alarms and displays in a credit card size device.

3. SYNKERA SENSOR DEVELOPMENTS

3.1 METAL OXIDE

The Phase II, as proposed, was aimed at producing metal oxide sensors in a unique multilayer structure. This was successfully accomplished, however due to some practical difficulties with regard to packaging the sensor elements two other fabrication methods were investigated. The first alternative was a standard planar architecture. This method was evaluated because it fits in with our current manufacturing capabilities for other metal oxide sensors that Synkera sells (hydrogen, NO_x, ammonia, VOCs) and had the potential to produce cheaper, more robust sensors than was possible with the multilayer architecture. The third architecture investigated was based on a microsensor platform unique to Synkera. This sensor platform has the ability to reduce the power necessary to operate a metal oxide sensor by 60% or more, while allowing for easy and reliable packaging techniques.

The following section presents general information regarding metal oxide sensors which is applicable to all three architectures. Following this is information specific to each architecture regarding fabrication, testing results, costing information, and advantages and disadvantages of each sensor.

Metal Oxide Sensor Background

Most semiconductor metal oxides undergo surface interactions (physisorption and chemisorption) with gas molecules at elevated temperatures. These interactions result in a change in electron (or hole) density at the surface (i.e., a space charge forms), which in turn results in a change in overall conductivity of the semiconductor oxide. An example of this is the interaction of SnO_2 or TiO_2 with molecular oxygen. O_2 chemisorbs on these materials, producing negatively charged oxygen ions, O_2^-, via removal of an electron from the conduction band of the metal oxide. Thus, there are fewer electrons in the surface space-charge region, and the overall conduction of the material is reduced. In the band gap model, the loss of electrons from the conduction band raises the conduction band energy, and thus widens the band gap. A similar interaction reaction occurs when reducing gases, such as H_2, interact with semiconductor surfaces, resulting in adsorbed positive ions, H_2^+ on the surface, and consequent donation of electrons to the conduction band, with a corresponding reduction in the band gap. In both cases, the nature of the interaction is ionic, and the presence of a gas changes the electronegativity of the metal oxide and the width of their band gaps. The accumulation of negative charges in n-type semiconductor oxides creates a narrowing of the band gap and an increase in conductivity, while a depletion of negative charges widens the band gap and thus results in a decrease in conductivity.

Sensors based on these gas-solid interactions have been commercially available for years for detecting such gases as carbon monoxide, ammonia, and methane. However, these sensors, which are largely based on SnO_2, have suffered from a lack of selectivity due to the nature of the chosen semiconductor. More recently, selectivity and sensitivity have been "enhanced" via materials selection and mixing of metal oxides and additions of catalysts (usually metals) or dopants (materials with different electron affinity). In addition, in combination with close control of operating conditions, it has been proven possible to "tune" a metal oxide sensor to respond more selectively to one gas versus another.

By controlling the crystallite size and morphology of the semiconductor to nanoscale levels (<100 nm) the sensing material has a very large surface area, which allows for the increased interaction between vapor molecules and the semiconductor material. This, in turn, increases the amount of physisorption and chemisorption that occurs, leading to a greater change in the semiconductor's conductivity in the presence of the gas. This increase in sensitivity is desirable as it improves the lower detection limit to the target gas. In order to take advantage of this phenomenon, we purchased tungsten oxide (WO_3) from Sigma-Aldrich and attrition milled it to reduce the particle size. After milling the WO_3 was on the order of 70 nm and had a surface area of $\sim 16\ m^2/g$, a ten-fold increase over the as-received powder. This milled powder was used for the fabrication of all three metal oxide sensor architectures.

Advantages/Disadvantages of Metal Oxide Sensors

Metal oxide sensors have numerous strengths and are widely used in fixed applications. Some of the advantages include: high sensitivity, robustness, long life, and low cost. However, typical metal oxide sensors have several important drawbacks, typically including lack of selectivity and high power consumption, that leaves them ill suited for portable applications. Through our development effort we have retained the advantages of this type of sensor while largely overcoming the selectivity issue. Although we tried, we were unable to develop a metal oxide sensor with sufficient performance at a low enough operating temperature (power consumption) in order to use the sensor in a credit card sized portable device. The microsensor design is sufficiently low power for many, larger, portable applications.

Testing of Metal Oxide Sensors

All testing was performed using Synkera's automated sensor testing equipment, allowing for multiple sensors to be evaluated at the same time, and greatly increasing the amount of data we were able to collect and analyze. This test equipment has provisions for transducing resistance changes in chemiresistive sensors into 0-5 VDC signals compatible with off-the-shelf data acquisition instrumentation, and also allows precise control of heater voltages applied to the sensors. In addition to the computer control of the sensor operation, the system also controls the gas switching making the testing procedure fully automated. The following are explanations of the various type of tests performed to evaluate sensor performance.

Sensitivity

The topic of sensitivity encompasses the testing of the sensors to determine their dynamic range, linearity and detection limits. The sensors were tested over a range of <1 to 100 ppm H_2S.

Sensitivity is calculated from the change in resistance of the sensor when exposed to a background of air and when exposed a vapor species in air as follows:

$$Sensitivity = \frac{R_a}{R_g} \tag{3}$$

where: R_a is sensor resistance in background air

R_g is sensor resistance when exposed to vapor species in air

The linearity is typically calculated by exposing the sensors to 3-6 different concentrations of challenge gas over a range of at least two orders of magnitude. The sensor response vs. concentration for metal oxide is generally linear when plotted on a log-log scale over a wide range, until the sensor response becomes saturated at higher concentrations.

The detection limit is the lowest concentration that the sensor can reliably detect at a signal level equal to three times the noise. The detection limit can be determined experimentally by plotting the log of resistance versus log of concentration and performing a linear fit. The linear equation is then used to predict the concentration of gas required to generate a signal exceeding three times the root mean square noise level.

Response and Recovery Time

The response time is the time it takes the sensor to detect a change in the surrounding environment. It is typically determined as the time required to reach either 50% or 90% of the eventual minimum resistance (R_g). The recovery time is defined as the time required for the sensor resistance to return to within 10% of its original resistance in air. Sensor response times are typically faster for higher concentrations of challenge gas, so we will calculate the typical response and recovery times at a relatively low gas concentration. For a step change response from 0 to 10 ppm H_2S, the t-90 (time to reach 90% of full scale response) is approximately 5 seconds.

Selectivity

Exposing the sensors to a wide variety of challenge gases and measuring the responses will establish the selectivity of the sensors to H_2S. Selectivity is determined based on a comparison of the sensitivity to the target gas (H_2S) to the sensitivity to an interferent gas (at the same operating conditions). Numerous interferants such as CO, NO_x, CH_4 and selected VOCs were used for determining selectivity. These interferent gases were chosen based on application requirements.

Environmental Effects

The response of the sensors to environmental factors such as temperature and humidity were evaluated. The sensors were tested at temperatures from –40 to +60°C and 0 to 95%RH. These conditions represent the extremes most likely to be encountered if the sensors are used outdoors. Both the changes in baseline resistance and sensitivity to H_2S were considered.

Reproducibility/Stability

The reproducibility of the sensor response is an important measure of reliability. To evaluate this aspect of sensor behavior, sensors were repeatedly exposed to H_2S challenge gases. Both short-term reproducibility (over the course of hours and days) and long-term reproducibility (over the course of weeks and months) experiments were performed. Variations in the resistance in both air (baseline) and the challenge gas were evaluated.

3.1.2 Multilayer Metal Oxide Sensors

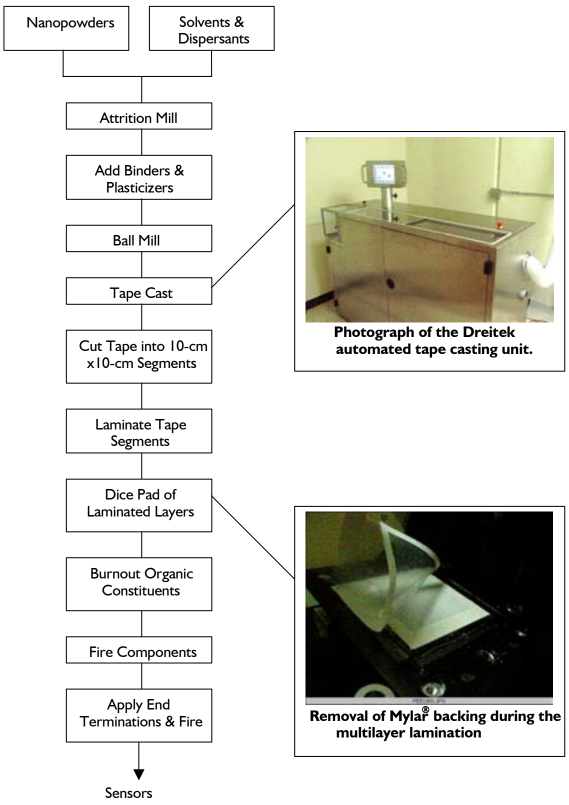
Fabrication

A formulation amenable to ceramic tape casting was developed in Phase I, in which relative concentrations of the raw material (WO_3), a binder, a plasticizer, a dispersant, and a solvent were combined. Each material has a unique function in the process, and thus the appropriate quantities must be used to ensure that the formulation can be used to successfully produce multilayer sensor elements.

In this procedure, outlined in Figure 1, the ceramic powder is first dispersed in the organic solvent, and the resulting slurry is milled to break up any powder agglomerates and to fully disperse the powders. Next, the binder and plasticizer are introduced, and the slip is ball-milled for an additional length of time to completely dissolve the materials.

The slip is cast using a Dreitek 101 tape casting unit onto a silicone-coated Mylar® carrier film in a continuous process, producing 10-cm wide tape. As the tape is cast, it is dried and rolled onto spools for later use. The tape is then cut into 10-cm x 10-cm sheets. Electrodes are screen printed onto one side of each sheet; ceramic devices are then fabricated by stacking and laminating the sheets together, removing the Mylar® backing after each lamination step. Once the build-up is complete, the array is diced into individual components.

The organic materials are removed using a low-temperature burnout process, in which the elements are heated in flowing nitrogen to a maximum temperature of 550°C using a series of ramps and holds. Slow heating rates are used, coupled with intermediate soaks. After binder removal, the sensors are fired to higher temperatures for densification. A typical firing temperature used for the WO_3 sensor elements is 1050°C. Sensor elements are shown in Figure 2.



Photograph of the Dreitek automated tape casting unit.

Removal of Mylar® backing during the multilayer lamination

Figure 1: Flow diagram showing the multilayer sensor fabrication process.

After firing, the electrodes were terminated using platinum paste and fired to 850°C to cure the paste. The sensors were then packaged for testing in Synkera's hazardous test system.. TO-39 headers were chosen for the package. The first step was to prepare alumina substrates (0.10″ square) that had electrodes for a heater connection, a resistive heater, and

Figure 2: WO_3 sensor elements.

electrode pads for the sensor element. The electrodes were gold and the heater was printed using a commercial thermistor paste designed to carry current. Gold ribbon was resistance welded to each of the four electrode pads; then the wired alumina substrate was mounted, heater down, onto the TO-39 header. The terminated multilayer sensor element was then attached to the substrate using high temperature epoxy (maximum operating temperature of 350°C). Finally, a conductive epoxy was used to connect the termination on the sensor element to the proper pad/pin/ribbon. Packaging sensors in this fashion allows for the heating of the sensor (by applying current to the resistive heater) from the bottom of the element with an insulator (alumina) between the heater and the sensor. The proposed plan was to incorporate the heater directly into the element itself, however, from experience in a intermediate development effort it was found that there was cross-interference between the sensor signal and heater current, particularly for lower resistance sensor elements (which the WO_3 elements could be classified as). A picture of a mounted sensor is shown in Figure 3. Note in the bottom photo the exposed platinum electrodes on the edge of the sensor element.

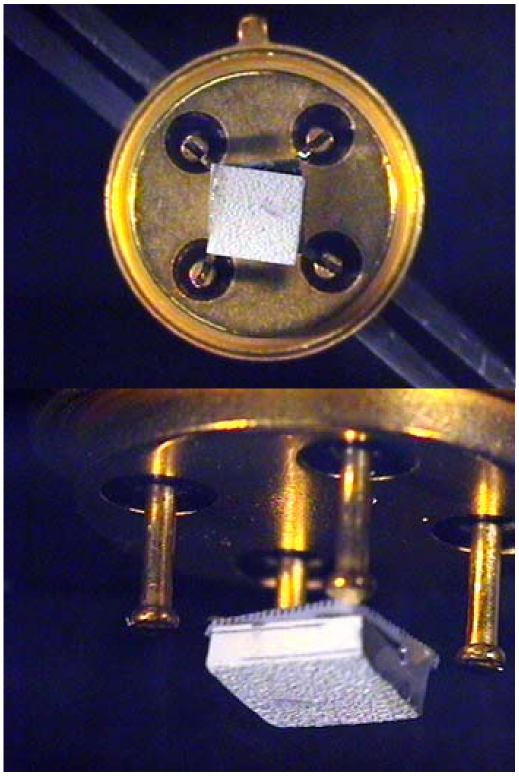


Figure 3: Packaged multilayer H_2S sensor.

Data

Testing conducted on the multilayer sensors included operating power/temperature studies, to define the input heater voltage at which to run the sensor for the best performance, linearity, selectivity, and the effect of environmental humidity. A heater voltage of 7.5V, corresponding to a power of approximately 1 watt was selected for sensor operation. At this setting the sensor showed good sensitivity with good response and recovery times. It should be noted that at lower temperatures the sensor is more sensitive to H_2S, but the response time and particularly the recovery times suffer. The following figures present a typical response curve, linearity data, the effect of humidity on linearity, and selectivity. This data shows that the sensors have sufficient sensitivity and response time to detect the low levels of H_2S necessary for the sensor to be used in health and safety applications. The signal to noise ratio at 0.3 ppm H_2S (the lowest concentration tested) is over 100. It is seen that the effect of humidity is minor, especially at concentrations of 5 ppm and above. Finally, the sensor is adequately selective, with high levels of alcohol being a potential problem. Note that there is also a fairly significant response to NO_x, however it is in the opposite direction as the response to H_2S, and thus would not set off an alarm as the signal could be buried in the baseline of the electronics processing.

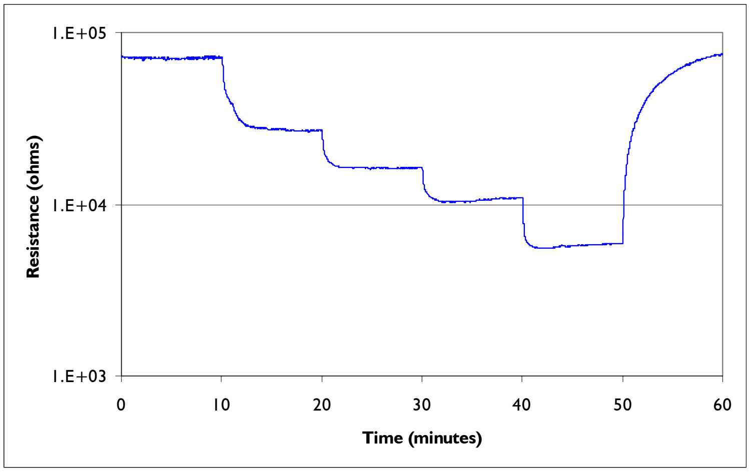


Figure 4: Typical response curve of multilayer sensor to 2, 5, 10, and 25 ppm H_2S with exposure to clean air at beginning and end of test.

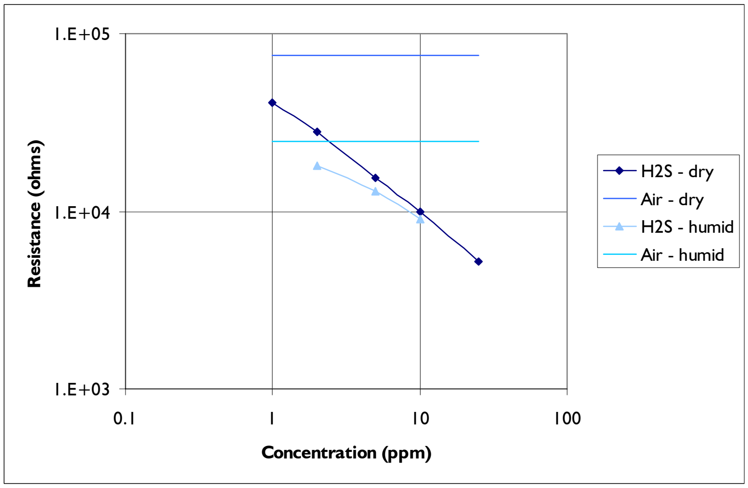


Figure 5: Linearity and humidity effect of multilayer H_2S sensors.

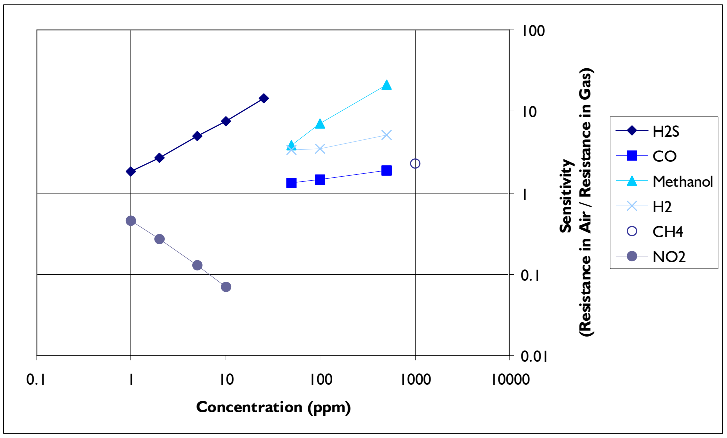


Figure 6: Selectivity of multilayer H_2S sensors.

Costing

In order to determine the manufacturing cost of multilayer metal oxide sensors, the cost of of materials, labor and overhead were evaluated. While many sensor elements (300 or more) can be produced in a single pad, there are other limiting steps in the production of the sensors. The two major limiting steps are the packaging of the sensor elements and the testing of the packaged sensors. Because of the time involved in these steps costing per sensor was calculated using a batch of 24 sensors as the basis. To produce 24 sensors it takes 9.1 hours of labor, the materials cost is $3.48, and assuming a 90% yield brings the total cost per sensor to $30.45. It is estimated that with modest improvements to the current capabilities available at Synkera that the per sensor cost could be reduced by $15 when sensors were produced in larger batches (100 sensors per batch).

Advantages/Disadvantages

The major advantage of the multilayer metal oxide sensor lies in the ability to produce sensor elements very inexpensively. Another proposed advantage was in the sensor to sensor reproducibility, as witnessed by multilayer capacitors produced using the same fabrication technique. Unfortunately, several things mitigate this potential advantage in practice. First is the fact that to achieve good sensitivity the sensor elements cannot be fired to full density. It is believed that the differences in microstructure that exist from part to part because of this porosity create sensor resistances that are somewhat variable. The second characteristic that causes the reproducibility to be less than expected is the fact that the sensors must be heated to operate. Inconsistencies in heater resistances and mounting of the sensor elements onto the heater substrate lead to additional sensor to sensor variations. Note that even though the desired consistency was not achieved through this fabrication method, the reproducibility is no worse than metal oxide sensors made by more traditional methods.

Without the major advantages expected from this fabrication technique, there are several significant disadvantages when compared to traditional methods that make this sensor unsuited for commercial applications. The most important is that the sensor is not very robust once packaged. This is due to the large mass of the multilayer sensor element and the stress that mass puts on the wires when physical shock occurs, causing one or more of the connections to break. A second disadvantage associated with the large mass of the sensor element is the need for relatively high power to heat the sensor. Traditional metal oxide sensors are not considered low power devices, and the multilayer sensor can draw an additional 33 to 50% power to be heated to the same operating temperature. Finally, though the cost to fabricate the sensors elements can be quite inexpensive, packaging the sensor element with a heater is labor intensive and actually makes a multilayer sensor more expensive to produce than a planar sensor.

The one situation where multilayer sensors could be competitive with other metal oxide sensors is in application in which the sensor element could be surface mounted and the heating of the sensor accomplished by the environment. In this case the robustness of the sensor would be excellent, the power consumption a non-issue and the cost very attractive.

3.1.3 Planar Metal Oxide Sensors

Fabrication

Planar sensors were prepared in the same manner as Synkera's other commercial metal oxide sensors. A screen-printable paste was prepared from the same milled WO_3 powder used for the multilayer sensors. To prepare this paste the powder was mixed with a commercially available screen-printing vehicle and then milled, on a three-roll mill, to make sure the paste was well mixed and to break up agglomerates in the powder. The substrates used for the sensors are 10 mil thick alumina that is 0.10″ x 0.10″ square. These substrates are patterned by an outside vendor to have gold electrodes for a heater element on one side and gold electrodes for the sensor element on the opposite side. Using a through-hole design the contact pads for both electrodes (4 pads total) are on the same side of the substrate. Having all contact pads on the same side makes packaging easier. These small substrates are produced in a 1″ square array of 100 elements and laser scribed so that many elements can be processed at the same time and then be singulated into the individual elements once complete. When the patterned substrates are received the heater is screen-printed, using a commercially available thermistor paste, and fired on a belt furnace to 850°C. After the heaters are prepared they are shipped out and the heater resistance is laser trimmed to 30Ω. This step brings all the heater resistance to within 0.5% of each other. This consistency in the heater resistance allows for more consistent sensor to sensor heating and thus more consistent sensor performance. After the heater is trimmed the WO_3 paste is screen-printed over the sensor electrodes and dried at 150°C. The sensor elements are then singulated.

The sensor elements are packaged into commercially available TO-39 headers using 10 x 1 mil gold ribbon. Short sections of ribbon are resistance welded onto each of the four contact pads, and then the wired element is resistance welded to the header. The mounted sensor is then covered with a cap that has a hole covered by a stainless steel mesh to protect the sensor from debris, but still allow gas to flow freely to the sensor element. Finally, the sensor is fired to an elevated temperature using the resistive heater. The planar H_2S sensors are fired at 9.0V for 15 minutes. Figure 1 shows both capped and uncapped planar sensors.

Figure 7: Capped and uncapped planar sensors.

Data

The testing conducted on the planar sensors was very similar to the testing on the multilayer sensors. The first step was to look at operating power/temperature, to define the input heater voltage at which to run the sensor for the best performance, linearity, selectivity, and the effect of environmental humidity. A heater voltage of 7.0V, corresponding to a power of approximately 900 mW, was selected for sensor operation. Although the power is lower than the multilayer sensor, the operating temperature is probably very similar due to the differences in the mass of the sensor element type. Like the multilayer sensors, at lower temperatures the planar sensor is more sensitive to H_2S, but the response time and particularly the recovery times suffer. The following figures present response curves, linearity data, the effect of humidity on response, selectivity, and long-term stability data. It is seen that the sensors have sufficient sensitivity and response time to detect the low levels of H_2S necessary for the sensor to be used in health and safety applications. It has been shown that the effect of humidity is quite low. The worst shift is seen between air with no water vapor (from a cylinder) to air with any level of humidity. Once water vapor is present the shift with changing levels is minor. Finally, the sensor is adequately selective, with high levels of organics being a potential problem. As with the multilayer sensor there is also a fairly significant response to NO_x in the opposite direction. Temperature testing of the sensors (from -40° to 60°C) has shown that the sensor responds over a wide range of environmental temperatures. However, our work has indicated that it is advantageous to implement some sort of temperature control over the sensing element, in order to obtain a more consistent response.

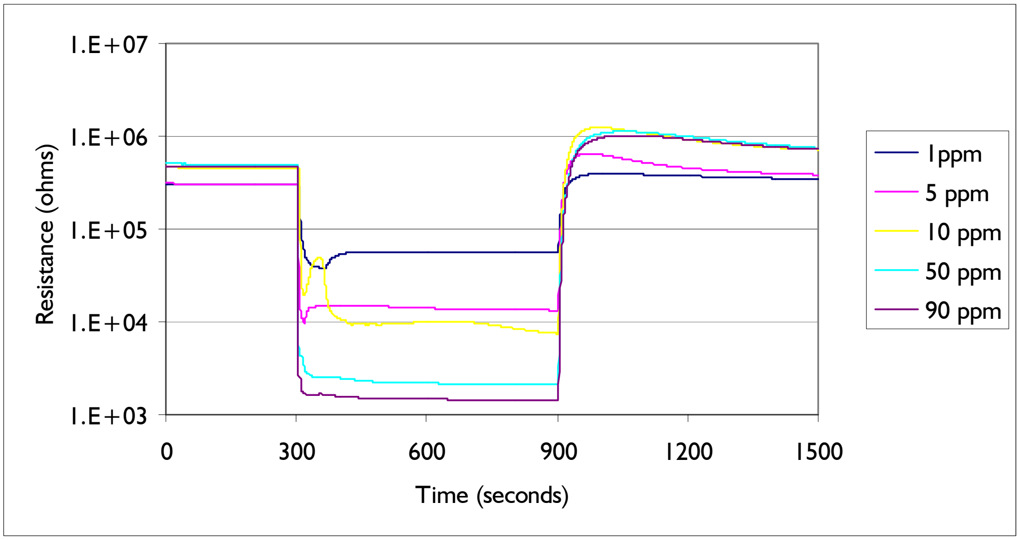


Figure 8: Response curves for planar H_2S sensors.

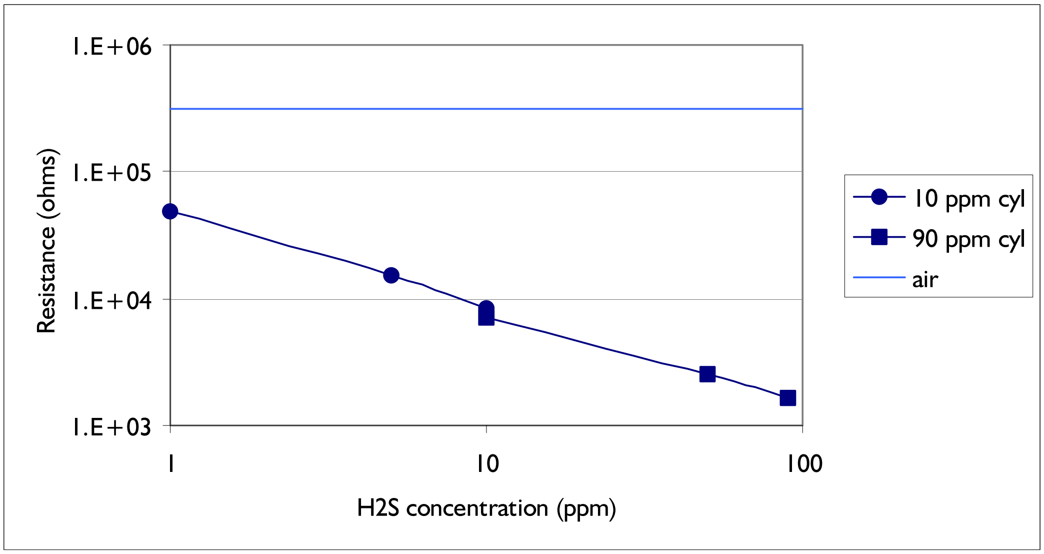


Figure 9: Linearity of planar H_2S sensors. Note use of two different cylinders to cover range.

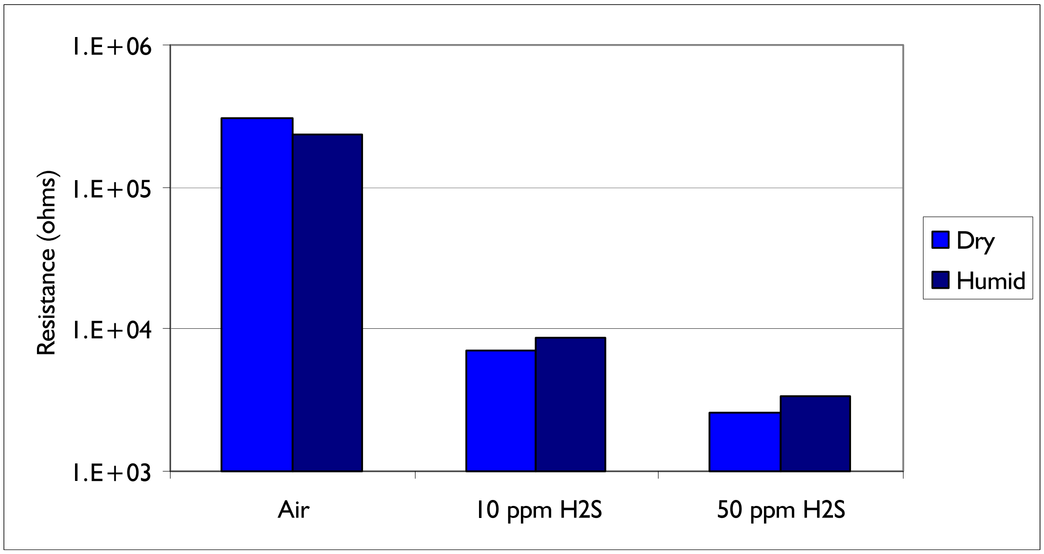


Figure 10: Planar H_2S sensor dependence on humidity.

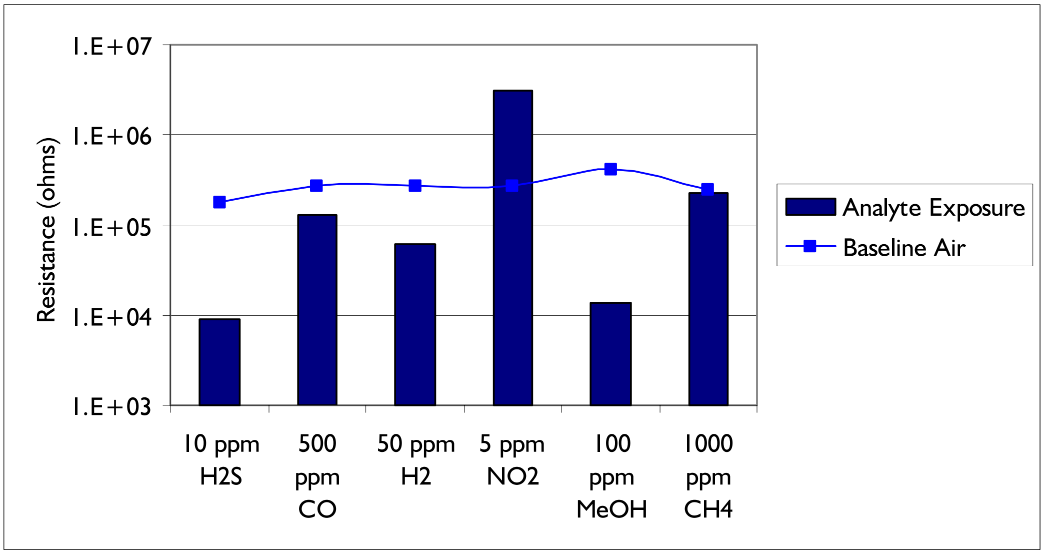


Figure 11: Selectivity of planar H_2S sensors to various interferent gases.

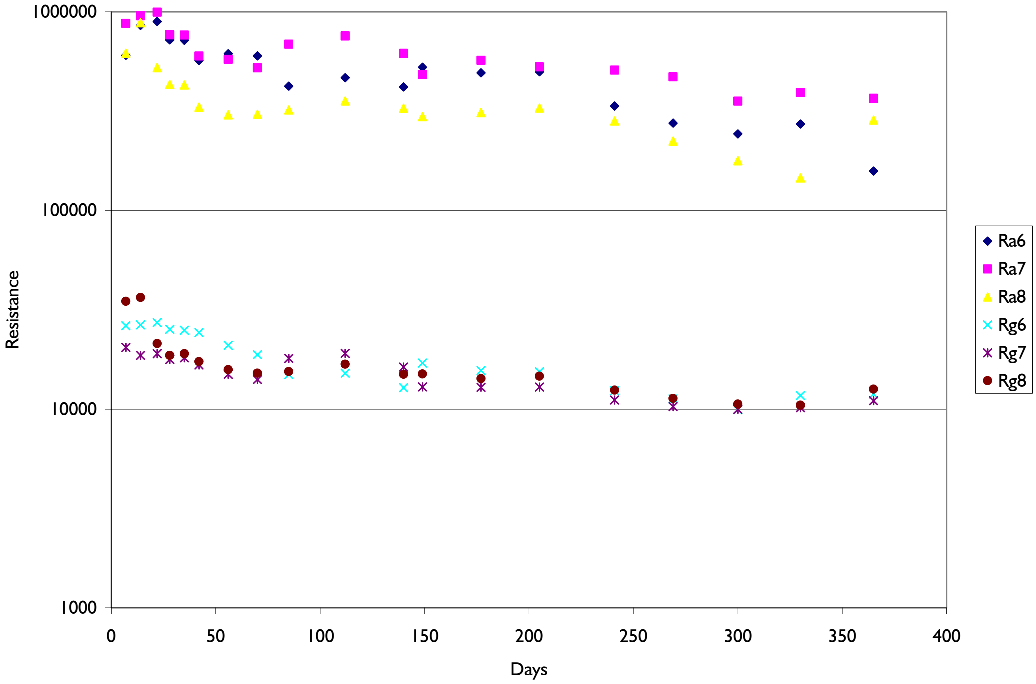


Figure 12: Long-term test data for three planar H_2S sensors.

Costing

The cost of producing planar sensors, taking into account labor, materials and overhead, has been calculated. Like multilayer sensors, many sensor elements can be produced, via screen-printing, very quickly, but the two limiting steps in production are packaging and testing. Because of the time involved in these steps costing per sensor was calculated using a batch of 24 sensors as the basis. To produce 24 sensors it takes 8.2 hours of labor, the materials cost is $3.28, and assuming a 90% yield brings the total cost per sensor to $28.37. It is estimated that with modest improvements to the current capabilities available at Synkera, the per sensor cost could be reduced by approximately $20 when sensors were produced in larger batches (100 sensors per batch). Note that in reasonable quantities (50 or fewer sensors) Synkera now sells planar sensors for $45 each, with appropriate price reductions for larger quantities.

Advantages/Disadvantages

The advantages of the planar metal oxide H_2S sensor include the fact that the sensor is considerably more robust than the multilayer geometry and easily withstands moderate physical abuse. Also, the geometry allows for more even heating of the entire sensing material, potentially leading to more consistent sensor response. In addition, the manufacturing costs are several dollars less than the multilayer sensor. Finally, from a manufacturing standpoint at Synkera, the planar geometry fits right in with our line of traditional metal oxide sensors, meaning there was no need to invest in additional capital equipment in order to add the H_2S sensor to our product line for small scale manufacturing (up to 5,000 units per year).

The biggest disadvantage of the planar sensor is its high power consumption. The required heater power of ~900 mW means that the sensor cannot be used effectively in portable applications. However, the sensor is easily integrated into fixed instruments, and several sensor instrument companies have done, or are doing so (see section 4.1). These companies include: Detector Electronics (Minneapolis, MN), Scott Instruments (Monroe, NC), and Net-Safety Monitoring (Calgary, AB). The primary use of these instruments is in the gas & oil industry in locations where traditional electrochemical sensors do not perform well (very high or low temperatures, and very low and high humidity). In addition to the performance at extreme environmental conditions, Synkera's planar, metal oxide sensor does not show "go to sleep" behavior, where other metal oxide sensors on the market do. "Go to sleep" behavior is when, after long periods of operation without being exposed to H_2S, there is a significant response delay when H_2S becomes present.

3.1.4 Metal Oxide Microsensors

Fabrication

Synkera uses proprietary procedures to micromachine anodic aluminum oxide (AAO) into microsensor platforms. AAO is an ideal sensor substrate material due to its high aspect ratio nanopores, secondary porosity, and ability to be micromachined into useful structures. Since miniaturization of sensor design is enabled through advances in MEMS technologies, great benefits can be realized. However, difficulties with micromachining of traditional materials (silicon) and less than desirable materials properties (such as a limited upper temperature range) have prohibited their widespread application to gas sensing. The ceramic micromachining of anodic alumina utilized by Synkera produces microsensors on a monolithic ceramic substrate with superior thermal, chemical and mechanical stability compared to conventional approaches to MEMS sensors.

Synthesis of nanoporous AAO requires high-purity (at least 99.99%) aluminum. The temper, texture, surface quality and flatness of the raw aluminum foil all have a significant influence on the long-range pore order, pore diameter distribution, mechanical properties of the resulting alumina film and its ability to withstand thermal shocks without cracking. Fabrication of planar, homogeneously structured and defect-free alumina films, suitable for high-yield micromachining of anodic alumina that can withstand annealing and provide robust sensor substrates requires special preparation of aluminum foil. Commercially available foil (Beckromal, 99.99%, 200 μm thick) is processed via proprietary procedures involving rolling and pressure annealing to the Tamman temperature (2/3 of melting point in Kelvin), followed by electrochemical removal of 10-20 μm of aluminum from the surface.

Sensor substrates are then produced using localized anodization. The basic processing sequence includes the following steps: (1) creating a thin adhesion layer of AAO (0.5 μm) on the Al surface; (2) spin-coating, pre-baking, exposing, developing and baking photoresist to create desired pattern; (3) anodizing the exposed Al foil to the required thickness and pore morphology; (4) applying proprietary electrochemical techniques to open the barrier layer; (5) striping the photoresist, and selectively etching the aluminum to release individual sensor substrates; (6) thoroughly rinsing and drying the sensor substrates.

Microheater platforms are produced by first performing localized anodization using an intermediate photoresist mask that exposes only the sensing element. The resulting oxide is then etched away, forming the required relief. The substrate is then masked with a conventional mask, and anodization is carried out to produce the full thickness of the sensing element.

Anodization of patterned aluminum foil is performed using a computer-controlled setup that includes a power supply, recirculating chillers, and anodization baths. A flexible LabView interface is used to control the processing variables and to collect the process data. The electrolyte composition, temperature, and anodization voltage are chosen depending on the required morphology of anodic alumina. The thickness of the films is controlled by the charge density, and pore diameter is controlled by anodization voltage and electrolyte composition. An image of a microsensor platform is shown in Figure 13.

Figure 13: Microsensor platform prior to electrode deposition.

Platinum is used to form the microsensor heating element, and is well suited for most applications. In a standard microheater design, thin platinum films are sputtered through a shadow mask. Sensing electrodes are deposited onto the opposite side of the sensing element.

Figure 14: Uncapped microsensor.

Once electroded the microheaters are packaged on commercial TO-39 headers in order to take advantage of the rapid heating and temperature cycling uniquely available as a function of the microheater geometry. The microheater substrates are fabricated with mounting holes in the corners, which slip over the pins of the TO-39 headers. The substrate is oriented sensor electrode side up. Then electrical and mechanical connections are made with conductive epoxy. After mounting the elements the platinum film used for the heater is thermally treated in order to densify the film. To do this current is passed through the heater and the element is heated to ~650°C.

Finally, the sensing film is applied to the sensor. The same screen-printing paste used for the planar sensor is brushed in a relatively thin film across the sensor electrodes. The film is then dried at 150°C before it is fired, using the microheater, to approximately 500°C. A picture of a mounted microsensor is seen in Figure 14. As with the multilayer and planar sensors, the microsensors are capped prior to testing.

Data

The testing conducted on the microsensors was the same as testing on the multilayer sensors. The first step was to look at operating power/temperature, to define the input heater voltage at which to run the sensor for the best performance, linearity, selectivity, and the effect of environmental humidity. A heater voltage of 2.3V, corresponding to a power of approximately 250 mW was selected for sensor operation. This is a significantly lower power consumption than either the multilayer or planar sensor configurations. This is due to the considerably lower mass of the sensor element type. The following figures present response curves, linearity data, the effect of humidity on response, and selectivity. It has been shown that the sensors have sufficient sensitivity and response time to detect the low levels of H_2S necessary for the sensor to be used in health and safety applications. The effect of humidity is greater than the planar sensors. This is possibly due to the AAO affinity for water vapor (Synkera offers a humidity sensor that utilizes AAO). Finally, the sensor is somewhat less selective to potential interferents than is the planar sensor. This is likely due to a slightly different operating temperature. It is expected that with further work that the cross-sensitivity of the microsensor can be reduced.

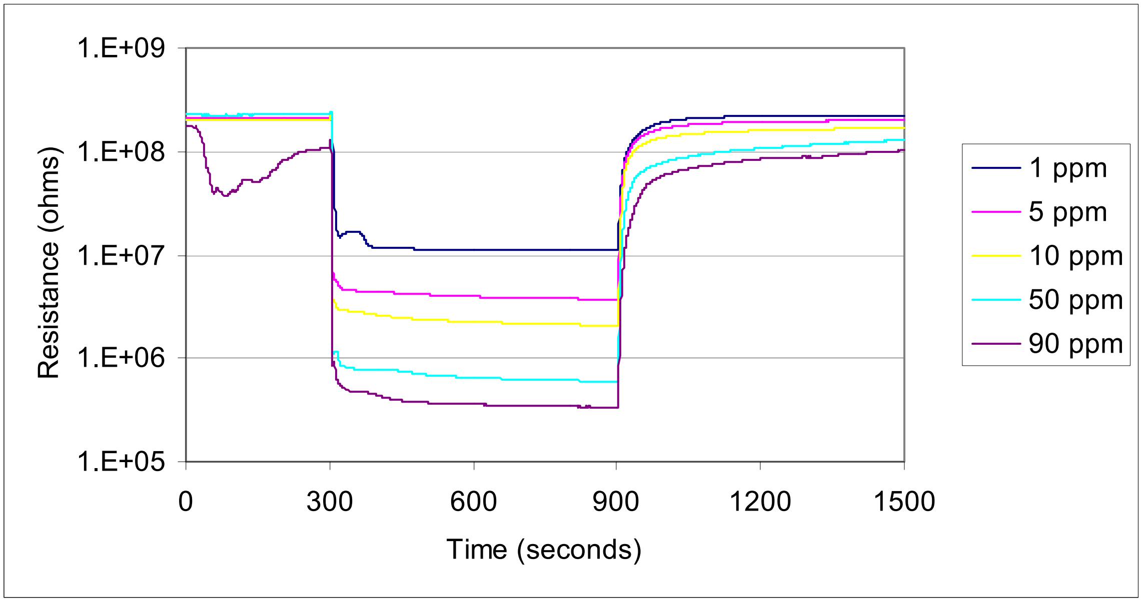


Figure 15: Response curves for micro-H_2S sensors.

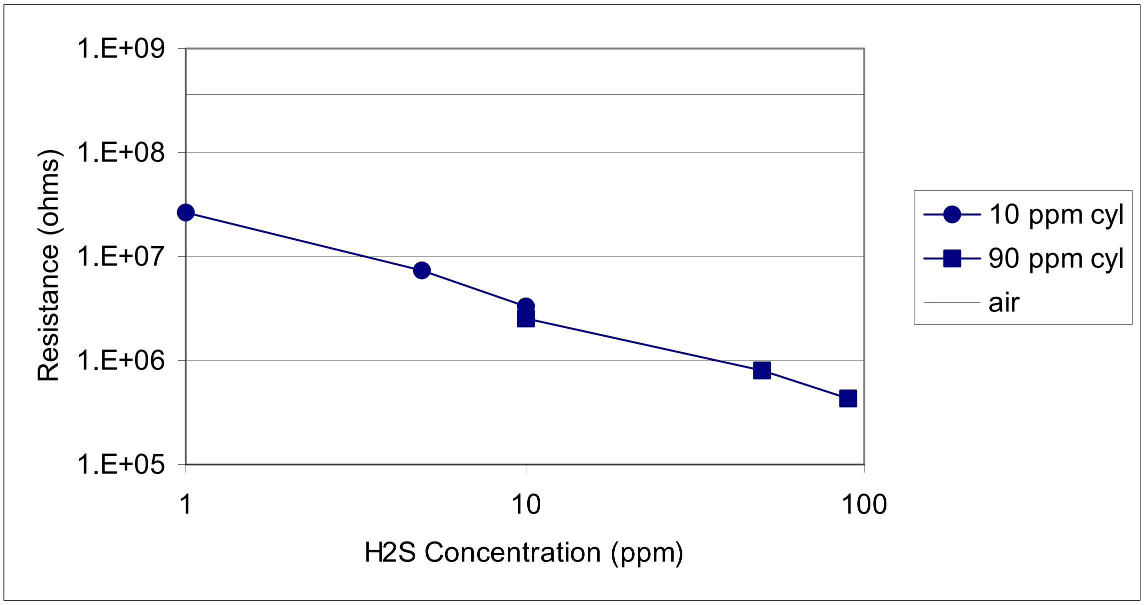


Figure 16: Linearity of micro-H_2S sensors. Note use of two different cylinders to cover range.

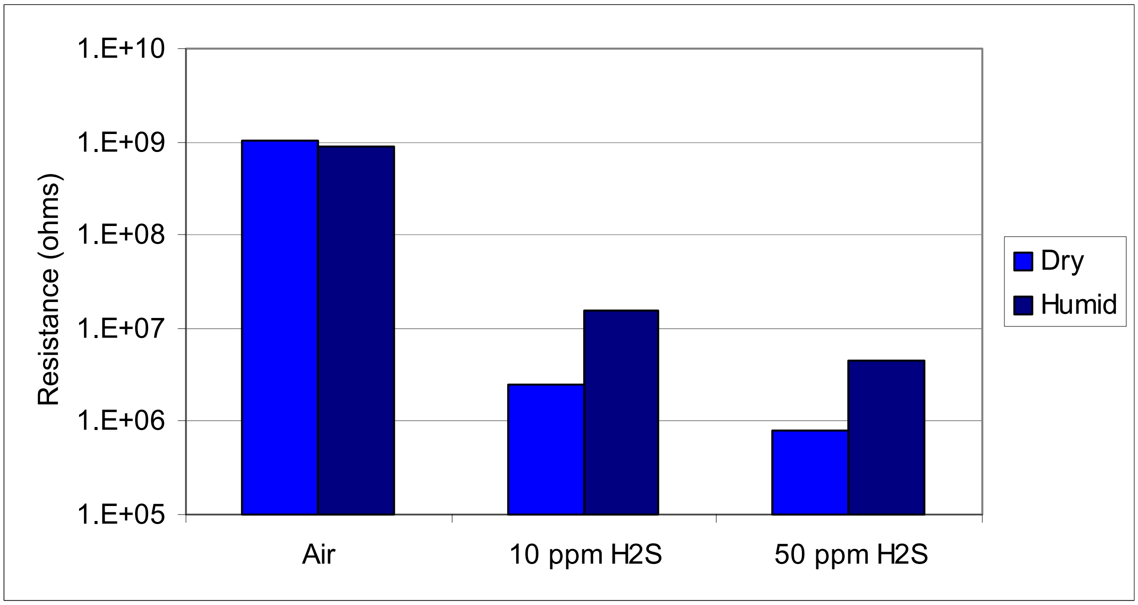


Figure 17: Micro-H_2S sensor dependence on humidity.

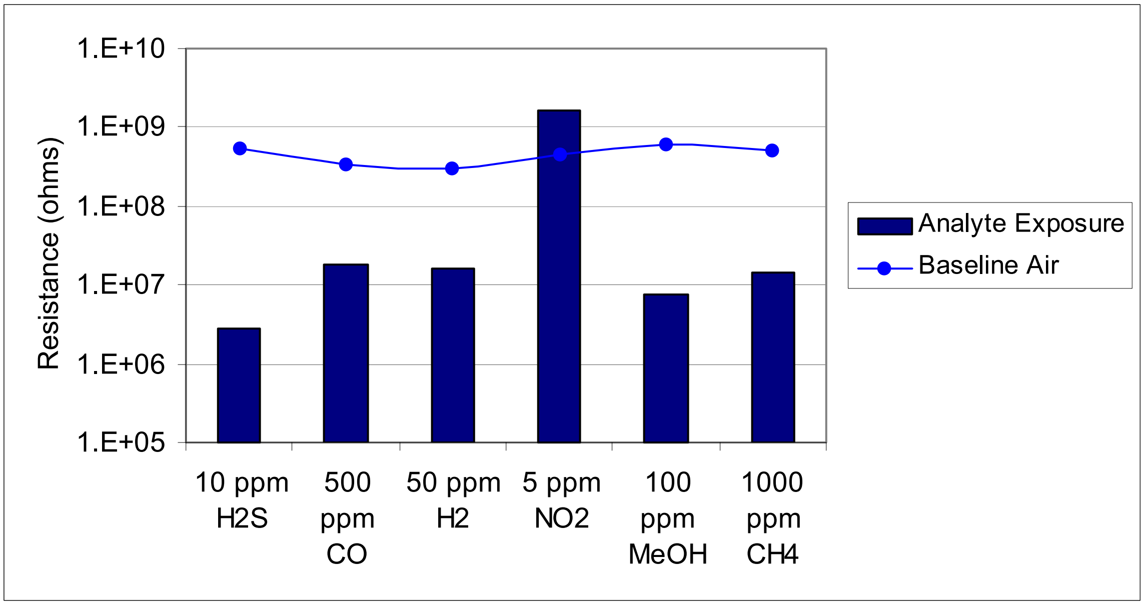


Figure 18: Selectivity of micro-H_2S sensors to various interferent gases.

Costing

Our current cost to produce microsensors was determined taking into account materials cost, labor, and overhead. In the R&D stage we are currently at with this technology the two main limiting steps are the electroding of the platform and the conditioning of the heater. As with multilayer and planar sensors, testing is also somewhat of a bottleneck. Because of the time involved in these steps costing per sensor was calculated using a batch of 24 sensors as the basis. To produce 24 sensors it takes 13 hours of labor, the materials cost is $2.94, and assuming a 90% yield brings the total cost per sensor to $18.23 in direct costs. This translates to $48.61 when overhead is accounted for. It is estimated that with modest improvements to the current capabilities available at Synkera, the per sensor cost could be reduced to $20 or less when sensors were produced in somewhat larger batches (81 sensors per batch). To reach this price would require improvements in sputtering and conditioning processes, along with expansion of Synkera's testing capabilities.

Advantages/Disadvantages

The biggest advantage of the H_2S microsensor over the planar metal oxide H_2S sensor is that with the current design the heater power consumption is approximately 25% of the planar design (or 225 mW). Synkera has shown that with smaller designs the microsensor power can be reduced even further. It is expected that this can be accomplished without affecting the performance of the sensor. This substantial reduction in power makes the microsensor suitable for some portable applications. In addition, implementation of power cycling schemes could reduce the power consumption by an additional 75% or more.

The biggest disadvantage of the microsensor stems from the point in development we are currently at. In the current R&D stage the cost of manufacture is high, and the sensor-to-sensor reproducibility is not as good as for the other two types of sensors (due to the hand application of the sensor film and the inability to trim the heaters to within 1%). However, we believe that with further development this, and other metal oxide microsensors, will be an important part of our product line. We are currently in discussion Net-Safety Monitor regarding funding for the development of H_2S microsensors for use in their permanent instruments. In addition, Synkera has recently been awarded several SBIR Phase I grants for sensor developments that are centered on the microsensor platform.

3.2 SOLID POLYMER ELECTROLYTE ELECTROCHEMICAL SENSORS

During the Phase II Synkera began developing solid-state electrochemical sensors through other funding. Because of the potential applicability of this technology to H_2S detection we looked at the development of a H_2S sensor for personal monitoring applications. Such a sensor is ideal for this application as it can be produced, in volume, at a very low price and it requires essentially no power to operate. A solid-state H_2S electrochemical sensor was successfully developed, and a design for a "*Smart H_2S Card*" personal monitor, built around this sensor, has been prototyped and tested. Below is general information regarding this type of sensor.

Background

Synkera's work with solid-state electrochemical sensors builds upon the current commercial success of electrochemical sensors and recent technology developments to create a next generation product that is significantly smaller, faster, more sensitive, stable and lower cost than anything available today. There are four unique aspects to this innovation: integration of a solid polymer electrolyte for leak-free, stable operation; the use of micro-band electrodes for increased sensitivity; novel manufacturing techniques for low cost, reproducible mass production in a novel architecture; and integration of the sensor directly into the electronic operating circuit.

Figure 19 shows the orientation of the microelectrodes in a chip made of solid polymer electrolyte (SPE). End terminations are used to provide electrical connections. This is similar to the multilayer metal oxide sensors described above.

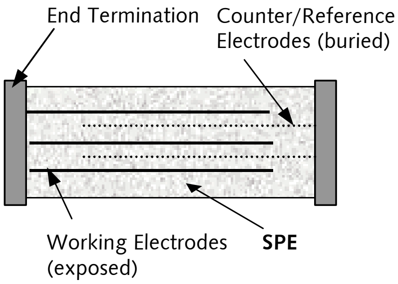


Figure 19: "SPE Sandwich Sensor"- Electrode layers are embedded in SPE.

Solid Polymer Electrolyte and Microband Electrodes

Commercial fuel cell sensors use liquid electrolytes (often sulfuric acid), and are widely known in the sensor industry to suffer from electrolyte leaks under certain conditions. Indeed, the need to make electrical connections and allow gas into the sensor inevitably creates several opportunities for leak paths to develop. Additionally, because sulfuric acid is hygroscopic, the volume of the electrolyte changes with relative humidity, leading to changes in the sensitivity of the sensor response. The best solution to this problem is to use a solid electrolyte, an area that is being increasingly addressed in the literature. During Phase II we investigated the performance of several variations on nanocomposite solid polymer electrolytes (SPE) with our microband electrodes. The materials were based upon polyethylene oxide (PEO) combined with appropriate inorganic supporting electrolyte (e.g. $LiClO_4$). These polymer electrolytes were modified with nanostructured inorganic materials, such as alumina or titania, to form composites for optimum conductivity, stability and sensor performance. The use of an all-solid state sensor based on SPE eliminates the need for a separate membrane to contain the liquid electrolyte, thus enhancing response times.

The significant advantages of using ultra-microelectrodes for electrochemical analysis have been recognized for many years. Ultra-microelectrodes are generally defined as electrodes where at least one dimension is on the micron scale. The advantages of these electrodes include increased temporal resolution (fast response), an ability to operate in less conductive electrolytes, and higher signal to noise ratios due to an increase of faradaic currents relative to non-faradaic currents. Ultra-microelectrodes can take the form of disks, cylinders or bands and have commonly been prepared by sealing fine wires in glass tubes or by photolithography, both relatively expensive techniques. Arrays of microelectrodes are commonly formed via photolithography techniques, leading to an increase in current output. Ultra-microelectrodes with a band geometry, such as those used by Synkera, are highly desirable because they are small in only one dimension. Increasing the length of the microband electrode increases the current flow, leading to higher and more easily measured currents.

Ultra-microelectrodes are a widely used tool for laboratory based electroanalytical chemistry. These electrodes have not yet been commercialized as gas sensors, largely due to the high cost of traditional ultra-microelectrode manufacturing techniques. The creation of high-quality arrays of microband electrodes using standard mass manufacturing techniques allows for the production of innovative, next-generation gas sensors at very low costs. In this innovation, the micro-band electrodes enable increased sensitivity and the use of less conductive electrolytes, such as the polymers investigated.

Multi-layer processing

Synkera's solid-state electrochemical sensors have been built using multilayer processing, similar to the multilayer metal oxide sensors, but modified for the polymer materials of interest. The novel architecture allows for the production of low-cost, highly reproducible sensors that take advantage of the potential for the fabrication of microelectrodes. Overall, the multilayer manufacturing techniques enable the production of high quality, micro-band electrodes and lead to very low cost, miniature, reliable and reproducible solid-state amperometric sensors.

The polymer electrolyte is cast in thin sheets and is used as the support material between the electrodes (instead of the ceramic tape for the metal oxide multilayer sensors). Gold and platinum electrodes are printed on some of the sheets, and then a "pad" is built via the successive lamination of individual sheets. Sensor preparation is completed by dicing the pad into individual components to expose the working electrode edges, while the counter/reference electrodes are buried within the SPE body.

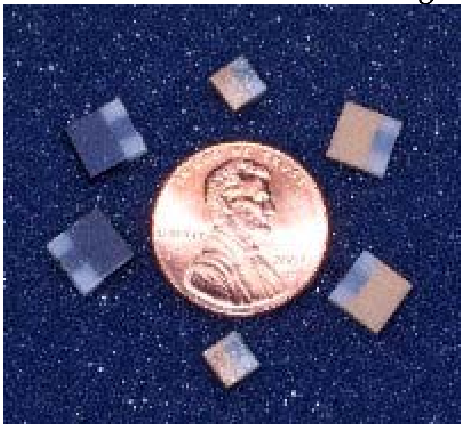


Figure 20: Synkera's solid –state amperometric sensors

Integration of sensor into electronic circuitry

Another unique feature of the solid-state electrochemical sensors produced by Synkera using multilayer fabrication methods is that the geometry of these devices is such that they can be directly mounted to a circuit board, simplifying requirements for packaging, and greatly reducing module cost. Several sensor sizes and materials combinations are depicted in Figure 20.

Fabrication

As discussed in the earlier section on metal oxide sensors, multilayer processing involves the production of chip-style devices with an internal electrode structure. These components are typically produced using a tape casting process in which thin sheets of ceramic material are cast using a doctor blade. Screen printing is then used to deposit the internal electrodes, and the multilayer structure is built by stacking and laminating individual sheets to form a "pad" of the desired thickness. To produce solid polymer electrolyte electrochemical sensors we replaced the ceramic materials with polymeric ones and in doing so found it necessary to alter several of the fabrication steps.

Preparation of a "slip" is the first step in the fabrication process, and involves combining the polymeric materials and electrolyte salts with organic solvents. The casting and laminating process requires materials that can be uniformly cast into a thin film. The slip is cast onto mylar between two shims (0.020" thick), being spread out under a second sheet of mylar. Once cast, the top sheet of mylar is removed and the tape is allowed to dry. Because the cast material will ultimately form the electrolyte of the sensor, the mechanical and electrical properties resulting from the preparation process are critical for good sensor performance. As an example, the degree of crystallinity in the polymer is correlated with ionic conductivity in the finished material. Thus, inert nanostructured ceramic materials (e.g. alumina) may be used to reduce the crystallinity and improve the ionic conductivity while simultaneously improving the processing properties of the cast polymer films. The anion(s) incorporated into the polymer electrolyte affect sensor processing and performance and were also explored. The primary electrolyte salt used was lithium perchlorate, with other anions such as triflate, tetrafluoroborate, and chloride considered.

Once dry, the tape is cut into squares and pressed, using high pressure, onto a paper backing. This paper backing allows for the layers to be processed using the standard multilayer processing equipment available at Synkera.

Next is the screen-printing step where the appropriate electrodes are printed on to the polymeric tape. Custom inks of platinum and gold, using high surface area starting materials, were prepared. The gold was used for the working electrode and the platinum was used for the counter/pseudo reference electrode. The specific formulation of the inks used has an important impact on sensor performance. The formation of “triple points” of working electrode (solid phase), electrolyte (solid phase) and analyte (gas phase) are the key to good sensor performance, and as such the interface between the micro-band electrodes and the electrolyte are critical. Commercial high surface area precious metal powders were combined with water and a small amount of the electrolyte material to produce a screen printable paste. The electrolyte material was added in order to enhance the formation of triple points, without hindering the conductivity of the electrode.

After the electrodes are applied to the appropriate layers, the multilayer structure is built up through a process call stacking and tacking. In this process the various layers are stuck together under slightly elevated temperature (~40°C) and pressure (~60 psi). Then, after all the layers are stacked together, the monolithic pad that has been formed undergoes a lamination process in which it is exposed to considerably higher pressure (2000 psi) to ensure that defects between the layers are eliminated. This is particularly important with the incorporation of electrodes, which lead to localized areas of poor adhesion between adjoining layers.

Once the multilayer lay-up is complete, the pad is diced into a large number of individual components. We produced two sizes of parts, 0.25″x 0.25″ squares and 0.175″x 0.175″ squares. The electrode patterns are defined so that upon dicing, the appropriate electrode faces and terminations are exposed for gas detection and further processing. An example of the electrochemical sensor elements are shown in Figure 21.

Figure 21: Electrochemical sensor elements.

The sensor elements were then packaged for testing. Available TO headers were used. Two of the four upset pins were clipped, providing contacts for the working and counter/reference electrodes on opposite sides of the header. The termination side of each electrode was terminated with silver powder, mixed with water. The element was then mounted to the header using epoxy, the upset pins were pressed against the termination, to create electrical contact, and then this connection was reinforced using conductive silver epoxy. A cap was then placed over the senor and cemented down. The cap serves two purposes; to protect the sensor element and to limit diffusion of H_2S to the sensor element. Diffusion limiting is important as it extends the upper detection range by preventing the sensor from becoming saturated

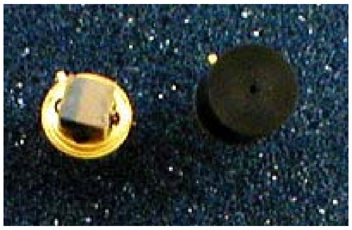


Figure 22: Uncapped and capped electrochemical sensors.

with gas. An uncapped sensor along side a capped sensor is shown in Figure 22.

Testing Description

For the testing of the electrochemical sensors we utilized a simple but effective control circuit that had been previously designed. The circuit is based on the classic potentiometric control circuit shown in Figure 23. For the solid-state electrochemical sensors being developed, the voltage at V_{CTRL} works in conjunction with the reference electrode R to keep a fixed potential between the counter electrode C and the working electrode W. (Note that owing to small currents we largely used a combined counter-pseudo-reference electrode.)

V_{out} is proportional to the current through the cell, and can be ranged via selection of R_M. This circuit had been previously implemented at Synkera in a two-electrode fixed potential solid-state sensor transducer, and was shown to be stable and reliable for current measurements as low as 50 pA. This potentiostatic control circuit was built into sensor test boards and interfaced with Labview programming to allow testing of multiple (up to 8) sensors simultaneously for statistical evaluation.

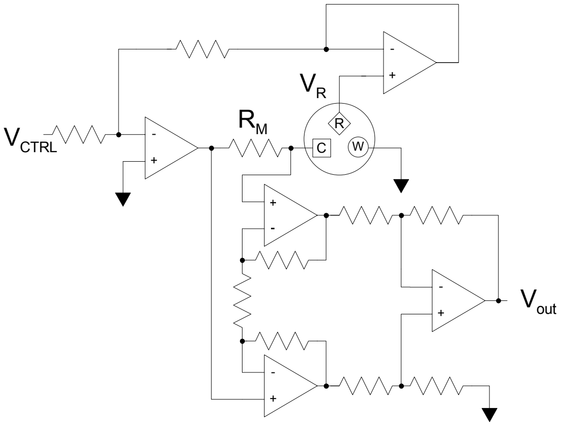


Figure 23: Potentiostatic control circuit

Sensors were characterized in order to establish the sensitivity, repeatability, response time, detection limit, linearity, dynamic range, selectivity and humidity and temperature dependence. Additionally, several sensors have been tested for their long-term stability.

The following definitions apply testing:

Sensitivity: The sensitivity is calculated as the current flow divided by the concentration of the challenge gas.

$$Sensitivity = \frac{i}{C}$$

where i is the current in μA and C is the concentration of challenge gas applied in ppm

Selectivity: The selectivity is a comparison of the sensitivity of an individual sensor to two different vapor species.

$$Selectivity = \frac{Sensitivity_A}{Sensitivity_B}$$

Detection Limit: The lowest concentration of vapor species that the sensor can reliably detect at a signal greater than three times the noise level.

Response Time: The response time is the time it takes for the sensor to detect a change in the surrounding environment. It is usually determined as the time required to reach 90% of the eventual peak current (i_{max}).

Recovery Time: The recovery time is the time it takes for the sensor to return to its base current after exposure to a challenge gas. It is defined as the time required to fall below 10% of the peak current.

The following tests were carried out on the solid-state electrochemical sensors:

Sensitivity: The sensitivity of the sensors was determined by exposing them to a wide range of H_2S concentrations, from <1 ppm to 100 ppm.

Repeatability: The repeatability of the sensors was examined by exposing them to the same gas concentration at multiple times.

Response and recovery time: The response and recovery times as described above were calculated for each gas exposure.

Selectivity: Selectivity to the challenge gas of interest is an important feature in nearly all sensor applications, fortunately, electrochemical sensors are generally considered inherently selective in most applications. The careful selection of electrode material and operating potential influence the selectivity of the sensors. The challenge gases evaluated for the selectivity included: hydrogen, carbon monoxide, various VOCs, NO_x, ammonia, and sulfur dioxide.

Response to humidity: The effect of humidity on sensor performance was studied. Short-term effects were looked at by introducing air containing water vapor at levels corresponding to approximately 15%, 50% and 90% relative humidity as challenge gases. In addition, the sensor response to target gases was also examined in a humid gas stream to determine the effect of environmental humidity on sensitivity.

The results of humidity tests are extremely important, as some polymeric electrolytes (i.e. Nafion) are known to change conductivity as a function of water content. However, results have shown that the conductivity of PEO based electrolytes is largely unaffected by water vapor, and the use of ultra-microelectrodes is less demanding of highly conducting electrolytes.

Response to temperature: The response of the sensors to the effects of environmental temperature were be studied. Short-term effects of temperature were studied by operating the sensors over the range of -20°C to +50°C and exposing them to challenge gases.

Data

The following figures present response curves, linearity data, the effect of humidity on response, and selectivity. It is seen that the sensors have sufficient sensitivity and response time to detect the low levels of H_2S necessary for the sensor to be used in health and safety applications. Responses to less than 1 ppm of H_2S were observed. The effect of humidity is fairly minor, particularly compared to traditional electrochemical sensors and SPE sensors that utilize Nafion as part of the electrolyte. The selectivity is very good when tested for gases potentially present in the expected application. Although not shown, it was seen that the sensor performance over the range of -20° to 50°C was good. However, below -20°C it seems that the electrolyte suffers from very low ionic conductivity and does not perform well. Finally, SPE electrochemical sensors have been operated in a laboratory environment for over a year and the sensors continue to function.

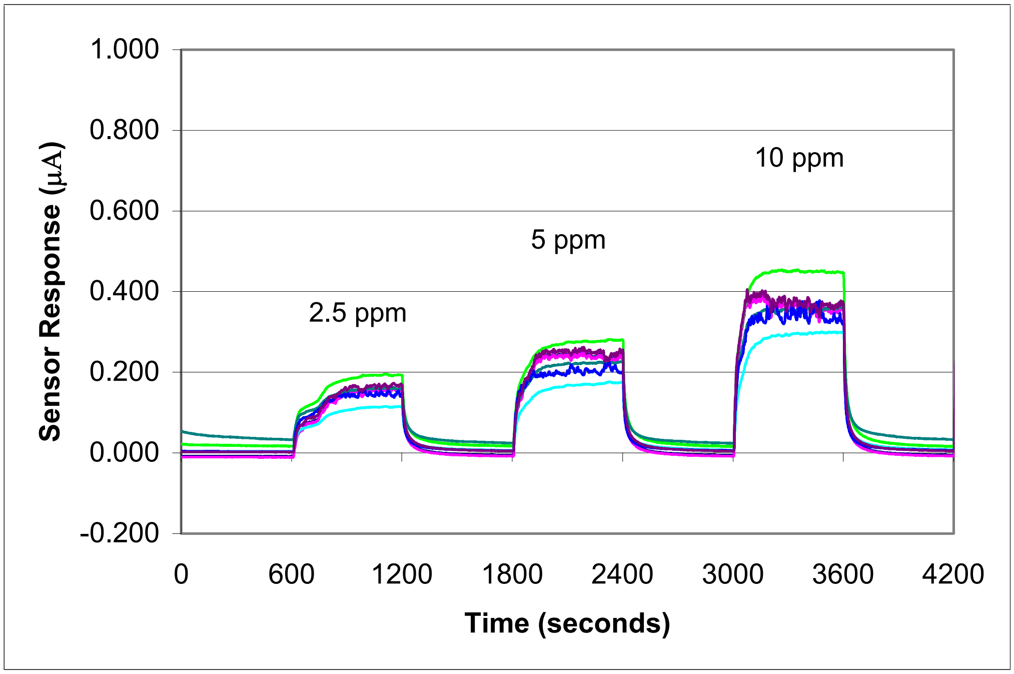


Figure 24: Electrochemical H_2S sensor response to varying gas concentrations.

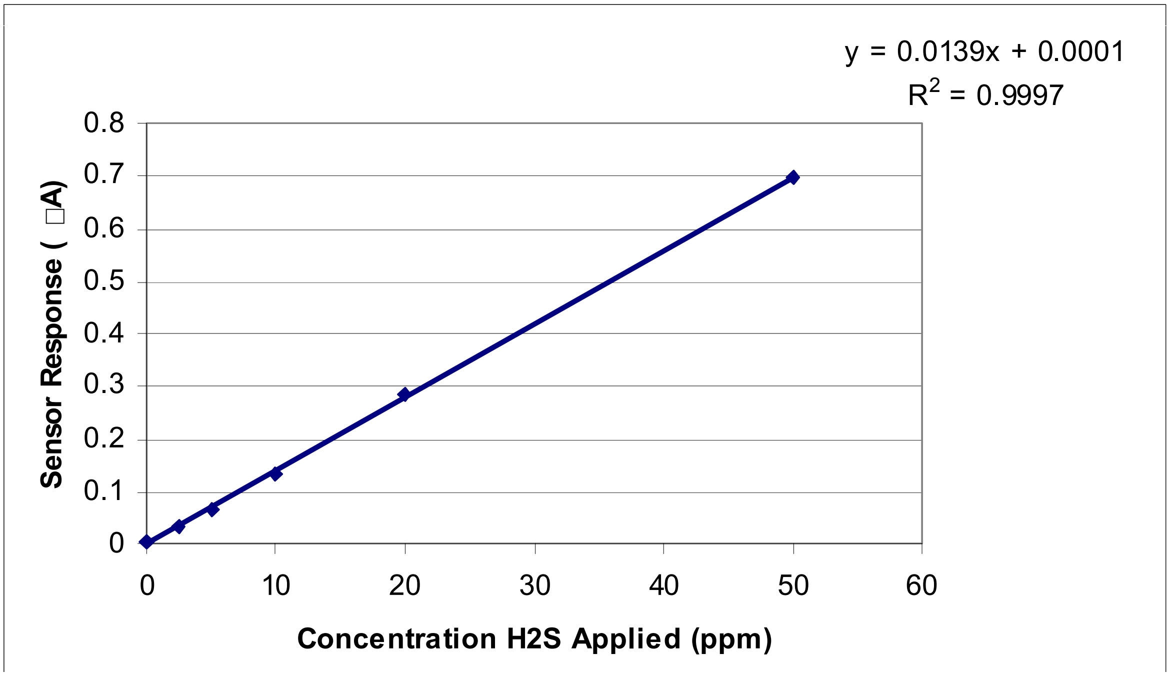


Figure 26: Linearity of electrochemical H_2S sensor.

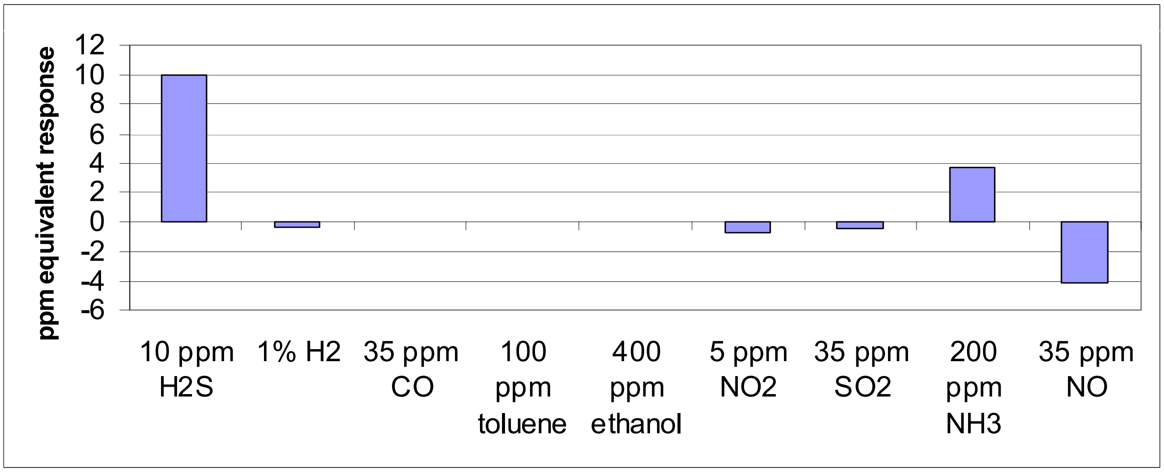


Figure 28: Selectivity of electrochemical H_2S sensor.

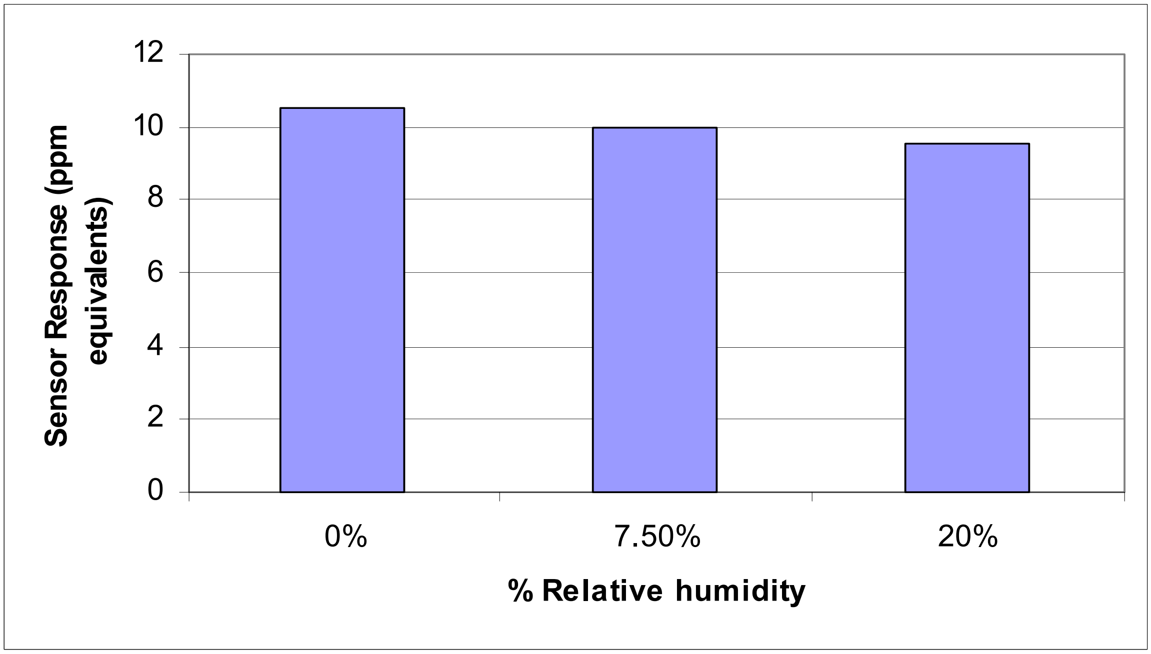


Figure 30: Humidity performance of electrochemical H_2S sensor.

Costing

The cost of producing solid-state electrochemical sensors, taking into account labor, materials and overhead, has been calculated. Like the metal oxide sensors, many sensor elements can be produced, via multilayer processing, very quickly, but the two limiting steps in production are packaging and testing. Because of the time involved in these steps costing per sensor was calculated using a batch of 20 sensors as the basis. To produce 20 sensors it takes 6.5 hours of labor, the materials cost is $6.35, and assuming a 90% yield brings the total cost per sensor to $30.82. This is for packaged sensors, not just the sensor elements as would be appropriate if they were packaged directly with the electronics. In small lots the element cost is about $22. It is estimated that with improvements necessary to produce the numbers of sensor elements for personal monitoring devices they can be produce for $3.10 per element. This is for quantities of 20,000 sensors, which is not an unreasonable lot size based on our market research.

Advantages/Disadvantages

The primary advantage of the SPE electrochemical H_2S sensor when compared to the metal oxide sensors is that it operates using essentially no power. This makes this type of sensor applicable to portable and personal monitors. When compared to traditional electrochemical sensors that utilize liquid electrolytes the SPE sensor has significant advantages in performance over a wide range of environmental humidity, its small size, low cost, and the fact that the electrolyte cannot evaporate or leak (which leads to changing performance over time). These advantages make it possible to incorporate this sensor into small, inexpensive personal monitors. The methods employed to fabricate the SPE electrochemical sensors are very amenable to mass manufacturing, thus the cost of these sensors has the possibility to be significantly less than traditional electrochemical sensors or metal oxide sensors.

Disadvantages of SPE electrochemical sensors compared to metal oxide sensors include short lifetimes (1-2 years compared to 5-10 years) and poorer performance at temperature extremes. When compared to traditional electrochemical sensors, the most significant disadvantage is that this new, unique sensor needs to find market acceptance.

Potential Improvements

Improvements to the SPE electrochemical H_2S sensors in a Phase III effort will center on refining and expanding the manufacturing procedures used. Manufacturing improvements will lead to better sensor-to-sensor reproducibility and will bring costs down. The key areas to consider include: ability to cast larger quantities of polymer tape, improved electrode ink formulations, ability to dice elements from larger pads, more efficient termination of diced parts, and automated packaging of sensor elements. In addition, improved sensor testing facilities will be required. All of these items, and others, are being considered through a business plan being written to solicit Phase III funding for the further development and product introduction of the *Smart* H_2S *Card*. Through the business planning the necessary improvements are being considered in detail.

4. OUTSIDE EVALUATIONS

4.1 METAL OXIDE

Numerous companies have been sampled, or purchased, planar metal oxide sensors for independent evaluation. The primary area of interest has been for the detection of H_2S in oil & gas fields. The three most interested companies are Detector Electronics Corporation, Net-Safety Monitoring, and Scott Instruments. They have all been pleased with the performance of the sensor and are in various stages of building instruments around it. Some of the major advantages of our sensor, in the opinion of these companies, are the fact that it has a minimal response to changing humidity levels, it has a very fast response time, and it does not "go to sleep" (a condition where the sensor is very slow to respond to gas if it has not been exposed for some period of time).

4.2 ELECTROCHEMICAL

Two companies evaluated the solid-electrolyte electrochemical H_2S sensor, Kidde Corporation and Scott Instruments. Both were encouraged by the test results. Kidde provided the most feedback regarding the performance of the sensor. Synkera's sensor was tested in their lab head-to-head with a City Technology 4-series electrochemical sensor and it exhibited comparable performance. City Technology is arguably the world leader in electrochemical gas sensors, so this is a very positive verification of our novel sensor. In particular, Kidde liked the fact that the solid-electrolyte sensor will not suffer from the drying out that is endemic to traditional electrochemical sensors and they also liked the small size. As we were aware, they need the sensor to be packaged in a more robust manner. Once that is accomplished they are interested in further evaluating the sensor with the intention of incorporating it into their sensor line. They are also quite interested in future development of an analogous sensor for carbon monoxide, that they can incorporate into home CO detectors, an area in which they are a major player in that very large market already.

5. *SMART H_2S CARD* DEVELOPMENT

A significant goal in the Phase II proposal was the creation of a prototype device for sensing of H_2S gas. The aim was to develop a *smart-card* size and style device that would extend reliable toxic gas sensing into the under $100 per measurement point range. Detailed market analysis efforts (separate to the project) have indicated that such a sensing device has a potential market impact of $50 to $100M annually, and subsequent contact with sensing industry leaders has resulted in strong interest in the concept. By the end of the Phase II project, we completed design, development, and fabrication of a working prototype of a *Smart H_2S Card*. This prototype is the basis for an important commercialization effort on the part of Synkera, and is the subject of extensive ongoing efforts. This section of the Phase II final report details the work performed and results obtained as part of the Phase II project.

Requirements

Based upon separate market survey estimates, the following requirements were developed for the *Smart H_2S Card*:

- 10 ppm alarm point – More or less determined by existing regulatory exposure standards.
- Simple – Going to be used for safety applications, will be ignored until it alarms.
- Reliable – Bump test and false alarms will be metrics for this, along with mechanical integrity.
- Robust – Will be used in relatively harsh environments, and thus will need fabrication and packaging methods to withstand the rigors of these environments.
- Price – Must be manufactured for <$30, sold in the $50 - $100 range.
- Alarms & Display – Although end-users have expressed significant differences of opinion with respect to this, it's clear that there is a general ranking of alarm

importance: audible > vibratory > visual. Display (alphanumeric or bar graph) is not required in most applications, and is undesirable in many.

- Size and weight - The size and weight was initially defined as “credit card-like”. However, in view of the probable power requirements of alarms, battery considerations will limit the minimum size and weight possible.
- Lifetime – The card must operate for a minimum of 2 years before needing replacement, less if it has alarmed for a long period. Recalibration should not be required within that period, but the product must be compatible with quality assurance methods (“bump tests”) that verify correct operation of the sensing device.

This list of requirements was used as the starting point for prototype development.

Prototype Design

The block diagram in Figure 31 summarizes the overall structure of the *Smart H_2S Card*.

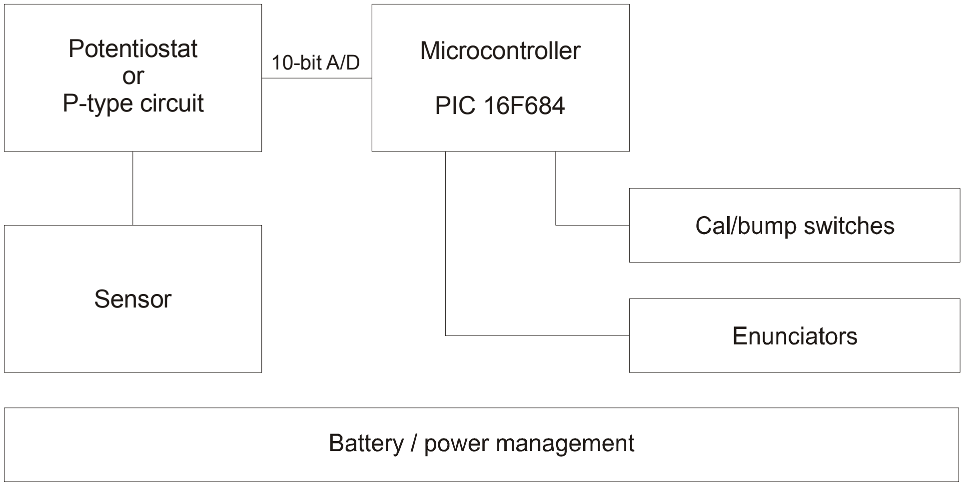


Figure 31: Block Diagram of the *Smart H_2S Card*.

Each of the sections is separately described below.

Potentiostat

A high performance, low-cost potentiostat is at the heart of the device. While prior work at Synkera had produced simple but effective potentiostat circuitry for measurement of small electrochemical sensor signals, these designs were not intended for use with portable/low power implementations. Specifically, a potentiostat compatible with use in the *Smart H_2S Card* must exhibit the following features:

- Ability to work with sensor currents in the 10 to 100 nA range
- Micropower operation (<10μA continuous current draw)
- Compatibility with supply voltages of 3V, discharging over time to 2.5V

- Ability to operate at the temperature extremes expected in user environments (-40 to +50°C)

Extensive modeling work was performed on potentiostatic designs collected from various published sources, along with original design work previously performed at Synkera. As a result of that work, in combination with breadboard circuitry testing using actual SPE H_2S sensors, it was determined that the circuit shown in Figure 32 met the needs of the *Smart H_2S Card*:

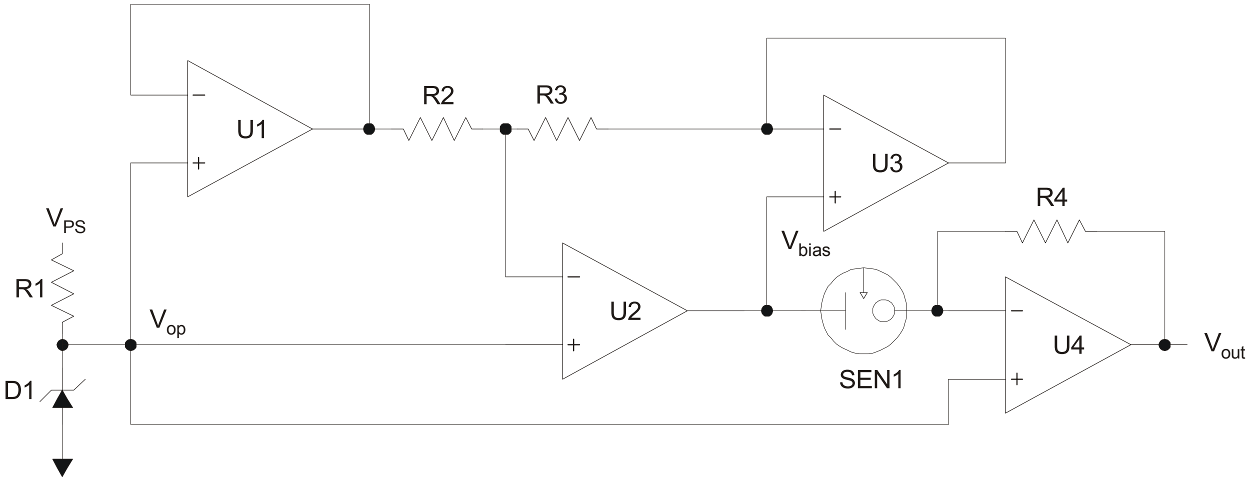


Figure 32: Potentiostat for the *Smart H_2S Card*.

U1 through U4 are included in an LT1496, which is an ultra-micropower (<1.5 µA/amplifier) quad package, with a worst-case input bias of 200 pA and rail-to-rail performance in single-sided designs. D1 is an LT1389, a micropower 2.5V reference. Taken together, these two components allow continuous operation of the potentiostat circuit on approximately 4.5 µA of current @ 3.0V. This equates to a 4 year operating time using a CR2032 Lithium battery. The circuit has been demonstrated to be functional with SPE sensors, and it has further been shown that noise and stability are limited by the sensor, which is a key performance criteria for the potentiostat. Cost of the circuit is higher than desired (the selected op-amps are approximately $1/amplifier in 1000's quantity), but this is acceptable for the prototype, and could be lowered by selecting a less "gold plated" part.

Microcontroller

A PIC16F684 was selected for the *Smart H_2S Card* because of it's micropower features, its capability match with the required tasks, and it's low cost (<$1 in quantities of 1000). It also has flash memory compatible with direct programming via a 5-wire connection to a PC, which makes testing and debugging of the prototype code easy and efficient. The built-in 10-bit A/D converter allows digitization of the potentiostat signal without additional external parts. By using the sleep capability of the controller to power down for the 1 to 5 second period between sensor readings, it will be possible to operate the microcontroller on an average current draw of 10µA; in combination with the potentiostat current usage, we are still well within our 2 year battery lifetime requirement.

Enunciators and Switches

Both a small LED and a piezoelectric (audible) enunciator are included in the prototype; implementation of a vibratory enunciator was deferred until a later time. The current draw for the LED is approximately 10 mA, although this can be reduced by a factor of 10 if strobing techniques are used. The audible enunciator draws 2mA of current in continuous operation; this value can similarly be reduced by using low duty cycle pulsing of the enunciator. Two momentary contact switches are included in the prototype for testing and calibration purposes.

Battery and Power Management

A CR2032 coin-type lithium cell is used to supply power to the device. No further power conditioning is required, since the prototype does not include battery recharging as a feature. The CR 2032 battery is widely used in personal computer implementation, and is consequently widely available and very low cost. A slightly larger, 3.6V battery has also been tested for use with the prototype circuitry, and shown to operate well. The higher capacity of this battery approximately doubles the lifetime of the prototype, allowing operation for up to 4 years.

Prototype Construction

The prototype was constructed using SMT parts on a 0.0625 inch thick FR-4 printed circuit board. The board utilized the 3.375 x 2.125 inch form factor specified in both the credit card and Smart Card industries. A manufacturing estimate of \$27 per prototype assembly (quantities of 1000) has been obtained from a Colorado-based contract circuit assembly manufacturer, and it is expected that this price can be lowered to less than \$20 through continuing engineering beyond the prototype stage. A photo of the completed prototype is shown in Figure 33.

Figure 33: *Smart H_2S Card* prototype.

Coding and testing of the prototype is in progress as of the end of the Phase II project. We anticipate that the prototype, along with a well-developed commercialization plan nearing completion, will be presented in the next few months to potential business partners with marketing and sales capability in the industrial health and safety/portable instrument business. We further anticipate that this commercialization effort will lead to a successful joint venture and commercial sales of the *Smart H_2S Card* by the first quarter of 2008.

6. BUSINESS GENERATION

6.1 METAL OXIDE

6.1.1 Generated To Date

Synkera has been selling planar metal oxide sensors since April of 2005. To date we have achieved revenue in excess of $14,000. We also have a pending order in place that will guarantee the sale of 400 more sensors ($18,000).

6.1.2 Projected

The projected sales for the planar metal oxide sensor to our three primary customers for instruments for the Oil & Gas industry are between 4000 and 10,000 units per year. The revenue from these sales will be somewhere in the range of $175,000 to $400,000 per year.

6.2 ELECTROCHEMICAL

We are currently pursuing funding for the appropriate packaging of the electrochemical sensors. This follow-on funding will likely be in the range of $150,000 to complete the development of the sensor. It is expected, that once the electrochemical sensor is ready for sale, that the market for this sensor will be comparable to the planar metal oxide sensors. Thus, that sensors could generate revenues up to half a million dollars per year.

6.3 *SMART H_2S CARD*

Synkera is actively seeking funding for the Phase III commercialization of the *Smart H_2S Card*. Based on independent market research this is a $50-100M market opportunity for H_2S personal monitors alone. This very large estimate is due to the fact that the monitors are expected to be low cost enough that it will allow for all workers, not just team leaders, in the Oil & Gas industry to be equipped with the device. In addition to the Smart H2S Card for H_2S, Synkera plans to build on this concept for carbon monoxide, oxygen, and combustible gas with sensors in development under other funding.

7. ACKNOWLEDGEMENTS

Synkera would like to thank the CDC for funding the successful development of several types of H_2S sensors that will find use in the area of health & human safety. This development effort has generated significant interest from commercial instrument manufacturers and has allowed us to begin seeking Phase III funding for the commercialization of these sensors and personal monitors.

Synkera would also like to acknowledge Sporian Microsystems for their consultation during the early stages of the *Smart H_2S Card* concept.

Finally, without the willingness of the commercial partners developed during the course of the project (Scott Instruments, Detector Electronics Corporation, Kidde Corporation and Net-Safety Monitoring) to provide application information, evaluate sensors, and share data from these external evaluation, the project likely would not have been nearly so successful.

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i. American National Standards Institute (ANSI) Standard No. Z37.2-1972

ii. cdalloz.com/9810.html

iii D. Fuller and A. Suruda, “Fatal Work-Related Deaths from Hydrogen Sulfide 1984-1994, apha.confex.com/apha/128am/techprogram/paper_12231.htm

iv. P. Szymanski, “H_2S Monitoring/Datalogging in Manholes and Lift Stations,” Industrial Hygiene News, www.intlsensor.com/h2smonitoring.html