

VIII.8 Leak Detection and H₂ Sensor Development for Hydrogen Applications

Eric L. Brosha (Primary Contact)¹,
Fernando H. Garzon¹,
Robert S. Glass (Primary Contact)²,
Rangachary Mukundan¹, Catherine G. Padro¹,
Praveen K. Sekhar¹, and Leta Woo²

¹Los Alamos National Laboratory (LANL)
MS D429, P.O Box 1663
Los Alamos, NM 87545
Phone: (505) 665-4008
E-mail: brosha@lanl.gov

²Lawrence Livermore National Laboratory (LLNL)

DOE Manager

HQ: Antonio Ruiz
Phone: (202) 586-0729
E-mail: Antonio.Ruiz@ee.doe.gov

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FY 2011 Objectives

- Develop a low-cost, low-power, durable, and reliable hydrogen safety sensor for vehicle and infrastructure applications.
- Demonstrate working technology through application of commercial and reproducible manufacturing methods and rigorous life testing results guided by materials selection, sensor design, and electrochemical research and development investigation.
- Recommend sensor technologies and instrumentation approaches for engineering design.
- Disseminate packaged prototypes to DOE laboratories and commercial parties interested in testing and fielding advanced commercial prototypes while transferring technology to industry.

Multi-Year Program Plan Technical Barriers from the Hydrogen Safety section (3.8) of the Fuel Cell Technologies Program

- (D) Liability Issues: Potential liability issues and lack of insurability affecting the commercialization of hydrogen technologies: need for reliable H₂ safety sensor.
- (A) Variation in Standard Practice of H₂ Safety Assessments: The requirement to calibrate and commercialize safety sensors.
- (G) Expense of Data Collection and Maintenance

Technical Targets

- Sensitivity: 1 vol % in air.
- Accuracy: 0.04-4% ± 1%.
- Response Time: <1 min at 1% and <1 sec at 4%; recovery <1 min.
- Temperature: -40°C to 60°C.
- Durability: Five years without calibration.
- Cross-Sensitivity: Minimal interference to humidity, H₂S, CH₄, CO, and volatile organic compounds.

FY 2011 Accomplishments

- Completed testing of FY 2009 and FY 2010 laboratory and pre-commercial prototypes for long-term evaluation (>3,000 hrs, LLNL and 4,000 hrs, LANL including temperature cycling) including comparison of mixed potential and impedance modality in laboratory prototypes: down-select to mixed potential.
- For laboratory prototypes, evaluated impregnated composite electrodes for better long-term stability and demonstrated stability and reproducibility to over 3,000 hrs in laboratory testing.
- Designed more advanced sensor substrates incorporating on-board temperature control and completed initial calibration procedures for pre-commercial prototypes.
- Effective packaging scheme adopted for pre-commercial prototypes.
- Partnered with BJR Sensors and co-developed an algorithm using a novel approach to eliminate the cross interference affecting existing technologies.
- Fabrication of multiple pre-commercial prototype devices for National Renewable Laboratory (NREL) testing; six devices prepared with high level of reproducibility.
- First round of devices shipped to NREL for testing; devices returned and durability studied.
- Positive NREL feedback already used to improve sensor platforms and to prepare for Round 2 NREL testing – focus on electronics.
- Calculated an estimate of sensor element cost for large scale up in production.
- Designed and constructed prototype sensor electronics (impedance buffer and controlled heater circuit) in preparation of Round 2 NREL testing.



Introduction

Recent developments in the search for renewable energy coupled with the advancements in fuel cell vehicles (FCVs) have augmented the demand for hydrogen safety sensors [1]. 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 [2-8] 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 sec [9] targets for infrastructure and vehicular. Further, a review of electrochemical hydrogen sensors by Korotcenkov et al [10] and the report by Glass et al [11] suggest the need for inexpensive, low power, and compact sensors with long-term stability, minimal cross-sensitivity, and fast response. 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 [8] 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 no response to CO_2 or 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 H_2 sensor prototype based on 'ITO/yttria-stabilized zirconia (YSZ)/Pt' configuration is detailed. The device fabricated on an alumina substrate integrates a resistive Pt heater to achieve precise control of operating temperature while minimizing heterogeneous catalysis. Targeting fuel cell-powered automotive applications, the safety sensor was subjected to interference studies, temperature cycling, operating temperature variations, and long-term testing over 4,000 hrs. The sensor responded in real time to varying concentrations of H_2 (1,000 to 20,000 ppm). Among the interference gases tested such as nitric oxide (NO), nitrogen dioxide (NO_2), ammonia (NH_3), carbon monoxide (CO), and propylene (C_3H_6), the sensor showed cross-sensitivity to C_3H_6 . Analyzing the overall device performance over 4,000 hrs of testing for 5,000 ppm of H_2 , (a) the sensitivity varied between 0.135 to 0.17 V with a minimum low of 0.12 V, (b) the baseline signal ranged from 0 to 0.04 V, and (c) the response rise time fluctuated between 3 to 47 s.

The salient features of the H_2 sensor prototype developed by LANL are (a) the low power consumption, (b) compactness to fit into critical areas of application, (c) simple operation, (d) fast response, (e) a direct voltage read-out circumventing the need for any additional conditioning circuitry, and (f) conducive to commercialization.

Approach

The sensor design approaches from LANL and LLNL were used to develop devices with superior performance.

LANL Design: Controlled Electrode/Electrolyte/Gas Interface

At LANL, 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 [12]. 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 of LANL sensors [13] derives 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 tripe 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), the LANL 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 fabricated at LANL will typically involve one electrode with fast (Pt) and another with slow (Au or $LaCrO_3$) O_2 reduction kinetics aimed to improve the sensitivity.

LLNL Design

In the LLNL design, a new impedance-based measurement technique, originally developed 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. LLNL has also 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

Commercial Platform Packaging and Preparation of Multiple Devices

In order to facilitate the transfer of sensors to testing partners, a ceramic packaging was devised. A two-piece packaging made from a commercial machinable ceramic material. The sensor element was supported from its heater and sense wires using four metal posts that protruded from the case such that long lead wires could easily be soldered to the device. A ceramic cap with a 0.5" stainless-steel mesh was then affixed to the lower packaging using a ceramic adhesive. Figure 1 shows the completed, 1" diameter, packaged H₂ sensor. The packaging is insulating and at normal sensor operating temperature, the safety sensor may be handled comfortably without personal protective equipment.

A new method of characterizing hydrogen sensor response was developed to test sensor response in a non-flow, safety sensor mode. Figure 2 illustrates the approach adopted in preparation to transferring sensors to NREL for independent testing and validation. The sensors were placed into a 1.7 ft³ plexiglas enclosure with dry or humidified air entering through a 0.25" pass-through. The enclosure was fitted with several 0.25" pass-through holes for venting. When commended to do so, H₂ was added to the air stream such that resulting hydrogen concentration was 2%. Figure 2 also shows the sensor response and the actual hydrogen concentration present immediately in front of the packaged sensor.

A total of six packaged H₂ sensors were prepared (four with ITO working electrode and two with lanthanum

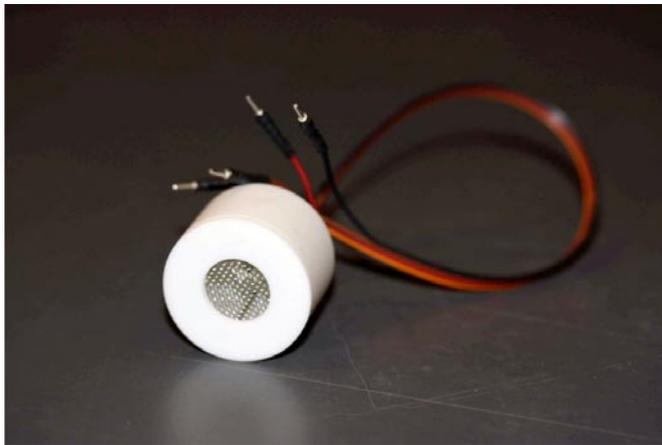


FIGURE 1. Photograph of a Packaged LANL/LLNL Mixed-Potential, Electrochemical H₂ Safety Sensor

manganese oxide working electrodes) for parallel testing at LANL, LLNL, and NREL.

Transfer of Packaged, Pre-Commercial H₂ Safety Sensors to NREL for Testing

Two packaged, pre-commercial H₂ safety sensors were shipped in October 2010 to NREL for testing and validation (Figure 3). Earlier, a mock-up of the packaging without sensor element was shipped to NREL to insure that test ports on the NREL apparatus would accept the LANL/LLNL sensors without complications. Testing commenced in January of 2011 and one of the heater leads of one of the packaged sensors broke during transport. That sensor was quickly replaced with a back up unit. The sensor's response to H₂, relative humidity influence, barometric pressure, and changes in ambient temperature were subsequently

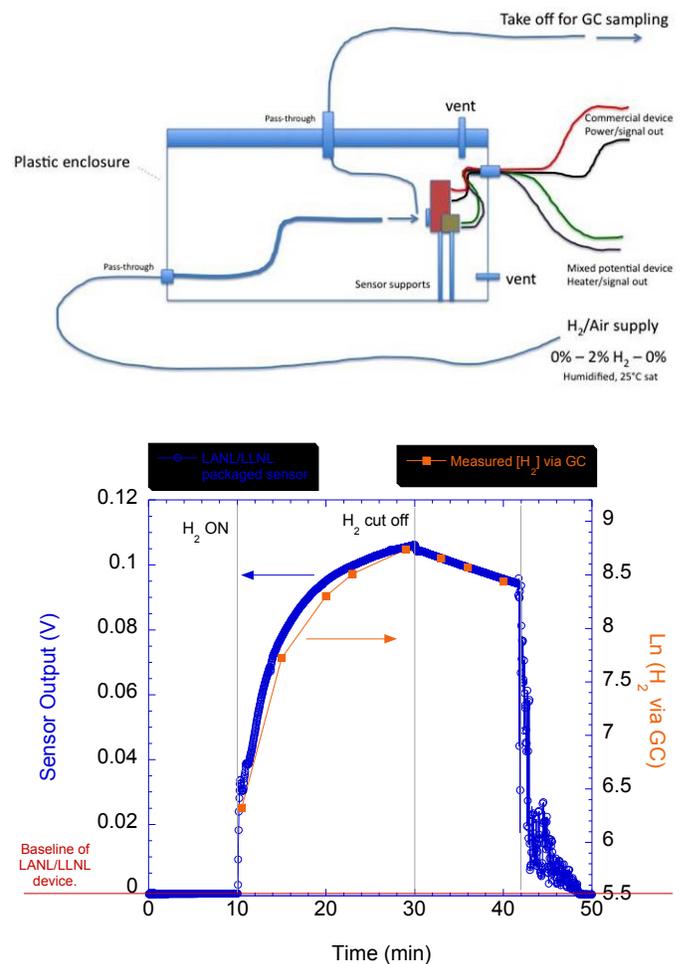


FIGURE 2. (top) A schematic of a test 1.7 cubic ft test enclosure cable of testing a pre-commercial, electrochemical-based LANL/LLNL H₂ sensor simultaneously with other technologies while extractive gas chromatograph measures actual hydrogen concentrations. (bottom) The response of a packaged, pre-commercial LANL/LLNL sensor while simulating a leak of hydrogen (2% H₂/air mix) into the enclosure.

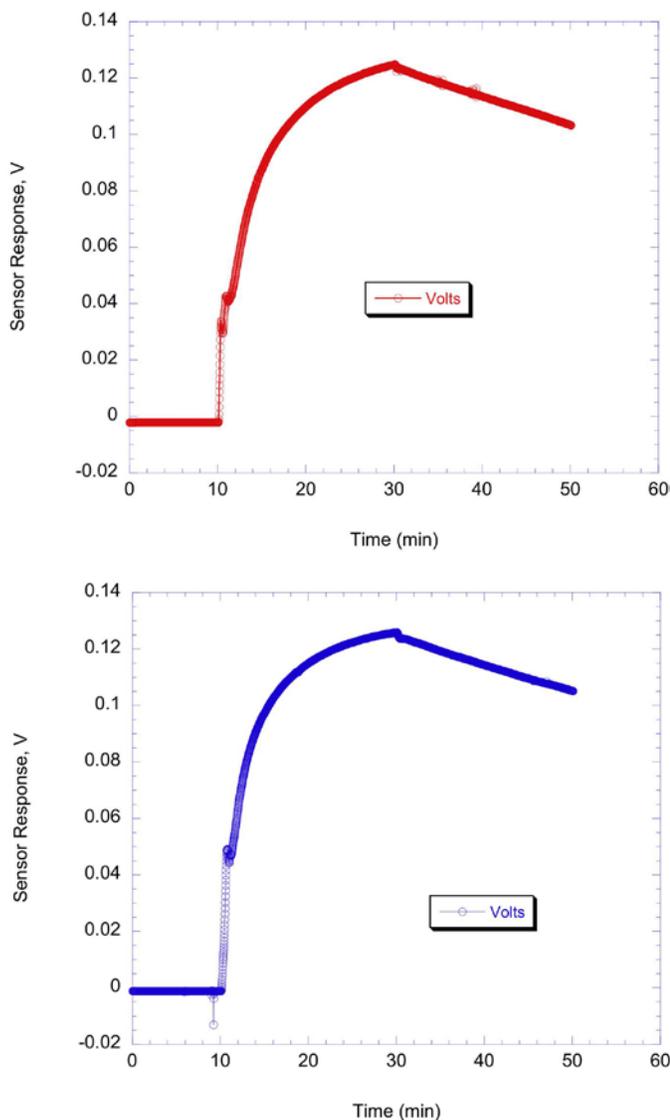


FIGURE 3. Comparison of the response of two packaged LANL/LLNL H_2 sensors to identical experiment profiles. Due to slight differences in positioning of the sensor element within the packaging and possible differences in heater resistance, the applied heater currents differed slightly (5 V/0.64 A top and 5 V/0.65 A bottom).

measured. The behavior of both sensors were similar as was predicted based on results shown in Figure 2. The sensors' response were insensitive to changes in relative humidity and the H_2 response to changes in ambient temperature of the testing chamber were as predicted (these devices did not have active temperature control). This latter result will be corrected once active temperature control is available using resistive thermal device (RTD) embedded in the sensor platform. However, there was a large non-zero baseline voltage not previously seen in these devices. This anomalous baseline voltage in air (no hydrogen) has never been seen at sensor testing at LANL or LLNL and may be attributed to impedance mismatches with the data acquisition system or



FIGURE 4. Custom-designed sensor impedance buffer circuit to isolate electrochemical sensor from external electrical influences. Photograph provided by Custom Sensor Solutions, Inc.

stray currents or voltages in some component of the NREL system since both sensors did not exhibit this behavior upon return to LANL after NREL testing. Based on these experimental results, a new high impedance/buffer circuit was designed to isolate the sensors from external influences. In addition, a circuit was designed to use the RTD output to control sensor operating temperature thus eliminating sensor response to changes in ambient testing temperature in the next round of testing at NREL.

Sensor Electronics: Circuit Design/Prototyping

Figure 4 shows an actual photograph of the completed high impedance buffer board. As of this report, multiple boards have been received from Custom Sensor Solutions, Inc. and compatible shielding and cables are being selected prior to testing and optimization. New, packaged sensors will be prepared and tested using this circuitry. Once the baseline response is well characterized on sensor test stations at LANL and LLNL (with and without impedance buffer to understand what effect – if any – the circuit has on sensor response), sensors and electronics will be transferred to NREL for the next round of testing/validation.

Conclusions

- All FY 2011 milestones on target to be completed this year.
- Improved electrode materials with potentially better performance were investigated where dense electronically conducting oxide (lanthanum strontium manganite) counter electrode showed better long-term stability.
- An alternate impedancemetric sensing modality was explored to evaluate improvements in long-term performance and stability.
- A viable H_2 safety sensor technology has been developed on a pre-commercial sensor platform that continues to

improve. A pre-commercial H₂ 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.

- A sensor platform cost analysis was performed by commercialization partner (scale up of existing pre-commercial platform to production of 100K and 500K units) and sensor cost estimated to be in the \$6 to \$9 range in line with a modern automotive lambda sensor.
- Multiple sensors were prepared and packaged that exhibited excellent response and device-to-device reproducibility.
- Sensors were prepared and transferred to NREL for independent testing and validation. Valuable feedback was obtained and used to design sensor isolation/impedance matching electronics and for sensor heater control.
- Device technology advanced from naked sensor to near-commercial state.
- Novel attributes of mixed electrochemical, mixed-potential sensor exploited in conjunction with novel pulse discharge technology as a method to reject influence from interference gases.

Future Directions

- Fabricate new sensors on platform with embedded temperature feedback sensor (RTD).
- Improve pre-commercial sensors and packaging using results from NREL testing.
- Work with NREL partners to develop testing protocols for mixed potential type, electrochemical gas sensors.
- Work with NREL to test prototype electronics (circuit and board design validation) for mixed potential type, electrochemical gas sensors:
 - Fabricate electronics to protect sensors from external influences, leakage currents, etc.
 - Impedance matching and signal amplification, baseline adjustment, etc.
 - Design and test constant resistance feedback circuit for temperature control.
- Utilize on-board RTD and incorporate active temperature control for next round of NREL testing.
- Provide new sensors and electronics to NREL for Round 2 testing.

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.

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