VIII.8 Leak Detection and H_2 Sensor Development for Hydrogen Applications

Eric L. Brosha[1] (Primary Contact), Fernando H. Garzon[1], Robert S. Glass[2], Cortney Kreller[1], Rangachary Mukundan[1], Catherine G. Padro[1], and Leta Woo[2]

[1]Los Alamos National Laboratory (LANL)
MS D429, P.O. Box 1663
Los Alamos, NM 87545
Phone: (505) 665 4008
Email: Brosha@lanl.gov

[2]Lawrence Livermore National Laboratory (LLNL)

DOE Manager
HQ: Antonio Ruiz
Phone: (202) 586-0729
Email: Antonio.Ruiz@ee.doe.gov

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FY 2012 Objectives

- Develop a low-cost, low-power, durable, and reliable hydrogen safety sensor for a wide range of vehicle and infrastructure applications.
- Continually advance test prototypes guided by materials selection, sensor design, electrochemical research and development (R&D) investigation, fabrication, and rigorous life testing.
- Disseminate packaged sensor prototypes and control systems to DOE laboratories and commercial parties interested in testing and fielding advanced prototypes for cross-validation.
- Evaluate manufacturing approaches for commercialization.
- Engage an industrial partner and execute technology transfer.

This project addresses the following technical barriers from the Hydrogen Safety section (3.8) of the Fuel Cell Technologies Program Multi-Year Research, Development and Demonstration Plan:

(A) Limited Historical Database

(F) Safety is Not Always Treated as a Continuous Process

Technical Targets

Technical targets vary depending on the application [1,2], but in general include:

- Sensitivity: 1-4 vol% range in air
- Accuracy: ±1% full scale in the range of 0.04-4 vol%
- Response Time: <1 min at 1% and <1 sec at 4%; recovery <1 min
- Temperature operating range: -40ºC to 60ºC
- Durability: minimal calibration or no calibration required for over sensor lifetime (as defined by particular application)
- Cross-Sensitivity: minimal interference to humidity, H_2S, CH_4, CO, and volatile organic carbons

FY 2012 Accomplishments

- Designed, built, and tested high-impedance buffer (HIB) circuit boards to isolate sensor element from outside voltage and current influences; added baseline offset and gain control.
- Tested more advanced sensor substrates incorporating onboard temperature control and completed initial calibration procedures for advanced prototypes.
- Designed, built, and tested sensor power supply and heater control electronics.
- Made additional refinements to effective packaging scheme adopted for advanced prototypes.
- Fabrication of multiple advanced prototype devices with HIB circuits for Round 2 of National Renewable Energy Laboratory (NREL) testing; six devices prepared with high level of reproducibility.
- Conducted Round 2 NREL testing. Results of Round 2 successful: isolation electronics developed in FY 2012 successfully resolved issues identified in Round 1 FY 2011 NREL testing. Sensor protected from leakage currents present in data acquisition electronics; baseline and hydrogen response nominal with minimal humidity interference and response to variations in barometric pressure, exceptional low-level H_2 sensitivity, high signal-to-noise, and minimal influence from methane, ammonia, carbon dioxide, and carbon monoxide.

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Introduction

Recent developments in the search for sustainable and renewable energy coupled with the advancements in fuel cell-powered vehicles have augmented the demand for hydrogen safety sensors [2]. There are several sensor technologies that have been developed to detect hydrogen, including deployed systems to detect leaks in manned space systems and hydrogen safety sensors for laboratory and industrial usage.

Among the several sensing methods electrochemical devices [3-9] that utilize high temperature-based ceramic electrolytes are largely unaffected by changes in humidity and are more resilient to electrode or electrolyte poisoning. The desired sensing technique should meet a detection threshold of 1% (10,000 ppm) H_2 and response time of ≤1 min [10], which is a target for infrastructure and vehicular uses. Further, a review of electrochemical hydrogen sensors by Korotcenkov *et.al* [11] and the report by Glass and others [10,12] suggest the need for inexpensive, low power, and compact sensors with long-term stability, minimal cross-sensitivity, and fast response. This view has been largely validated and supported by the fuel cell and hydrogen infrastructure industries by the NREL/DOE Hydrogen Sensor Workshop held on June 8, 2011 [13]. Many of the issues preventing widespread adoption of best-available hydrogen sensing technologies available today outside of cost, derive from excessive false positives and false negatives arising from signal drift and unstable sensor baseline; both of these problems necessitate the need for unacceptable frequent calibration [13].

As part of the Hydrogen Codes and Standards sub-program, LANL and LLNL are working together to develop and test inexpensive, zirconia-based, electrochemical (mixed potential) sensors for H_2 detection in air. Previous work conducted at LLNL showed [9] that indium tin oxide (ITO) electrodes produced a stable mixed potential response in the presence of up to 5% of H_2 in air with very low response to CO_2 and water vapor. The sensor also showed desirable characteristics with respect to response time and resistance to aging, and degradation due to thermal cycling.

In this investigation, the development and testing of an electrochemical hydrogen (H_2) sensor prototype based on 'ITO/yttria-stabilized zirconia (YSZ)/platinum (Pt)' configuration is detailed. The device fabricated using commercial ceramic sensor manufacturing methods on an alumina substrate with an integrated Pt resistance heater to achieve precise control of operating temperature while minimizing heterogeneous catalysis and loss of hydrogen sensitivity. Targeting fuel cell-powered automotive applications, the safety sensor was subjected to interference studies, temperature cycling, operating temperature variations, and long-term testing now exceeding over 6,000 hrs for some sensor configurations. In FY 2012, the mixed potential electrochemical technology was independently validated at the hydrogen safety sensor-testing lab at NREL; two packaged pre-commercial prototypes were tested against a standard testing protocol including sensor resistance to cross-interferences such as CO, CO_2, CH_4, and NH_3. In general, NREL testing showed a fast response to H_2 with exceptional low-level sensitivity and high signal-to-noise, very little deviation in sensor response to changes in ambient conditions such as humidity and barometric pressure, and minimal response to some common interference gases.

The salient features of the H_2 sensor prototype developed by LANL and LLNL are (a) low power consumption, (b) compactness to fit into critical areas for some applications, (c) simple operation, (d) fast response, (e) a direct voltage read-out circumventing the need for complicated signal processing, and (f) a low cost sensor platform conducive to commercialization using common ceramic manufacturing methods.

Approach

Two alternative sensor measurement approaches were used to develop devices with superior performance.

Controlled Electrode\Electrolyte\Gas Interface for Potentiometric Sensors

In the first approach, electrochemical potentiometric modality is utilized for designing the sensors. Mixed potential sensors are a class of electrochemical devices that develop an open-circuit electromotive force due to the difference in the kinetics of the redox reactions of various gaseous species at each electrode/electrolyte/gas interface, referred to as the triple phase boundary [14]. Therefore these sensors have been considered for the sensing of various reducible or oxidizable gas species in the presence of oxygen. Based on this principle, a unique sensor design was developed. The uniqueness these sensors, originally developed at LANL [15], derive from minimizing heterogeneous catalysis (detrimental to sensor response) by avoiding gas diffusion through a catalytically active material and minimizing diffusion path to the 3-phase interface (electrode/electrolyte/gas referred to as triple phase boundary). Unlike the conventional design of these devices that use a dense solid electrolyte and porous thin film electrodes (similar to the current state-of-the-art zirconia-based sensors and fuel cells), this design uses dense (either metal wires, oxide pellets or thin film) electrodes and porous electrolytes (bulk or thin film). Such a sensor design facilitates a stable and reproducible device response, since dense electrode morphologies are easy to reproduce and are significantly more stable than the conventional porous morphologies. Moreover, these sensors develop higher mixed potentials since the gas diffusion is through the less catalytically active electrolyte than the electrode. Further, the choice of electrodes is primarily based on their O_2 reduction kinetics. Sensors will typically involve one electrode with fast (Pt) and another with slow (Au or $LaCrO_3$) O_2 reduction kinetics aimed at improving the sensitivity.

Impedance Metric

In the second design, a new impedance-based measurement technique, originally developed at LLNL for electrochemical oxides of nitrogen (NO_x) sensors, was shown to generate more stable sensor responses and may be able to offer a way to compensate for cross-sensitivity effects. The technique is based on the measurement of parameters related to the complex impedance of the sensor in the frequency range of 1 Hz to 10 kHz. Measurements are typically made at a single frequency selected to maximize the desired sensitivity, although measurements performed at additional frequencies have been shown to be useful for correcting the response to interfering gases. It has been found in the NO_x sensor studies that it may be possible to use a wider variety of electrodes for the sensor in impedance-based sensing. Additional possible advantages included better tolerance to mechanical defects (such as delamination) and better longer-term stability.

Results

(a) Development of high impedance buffer board and testing with pre-commercial prototype

FY 2011 testing at NREL uncovered an unanticipated interaction of the sensor element with the data acquisition system used in the hydrogen sensor testing system. The first sensor testing and validation experiments showed data with an anomalously high baseline (when no H_2 was present) and poor sensitivity to H_2 (when H_2 was present). These behaviors were never seen in LANL or LLNL laboratory sensor development work and could only be explained if there was insufficient input impedance on the data acquisition system. As a result, an HIB circuit board was designed and built to isolate the naked electrochemical sensor from stray electric currents that would generate a high baseline voltage which, depending on the direction of the current flow, would induce an offset voltage that would reduce the sensor voltage generated in response to H_2 exposure. The HIB is designed around a Burr Brown INA116 electrometer amplifier integrated circuit and is designed to minimize leakage between the electrodes, and from the sensor itself to the electrometer circuit. The circuit was designed with built in offset and span adjustment. Figure 1 shows that implementation of the HIB board did not appreciably alter the characteristics of the sensor response when using a laboratory Keithley 2400 source-meter, which employ very high input impedance measurement circuitry, to record voltage vs. time.

(b) Transfer of packaged, pre-commercial H2 safety sensors to NREL for Round 2 testing

Multiple packaged advanced prototype sensors and two sets of HIB boards were prepared and used for Round 2 testing at the NREL sensor evaluation facility. In the first experiment, one of the sensors was placed into the NREL test chamber and connected directly to the data acquisition system and a simple on/off response to 2% H_2 was performed in air. The unusual and undesirable response characteristics reported in FY 2011 where immediately reproduced (bottom curve in Figure 2a). The HIB board was then connected to this sensor and placed alongside the sensor element within

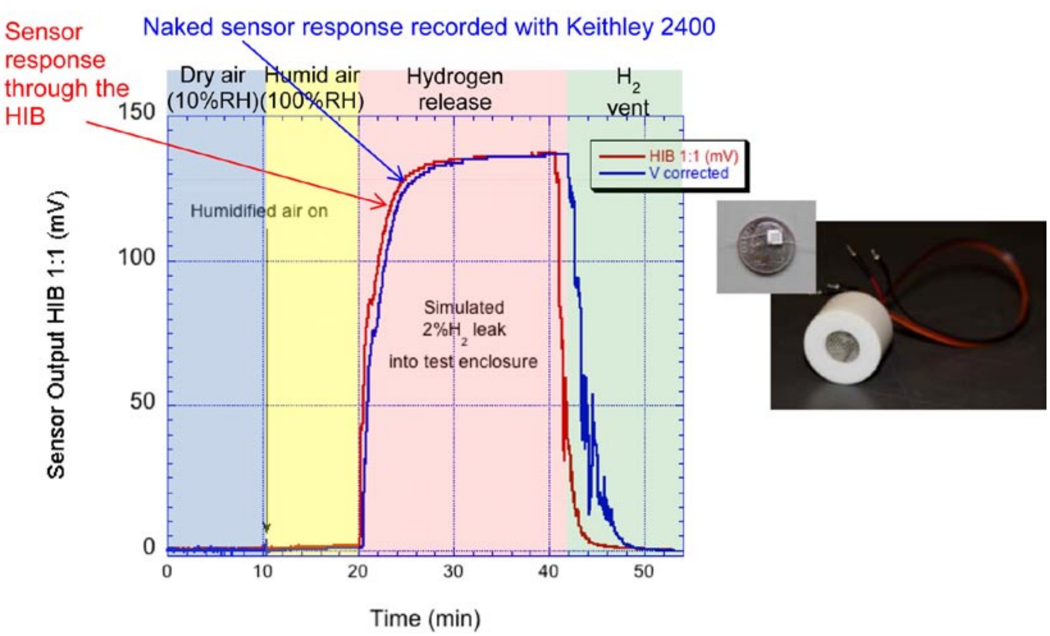

FIGURE 1. Testing of LANL/LLNL mixed-potential, electrochemical H_2 safety sensor with HIB board. Results show that the HIB isolates the electrochemical sensor from the measuring electronics without appreciably altering the response characteristics of the device. A photograph of the packaged prototype and naked sensor element is shown in the inset.

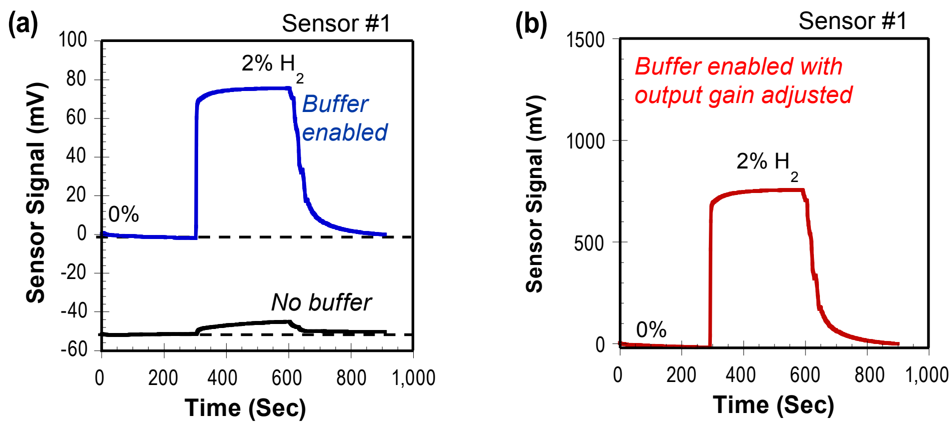

FIGURE 2. Data obtained at NREL of the mixed potential sensor performance of the packaged LANL/LLNL ITO/YSZ/Pt advanced prototype showing (a) use of HIB board to remove an anomalous baseline and recover sensitivity and (b) use of HIB board to magnify the output gain. The data in (a) clearly show the magnitude of the influence that the external data acquisition circuitry can impart on the measured sensor response.

the test chamber. A second H_2 sensor and HIB board was installed into the test chamber so that response data could be obtained from two devices simultaneously throughout the testing. The implementation of the isolation electronics immediately resolved the anomalous behavior and proves that the anomalous results obtained in Round 1 testing were introduced by undesirable influences imparted on the sensor from the NREL data acquisition system (Figure 2a).

The gain on the HIB board was the increased to amplify the signal from the device (Figure 2b). The large voltage signal produced by the sensor, high signal-to-noise, and fast response time are both very desirable qualities that will be easily exploited during subsequent stages of development and ultimate commercialization.

(c) Validation testing of the packaged LANL/LLNL pre-commercial prototype sensor and HIB electronics using NREL protocols: Round 2

Given the exception high H_2 sensitivity that the LANL/LLNL electrochemical devices exhibited, the standard NREL protocol to test device response and reproducibility to H_2 in air was modified. H_2 levels at 0.05%, 0.1%, and 0.5% were also tested, in addition to the standard NREL testing protocol using 0.2%, 1%, and 2% H_2 concentrations. While the overall results have been summarized in the FY 2012 Accomplishments section above, one particular test – effect of relative humidity (RH) changes – is highlighted below. The effects of changes in RH can have a dramatic effect on rates of false positives; for example, metal oxide-based semiconducting explosimeter sensors will easily trigger a false positive response to the moisture in human breath.

Two LANL/LLNL H_2 sensors were placed into the NREL H_2 sensor test chamber and were subsequently tested using the standard NREL protocols used for other H_2 sensor technologies [1]. Standard tests included: H_2 sensitivity, H_2 response reproducibility, humidity response, effects of changes in ambient conditions such as temperature and barometric pressure, effect of likely interference gases such as CO_2, CO, ammonia, and methane, and an extreme anaerobic durability test where the sensor is subjected to hours of operation in pure H_2. Figure 3 is an example of how well the LANL/LLNL H_2 safety sensor responded to a comprehensive NREL humidity test. The lack of intrinsic response to changes in humidity for the prototype sensors was shown in Figure 1. In this quick test of the sensor/HIB boards, the air base gas was switched from very dry 10% water content to a humidified air stream (100% RH at 25°C). The data in Figure 1 show no change in sensor baseline despite the abrupt change in RH. Figures 3a and 3b show the mixed potential sensor performance in more rigorous RH testing, with two sensors (Sensor #1 and Sensor #2) tested side-by-side in the NREL test stand using separate HIB boards with the output gain adjusted. To monitor system environmental variability from nominal set parameters, a humidity sensor and thermocouple continuously monitored water and temperature in the chamber (Figures 3c and 3d). In Figures 3a and 3b, the mixed potential sensors show good and reproducible response to hydrogen in the concentration range of 0.01-1% in both dry conditions and in the presence of water up to 2%.

In follow-on, Round 3 testing, emphasis will be placed expanding the tests to include additional interference gases, including those that are potentially corrosive in nature.

Conclusions

- All FY 2012 milestones were completed this year.
- A viable H_2 safety sensor technology has been developed on an advanced sensor platform that continues to

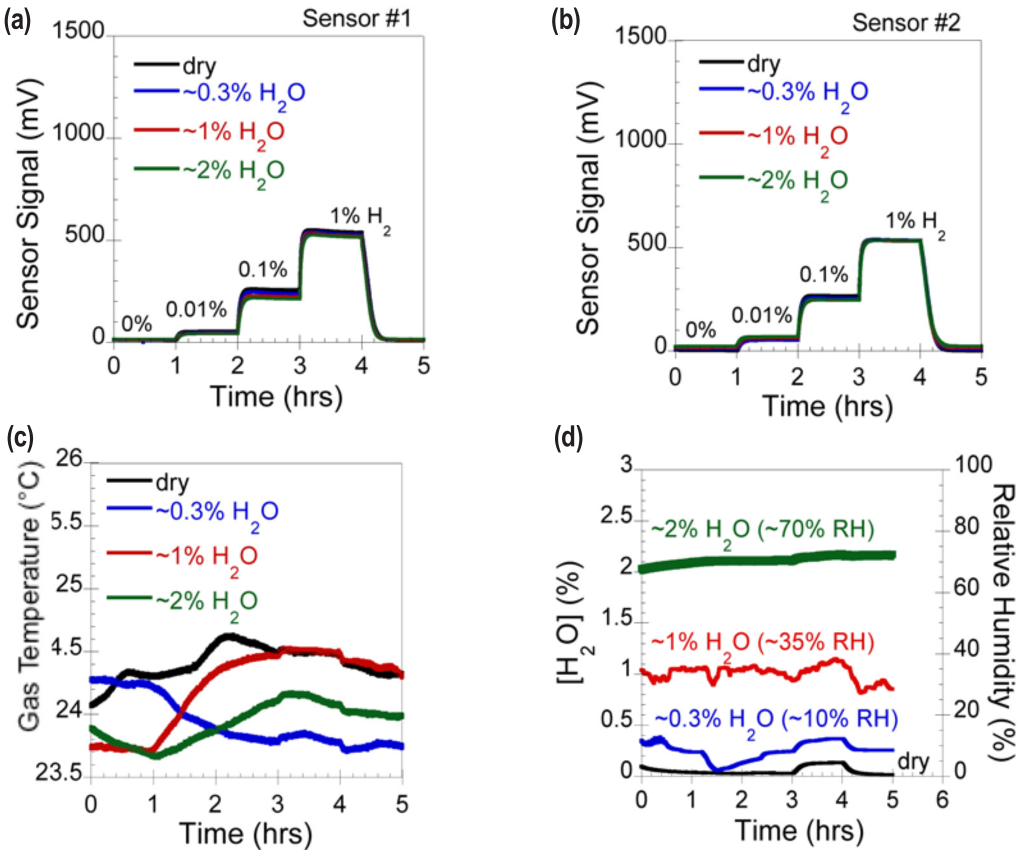

FIGURE 3. Mixed potential sensor performance of packaged LANL/LLNL ITO/YSZ/Pt advanced prototype, (a) Sensor #1 and (b) Sensor #2, with corresponding (c) gas temperature and (d) water concentration measurements under dry conditions and in the presence of ~0.3, ~1, and ~2% water.

improve. An advanced H_2 sensor prototype was fabricated on an alumina substrate with ITO and Pt electrodes and YSZ electrolyte with an integrated Pt heater to achieve precise operating temperature and minimize heterogeneous catalysis.

- Multiple sensors were prepared and packaged that exhibited excellent response and device-to-device reproducibility.
- Sensors and electronic packages were prepared and underwent cross-validation Round 2 testing at the NREL sensor test facility.
- Anomalous sensor behavior observed in Round 1 NREL testing in FY 2011 was reproduced and attributed to the presence of stray leakage currents in the data acquisition system, which introduced an undesired voltage between the sensor electrodes. HIB board electronics were designed, constructed, and tested in FY 2012, and they effectively eliminated these anomalies.
- NREL Round 2 testing show excellent sensitivity to H_2, reproducible device response with high signal-to-noise, minimal interferences to changes in relative humidity and barometric pressure, and good rejection of potential interference gases CO_2, CO, NH_3, and CH_4.

Future Directions

- Assemble complete sensor systems for field trial experiments in fuel cell laboratories and refueling facilities (e.g. power supply, HIB board, wireless internet protocol transmission of sensor signal, and data recording, display, and alerting algorithms).
- Identify commercialization partners and plan for a path forward.
- Improve power supply electronics to use single input control point.
- Reduce size and power consumption of the sensor element.
- Work with NREL partners to develop testing protocols for mixed potential type, electrochemical gas sensors.
- Provide new sensors and optimized electronics for Round 3 testing at NREL.

Collaboration and Coordination with Other Institutions

- Los Alamos National Laboratory
- Lawrence Livermore National Laboratory
- National Renewable Energy Laboratory
- ESL ElectroScience, Inc.
- BJR Sensors, LLC.
- Custom Sensor Solutions, Inc.

FY 2012 Publications and Presentation

1. L.Y. Woo, R.S. Glass, E.L. Brosha, R. Mukundan, F.H. Garzon, W.J. Buttner, M.B. Post, C. Rivkin, and R. Burgess, "Humidity Tolerance of Electrochemical Hydrogen Safety Sensors Based on Yttria- Stabilized Zirconia (YSZ) and Tin-doped Indium Oxide (ITO)," submitted ECS Transactions, Summer 2012.

2. L.Y. Woo, R.S. Glass, E.L. Brosha, R. Mukundan, F.H. Garzon, W.J. Buttner, M.B. Post, C. Rivkin, and R. Burgess, "Humidity Tolerance of Electrochemical Hydrogen Safety Sensors Based on Yttria- Stabilized Zirconia (YSZ) and Tin-doped Indium Oxide (ITO)," 221st Meeting of the ECS, Seattle, WA May 9, 2012.

3. P.K. Sekhar, E.L. Brosha, R. Mukundan, H. Mekonen, B. Farber, C. Kreller, and F.H. Garzon, "Packaging and Testing of a Hydrogen Safety Sensor Prototype," in preparation summer 2012.

4. P.K. Sekhar and E.L. Brosha, "Electrochemical Gas Sensor based Detection and Discrimination of Trace Explosives and Energetic Materials," 221st Meeting of the ECS, Seattle, WA May 9, 2012.

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