IX.12 Safe Detector System for Hydrogen Leaks

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Objectives

- Select and finalize the hydrogen sensor chemistry that possesses the optimum sensitivity, reliability, reproducibility, and aging performance.
- Design and fabricate optoelectronic board for hydrogen leak sensor.
- Assemble and test the optoelectronic interface for the sensor prototype.
- Test and validate the fully packaged prototype performance at the National Renewable Energy Laboratory (NREL).

Technical Barriers

This project addresses the following technical barriers from the Hydrogen Safety section of the DOE Fuel Cell Technologies Program Multi-Year Research, Development and Demonstration Plan (MYRDDP), page 38-7:

(D) Liability Issues: Potential liability issues and lack of insurability are serious concerns that could affect the commercialization of hydrogen technologies.

(E) Variation in Standard Practice of Safety Assessments for Components and Energy Systems: Variations in safety practices and lack of standardization across similar hydrogen technical projects increase the risk of safety related incidents.

Barriers addressed by this project from other sections of the MYRDDP include:

- Delivery:
  - (I) Hydrogen Leakage and Sensors (page 3.2-20)
- Storage:
  - (H) Balance of Plant (BOP) Components (page 3.3-14)
- Manufacturing R&D:
  - (F) Low Levels of Quality Control and Inflexible Processes (page 3.5-11)
- Technology Validation:
  - (C) Lack of Hydrogen Refueling Infrastructure Performance and Availability Data (page 3.6-8)

Contribution to Achievement of DOE Safety, Codes & Standards Milestones

This project will contribute to the achievement of the following DOE milestones from the Hydrogen Safety/Leak Detection Technology section of the Fuel Cell Technologies Program MYRDDP:

- Milestone 2: Develop sensors meeting technical targets. (4Q, 2012)
- Milestone 3: Develop leak detection devices for pipeline systems. (4Q, 2015)

Accomplishments

This continuation of a project that was initiated on June 1st, 2008 has been extended through November 2010. The initial work focused on exploring a family of colorimetric hydrogen sensor formulations and physical embodiments for different venues and markets. These included porous glass "optrodes" for integration with optical fiber sensors, polymer integrated optic chip sensors, and fully-distributed fiber optic sensors. Work on the latter has been Presented by R.G. Zalosh and N.F. Barilo [1] from the Pacific Northwest National Laboratory at the International Hydrogen Conference in France, 2009.

In the past year, IOS has focused on developing and testing an optrode-based point H_2 detector technical accomplishments for the past 12 months are summarized below:

- A process for reproducible fabrication of hydrogen sensor substrates was optimized and tested. The statistical variance in different batches of sensor elements was observed to be (~0.04±0.01) from batch-to-batch.

- The development of the optoelectronic readout device was finalized. Two generations of fully functional hydrogen sensor prototype devices were fabricated, tested and optimized.
- Signal processing algorithms were developed to linearize optrode response under various environmental conditions. The algorithms are currently undergoing validation and optimization testing before release of the final version.
- The hydrogen sensor was tested and validated, for reversibility, repeatability, accuracy, and environmental dependence, confirming IOS results at NREL.
- IOS presented a briefing, and a working prototype unit, during the 2010 Hydrogen and Vehicle Technologies Annual Merit Review in Washington, D.C. During this review, we met with a number of parties interested in the hydrogen sensor and its performance.

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Introduction

Hydrogen safety is an important key to commercializing hydrogen energy technologies, and to facilitate the use of hydrogen as a green energy source. The principal objective of this DOE project is to integrate IOS' proprietary hydrogen indicator chemistry with optical and optoelectronic designs, and advanced signal processing, to create a prototype point-sensor system with well-defined sensing characteristics for various markets, including fuel cell-powered passenger vehicles, hydrogen generation and refueling stations, storage locations, and other situations.

Each IOS hydrogen sensor uses an optoelectronic platform to monitor an optically conductive matrix hosting a colorimetric indicator. Upon hydrogen exposure, the sensor element changes color, and the sensor uses the resulting optical signal to calculate hydrogen concentration.

IOS' hydrogen sensor approach is unique in many aspects. First, it uses an intrinsically safe sensing element that functions without the heat required by many electronic hydrogen sensors, and can be remotely read without any electrical connection. Second, the unit has a faster response time and higher sensitivity levels, over a wide range of environmental conditions (i.e., temperature and humidity) than its counterparts. The sensor module can also be cabled to a readout unit for remote monitoring applications.

Approach

IOS has studied three formats for hydrogen sensors: porous glass substrates (optrodes), evanescent-field polymer-clad silica optical fiber sensors (distributed sensors), and integrated-optic chip sensors.

A comparative evaluation of the three sensor matrices revealed that, overall, the more technologically mature porous glass optrodes performed the best, and thus the optrodes were chosen as the hydrogen indicator matrix for the final product prototype. Sensor prototypes, each designed to accommodate both a hydrogen-sensitized optrode and an undoped porous glass "reference optrode," were fabricated and tested. The optrode response time is rapid (time to reach 90% of full scale: T90 ≈5-8 seconds); software routines have been developed to provide a user-settable detection alarm at low hydrogen levels (down to 0.02% hydrogen in air).

Results

Optrode development focused on optimizing the optrode substrate fabrication steps to achieve the optimum response characteristics, a reproducible fabrication process, longer shelf-life times, and better resistance to chemical gas interferences. The operational specifications are summarized in Table 1.

TABLE 1. Summary of Current Optrode Specifications

Operating Range	0.1% to 10% H_2 in Air, N_2, or Helium $LOD_{>20\%RH} = 0.05\%\ H_2$ $LOD_{<20\%RH} = 0.1\%\ H_2$
Accuracy	2% of Concentration (0 to 3% Range) 5% of Concentration (3 to 10% Range)
Response Time: Alarm Measurement T_{90}	 2-3 seconds 5-8 seconds
Recovery Time T_{90}	5 seconds
Environmental Correction	Compensated for temperature and humidity
Temperature Range, Operating	-30°C to 50°C (compensated)
Humidity Range, Operating	0-80% RH, Non-Condensing (compensated)
Product Life	>6 months

LOD – limit of detection; RH – relative humidity

The design, fabrication, assembly, and testing of the optoelectronic readout unit resulted in the construction of two hardware generations. After successfully testing and characterizing the first generation development prototype, we then developed the second generation (final prototype) unit shown in Figure 1. Among other requirements, the new version was designed with scaled up manufacturability and mass production in mind. Multiple user-friendly features, such as the replaceable sensor module, were also added. Figure 1 shows the fully functional final prototype in an anodized aluminum enclosure. The new prototype is smaller than the

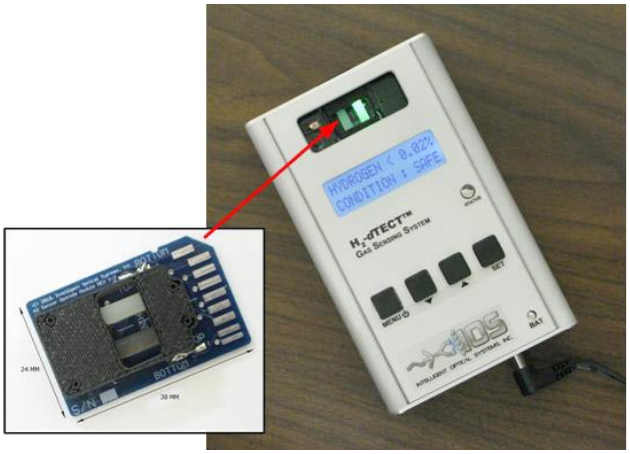

FIGURE 1. New Generation Hydrogen Sensing Unit (right), Replaceable Hydrogen Sensor Module (left), Top Optrode: Undoped (reference); Bottom Optrode: Hydrogen-Sensitive.

previous version. The new device can be powered with a wall plug adapter, a universal serial bus, or the built-in rechargeable battery. This unit is an ideal handheld device that can also be used as a wall mounted unit. The detachable sensor module is mounted on a printed circuit board that was adapted from the design of a secure digital memory card, which is commonly used in today's consumer electronics. The sensor module is inserted into the main measuring module using a push-push locking and removal mechanism. The replaceable sensor module containing a hydrogen-sensitive optrode and a reference optrode is shown in Figure 1.

Repeatability/Reversibility

Excellent signal reversibility and repeatability are now being observed for our optimized optrodes, as illustrated by the test data shown in Figure 2. High degree of reproducibility in sensor fabrication was achieved by controlled sensors preparation protocol. Figure 3 illustrates the signal changes for two various batches, error bars represent the standard deviation from the average value (~0.04±0.01).

Environmental Stability

The detection and quantification of hydrogen was observed under a wide range of humidity and temperature, as shown in Figure 4; some degree of dependence on RH was noted, while at different temperatures, variations in the relative humidity were also observed (from 30 to 45%), and therefore, the sensor signal was not only affected by the temperature, but also by the humidity. Because of this factor, an accurate calibration curve for temperature dependence alone cannot be extracted from these tests; however, we have qualitatively identified the thermal dependence of the sensor.

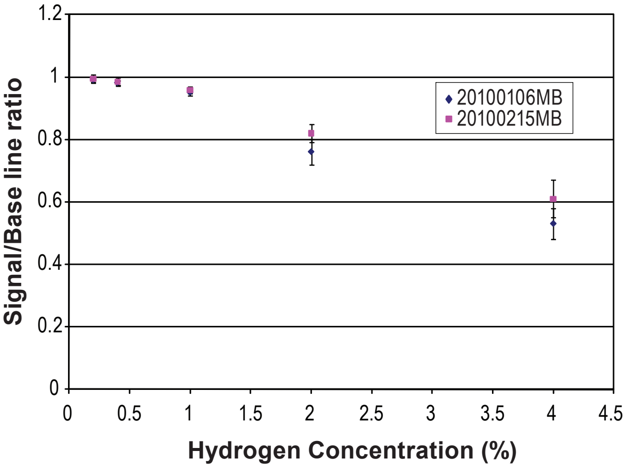

FIGURE 3. Average of Optical Signal of Two Sensor Batches as a Function of Hydrogen Concentration

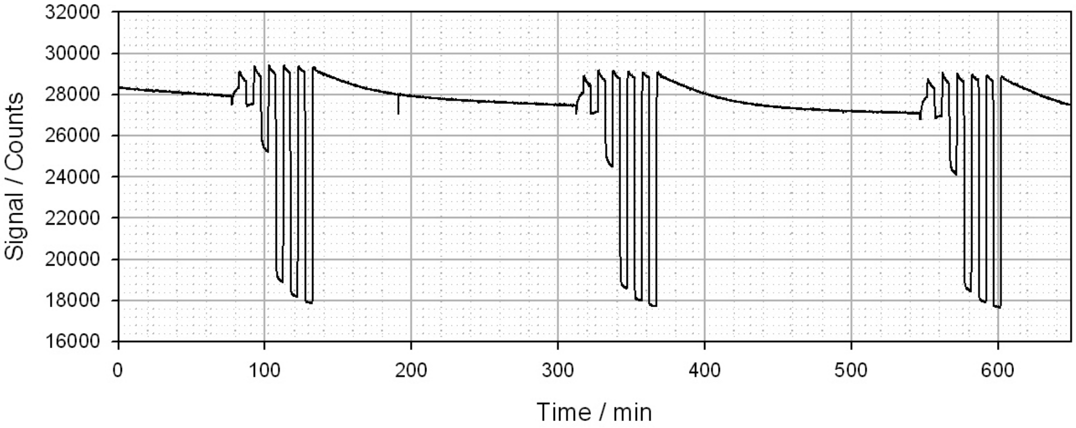

FIGURE 2. Reversible/Repeatable Performance of IOS Hydrogen Sensor

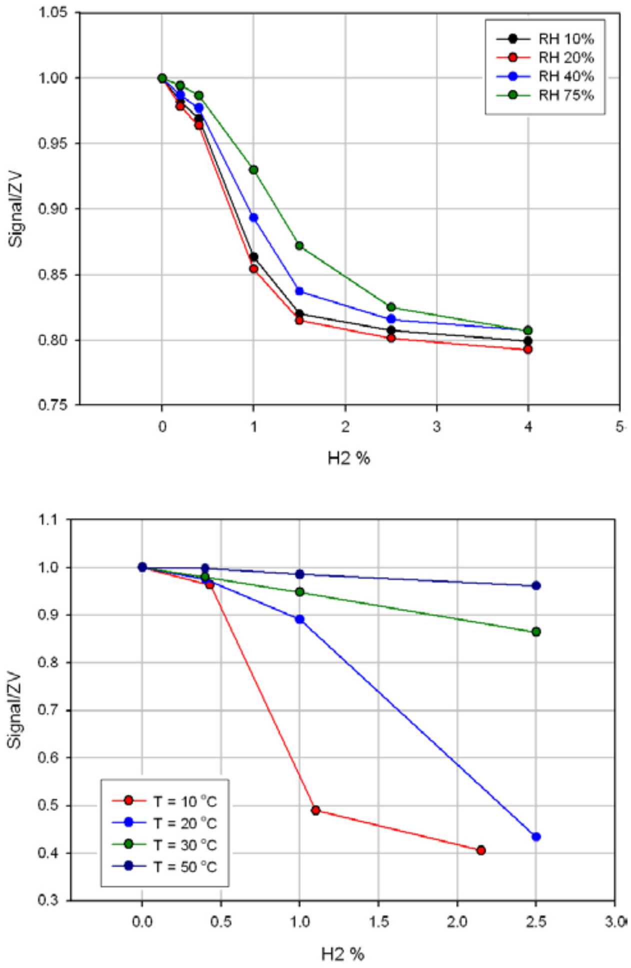

FIGURE 4. Environmental Effects on Hydrogen Sensor Response; Top: RH (temperature held constant at 25°C); Bottom: Temperature (RH = 37±7%)

Reproducible Fabrication/Longevity Studies

Fabricated hydrogen sensor optrodes were placed in long-term longevity studies where the optrodes were exposed to various levels of hydrogen (0.2 and 1.0%) at standard conditions (RH ~40%, and T=25°C). The signal change at a fixed hydrogen concentration showed no noticeable change over an aging period of five months (see Figure 5). We envision that a minimum longevity time of one year can be obtained. The accuracy and precision of hydrogen optrode measurements are listed in Table 2. A high degree of optrode fabrication reproducibility was achieved; data summarizing the inter-batch performance versus the intra-batch performance is shown in Figure 6.

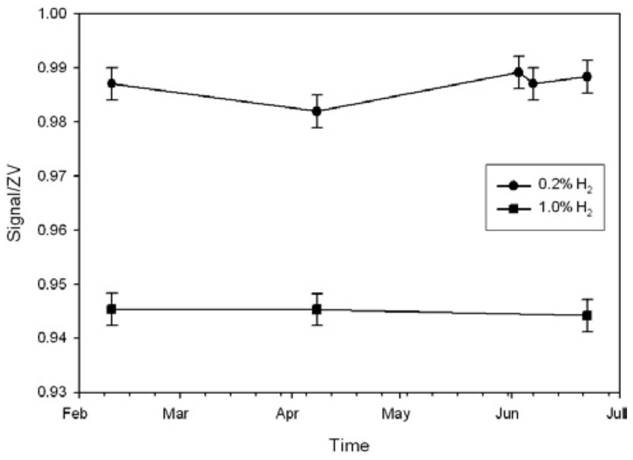

FIGURE 5. Aging Studies of Hydrogen Sensor Element

TABLE 2. Hydrogen Optrode Accuracy/Precision

	Hydrogen (%)		
n	0.2	1	2
1		0.99	1.97
2	0.16	0.94	1.98
3	0.15	0.99	1.99
4	0.22	1.01	2.01
5	0.21	1.02	2.02
6	0.27	1.06	2.03
Average	0.20	1.00	2.00
StDev	0.05	0.04	0.03

Calibration Function: Linear interpolation on batch #20100106MB-A2 tested at NREL; StDev – standard deviation

Conclusions and Future Directions

We have developed sensitive, stable, reversible colorimetric hydrogen optrodes, and incorporated them in unique compact, hydrogen sensor units. Future directions include:

- "Map" the temperature/humidity parameter space using formally designed experiments to provide complete coverage.
- Develop, test, and optimize data processing algorithms to fully compensate for environmental effects.
- Perform field tests to validate sensor performance in a variety of environments and applications.
- Explore commercial possibilities for the different hydrogen sensor embodiments.

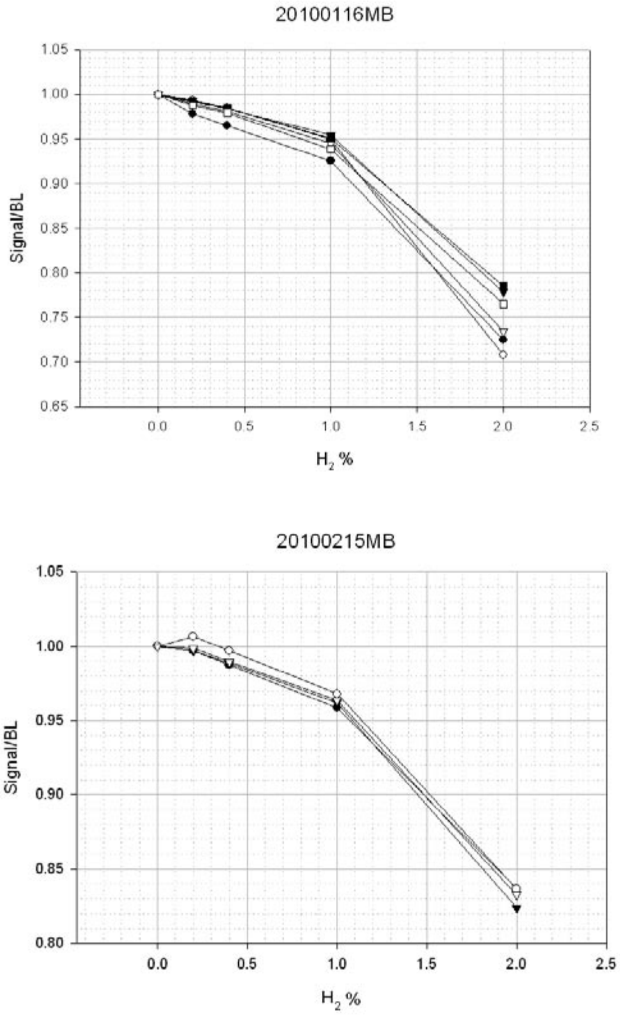

FIGURE 6. Response of Different Optrodes from Two Batches to 0–2% H_2 in Air at 40-45% RH

Special Recognitions & Awards/Patents Issued

An application is currently under examination in the United States Patent Office (USPTO); during this quarter, IOS did not receive any communications from the USPTO on this matter.

FY 2010 Publications/Presentations

1. 2010 Annual Merit Review Proceedings, poster presented June 09, 2010.

References

1. R.G. Zalosh and N.F. Barilo, "WIDE AREA AND DISTRIBUTED HYDROGEN SENSORS," PNNNL – SA-65498, International Conference on Hydrogen Safety, Ajaccio, Corsica, France, September 16018, 2009.