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EVALUATION OF A HYDROGEN SENSOR FOR NUCLEAR
REACTOR CONTAINMENT MONITORING

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ABSTRACT

Measurement of hydrogen (H_2) concentration in containment atmospheres in nuclear plants is a key safety capability. Current technologies require extensive sampling systems and subsequent maintenance and calibration costs can be very expensive. A new hydrogen sensor has been developed that is small and potentially inexpensive to install and maintain. Its size and low power requirement make it suitable in distributed systems for pinpointing hydrogen buildup. This paper will address the first phase of a testing program conducted to evaluate this sensor for operation in reactor containments.

I. INTRODUCTION

Title 10 of the Code of Federal Regulations, Part 50 (10CFR50), Appendix A, General Design Criterion 13 includes requirements to monitor parameters that are relevant to containment integrity. For both Pressurized-Water Reactors and Boiling-Water Reactors, U.S. Nuclear Regulatory Commission (USNRC) Regulatory Guide 1.97 classifies containment H_2 concentration as a Type C variable (i.e. a variable providing information indicating the potential for breach of a fission product barrier). Hydrogen monitoring will continue to be a requirement for many advanced reactor designs.

Current technologies for measuring hydrogen gas concentrations are based upon thermal conductivity measurements between reference and catalyzed sensing cells or measurement of current flow through an electrolyte exposed to a sample of the containment atmosphere. These technologies require extensive sampling systems. Maintenance and testing of these measurement systems have been very costly to the nuclear industry; plant outage costs as high as \$100,000 have been documented relative to

preventive and corrective maintenance and testing.¹ Development and use of a low-cost, reliable, and accurate hydrogen concentration sensor requiring no sampling systems would present the opportunity for the nuclear industry to realize substantial cost savings.

A solid-state H_2 sensor, developed at the Oak Ridge National Laboratory (ORNL), is currently under evaluation for use in nuclear reactor applications. This sensor is small and relatively inexpensive (the sensor can be made in quantity for less than \$10), thus it is suitable for distributed systems. Its current drain of ~100mA at 9 volts is low enough for battery-backup powered operation. Future embodiments of the sensor can conceivably reduce power consumption much further. Current sensor prototypes are fabricated on ceramic substrates using thick film techniques, which yield an inexpensive and sturdy device, capable of withstanding temperatures to 200°C.

The scope of work presented here includes tests designed to demonstrate sensor operability under conditions representative of design basis accidents defined in regulations. For the purposes of this project, tests were conducted to examine sensor performance at discrete hydrogen concentrations over a range from 0-30%, namely, 0.5, 1, 2, 3, 4, 10, 20, and 30% hydrogen. Sensor response time, repeatability, and reliability are also addressed. The test matrix was devised for measuring sensor response to these concentrations of hydrogen at a range of relevant temperatures from ambient to 200°C, dry, and also in the presence of steam. Future work may focus upon sensor performance in more severe accident conditions. These tests would also include an evaluation of sensor life-span, cross-sensitivity to other gases, and survivability during prolonged exposure to post accident conditions.

II. SENSOR DESIGN AND OPERATION

The scientific basis for many hydrogen sensors relies on the reversible solubility of hydrogen in palladium.^{2,9} Most hydrogen partial pressures of interest (7 to 7000 n/m² or 10⁻³ to 1 psia) will be in equilibrium with the palladium-hydrogen solid solution (α phase) at ambient temperatures. In this range, hydrogen molecules dissociate on the Pd metal surface and atomic hydrogen is quickly absorbed as an interstitial solute in the Pd until equilibrium is reached. The dissolved hydrogen increases the electrical resistivity of the Pd in a known, quantitative way.¹⁰ In prior work, a thin-film hydrogen sensor based on this phenomenon was developed at ORNL and demonstrated for hydrogen concentrations up to the lower explosive limit (LEL) in air (about 4%).^{11,12}

A later project continued the sensor development. We recognized that a thick-film sensor similar to the original thin-film device would be inherently simpler, more robust, and less expensive to manufacture. Most of the needed thick-film compositions, or "pastes," were off-the-shelf products; however, the sensor required one completely new paste containing pure Pd and a very durable glass frit. We successfully formulated a sensor paste by combining a commercial silver-palladium-based conductor composition with fine Pd power and then teamed with DuPont Electronics (Research Triangle Park, North Carolina) to specify and develop an optimized composition for mass production.^{13,14} Because the components of the sensor are sintered at high temperatures, they are refractory and quite stable in air under ambient conditions, giving the device an inherent advantage for operation in harsh environments. Details of the sensor fabrication are presented elsewhere.¹⁵ In preliminary tests, these thick film sensors had a linear response to increasing concentrations of hydrogen (0.5% to 4% in an argon/air matrix).

The hydrogen sensor design is similar to that of a classical strain gauge with active and reference components. Four palladium conductors are deposited as serpentine patterns and connected as a Wheatstone bridge to increase measurement sensitivity and provide temperature compensation (Figure 1). One or two of the palladium legs are "active" and are exposed to ambient conditions. The remaining serpentine legs are "reference" legs and are passivated by a dielectric layer impermeable to hydrogen. dc power is applied to opposite nodes of the circuit, and the bridge voltage is measured across the remaining nodes, as indicated in Figure 1.

In a typical bridge circuit, the objective is to measure the resistance change of one resistor. The model for this change is:

$$V_{bridge} = \frac{V_{applied}}{2} \left(\frac{\Delta R}{2R + \Delta R} \right), \quad (1)$$

where $R + \Delta R$ is the resistance of the active leg in the presence of hydrogen. For a sensor circuit, the sensitivity can be doubled by having two active resistor legs. In this case, the equation becomes:

$$V_{bridge} = V_{applied} \left(\frac{\Delta R}{2R + \Delta R} \right), \quad (2)$$

where V_{bridge} and $V_{applied}$ correspond to sensor voltages across the bridge as indicated in Figure 2.

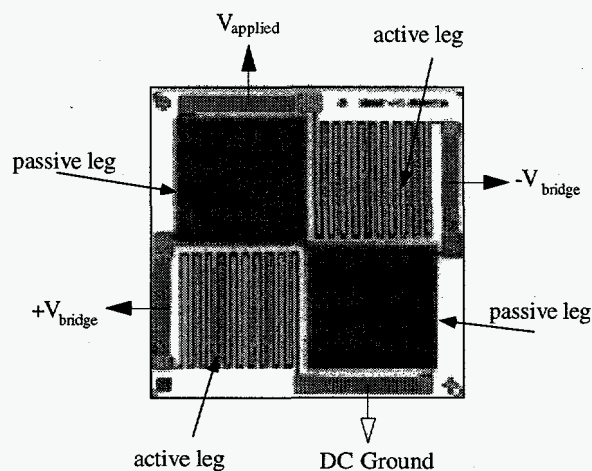


Figure 1. The ORNL hydrogen sensor (1.6 \times actual size), consists of four palladium resistors connected as a Wheatstone bridge. Two of the resistors are passivated by a hydrogen-impermeable coating to act as reference resistors.

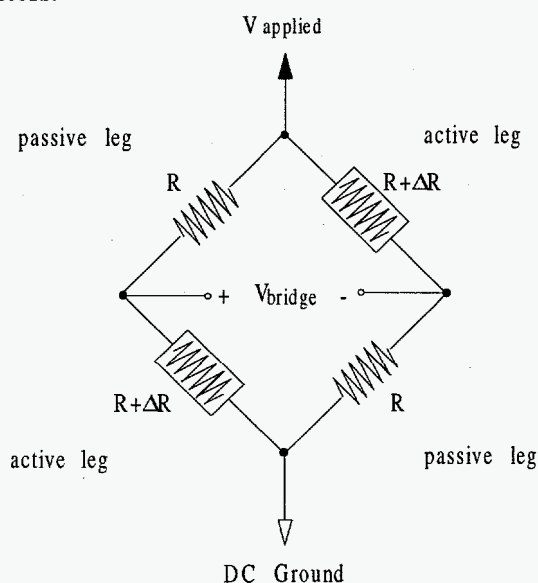


Figure 2. Schematic representation of the hydrogen sensor. Two resistors are fixed (passivated by the

impermeable glass layer) and two are active (resistance varies in response to changing concentrations of ambient hydrogen).

III. EXPERIMENTAL TEST BED DESCRIPTIONS

A. The Harsh Environment Test Bed (HETB)

Sensor tests were conducted at two separate facilities at ORNL, the HETB and the Metrology Research and Development Laboratory (MRDL). The HETB is an ORNL-fabricated stack/vent simulator, i.e., harsh environment laboratory, consisting of two sections, a generator section and a stack section. The generator section is a horizontally mounted 5-cm (2-inch) stainless steel pipe through which gases and matrix modifiers, such as water vapor, may be introduced into the system. The generator section is flanged to the vertical stack section, a 10-cm (4-inch) diameter stainless steel pipe that contains twelve ports positioned at three different heights along the stack. Both the generator and the stack sections are equipped with sufficient heating to allow system operation up to about 250°C. For our tests, flows were controlled from two to 15 liter/min depending upon the hydrogen concentration desired. The time constant or volume replacement time for this test configuration varied from 2 to 6 seconds, depending upon flow velocities. A commercially available blend of 4% hydrogen in argon was used to provide hydrogen to the system. Nitrogen was used as a diluent gas where necessary.

The HETB test outline called for a series of sensor tests at three temperatures, (20°C, 90°C, and 200°C) matrixed against relative humidities of 0%, 80%, and 100%. However, not all of these moisture levels were obtainable at all stack temperatures. At 20°C and 90°C we were able to obtain arid, 40%, and 80% relative humidity but only arid conditions at 200°C. Power to the sensors was supplied by a dc power supply at 8 volts. Data acquisition was effected through an ORNL-developed system using National Instruments' LabView™.

B. Metrology Research and Development Laboratory

Other tests were performed at the MRDL facility, in which a pressurized test chamber provided the high temperature and high humidity conditions not achievable at the HETB. Evaluation of the thick-film hydrogen sensor consisted of parametric tests to quantify sensitivity, time response, long and short term drift, reliability, and pressure/humidity sensitivity of the sensor under conditions representing some worst-case scenarios for accident conditions in a nuclear power reactor. Included within the matrix were high temperature conditions of 50°C, 100°C,

150°C, and 200°C, combined with relative humidity requirements approaching 100% RH. To accommodate the highest temperature condition, testing pressures of approximately 1800 kPa were required to maintain near saturation conditions around the sensor. Precautions were required to ensure safe operation throughout these harsh conditions of the tests, while operating within the potentially explosive concentrations of 4 to 30%.

An easily reconfigured, explosion-proof gas flow loop was constructed to accommodate the wide range of conditions needed for this testing program. A test chamber, for housing the sensor and integral to each testing configuration, was fabricated. This housing consisted of a short section of 5-cm (2-inch) schedule-40 stainless steel pipe, approximately 10-cm (4-inch) in length and capped on each end with a modified pipe cap, as presented in Figure 3.

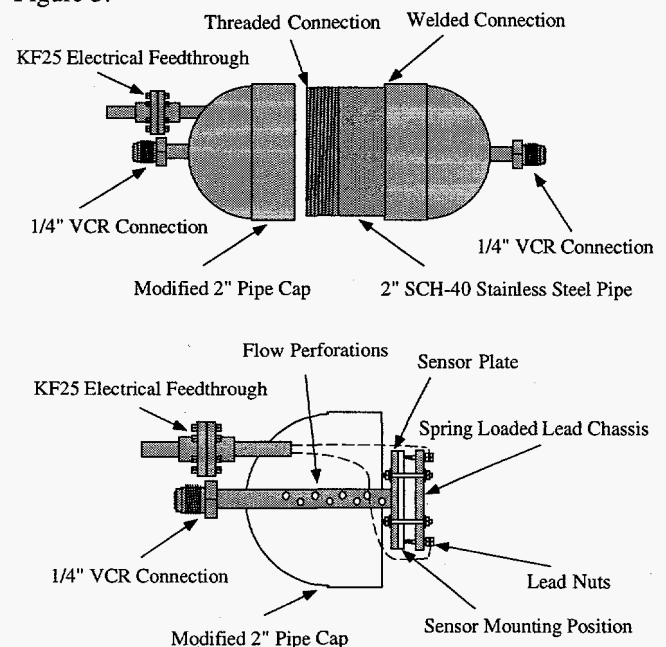


Figure 3. External and Interval Views of High-Pressure Sensor Housing Chamber.

Overall housing volume was maintained at a minimum to decrease the thermal and pneumatic inertia of the system. Plumbing connections to the test chamber were provided via 63.5-mm (1/4-inch) vacuum compression ring components. Electrical connections, including a 9-volt dc excitation pair and a low level signal pair, were supplied through a high-pressure/high-temperature electrical feedthrough, comprised of solid nickel-oxide clad copper wires embedded in a high-temperature epoxy resin. Electrical connections to the sensor pads were initially established using a silver based, high-temperature solder. However, solder joint failures often accompanied temperatures exceeding 150°C. These problems, combined

with an overall difficulty in achieving a good solder joint to the sensor pad, led to the use of a high-temperature, conductive epoxy and to the eventual development of a spring-loaded lead harness for wiring connections of later tests.

Using the sensor housing chamber, a variety of test configurations were employed to evaluate the sensor under various conditions. Tests for overall sensitivity and time response of the sensor were conducted using a flow-dilution configuration as presented in Figure 4.

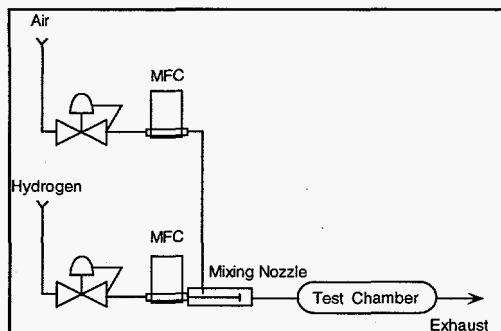


Figure 4. Sensitivity and Step Response Configuration.

In this configuration, two mass flow controllers regulate the concentration of hydrogen in the flow stream. The mass flow controllers, STEC Model SEC-7330, are 1-liter/min units calibrated respectively using air and hydrogen. To ensure adequate time response, the units were also checked for speed of response to a setpoint change against a high speed Honeywell Microswitch hot film device with a time response of approximately 10 ms. Time response of the flow controllers was consistently better than 0.25 seconds. The time constant for delivery of test gas to the test chamber was calculated at 7 seconds. Overall accuracy was better than 0.5% of full scale flow. Gas mixing was optimized using an annular mixing nozzle. Flow rates were maintained at 1-liter/min for all hydrogen concentrations, i.e., mix ratios, to standardize the effect of flow velocity over the surface of the sensor. To evaluate the sensor at various temperatures, the test chamber was mounted into a Precision Scientific Thelco oven with capability of temperatures from ambient to approximately 230°C, and stability of better than 1°C. This configuration, was used for only dry, non-moisturized, flow streams. Alternate configurations employed a saturator vessel upstream of the sensor housing to moisturize hydrogen flows.

Data acquisition and control of the tests were performed using a PC-based system, with National Instruments' AT-MIO-16X analog input board and AT-AO-6/10 analog output board. Input data was acquired

from the excitation power supply, the sensor output, and several type-J thermocouple measurements. Analog outputs controlled the flow setpoints of each of the mass flow controllers. The oven temperature was controlled through serial communication. National Instruments' LabWindows™ environment automated test control and data acquisition, which consisted of timed mixing concentration sequences and periodic data logging.

IV. RESULTS AND DISCUSSION

A. Sensor Performance

1. Stability.

Figure 5 shows the "resting," i.e., no hydrogen excitation, outputs of two sensors that experienced all of the temperature and humidity excursions at the HETB. The sensor outputs differ because the Wheatstone bridge was not balanced for either sensor. The resulting dc offset was not subtracted from the outputs. Tests in the April and August periods included temperature ranges from 20 to 200°C, humidity conditions to saturation, and repeated exposures to hydrogen/argon/nitrogen/air mixtures between hydrogen concentrations of 0.5% to 3%. The outputs of Sensor A, in between hydrogen excitation, varied little over time. The outputs of Sensor B remained stable until the solder joints failed during the highest temperature regimes on April 9, after which the sensor connection failed completely. A couple of other sensors placed in this test environment also lost connectors when the solder failed at elevated temperatures, and stability measurements could not be made for them.

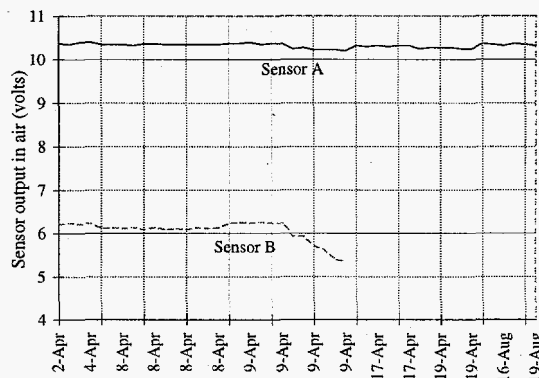


Figure 5. Sensor Stability in Air Over a 4 Month Interval.

2. Response time.

Theoretically, the diffusion of hydrogen into a thin layer of palladium occurs on the order of milliseconds; in laboratory tests, however, the test setup can prevent direct

observation of the actual response time of the sensor. Often the overall time response is the time constant of the test chamber, tubing, etc. The HETB time constant is between 2 and 6 seconds depending upon the flow rates dictated by gas mixing; in the MRDL, the time constant is 7 seconds. Other factors also have an effect. In Figure 6, we observe that temperature has some effect on the response time of a sensor. This chart consists of many responses for several sensors. There is a modest trend of slightly faster response at higher temperatures, as one would expect from kinetic theory. At ambient, a slower time response is noted for several sensors. These points correspond with first trials of unexposed sensors, and indicate that a "conditioning" run may be required to activate previously unexposed sensors. The explanation for this may be that moisture or oxygen adsorbed on the active palladium prevent a "normal" hydrogen gas dissociation into the sensor. For most of these points, however, the time to reach 90% of the maximum change in the hydrogen atmosphere is less than 30 seconds. All of the measurements in Figure 6 were made under dry conditions.

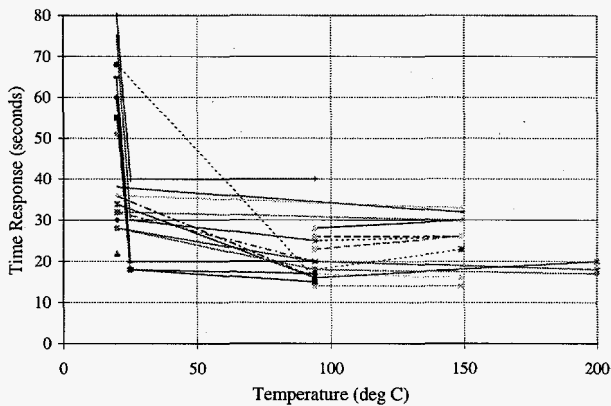


Figure 6. Temperature Dependence of Step Response Time to 90% of Steady State Value for Multiple Test Sensors.

Step response is slightly dependent on hydrogen concentration, as indicated in Figure 7. At the low end of concentrations, sensor time response is slower. No discernible trend is evident at higher concentrations. This might indicate the effect of adsorbed oxygen on the Pd surface. Larger H_2 concentrations would presumably remove this oxygen faster.

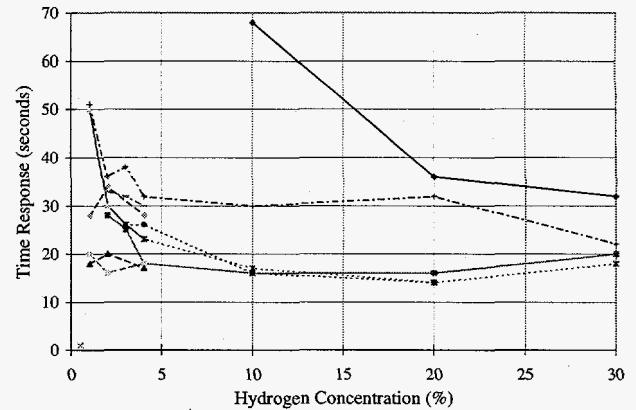


Figure 7. Concentration Dependence of Sensor Step Response for Multiple Test Sensors.

Response times for an individual sensor at three humidity levels, 0, 80%, and 100%, shown in Figure 8, indicate that the sensor is somewhat slower as the relative humidity increases. The time to reach 90% of the equilibrium response for each concentration is still less than one minute for all of the tests. Recovery times in air do not indicate any discernible trends. These initial tests are encouraging; nevertheless it will be important to understand more about the sensor reaction and life span under humid conditions, because humid conditions or conditions of varying humidity, are common to many industrial environments.

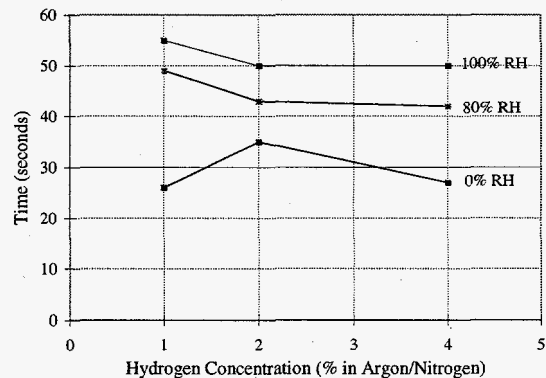


Figure 8. Dependence of Step Response on Humidity Level for an Individual Test Sensor.

3. Linearity.

Functional tests of the sensor indicate good correlation between sensor output and hydrogen concentration. This correlation was consistent for concentration step change data, as well as for steady state sensor output. In addition to response to a step change in hydrogen concentration, tests were also conducted to evaluate the sensor response to slow, gradual

accumulations of hydrogen gas. Such conditions would be typical, for example, of the evolution of hydrogen from overcharged lead acid batteries, or the accumulation of hydrogen in a sealed environment. Tests indicated excellent linearity of the sensor to gradual accumulations of hydrogen as presented in Figure 9.

Figure 10 shows the responses for a sensor repeatedly exposed to a range of hydrogen concentrations in air (0.5 to 3%), at room temperature. Another sensor was tested through the range of 0.5% to 30% H₂ in air (Figure 11). A promising result is that even at 30% hydrogen, the sensor does not appear to saturate. On the other hand, the reading for 0.5% hydrogen never appears to move beyond a zero change (not shown). Other test results have also shown lower than expected readings for this level of concentration. Subsequent tests indicate that this is a limitation of the mass flow controller, which was selected for response time rather than accuracy at the lower concentrations. Prediluted hydrogen gas sources were used to raise the flowrate, and thus control accuracy, of the hydrogen supplying the mass flow controller. Using this setup, improved linearity of the flow system was achieved, improving sensor data at the low end.

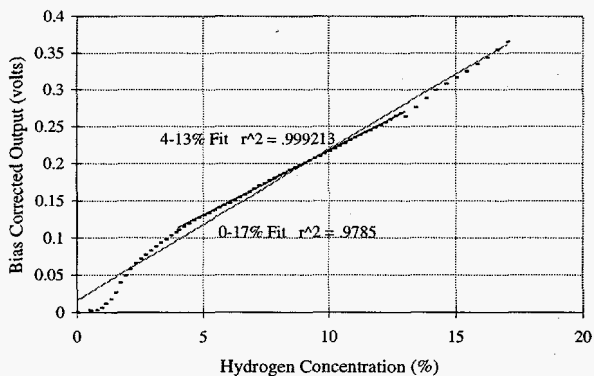


Figure 9. Linearity of Sensor Response Under Gradual Accumulation Conditions.

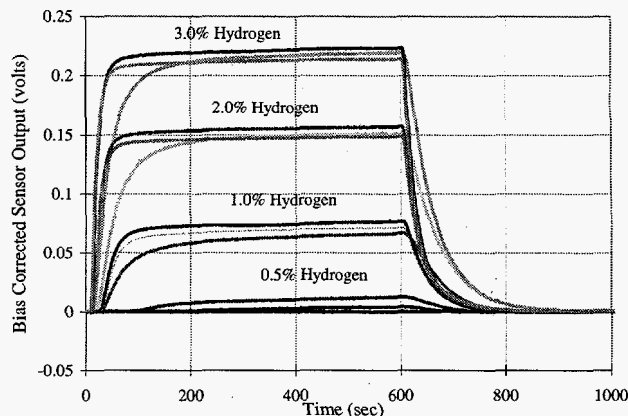


Figure 10. Typical Sensor Response Curves to Step Concentration Changes.

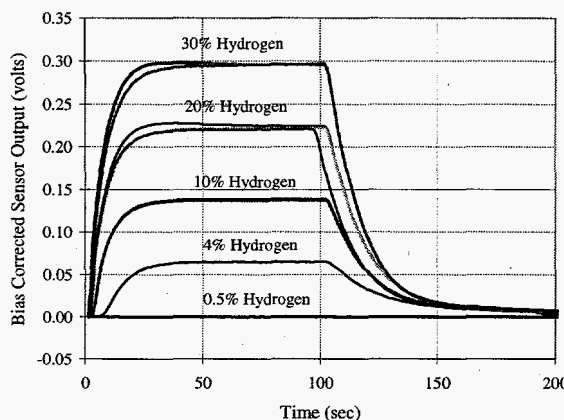


Figure 11. High Hydrogen Concentration Sensor Performance.

4. Elevated temperatures.

As temperature increases, the amount of hydrogen dissolved in Pd at a given hydrogen partial pressure decreases.¹⁰ This is demonstrated for one sensor in Figure 12. Obviously, if the sensor is to be used quantitatively, appropriate calibration curves will have to be developed for the intended sensor environment.

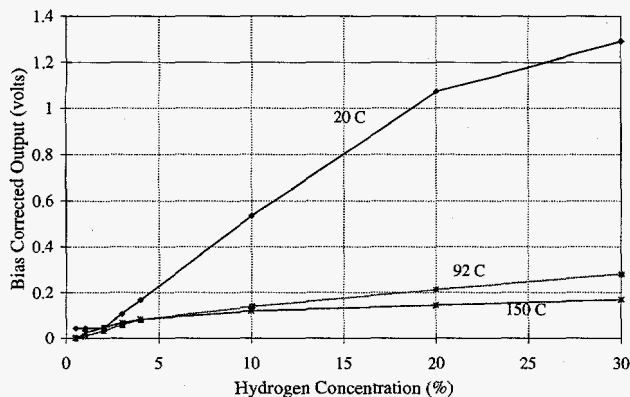


Figure 12. Temperature Dependence of Steady State Response.

B. Packaging Issues

Packaging design will inevitably be driven by the intended application domain. Connections to the sensor must be secure and reliable at all intended operating temperatures. Most solders will not perform above 200°C. We are experimenting with conductive epoxies, but believe that wire-bonding attachments are probably the most promising long-term approach.

Experimental data indicate that, over time, moisture adsorbing to the sensor surface is detrimental to the sensor speed, slowing response by up to 10x. We have proposed covering the active palladium legs with Teflon or other hydrogen-permeable materials to exclude moisture and other possible contaminants. However, the effect of coverings on response time must be investigated.

We are currently designing a sensor layout for a 160-mm² (0.25-in²) substrate. This size is convenient for commercial packages and connectors used by some sensor manufacturers. Ideally, the sensor can be mounted in a commercial package or monitor housing, and accompanying off-the-shelf electronics can be tuned or programmed to operate the new sensor.

The results of these tests point to several areas for more in-depth studies of this sensor technology. We will continue to study the competing thermodynamic and kinetic effects through parametric studies. Failure analysis by electron microscopy will provide valuable insight into the behavior of the device, including damage associated with high H₂ concentrations. A fundamental high upper limit is associated with volumetric expansion effects and associated cracking of palladium traces. Other palladium alloys can likely extend the operation of the sensor into higher hydrogen concentration levels.

Packaging issues generally depend upon the requirements of individual applications. The sensor itself is rugged and mechanically stable, and is inherently well suited to a large range of environment conditions. Normal temperature and humidity variations in buildings, out of doors, or in environmental enclosures containing heat-producing electronic equipment do not appear to be a barrier to operation and ultimate commercialization of the sensor. Similarly, the potential for high temperature and/or high humidity conditions in reactor containment areas appear to not pose significant problems for sensor implementation. Other potential insults, such as radiation, will be addressed in future work.

Thick film techniques, in general, are mature and relatively inexpensive for quantities in the hundreds of units. The relatively high processing temperatures (500 to 1000°C) renders a device able to survive wider thermal ranges than commercially available sensors. The sensor mechanism is selective for hydrogen, although definitive studies of cross-sensitivity of the sensor are planned. The sensor fabrication is compatible with many sensor and detector packaging schemes, and promises a cheap and effective method for a wide variety of hydrogen sensing applications.

V. CONCLUSIONS

In general, current evaluation of the palladium-based thick film sensor indicates several favorable results:

- Response Time—typical response times are 20-30 seconds and recovery times are of the same magnitude. Further study is required to promote understanding of the “activation” mechanism required by unexposed sensors.
- Linearity—sensor features good linearity over a wide range of use (1%-30% hydrogen). Questions remain regarding linearity of response at the low end (<1%), as well as upper limit of operation.
- Stability—sensor output remains very consistent in low hydrogen atmospheres (<3%). Baseline shifting due to higher concentrations warrant further investigation. A better understanding of the degradation mechanism is required.
- Temperature—sensor performs reliably over a wide range of temperatures (ambient-200°C). Sensor response is affected predictably by temperature, promoting the use of temperature compensation for maximum sensing accuracy.
- Humidity—sensor response time is affected by humidity at the sensor surface. Further investigation of protective coatings may be necessary to optimize performance in high humidity or steam-saturated environments.

ACKNOWLEDGMENTS

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