VIII.14 Hydrogen Leak Detection System Development

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Contract Number: DE-FG36-08G088098

Project Start Date: June 1, 2008
Project End Date: November 30, 2011

Overall Objectives

- Integrate hydrogen indicator chemistry into a complete optoelectronics package with well-defined sensing characteristics and a known end-use market.
- Develop signal processing and user interface software/firmware to assure sensor meets appropriate standards for commercial acceptance.

Fiscal Year (FY) 2011 Objectives

- Select and finalize hydrogen sensor components and outline scalable cost analysis.
- Finalize sensor data processing algorithms with minimum false alarms.
- Fabricate, test, and validate performance of 14 fully packaged prototypes.
- Deploy prototypes at four different field test sites.
- Collect and analyze real-time test data under various deployment conditions.
- Reach end-users through field demonstrations and field trails.

Technical Barriers

This project addresses the following technical barriers from several sections of the Fuel Cell Technologies Program Multi-Year Research, Development and Demonstration Plan (MYRDDP):

- **Delivery: Barrier I.** Hydrogen Leakage and Sensors (MYRDDP page 3.2-20: "Low cost hydrogen leak detector sensors are needed")
- **Storage: Barrier H.** Balance of Plant (BOP) Components (MYRDDP page 3.3-14: "Light-weight, cost-effective… components are needed…These include… sensors")
- **Manufacturing R&D: Barrier F.** Low Levels of Quality Control and Inflexible Processes (MYRDDP page 3.5-11: "Leak detectors… are needed for assembly of fuel cell power plants.")
- **Technology Validation: Barrier C.** Lack of Hydrogen Refueling Infrastructure Performance and Availability Data (MYRDDP page 3.6-8: "…the challenge of providing safe systems including low-cost, durable sensors [is an] early market penetration barrier")

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 Multi-Year Research, Development and Demonstration Plan:

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

FY 2011 Accomplishments

The hydrogen safety sensor being developed in this project has advanced from the applied research stage (DOE technology readiness level, TRL, 3) to the engineering prototype (TRL 6) stage. 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," polymer integrated optic chip sensors, and hydrogen-sensitive optical fibers many meters in length (Figure 1). Economic and regulatory considerations led to the selection of an optrode-based handheld/wall-mounted format for the engineering prototypes. Key accomplishments during the past year include:

- Hydrogen safety sensor prototype refined/ruggedized.
- Optrodes have high sensitivity and rapid hydrogen response.
- Sensor repeatability/reversibility validated in third-party (National Renewable Energy Laboratory, NREL) tests.
- Hydrogen alarm algorithm developed and validated in field tests.
- Potential for high-accuracy concentration measurement demonstrated.

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Introduction

Assuring safety is critically important to fostering commercial acceptance of hydrogen energy technologies, and to sustaining the use of hydrogen as a green energy source. A key to maintaining safety in hydrogen vehicles and installations is the ability to detect and warn of potentially hazardous conditions.

The overarching goal of this project is to create a reliable, cost-effective, alarm that warns of hydrogen leaks before they reach flammable concentrations. In the course of meeting this goal, we have demonstrated a proprietary hydrogen indicator chemistry that can be deployed in variety of optical formats, suitable for applications ranging from wide-area monitoring to point detection. Under DOE guidance, we have integrated a miniaturized indicator-bearing optical transducer with optoelectronic hardware and advanced signal processing software into a compact "smoke-detector-style" unit that will meet DOE- and customer-specified goals for sensitivity, response time, and reliability. This safety sensor will find use in many environments, including fuel cell-powered industrial vehicles, stationary power units, hydrogen generation and refueling stations, and storage locations.

Approach

- The hydrogen alarm sensor uses an optoelectronic platform (Figure 2) to monitor a porous glass sensor element ("optrode") hosting a colorimetric indicator. Upon hydrogen exposure, the optrode changes color, and the sensor unit uses the resulting optical signal to calculate hydrogen concentration. A second porous glass element, not containing the hydrogen indicator, gives the sensor an "internal reference" that minimizes environmentally induced false alarms (Figure 1).
- IOS' hydrogen sensor approach is unique in many aspects. First, each sensor unit uses an intrinsically safe low-power sensing element that functions without the heat required by many electronic hydrogen sensors. The unit employs another porous glass element, not containing the hydrogen indicator, gives the sensor an "internal reference" to minimize environmentally induced false alarms. Second, the unit has a faster response time and higher sensitivity levels, over a wider range of environmental conditions (i.e., temperature and humidity), than most of its counterparts. The sensor module can also be cabled to a readout unit for remote monitoring applications.

Results

In preparation for construction and delivery of 14 hydrogen sensor alarms for field testing, several elements

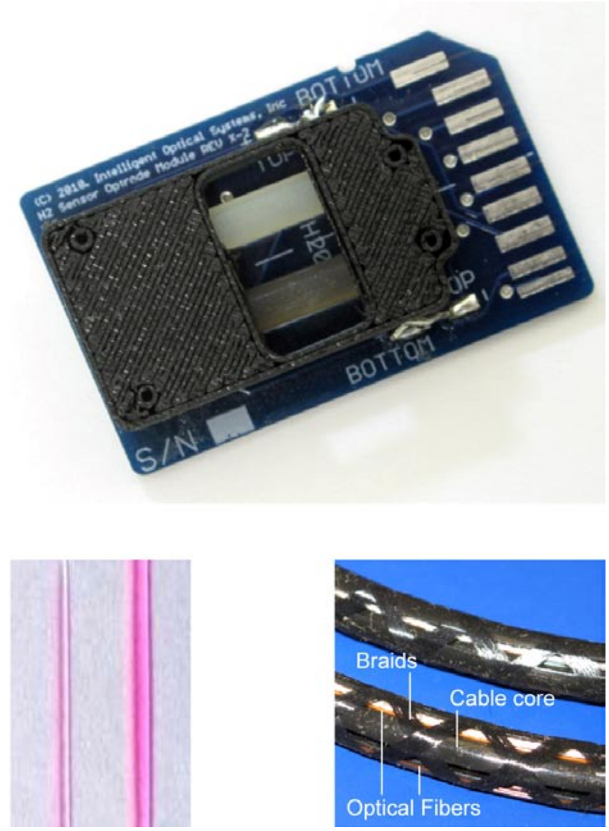

FIGURE 1. Optical Hydrogen Sensor Formats Top: optrodes in prototype mount; Bottom Left: integrated optic polymer waveguides; Bottom Right: extended-length sensor cable.

FIGURE 2. Compact Hydrogen Safety Sensor Unit

of the second-generation compact sensor were upgraded. Most notably, "noise" and "drift" in optical signals has been significantly reduced by redesigning the quick-connect optrode holder (Figure 1, top) to improve optical coupling between sensor elements and optoelectronic components. Changes in printed wiring board design were also implemented to simplify construction and address issues uncovered during testing of earlier versions. The result is a fully finalized physical and electronic design. All components have been procured, and construction of the field-test prototype units has begun. We project a mass-produced unit sale price of $100-$400, depending on features.

Sensor element materials and processing have also been finalized; a fabrication procedure has been selected that reproducibly generates optrodes of uniformly high quality. These transducers can respond to hydrogen at very low concentrations (Figure 3, top), and have been used to implement a high-speed alarm algorithm (Figure 3, bottom). Alarm response times are shown in Table 1. For all hydrogen concentrations at or above 10% of the lower flammability limit, (4% H_2 in air), the hydrogen leak detector sounds an alarm in less than 5 seconds.

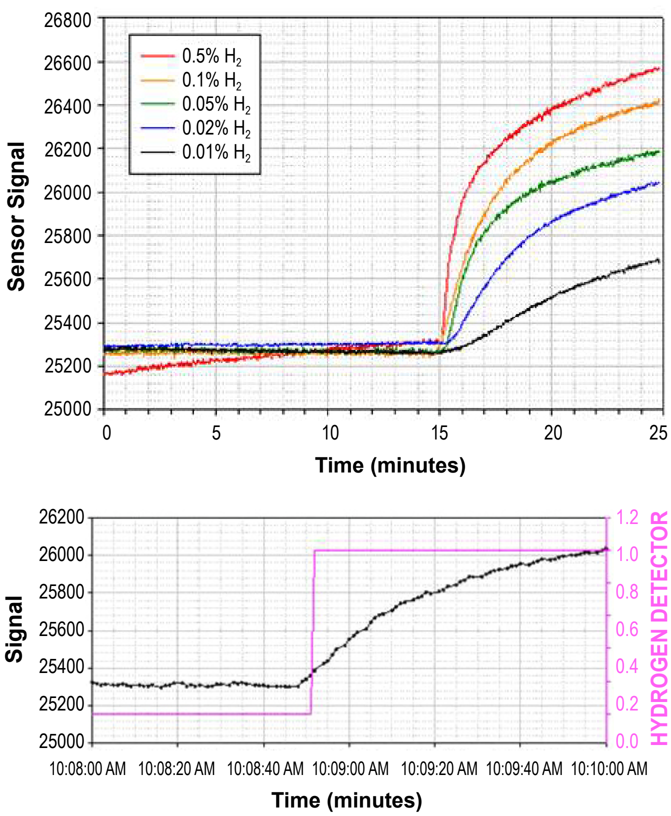

FIGURE 3. Rapid Response and High Sensitivity Top: response to low concentrations of hydrogen (0.01% H_2 = 0.25% of lower flammability limit; 0.5% H_2 = 12.5% lower flammability limit); Bottom: alarm algorithm (red line) triggers rapidly as optrode responds (black line) to 0.4% H_2 (10% lower flammability limit).

TABLE 1. Hydrogen Alarm Response Times

H_2 (%)	Detection Time (s)*
4.0	3
2.0	3
1.0	3
0.5	3
0.1	10
0.05	10
0.02	30
0.01	120

Determinations of sensor response and alarm algorithm function carried out at IOS have been independently verified in third-party tests carried out at NREL. Measurements of optrode signal sensitivity (Figure 4), repeatability, and reversibility (lack of hysteresis), have produced identical results to within the precision of the measurement apparatus. Multiple exposures to hydrogen release at NREL also showed the robustness of the rapid-response alarm algorithm (Figure 5). Preliminary tests of sensor response to simulated real-world leaks were carried out during a controlled release of hydrogen into a building at Sandia National Laboratories' Livermore facility. Optrode response closely tracked the hydrogen concentration in the building (Figure 6), verifying the feasibility of using optrodes not only for the development of safety alarms, but in high-accuracy hydrogen concentration sensors as well.

Conclusions and Future Directions

The prototype hydrogen leak alarm design is complete, and incorporates several upgrades based on results from IOS, NREL, and Sandia National Laboratories tests of earlier test units. Preliminary verification of the alarm

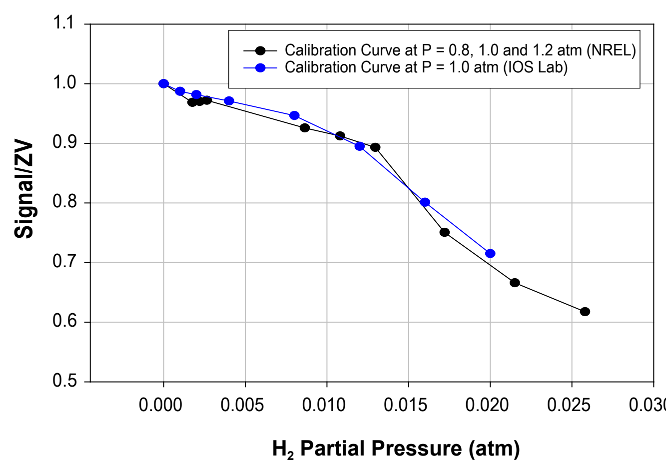

FIGURE 4. Optrode Response Validation Blue – Data taken at NREL; Black – Data taken at IOS.

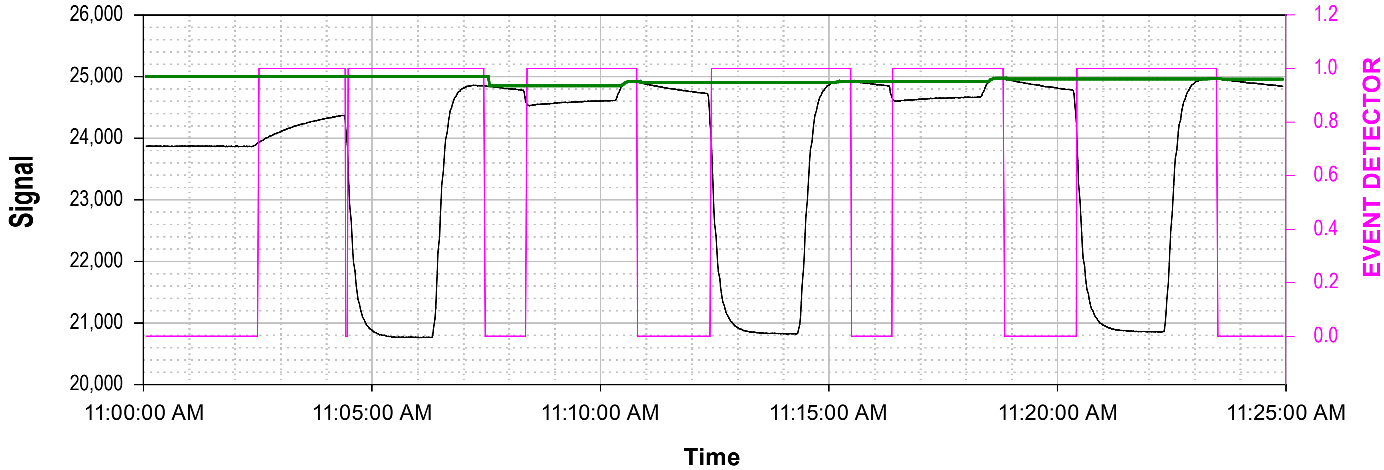

FIGURE 5. Hydrogen Alarm Algorithm Validation Black: optrode response; Red: alarm algorithm signal. Trigger point set at 2% H_2 (50% lower flammability limit, NREL data).

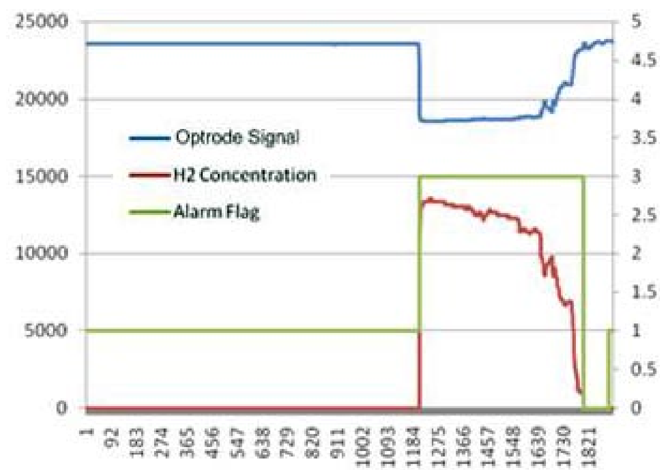

FIGURE 6. Building Release Trial at Sandia National Laboratories

algorithm has confirmed rapid response to all hydrogen concentrations of interest for safety monitoring. Remaining work in the project, which will advance the hydrogen detection leak system to TRL 7 includes:

- Development and installation of upgraded signal processing software.
- Assembly and delivery of 14 prototypes for field testing at DOE–selected sites.
- Extended temperature- and humidity-range testing of detector performance.
- Post-test upgrade of signal processing algorithms and final delivery of prototypes.

Patents Issued

1. "Sensor for Detection of Gas Such as Hydrogen and Method of Fabrication," U.S. Patent No. 7,897,057, issued March 1, 2011.

FY 2011 Publications/Presentations

1. "Intrinsically safe oxygen and hydrogen optical leak detector," M. Beshay, S. Garon, D. Ruiz, L. U. Kempen, Proc. SPIE Vol. 8026: Photonic Applications for Aerospace, Transportation, and Harsh Environment II, Alex A. Kazemi; Bernard Kress; Eric Y. Chan; Nabeel A. Riza; Lothar U. Kempen, Editors, 802605; 2011.

2. "Miniaturized real-time monitor for fuel cell leak applications," M. Beshay, J. G. Chandra Sekhar, J. Delgado Alonso, C. Boehr, R. A. Lieberman, Proc. SPIE Vol. 8026: Photonic Applications for Aerospace, Transportation, and Harsh Environment II, Alex A. Kazemi; Bernard Kress; Eric Y. Chan; Nabeel A. Riza; Lothar U. Kempen, Editors, 802606; 2011.