VIII.11 NREL Hydrogen Sensor Testing Laboratory

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Project Start Date: October 1, 2012 Project End Date: Project continuation and direction determined annually by DOE

Overall Objectives

- Quantify performance of commercial hydrogen safety sensors relative to DOE metrics.
- Collaborate with industry, universities, and government researchers to develop improved hydrogen sensor technologies.
- Educate the hydrogen community on the proper use of hydrogen sensors.
- Support development and updating of hydrogen sensors codes and standards.
- Support infrastructure deployment by providing expert guidance on the use of hydrogen sensors.

Fiscal Year (FY) 2013 Objectives

- Quantify performance metrics of developmental sensor technologies supported by DOE.
- Support infrastructure deployment by providing sensor testing capability and guidance to stakeholders.
- Support fuel cell electric vehicle deployment by assessing safety sensor requirements specified in the Global Technical Regulation (GTR) for hydrogen-powered vehicles.
- Facilitate the commissioning of the NREL Energy System Integration Facility (ESIF) by working with NREL Environmental, Health and Safety to review and validate the chemical detection system.
- Transfer and establish the NREL Sensor Laboratory to ESIF.

Technical Barriers

This project addresses the following technical barriers identified in the Hydrogen Safety, Codes and Standards section 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
- (F) Enabling National and International Markets Requires Consistent Regulations, Codes and Standards
- (G) Insufficient Technical Data to Revise Standards
- (H) Insufficient Synchronization of National Codes and Standards
- (K) No Consistent Codification Plan and Process for Synchronization of R&D and Code Development

Contribution to Achievement of DOE Safety, Codes and Standards Milestones

This project contributes to achievement of the following DOE milestones from the Hydrogen Safety, Codes and Standards section of the Fuel Cell Technologies Office's Multi-Year Research, Development, and Demonstration Plan:

- Milestone 2.6: Develop sensors meeting technical targets (4Q, 2013)
- Milestone 2.12: Develop leak detection devices for pipelines (4Q, 2015)
- Milestone 2.15: Develop holistic design strategies (4Q, 2017)
- Milestone 3.1: Develop, validate, and harmonize test measurement protocols (4Q, 2014)
- Milestone 4.9: Completion of GTR Phase 2 (1Q, 2017)
- Milestone 5.1: Update safety bibliography and incidents databases (4Q, 2011-2020)

FY 2013 Accomplishments

- NREL and the European Union Joint Research Centre's Institute for Energy and Transport (IET) completed a 2-year Memorandum of Agreement (MOA) to collaborate on hydrogen safety sensor research; the MOA is being renewed.
- Completed numerous topical studies on the proper use of hydrogen sensors under the auspices of the NREL-IET MOA.

- Completed a critique on the use of oxygen sensors to correlate changes in oxygen concentration to hydrogen levels with strong arguments as to why this approach should not be used.
- Completed a survey of the impact of depressed oxygen on sensor performance for the major sensor platform types. Some sensors will not function in the absence of oxygen, which can lead to a potentially dangerous situation. Many stakeholders are not aware of this requirement.
- Completed a study of the impact of miniaturization via micro-machining on sensor performance.
- Initiated a fourth topical study surveying the impact of interferences and poisons on performance of the major sensor platform types.
- Completed the round robin testing with IET of commercial hydrogen sensors.
- Contributed to the white paper "Advancing the Hydrogen Safety Knowledge Base" summarizing the accomplishments of the International Energy Agreement, Hydrogen Implementation Agreement--Task 31 Hydrogen Safety.
- The NREL sensor laboratory proposed to the U.S. representative on the GTR (Nha Nguyen, Department of Transportation) that endorsement on the use of oxygen measurements to track hydrogen/helium leaks be removed from the GTR text.
- Supported the commissioning of the NREL ESIF by reviewing the chemical sensor detection system and assisting in validating its performance.
- Established the NREL sensor laboratory in the ESIF.

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INTRODUCTION

Safety is a major concern for the emerging hydrogen infrastructure. A reliable safety system is comprised of various elements that can include intrinsic design features (e.g., pressure control systems), engineering controls (e.g., sample size minimization), and the use of hydrogen sensors to monitor for releases. Both the IFC 2009 and National Fire Protection Association (NFPA) 2 require hydrogen sensors for numerous applications, thus sensors will be mandatory in all jurisdictions that adopt either IFC or NFPA. To assure the availability of reliable safety sensors, NREL established the Sensor Test Facility. The NREL Sensor Test Facility provides stakeholders (e.g., sensor developers and manufacturers, end users and code officials) an independent, unbiased evaluation of hydrogen sensor technologies. Test protocols are guided by the requirements in national and international sensor standards, as well as sensor performance targets

established by DOE. In addition to laboratory assessment of sensor performance, a critical mission of the NREL sensor testing laboratory is to educate end users on the proper use of hydrogen sensors. This is achieved, in part, through topical studies designed to illustrate fundamental properties and limitations of various hydrogen sensor technologies. The NREL sensor laboratory also facilitates deployment by partnering with end-users to assist in the design of their sensor system.

APPROACH

Evaluation of hydrogen safety sensors is an on-going activity at NREL. The NREL sensor test apparatus was designed with advanced capabilities, including parallel testing of multiple hydrogen sensors, sub-ambient to elevated temperature, sub-ambient to elevated pressure, active humidity control and accurate control of gas parameters with multiple precision digital mass flow meters operating in parallel. The test apparatus is fully automated for control and monitoring of test parameters and for data acquisition with around-the-clock operation capability. Selected sensors are subjected to an array of tests to quantify the impact of variation of environmental parameters and chemical matrix on performance. Results are reported back to the developer or manufacturer to support their future development work. NREL sensor testing also supports end-users by qualifying technology for their application and by educating the hydrogen community on the proper use of hydrogen sensors. The importance of hydrogen safety sensors has been internationally recognized. The IET has also established a sensor test facility. To facilitate sensor analysis and dissemination of the results, the NREL and the IET sensor testing laboratories have formalized collaboration under an inter-laboratory MOA. The MOA synergizes the laboratories' independently programmed activities to maximize the benefit of their respective institutional interests through cooperative activities. Under the auspices of the MOA, numerous topical studies have been initiated and jointly presented at meetings and published.

RESULTS

In order to support hydrogen deployment, the NREL Sensor Test Facility strives to assure the availability of hydrogen sensors to meet stakeholder needs. This is achieved in part by providing an unbiased assessment of performance to sensor developers and manufacturers as well as end-users. NREL has also performed numerous topical studies aimed at educating the hydrogen community on the proper use of hydrogen sensors. Results reported here summarize major studies completed in FY 2013 on the characterization and use of hydrogen sensors.

A round-robin test (RRT) of hydrogen sensors between NREL and IET produced quantitatively equivalent results,

thereby cross-validating the respective test systems and protocols. IET and NREL thus agreed to coordinate all future sensor evaluations so as to explicitly eliminate duplicate activity. The RRT also indicated a disparity between actual sensor performance and manufacture specifications; nearly one-third of the models considered for RRT did not meet the manufacturer accuracy specification. The protocol developed for the RRT stipulated that commercial, factory-calibrated sensors would be used without adjustment; on-site calibration would have lowered the number of sensors that were out of specification. Nevertheless, this observation emphasizes the need to verify sensor metrics prior to deployment.

One emerging approach to measure hydrogen releases has been to use oxygen sensors to monitor changes in ambient oxygen levels and then to equate this change to hydrogen. This approach has been explicitly cited in the draft GTR proposed for hydrogen-fueled vehicles {Section B.6.1.2: "Sensors are selected to measure either the build-up of the hydrogen or helium gas or the reduction in oxygen (due to displacement of air by leaking hydrogen/helium)"}. The use of oxygen sensors to measure hydrogen levels was evaluated. In spite of the endorsement in the GTR, this approach was found to be inappropriate for closed systems, such as automobile passenger compartments. This is shown in Figure 1 which plots the O₂ sensor reading in air (21 vol% O₂) at 0.8 bar (region A). At 0.4 hours, the system was pressurized with helium to 1.0 bar; no response was observed on the oxygen sensor in spite of the presence of 20 vol% helium (region B). At 0.75 hours, the chamber was maintained at 1.0 bar while purged with air (region C). As a result, NREL has recommended to the U.S. representative on the GTR panel to remove the endorsement of this approach from the GTR. In addition, it was found that the natural drift in the oxygen sensor response precludes using this approach for safety monitoring applications (e.g., indoor monitors). Complete details of this study, including recommendations for alternative technologies will be presented at the 2013 International Conference for Hydrogen Safety and published in the International Journal of Hydrogen Energy.

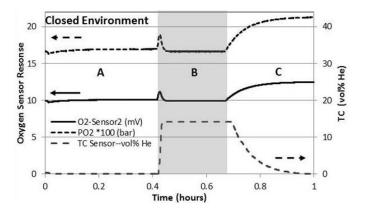


FIGURE 1. Insensitivity of the Oxygen Sensor to a Hydrogen Surrogate in a Closed Environment

Several critical sensor performance metrics remain elusive, such as the DOE target response time of 1 s. To achieve fast kinetics, sensor developers have invoked advanced manufacturing techniques such as micromachining to produce miniaturized devices. Such an approach can yield low-cost sensors through economy of scale manufacturing. It can also improve response times by minimizing the impact of bulk properties on the sensor response. NREL, in collaboration with IET and the Université du Québec à Trois-Rivières, evaluated the impact of miniaturization on sensor performance. Miniaturized sensors did indeed exhibit improved response times, however some developers tended to overemphasize the response time specification at the expense of other parameter since it was also observed that at least for some platform types, micromachining resulted in significant degradation in overall sensor performance. Preliminary results were presented at the World Hydrogen Energy Conference 2012 and a complete study was submitted to the International Journal of Hydrogen Energy in August 2013.

Hydrogen operations are often performed under an anaerobic atmosphere in order to minimize risks associated with the use of hydrogen. As an integral element in a safety system, sensor performance should not be compromised by operational parameters, but unfortunately many sensor platforms are deactivated when operated in an anaerobic atmosphere. On several occasions the NREL sensor laboratory had to inform an end-user that the sensor they proposed to use to measure hydrogen in a nitrogen purge would not work. This could lead to a false negative and potentially dangerous situation once the nitrogen purge is mixed with air. To educate the hydrogen community on the choice of hydrogen sensor platforms compatible for use in inert atmospheres, NREL and the IET completed an assessment of the oxygen requirements for the major sensor platform types. Preliminary results were presented at the 2011 International Conference for Hydrogen Safety and recently published in the International Journal of Hydrogen Energy.

In addition to topical studies, the NREL Sensor Test Facility supports sensor development by providing sensor developers and manufacturers with advanced sensor test capability. NREL provides reports and verbal briefings to sensor developers on the performance of their technology. The summary also includes an assessment of possible failure modes. The NREL Sensor Test Facility personnel have extensive experience in the design and use of chemical sensors, and can often identify faults that are missed by developers. Inasmuch as it is the policy of NREL not to identify a specific manufacturer, these reports are confidential and cannot be openly presented in an open forum such as the Annual Merit Review, but the data can be used, without reference to the sensor model, in topical studies and presentations. The NREL Sensor Test Facility has also worked with end-users on the design and verification of their

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hydrogen safety sensor system. Recently, the NREL Sensor Test Facility worked with the NREL Environmental Health and Safety Group to check out and validate the gas detection system implemented in ESIF.

CONCLUSIONS AND FUTURE DIRECTIONS

In the next year, the NREL sensor laboratory will build off its current accomplishment and capabilities via two main avenues—continued evaluation of commercial and developing sensor technologies and support of deployment by expanded collaborations with end-users of sensors.

- Manufacture/Developer Support
 - Commercial and developmental sensor technology performance validation
 - Wide area monitoring/distributed sensors
 - Process control sensors/fuel quality sensors (sensors for 0 to 100 vol% hydrogen)
- End-User Support to Support Deployment
 - Guidance on the use of hydrogen sensors in infrastructure deployments
 - Department of Transportation and the GTR on hydrogen vehicles
 - Barriers to sensor certification and the impact

FY 2013 PUBLICATIONS/PRESENTATIONS

1. Assessment of Commercial Micro-machined Hydrogen sensors to guide the Next Generation, H. El Matbouly, F. Domingue, V. Palmisano, L. Boon-Brett, M.B. Post, C. Rivkin, R. Burgess, and W.J. Buttner; presented at World Hydrogen Energy Conference 2012 and submitted to the International Journal of Hydrogen Energy (2013).

2. An Assessment on the Quantification of Hydrogen Releases Through Oxygen Displacement Using Oxygen Sensors, W. Buttner, M. Post, R. Burgess, C. Rivkin, L. Boon-Brett, V. Palmisano; to be presented at the International Conference on Hydrogen Safety (September 9–11, 2013) and published in the proceedings. **3.** Evaluation of Selectivity and Resistance to Poisons of Commercial Hydrogen Sensors, V. Palmisano, L. Boon-Brett, W. Buttner, M. Post, R. Burgess, C. Rivkin, to be presented at the International Conference on Hydrogen Safety (September 9–11, 2013) and published in the proceedings.

4. Inter-laboratory assessment of hydrogen safety sensors performance under anaerobic conditions, W.J. Buttner, R. Burgess, C. Rivkin, M.B. Post, L. Boon-Brett, G. Black, F. Harskamp, P. Moretto, International Journal of Hydrogen Energy 37 (2012) 17540-17548.

5. Steering Committee Progress Report on Hydrogen Sensor Performance Testing and Evaluation under the Memorandum of Agreement between NREL, U.S. DOE and JRC-IET, EC W. Buttner, M. Post, R. Burgess, C. Rivkin, L. Boon-Brett, V. Palmisano, C. Bonato and F. Harskamp Technical Report NREL/TP-5600-57207 (December 2012).

6. NREL/JRC MoA Steering Committee Meeting--Hydrogen Sensor Testing and Evaluation, W. Buttner, R. Burgess, C. Rivkin, M. Post L. Boon-Brett, P. Moretto, G. Black, V. Palmisano, F. Harskamp, C. Bonato, NREL/JRC Steering Committee-Annual Review Meeting (December 3, 2012).

7. U.S. Hydrogen Sensor Standards and Their Impact on Infrastructure Implementation, Kathleen O'Malley, William J. Buttner, H. Lopez, Julie Cairns, Robert Burgess, Carl Rivkin, and Robert Wichert, to be published as an NREL Technical Report (2013).