VIII.11 Hydrogen Safety, Codes and Standards: Sensors

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Project Start Date: Fiscal Year 2008
Project End Date: Fiscal Year 2015

Overall Objectives

- Develop a low cost, and low power electrochemical hydrogen safety sensor for a wide range of infrastructure and vehicle applications with focus on high durability and reliability
- Continually advance test prototypes guided by materials selection, sensor design, electrochemical research and development 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

Fiscal Year (FY) 2015 Objectives

- Complete construction and testing of prototype field trials units
- Test field trials unit, wireless system, and control software in laboratory setting
- Calibrate unit
- Install first field trials unit at Hydrogen Frontier Inc., Burbank, California location
- Collect data from field trials unit for minimum of one week and continue logging throughout rest of fiscal year
- Prepare follow on field trials units and site at Burbank facility
- Test new H_2 electrochemical sensor elements based on LANL working-electrode improvements

Technical Barriers

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

(A) Safety Data and Information: Limited Access and Availability

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

(K) No Consistent Codification Plan and Process for Synchronization of R&D and Code Development

(L) Usage and Access Restrictions

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 s at 4%; recovery <1 min
- Temperature operating range: -40°C to 60°C
- 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 compounds

FY 2015 Accomplishments

- Field trials were completed using two units, and the units were tested off LANL's site. Wireless communications and GoToMyPC® access to control LabView™ executable software developed by Agile Engineering and Zircoa Corporation were tested. By the end of the fiscal year, two units were installed: a hydrogen safety sensor inside a filling station dispensing island, and another located inside the compressor skid. An equipment-electronics locker was installed to house the LANL data acquisition computer and wireless receiver.
- No evidence of sensor baseline drift was detected during the field trials experiment.
- There were no false alarms or false positives that caused a signal exceeding 4% of H_2 (lower flammability limit). Exposure of sensor enclosure (and sensor) to significant and sometimes severe weather events was confirmed with no deleterious effects to the sensor or stable baseline of the sensor. These data confirm laboratory development data and National Renewable Energy Laboratory (NREL) testing data.
- Hydrogen Frontier station fill logs were obtained from November 7, 2014, through the end of November.
- We found excellent correlation of recorded H_2 release events with customers filling their fuel cell vehicles (FCVs). Multiple fill events were recorded in filling station logs and sensor resolution was good; each FCV fill even when spaced less than 15 min intervals was recorded.
- A statement of work was written and finalized with the South Coast Air Quality Management District (SCAQMD) to initiate a new project to install two sensor field trials units at two additional Los Angeles area hydrogen filling stations in FY 2016 as well as to expand testing at Hydrogen Frontier facilities.
- The FY 2015 Sensor Project milestone was met.

INTRODUCTION

Recent developments in the search for sustainable and renewable energy coupled with the advancements in FCVs have augmented the demand for hydrogen safety sensors initially to be placed at refueling sites and developed for incorporation on-board vehicles [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 commercially available or under development, electrochemical devices that utilize high temperature-based ceramic electrolytes have been shown to be robust, potentially low cost, have high sensitivity and good selectivity, the latter exemplified by tolerance to changes in humidity, and are more resilient to electrode or electrolyte poisoning [3-9]. 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 et al. [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 unstable sensor baseline; both of these problems necessitate the need for unacceptable frequent calibration [13]. As part of the Hydrogen Codes and Standards 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.

APPROACH

In this investigation, the development and testing of an electrochemical H_2 sensor prototype based on ITO/YSZ/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 vehicle infrastructure, the safety sensor was subjected to interference studies, temperature cycling, operating temperature variations, and long-term testing now exceeding over 6,000 h for some sensor configurations. In FY 2011, FY 2012, and FY 2013 the mixed potential electrochemical technology was independently validated at the hydrogen safety sensor-testing lab at NREL in three separate rounds of testing. In each round, two packaged precommercial prototypes were tested against a standard testing protocol including the effects changes in ambient temperature, pressure, humidity, and oxygen partial pressure and 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. However, potential weakness were found in the first two rounds of testing such as changes in sensor calibration with ambient temperature changes and complete sensor failure under the most harsh operating environment tested (anaerobic conditions, which would only happen under extremely unusual conditions) were identified. These last NREL-identified performance issues were ameliorated in FY 2013 and FY 2014. In FY 2013, a more chemically robust electrode was tested in a wide range of oxygen partial pressures (rich conditions to 100% O_2). The $La_{0.8}Sr_{0.2}CrO_3$ perovskite electrode was incorporated into new ESL devices and tested in FY 2015.

FY 2014 work focused primarily on the design, development, and testing of hardware required for field testing deployment at hydrogen refueling stations in California. In addition to technical work, pursuit of an indemnity agreement, commercial partner outreach, and planning for adherence to codes and standards in designing the prototype units were accomplished. A new circuit board design was prepared by Custom Sensor Solutions Inc. that combined the high impedance buffer circuit and sensor heater control board into one streamlined unit. The first of the new boards was delivered in May 2014 and testing and circuit revisions/optimization continued through June. At the end of June, all of the components were integrated into a commercially sourced, National Electrical Manufacturers Association Class 8 enclosure and systems testing began in July in the laboratory. A dedicated LabVIEW™-based software program was developed by a certified LabVIEW™ developer (Agile Engineering with software-wireless communications testing performed by Zircoa Inc.) This executable code was designed to accommodate up to three independent wireless hydrogen sensors at each deployment location. Given the exposure to outdoor environment at the primary California testing site, a ruggedized industrial computer with solid-state storage was selected and daily performance of the field trials unit will be carried out using remote access communication via the Internet.

The salient features of the H_2 sensor prototype developed by LANL and LLNL are (1) low power consumption, (2) compactness to fit into critical areas for some applications, (3) simple operation, (4) fast response, (5) a direct voltage read-out circumventing the need for complicated signal processing, (6) a low cost sensor platform, and (7) excellent stability and reproducibility all of which are conducive to commercialization using common ceramic manufacturing methods (8) low cost (9) technology readily lends itself to mass manufacturing protocols.

RESULTS REPORTED IN FY 2015

The sensor unit and data collection system were shipped to the Burbank filling station location and LANL staff members arrived several days after Hydrogen Frontier received the equipment. Installation began on November 4, 2014, and the sensor was brought online on November 5, 2014. The data acquisition system was installed inside of a properly rated steel enclosure above the existing control electronics bay for the filling station. The wireless system was brought online and the sensor was tested using a calibration gas provided by Hydrogen Frontier. The data acquisition computer was connected to a 1 GB/s Internet connection and control of the computer using GoToMyPC® software was tested using a laptop with cell modem communications. Figure 1 shows pictures of the installation.

FIGURE 1. (Left) Sensor unit installed inside dispensing island with cover closed. (Center) Cover open showing wireless transmitter and sensor and metal shielded power supply. (Right) Completed installation with dispenser unit enclosure sealed and ready for service.

The field trials experiment went online on November 5th and a new data file was typically started on each morning of each subsequent day of testing. After two to three days of testing, the LabVIEW™ program was remotely closed and the data files were downloaded to a laptop computer in New Mexico using the File Transfer Protocol provision in the GoToMyPC® program. Several characteristics in the sensor data were immediately apparent; the sensor baseline was stable and did not drift however there was some sensor activity that could not be attributed to noise. Also, several sharp responses were recorded almost immediately. Three significant releases of H_2 were detected in the first 20 hours and two of these exceeded 1,000 ppm. The same behavior was seen in the next 25 hours of data collection; five release events were recorded with one pair occurring within 20 minutes of each other and one exceeding 2,500 ppm. The sensor baseline on the second day, in between these spikes in H_2 concentration, was exceptionally stable with no drift. We requested that the station filling log data be made available and Hydrogen Frontier sent LANL data for November 7th. Several positive correlations to station filling activities were immediately noted and we requested more station filling log data. Figure 2 shows the sensor data collected for the file that was started in the morning of November 7, 2014, and continuous sensor logging was carried out for 34 hours. As indicated, each of the H_2 releases detected by the field trials sensor corresponded to a station customer filling his/her FCV. Every release detected is accounted for by matching the time that the sensor recorded an H_2 release and when the customer began or ended the FCV fill. Another significant observation to note is that there are no H_2 peaks that are not unaccounted for despite that fact that the filling station is located in a heavily congested downtown city environment. The facility is adjacent to the City of Burbank's facility for waste and municipal government operations that include heavy vehicle access to their facilities in close proximity to the station and sensor location. Since the computer software does not record a date/time stamp in the data file, the correlation of sensor time and station filling log time must be manually synchronized and there is a cumulative error of perhaps 2–3 minutes between the sensor log and station dispenser log however the error is much smaller than the average 12–15 minutes that the typical FCV fill would take. It is speculated that the H_2 releases being recorded are the result of H_2 diffusing from the vent line located well above the dispensing island enclosure after depressurization of the filling hose and nozzle. The station operators did not anticipate or expect these frequent incursions of H_2 inside the dispensing island enclosure and they have been made aware of these occurrences. To our knowledge, the commercial H_2 sensor located less than 12 inches from the LANL-LLNL field trials sensor, did not record these events.

A closer analysis of the event, the peak shape illustrates the detail that the field trials sensor unit was able to capture when FCV customers filled their hydrogen tanks. Figure 3 is an expanded view of the hydrogen dispensed on November 7, 2014, at 17:36. Figure 3 shows a deviation from the sensor baseline occurring within the time error of the station's filling log. There was a slow increase in sensor output for approximately 11 minutes at which time there was a large, rapid increase in H_2 to 1,300 ppm and then rapid decay in H_2 as the H_2 dissipated. Since the station filling log indicated that recharging the FCV storage tanks took 12 minutes, we believe that the field trials sensor accurately captures the pressurization of the delivery hose (and was sensitive enough to measure the hydrogen either diffusing through

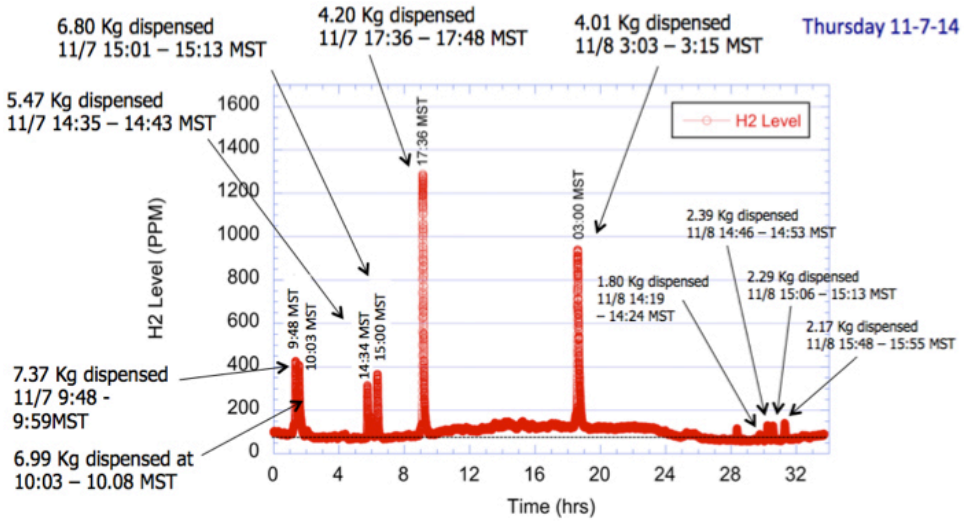

FIGURE 2. Data recorded from Thursday, November 7, 2014 field trials sensor unit. Each release of H_2 recorded (>100 ppm) is matched to the Hydrogen Frontier station filling log data for customers filling their FCVs. The station time and amount of H_2 dispensed is indicated.

the walls of the hose or is an indication of small leaks in the internal connections of the dispensing station) and the depressurization/venting of the system before the dispensing hose was decoupled from the vehicle.

These types of sensor behavior were seen throughout the next week of logging sensor data. Around November 12, 2014, the data became increasingly noisy and wireless communications dropouts began to be detected. This was apparent to us whenever the recorded sensor voltage would spike to +10 V, the default voltage produced by the Omega wireless received when the signal is lost from the Omega transmitter. By November 19, 2014, the signal was lost entirely for almost two weeks. On November 29th, communications were reestablished and sensor logging was restarted. Over the course of the next 280 hours of field trials data logging, there was a change in the behavior of the H_2 releases recorded by the sensor. These data are shown in Figure 4. An elevated and oscillating sensor baseline was seen; the concentration fluctuated between 200 ppm and 400 ppm of H_2 with a periodicity of about 24 hours. This behavior was seen for over 280 hours of continuous monitoring with several large releases of H_2 recorded (as high as 8,000 ppm). As before, the sensor baseline showed no drift over the course of this interval; the periodicity was very regular – suggesting this was a man-made cause – and the concentration of H_2 releases was much larger than any of the FCV-related activity.

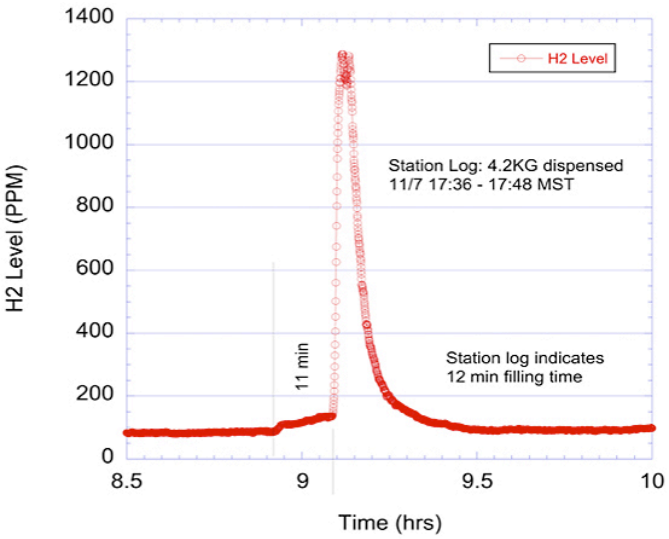

FIGURE 3. Expanded axes of the hydrogen release recorded on November 7, 201414 at 17:36 MST. There are two different sensor behaviors captured in these data showing FCV fueling and depressurization-hose release from the vehicle.

We contacted Hydrogen Frontier to discuss possible causes for this sensor behavior. We were informed that that station had gone back to onsite-generation of hydrogen using the station's methane reformer. When this occurs, the reformer operates continuously on a 600-hour duty cycle with periodic compression of the synthesized H_2 using the station's compressor systems. Moreover, during this enhanced level of station activity, the Burbank and Greater Los Angeles Area received significant severe weather over the course of a week that included high winds, downpours (leading to standing water inside the filling station dispenser enclosure) and even a recorded tornado. Time correlations of these events are indicated in Figure 4. Once again, the behavior of the field trials sensor can be explained by station activities. The fact that the periodic sensor baseline was not affected

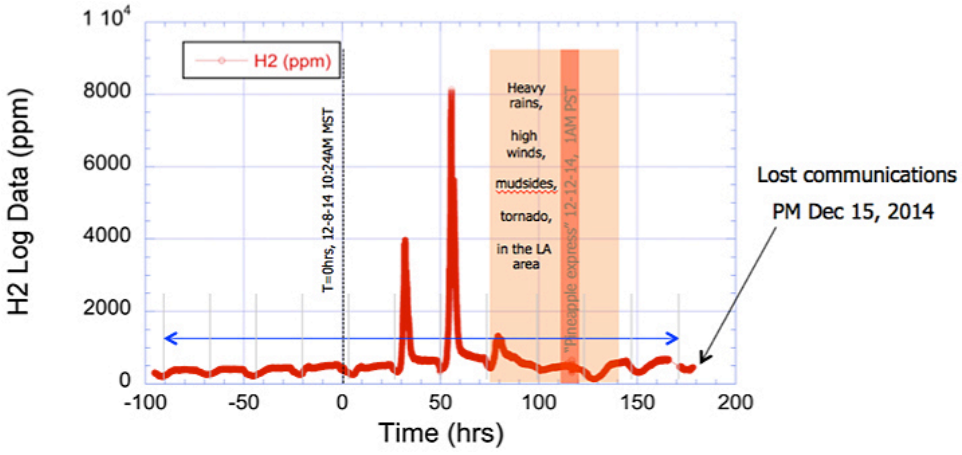

FIGURE 4. After communications were reestablished on November 29, 2014, a continuous run of 280 hours was successfully achieved that overlapped with known, significant weather events in the Burbank area. Elevated baseline and periodic oscillations are attributed to the Hydrogen Frontier station producing H_2 onsite with their methane steam reformer system.

by severe weather (arrival of a "Pineapple Express" weather phenomena indicated) is an excellent confirmation of our reported laboratory findings during the sensor development phase of this project and confirmation of NREL sensor testing results. Communications with the field trials unit went offline permanently on December 15, 2014. The FY 2015 milestone for the field trials experiment was achieved.

At the end of FY 2014, discussions were initiated with our sensor manufacturing partner, ESL Electroscience to design the next generation of H_2 safety sensor to further reduce sensor cost, increase performance, and to simplify the construction of future field trials test units. The present sensors are designed using an indium tin oxide-working electrode identified by LLNL early in this safety, codes and standards project. Since this material is not compatible with ESL's manufacturing process, the working electrode and solid electrolyte must be deposited at LANL subsequent to delivery of the substrates from ESL. As discussed before, this increases cost and complexity of making the H_2 safety sensors. A new La-Sr-Cr-O working electrode identified by LANL was substituted for the LLNL ITO electrode. Furthermore, it was identified in FY 2014 that some commercial alumina tape varieties in use by ESL could permit sufficient ionic or electronic leakage currents between the Pt resistive heater and the electrodes/electrolyte of the sensor as to cause anomalous behavior from the high-impedance buffer circuit. Work began at ESL on 20 complete devices in December using a new sensor design leveraged off of LANL NO_x/NH_3 sensor technology projects. These complete devices, as prepared, are fabricated using ESL's commercial high temperature co-fired ceramic method. The devices will supply subsequent field trials operations through FY 2015 and beyond.

CONCLUSIONS

- The FY 2015 milestone was completed this year.
- Field trials testing at Burbank, California, Hydrogen Frontier Inc. were successful with H_2 exposure results almost perfectly correlated to station activities; both FCV filling and on-site production of hydrogen could be tracked by examination of the field trials sensor response.
- No false positives or false negatives were detected during period of performance.
- There was no evidence of or obvious drift in sensor baseline voltage over the course of testing and known severe weather events did not affect the sensor.
- The on-site commercial sensor did not report recorded hydrogen releases/exposures.
- The Hydrogen Frontier dispensing island enclosure was selected because of anticipated quiescent conditions but hydrogen was present during normal station operations.
- The station's filling log data support conclusions that H_2 releases appear to be related to filling FCVs and production-compression activities.
- Changes in ambient relative humidity, temperature, and pressure did not appear to have an effect on sensor performance.
- The mixed potential, electrochemical sensor technology performed as designed.

FUTURE DIRECTIONS

- Return to Burbank site to install second field trials unit and to upgrade sensor element of the first field trials unit to a new sensor prepared entirely by ESL using the new, LANL-derived working electrode
- Install computer controlled weather station to correlate atmospheric conditions with sensor data
- Reorient/reposition system antenna of commercial wireless units to reduce signal dropouts
- Begin work with SCAQMD to expand field-testing at other California H_2 filling station locations
- Continue with commercialization/technology transfer efforts with webinars and commercial outreach
  - Responded to NineSigma call for H_2 sensing technology for fuel cell infrastructure

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