Overview of the U.S. DOE Hydrogen Safety, Codes and Standards Program Part 4: Hydrogen Sensors

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ABSTRACT

Hydrogen sensors are recognized as a critical element in the safety design for any hydrogen system. In this role, sensors can perform several important functions including indication of unintended hydrogen releases, activation of mitigation strategies to preclude the development of dangerous situations, activation of alarm systems and communication to first responders, and to initiate system shutdown. The functionality of hydrogen sensors in this capacity is decoupled from the system being monitored, thereby providing an independent safety component that is not affected by the system itself. The importance of hydrogen sensors has been recognized by DOE and by the Fuel Cell Technologies Office's Safety and Codes Standards (SCS) program in particular, which has for several years supported hydrogen safety sensor research and development. The SCS hydrogen sensor programs are currently led by the National Renewable Energy Laboratory, Los Alamos National Laboratory, and Lawrence Livermore National Laboratory. The current SCS sensor program encompasses the full range of issues related to safety sensors, including development of advance sensor platforms with exemplary performance, development of sensor-related code and standards, outreach to stakeholders on the role sensors play in facilitating deployment, technology evaluation, and support on the proper selection and use of sensors.

1.0 INTRODUCTION

The Fuel Cell Technologies Office (FCTO) [1] within the DOE Office of Energy Efficiency & Renewable Energy [2] is committed to the development of hydrogen as an energy carrier. Accordingly, the FCTO has numerous program areas which address technical issues with fuel cell technology. These programs cover major focus areas associated with hydrogen, including among others, hydrogen production, hydrogen storage, fuel cells, and safety codes and standards (SCS). One critical mission of the SCS program [3] is to facilitate the safe implementation of the hydrogen infrastructure. The SCS program supports the development of national hydrogen codes and standards that are harmonized to international standards as well as outreach programs designed to educate stakeholders on the regulations and best practices for the safe handling hydrogen. The SCS program is also actively supporting technology that is directly related to hydrogen safety, including research into hydrogen-compatible materials and components and hydrogen sensors.

1.1 Hydrogen Safety Sensors as an Enabling Technology

Hydrogen sensors are recognized as a critical element in the safety design for any hydrogen system. In this role, sensors can perform several important functions including indication of unintended hydrogen releases, activation of mitigation strategies to preclude the development of dangerous situations, activation of alarm systems and communication to first responders, and to initiate system shutdown. The functionality of hydrogen sensors in this capacity is decoupled from the system being monitored, thereby providing an independent safety component that is not affected by the system itself. The importance on the use of sensors, including the importance of selecting the right sensor for the application, has been demonstrated. A data base of hydrogen incidents maintain by PNNL [4] has identified several circumstances when a hydrogen-related event occurred because sensors were not used [e.g., 5] or on occasions when an inappropriate sensor was used [e.g., 6]. The importance of hydrogen sensors has been recognized by DOE and by the FCTO SCS program in particular, which has for several years supported hydrogen safety sensor research and development. The hydrogen sensor programs are currently led by the National Renewable Energy Laboratory (NREL), Los Alamos National Laboratory (LANL), and Lawrence Livermore National Laboratory (LLNL). The current SCS sensor program encompasses the full range of issues related to safety sensors, including development of advance sensor platforms with exemplary performance, development of sensor-related code and standards, outreach to stakeholders on the role sensors play in facilitating deployment, technology evaluation, and support on the proper selection and use of sensors. In collaboration with the European Fuel Cell and Hydrogen Joint Undertaking (FCH-JU), the SCS sensor program implemented the first formal international project with common objectives between the hydrogen programs in Europe and the U.S. The goals were to identify gaps in current sensor technologies and to identify pathways to make available effective, cost efficient sensors. The EU activity was performed under the auspices of *H2Sense* [7], a FCH-JU funded consortium of European sensor manufacturers and research laboratories. The U.S. activity was headed by the NREL Sensor Laboratory.

2.0 DOE Support of Advanced Hydrogen Sensors

Hydrogen sensors are commercially available in a variety of sensing platforms, defined primarily by the mechanism by which hydrogen interacts with the sensing element to produce an electrical signal. The most common hydrogen sensor types are metal oxide, electrochemical, catalytic bead, thermal conductivity, and devices based on palladium thin films. The strengths, weaknesses, and basic behavior of these sensors were recently reviewed [8, 9]. A more thorough summary of these hydrogen sensor platform types and other less common sensor platforms is currently in preparation [10]. One general conclusion on sensor performance is that while most commercial sensor platforms are excellent devices for the detection of hydrogen, none has been shown to meet all requirements for all applications. Thus, DOE has for several years supported the development of new sensing platforms for hydrogen, including a palladium thin film sensor, which have been successfully commercialized [11]; a mechanical zero-electrical power microcantilever sensing element that can be interrogated remotely with an optical probe [12] making it an ideal sensor for use in potentially explosive environments; and a unique electrochemical sensing platform being developed by LANL and LLNL, the mixed potential sensor [13], which is currently being field tested and explored for commercialization.

2.1 The Mixed Potential Hydrogen Sensor

The mixed-potential sensor is based upon different fundamental electrochemical reaction rates between specific electrode structures and the analyte. One significant advantage of this platform is the ability to tune the selectivity of the sensor by choosing electrode materials that have the desired properties with respect to the analyte of interest and potentially interfering contaminants. The LANL/LLNL technology is based on high temperature oxygen-ion conducting solid electrolytes like those used in automotive exhaust gas sensing technology. As such, the sensor is potentially very chemically and physically robust for operation in harsh environments and can be in principle a simple and inexpensive device. In an electrochemical cell, a polarization potential will develop as the reactant concentration is increased. This can be alleviated by increasing the area of the electrode or by using electrode materials with faster reaction rates (typically defined by the exchange current) for the specific reactant; thus the polarization potential for a specific reactant is very much dependent upon the electrode material. The basic phenomenon for mixed potential sensors was first reported by Fleming [14] and later suggested for the detection of carbon monoxide (CO) on an oxygen sensor. The fundamental theory behind the phenomena has been evolving since then. Researchers at LANL have made extensive advances in elucidating the fundamental theory of this class of sensors [13]. Mukundan and co-workers demonstrated that the potential that developed between two metal electrodes (e.g. gold and platinum) upon exposure to oxygen and oxygen with CO was directly correlated to the difference in polarization curves for platinum and gold that developed in the presence of CO (shown in Figure 1). As no electric current is permitted to flow between the electrodes, the oxidation and reduction reactions reach a steady state and a voltage is produced that is logarithmically proportional to the concentration of the CO.

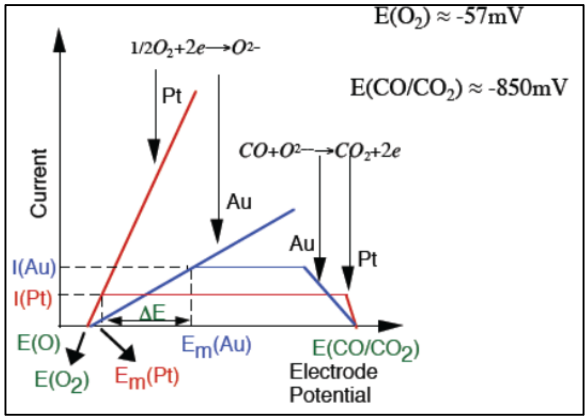

Figure 1: Illustration of the origin of the mixed potential at open circuit via the polarization curves of CO/O2 on Pt and Au electrodes [13], used with permission.

Typically, these structures are fabricated using solid-state oxide-ion conductors and thus are based upon the oxygen-oxide electrochemical equilibrium mediated by each electrode. Yttria-stabilized zirconia (YSZ) is often used as the electrolyte, which is a pure oxide ion conductor at temperatures above about 500°C. The polarization curves for each electrode are a convolution of the simultaneous reactions of oxygen reduction and CO oxidation. It was further shown that this difference was dominated by the gold electrode which exhibited a significant increase in overpotential upon exposure to CO relative to that observed on platinum. This work led to defining the requirements for a mixed-potential hydrogen sensor, including the use of an electrode which has minimal overpotential associated with hydrogen oxidation (e.g., platinum) and an electrode with a large overpotential associated with hydrogen oxidation. Gold meets the high over potential requirement in that gold has a much lower exchange current to hydrogen and oxygen than platinum. However, it is also necessary that the material be stable on operating temperature, and the gold-YSZ interface is not sufficiently stable for practical sensor applications at the required sensor operating temperature. Other electrode materials are being investigated, including indium tin oxide (ITO), which meets both the low oxygen exchange kinetics (e.g. behaves like Au) and thus generates a large mixed potential voltage in the presence of hydrogen, and exhibits a robust thermal stability requirement (ceramic material). A prototype mixed potential hydrogen sensor based on platinum and ITO (Figure 2) is now being developed and demonstrated [15], and considered for commercialization.

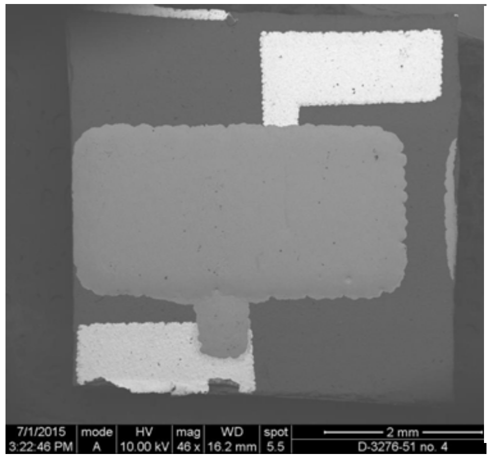

Photo by Eric Brosha, used with permission

Figure 2: The mixed potential sensor based on a commercial High Temperature Ceramic Co-fire (HTCC) process utilizing a metal oxide working electrode and an equilibrium Pt counter electrode supported on an alumina/YSZ platform.

2.2 Hydrogen Sensors and Infrastructure Deployment--the NREL Sensor Laboratory

Hydrogen sensors are not just laboratory curiosities, but are practical devices that enable hydrogen deployment by providing assurances of safety. Moreover, the use of sensors to detect unintended hydrogen releases is mandatory for several critical applications, for example in repair garages [16] or dispensing facilities [17]. The implementation of hydrogen infrastructure is accelerating with the imminent rollout of commercial fuel cell electric vehicles. Many of the stakeholders in the hydrogen community are not familiar with the selection, installation, and operation of hydrogen sensors. The NREL Hydrogen Sensor Test Laboratory [18] was established in 2008 to provide stakeholders (e.g., SDOs/CDOs, sensor developers and manufacturers, end users and code officials) a resource for the independent and unbiased assessment of hydrogen sensors. A main focus of the sensor laboratory was to assess the ability of commercial and developing sensor technology to meet critical performance metrics as defined by national [19] and international [20] standards, as well as critical performance metrics as identified by DOE [21]. The scope of the NREL Sensor Laboratory has expanded to encompass a full spectrum of hydrogen sensor support activities that include:

- Quantify performance of commercial hydrogen sensors relative to national and international standards and DOE metrics,
- Support development and assess performance of new and emerging sensor technologies,
- Support development and updating of hydrogen sensor codes and standards,
- Support infrastructure deployment by providing expert guidance on the use of hydrogen sensors,
- Educate the hydrogen community on the proper use of hydrogen sensors

The ultimate goal of the sensor laboratory is to assure that stakeholders in the hydrogen community have the sensor technology they need. Accordingly, evaluation of hydrogen safety sensors remains an on-going activity at NREL, which currently supports sensor developers and manufacturers as well as end-users. The NREL sensor test apparatus (Figure 3) was constructed with advanced capabilities, including parallel testing of multiple hydrogen sensors, sub-ambient to elevated temperature operation, sub-ambient to elevated pressure operation, active humidity control, monitoring of test conditions with traceable sensors, and accurate control of gas parameters with multiple precision digital mass flow meters operating in parallel. Representative test results are shown in Figure 4, illustrating the Dyanamic Range Test [22].

Additional standard test protocols have been developed [22], but these are customizable for specific applications. In addition, dedicated fixtures have been built to accommodate specialized testing, such as sensor operational lifetime and the impact of poisons.

NREL Photograph: XXXXX

Figure 3: The NREL Sensor Test Apparatus for basic sensor performance assessment was commissioned in 2009

To efficiently and effectively fulfill its mission, the NREL sensor laboratory has established numerous national and international partnerships with sensor manufacturers and developers, end-users, standards development organizations, and government laboratories covering both stationary and vehicle applications. The NREL Sensor Laboratory currently has six active or pending agreements with industrial partners whose applications range from development of fundamental sensor platforms to direct support of both infrastructure and vehicle deployment. The importance of hydrogen safety sensors has been internationally recognized, and the NREL sensor laboratory closely collaborates with international test laboratories including the Joint Research Centre Institute for Energy (IET) and Transport and the Federal Institute for Materials and Testing (BAM) in Berlin Germany.

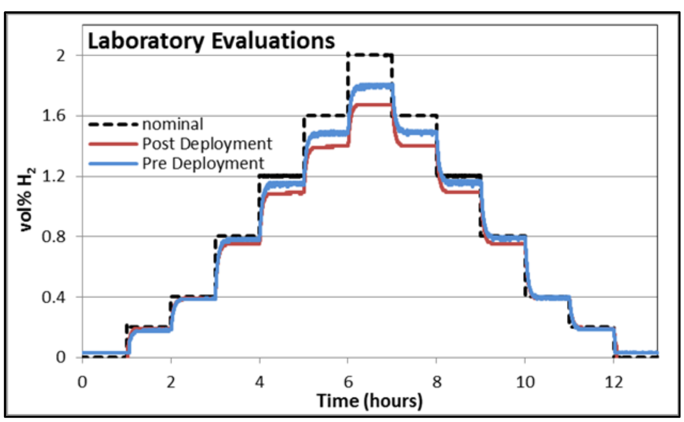

Figure 4: Response of a commercial H_2 sensor to various test gas concentrations prior to and following an actual field deployment [23].

One critical mission of the NREL sensor laboratory is to guide and educate the hydrogen community on the proper use of hydrogen safety sensors. To do this, numerous topical studies have been performed or on on-going to illustrate strengths/weaknesses and performance features of various hydrogen sensor platforms. Many of these studies were performed under the auspices of an international collaboration formalized by a memorandum of agreement with a comparable sensor test laboratory at the Institute IET [24]. The IET is operated by the European Union's Joint Research Center. Several such studies include:

- Impact of poisons and interferents on sensor performance and lifetime [23, 25]
- Support of the Global Technical Regulations [26] for hydrogen powered vehicles, including verification of sensing technology for vehicle crash tests [27, 28] and verification of tail pipe emission requirements [29].
  - The results of these studies directly supports the US Department of Transportation on the development of the Federal Motor Vehicle Safety Standard for hydrogen power vehicles
- Wide Area Monitoring (WAM), which is currently a literature study, has been initiated and on-going. WAM has the potential to simplify and be more cost effective for large facility-wide H2 monitoring than the use of point sensors.

3.0 SUMMARY

Sensors play a critical role in the DOE Hydrogen SCS program. In addition to the development of advanced sensors, the SCS sensor program also focuses on the addressing the needs of the end-users. Although evolving, the support of advanced technologies is continuing, with investigations into approaches such as wide area monitoring and risk assessment so as to define zone of hazards. Through outreach activity, including participation on code and standards development committees, topical publications and presentations, and direct interaction with stakeholders (including direct industrial partnerships), the NREL sensor laboratory is actively education the hydrogen community on the proper use of hydrogen sensors and best practices for their use.

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