

# **An Assessment on the Quantification of Hydrogen Releases through Oxygen Displacement Using Oxygen Sensors**

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## **Abstract**

Contrary to several reports in the recent literature, the use of oxygen sensors for indirectly monitoring ambient hydrogen concentration has serious drawbacks. This method is based on the assumption that a hydrogen release will displace oxygen, which is quantified using oxygen sensors. Despite its shortcomings, the draft Hydrogen Vehicle Global Technical Regulation lists this method as a means to monitor hydrogen leaks to verify vehicle fuel system integrity. Experimental evaluations that were designed to impartially compare the ability of commercial oxygen and hydrogen sensors to reliably measure and report hydrogen concentration changes are presented. Numerous drawbacks are identified and discussed.

## **1.0 Introduction**

The U.S. Department of Energy (DOE) Fuel Cell Technologies Program has taken the lead to support the development and deployment of hydrogen as an alternative energy source in the United States [1]. It functions as part of DOE's mission to ensure America's security and prosperity by addressing its energy and environmental challenges through transformative science and technology solutions [2]. Similarly, the European Commission (EC) has also identified the potential of hydrogen and fuel cells in the 2011 Technologies Map [3], which supports the Strategic Energy Technology Plan, the reference framework for developing energy research in Europe. The hydrogen infrastructure must develop safely if hydrogen is to be used successfully as an alternative fuel. One element of a hydrogen safety system is the use of sensors to detect unexpected releases. To ensure that hydrogen safety sensors are available to support infrastructure development, sensor test facilities were independently established by European Joint Research Centre (JRC) at the Institute for Energy and Transport (IET) [4] and by DOE at the National Renewable Energy Laboratory (NREL) [5]. Owing to the significant overlap of their respective missions to evaluate sensor technology and to educate the hydrogen community on the proper use of hydrogen sensors, the JRC-IET and NREL sensor laboratories have ongoing collaborative sensor research programs, formalized by a Memorandum of Agreement.

This paper presents the results of an investigation, performed under the auspices of the NREL-JRC Memorandum of Agreement, to critically assess the use of oxygen sensors for quantitatively monitoring hydrogen releases. Hydrogen releases are routinely detected using chemical sensors that respond directly to hydrogen. One emerging approach to detect and quantify hydrogen releases has been to use oxygen sensors to measure changes in ambient oxygen levels and then to equate this change to hydrogen [6, 7]. This approach has even been explicitly cited in the draft Global Technical Regulation (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)”} [8]. Some of the work that used the oxygen sensor for hydrogen monitoring was for controlled releases and not as safety monitors to detect unexpected releases and deployed for extended times. In controlled releases, helium is sometimes used as a surrogate for hydrogen.

Typically, the electrochemical oxygen sensor, also known as the *galvanic oxygen sensor* (because it operates in an amperometric mode), has been selected for this application. In this paper the term *oxygen sensor* refers to the galvanic oxygen sensor. The use of oxygen sensors for hydrogen determinations has some apparent advantages. As a mature technology, they are commercially available from a variety of manufacturers and with some impressive analytical performance specifications, including broad linear range to oxygen and reported response times of less than 1 sec for some models and modes of operation. Oxygen sensors are quite specific to oxygen and are not typically affected by chemical interferents. They are typically marketed for the measurement of ambient oxygen concentrations (typically given as approximately 20.9 vol%), but are also available with a range of 0 to 100%. Ambient oxygen levels decrease if air is displaced by a diluent gas such as hydrogen. Air displacement caused by hydrogen will be identical to that induced by an equivalent amount of helium, so helium can be used as a hydrogen surrogate without change of sensor or even recalibration. The oxygen sensing element is also extremely simple to use. Signal measurement requires nothing more than a voltmeter attached to a resistor connecting the anode and the cathode, although many sensor models include circuitry to improve signal characteristics. A simple, 2-point calibration procedure is often performed using ambient air (20.9 vol% O<sub>2</sub>) and an inert gas (e.g., nitrogen, helium) with 0 vol% O<sub>2</sub>.

The use of oxygen sensors to determine hydrogen seems to have advantages; however, some tangible limitations adversely impact their reliability for many—if not all—applications. This paper assesses some of these limitations; a more thorough assessment is in preparation. Signal drift and a limited operational lifetime are two major drawbacks of the oxygen sensor for hydrogen monitoring. It is concluded that oxygen sensors should not be used to detect and monitor hydrogen, especially for safety applications. Even in controlled investigations, including those where helium is substituted for hydrogen, the oxygen sensor is not the platform of choice for best data quality. Alternative technology is proposed that meets or exceeds the performance of oxygen sensors for hydrogen monitoring for many critical applications, including studies using helium as a hydrogen surrogate.

## **2.0 Experimental**

### **2.1 Sensor Selection**

This study used two commercial oxygen sensor models (labeled O2-Sensor1 and O2-Sensor2). Both sensors were operated according to the manufacturer’s recommendations. Specifically, the O2-Sensor2 signal was directly measured as a voltage across an internal integrated resistor connecting the anode and cathode. O2-Sensor2 was operated without additional circuitry, which could have amplified its signal and decreased signal noise, thereby improving overall analytical performance. O2-Sensor1 was interfaced to commercial control circuitry specifically designed for this sensor. Both sensors signals were in volts, which were logged by the sensor apparatus data acquisition system (DAQ). In addition, a thermoconductivity (TC) sensor marketed for the direct detection of hydrogen was used as control. The

TC sensor was selected because it was shown to be amenable to both hydrogen and helium detection [9]. The cross-sensitivity between helium and hydrogen is a property of the TC sensor platform. The TC sensor used in this study was factory calibrated for hydrogen with an output corresponding to equivalent vol% H<sub>2</sub>, but in-house calibration readily converted the response to vol% He [9]. The electronics of the TC sensor restricted its range to an equivalent response of 0 to 10 vol% H<sub>2</sub>. Due to a lower sensitivity, the helium range of the sensor corresponded to approximately 0 to 13.5 vol% He. This range is not a fundamental limiting value for the TC platform; there are some commercial TC sensors specified for 0 to 100 vol% hydrogen operation. The 0 to 10 vol% range is adequate for safety monitoring for nearly all hydrogen safety applications [10]. The apparatus and test protocols described in the following subsections were used to simultaneously test the three sensor models.

## 2.2 Sensor Test Fixture

Evaluation of hydrogen safety sensors is an ongoing activity within the sensor test facilities at the JRC-IET [4] and at NREL [5]. Both institutes designed and built sensor test apparatus with advanced capabilities, including parallel testing of multiple sensors, subambient to elevated temperatures (T), subambient to elevated pressures (P), active relative humidity (RH) control, and accurate control of gas parameters with multiple precision digital mass flow controllers operating in parallel. Probes that are certified to national standards were used to monitor test conditions (T, P, RH, and flow). Evaluations were conducted in the sensor chamber, which isolated the test sensors from the external environment. Typically, the test gas flowed continuously for the duration of the experiment, although the apparatus can also operate under static, no flow conditions. Both the NREL and JRC sensor test apparatus are fully automated for the control and monitoring of test parameters and for data acquisition. Both apparatus utilize data acquisition systems (DAQ) based upon LabView® and National Instruments hardware. Although different design and control features have been incorporated in the sensor test fixtures at JRC and NREL, round-robin testing of various sensor technologies has cross-validated the performance capability and accuracy of the respective apparatus [11].

## 2.3 Sensor Test Protocols

The three sensors were simultaneously deployed in the test chamber. The TC sensor and O<sub>2</sub>-Sensor2 were operated in diffusion mode, responding to changes in the bulk atmosphere of the test chamber. O<sub>2</sub>-Sensor1 was designed to function as a flow-through sensor such that the test gas was to flow continuously over its surface. Appropriate flow was achieved by connecting the inlet of the O<sub>2</sub>-Sensor1 sensor housing to the gas inlet of the test chamber. Incoming flow to the chamber was regulated to 1000 sccm.

Helium was used as a surrogate for hydrogen. Helium-air mixtures were generated from gas cylinders of synthetic air and ultra-high purity helium. Cylinders of ultra-zero air, produced by blending of oxygen and nitrogen by the supplier, were used for sensor testing and have a nominal certified oxygen concentration of  $21.0 \pm 1.5$  vol% O<sub>2</sub> with a balance of nitrogen and negligible concentrations of other gases (e.g., hydrocarbons, argon). For this study, air is considered to be 21 vol% O<sub>2</sub> in nitrogen, which closely approximates the typical ambient oxygen concentration of 20.9 vol%. The test gas composition was generated by the dynamic mixing of air and helium with the respective flow rates regulated by mass flow controllers. Typical test conditions were as follows:

Temperature (T):	25.0 ± 2° C
Pressure (P):	1.0 ± 0.05 bar
Relative Humidity (RH):	Dry (<5% RH)
Gas flow rate:	1000 sccm

Test conditions were varied for the investigation of the impacts of environmental parameters (e.g., T, P) on sensor response.

Sensor exposures were performed in discrete steps of fixed oxygen concentrations, which were adjusted by blending air with helium. The DAQ continuously logged the signals from the chemical sensors and environmental probes at a nominal rate of 1 pt/sec and stored them in an electronic data file. Each step was of one hour duration, a time sufficient for the sensor response to achieve steady-state. The steady-state signal (or *final indication* as defined by ISO 26140 [12]) was taken as the sensor response (SR) for a specific test condition and was extracted from the electronic data file as a 30-sec average of the logged data points collected during the final 2 min of a step. At the end of the 1-h step, the test gas concentration was adjusted. Step duration and gas composition were fully automated and controlled by the DAQ. Changes in environmental parameter set points (T, P, and RH) were also fully automated and controlled by the DAQ.

### 3.0 Results and Discussion

Hydrogen determination via oxygen monitoring is fundamentally an indirect analysis method. Assuming the oxygen concentration in air is 21 vol%, the total diluent concentration can be determined by eq 1:

$$\text{vol\% diluent} = 100 - \frac{100 * \text{vol\% O}_2}{21} \quad (1)$$

Because oxygen represents only 21% by volume of the total composition of air, the diluent concentration will be nearly 5 times greater than the measured change in the oxygen concentration. Although this implies a large sensitivity for the diluent determination, this dependency also amplifies the impact of sensor noise and drift. It also affects the accuracy of diluent determination because of the uncertainty associated with accurately resolving small changes in oxygen levels with the oxygen sensor. A 0.1 vol% limiting resolution for the oxygen sensor (e.g., the ability of the oxygen sensor to accurately differentiate between 21.0 vs. 20.9 vol% O<sub>2</sub>) would impart a lower detection limit (LDL) of 0.48 vol% for the diluent. For comparison, hydrogen safety sensors are often set to alarm at 0.4 vol%, which is 10% of the hydrogen lower flammability limit of 4.0 vol% H<sub>2</sub>. Thus, a sensor drift corresponding to only 0.084 vol% O<sub>2</sub> (e.g., 21.000 vs. 20.916 vol% O<sub>2</sub>) could result in a hydrogen false alarm. For reliability, alarm levels should not be set based on the sensor LDL, but rather on the limits of quantification (LOQ), although this is not necessarily performed for all deployments. Depending on the requirement, the LDL is typically defined as the sensor response that is 2 to 3 times greater than the background noise, while the LOQ corresponds to the response that is 5 to 10 times greater than the background noise. The analytical characteristics, especially noise and drift, of the oxygen sensor will limit its ability to determine diluent concentrations. Sensor signal noise considerations are critical for this application.

#### 3.1 Oxygen Sensor Response and Correlation to Diluent Concentration

The responses of all sensors were measured using mixtures of air and helium ranging from either 0 to 100 vol% He (extended range) or 0 to 13.4 vol% He (low range). The results of these tests are shown in Figures 1 and 2, respectively. Intermediate concentrations were included for each range. Evaluations were performed with dry gases and conditions regulated to 25 ± 2°C and 1.00 ± 0.05 bar P to assess sensor performance under highly optimal conditions. Helium was selected as the diluent because of its use as a surrogate for hydrogen. This allowed for a broader range of test gas concentrations to be used in this study since the sensor test facilities at NREL and JRC currently restrict hydrogen levels to 4 vol% or less in air. Oxygen sensors are often calibrated using only two concentrations: the typical ambient concentration of 21 vol% and an inert atmosphere such as nitrogen, argon, or helium with 0.0 vol% O<sub>2</sub>. The extended range data (Figure 1) could be used to obtain a 2-point calibration curve analogous to the typical procedure for oxygen sensors. The resulting calibration equations correlating the SR to oxygen concentration were:

$$\text{O2-Sensor1: Vol\% O}_2 = 26.131 * \text{SR} - 0.0203 \quad (2)$$

$$\text{O2-Sensor2: Vol\% O}_2 = 1.8024 * \text{SR} - 1.2164 \quad (3)$$

The respective calibration curves accurately determined all oxygen concentrations used in the extended range test, with a maximum absolute error of 0.08 vol% O<sub>2</sub>, and 0.09 vol% O<sub>2</sub> for O2-Sensor1 and O2-Sensor2, respectively. The extended range test demonstrated the analytical strengths of the oxygen sensor, including broad linear range, simple operation, and good *short-term* accuracy.

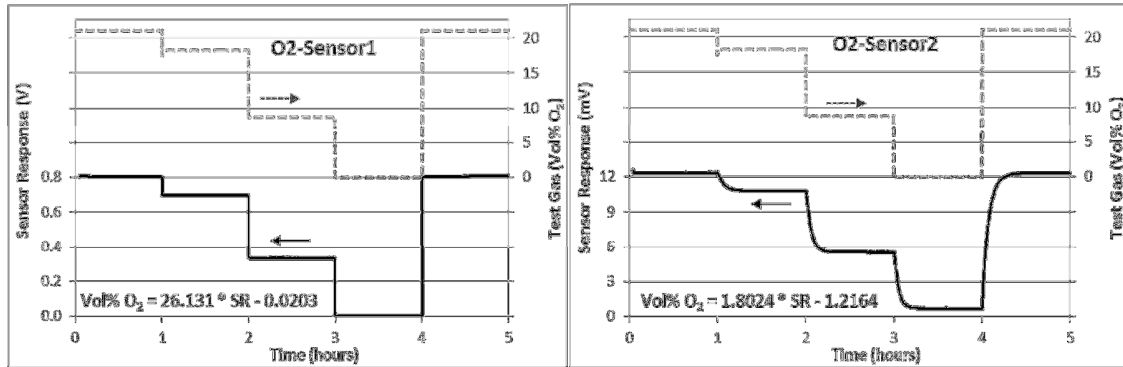


Figure 1: The Extended Range Test. Response of O2-Sensor1 (left) and O2-Sensor2 (right) to air/helium mixtures made up of pure air 21 vol% O<sub>2</sub> (0.0 vol% He), 18.17 vol% O<sub>2</sub> (13.48 vol% He), 8.76 vol% O<sub>2</sub> (53.30 vol% He), 0 vol% O<sub>2</sub> (100 vol% He), and a repeat of 21 vol% O<sub>2</sub>. The calibration curve relating the vol% O<sub>2</sub> to the SR was determined with a 2-point calibration using 21 vol% O<sub>2</sub> and 0 vol% O<sub>2</sub>.

Following the extended range test, the sensors were subjected to a variety of additional test sequences, including the low range test (0 to 13.4 vol% He) shown in Figure 2. This test was a more detailed survey of the oxygen sensor response to diluent concentrations relevant to hydrogen safety applications. It was performed to quantify the oxygen sensor's ability to resolve small changes in diluent levels. The extended range test and the low range test were performed under identical, highly regulated conditions. However, the optimal operational conditions employed in these evaluations would not be properly representative of most real-world applications, and this analysis should be viewed as a best-case scenario.

As presented in Figures 1 and 2, both sensors appear to exhibit repeatable responses to the test gas. Ideally, for a given test gas composition, the response of each sensor in the extended range test and low range test should be identical. However, the sensor performance was not ideally repeatable and real differences were observed under ostensibly identical conditions. This is illustrated in Figure 3, which shows an expanded view of the highlighted areas of Figure 2 to better illustrate the sensor signal in response to low levels of diluent (0 to 1.4 vol% He). The final indications for the sensor data shown in Figure 3 are presented in Figure 4. Several points are illustrated in Figures 3 and 4. First, the oxygen sensor response is prone to drift. Drift was observed even during the low range test, as indicated by a change in sensor response induced by identical test gas concentrations in the ascending and descending sequences. Although small, such drifts in sensor response were discernible and contribute to measurement uncertainty. The error bars indicated in Figure 4 correspond to 3 times the standard deviation (e.g., the LDL for the diluent) of the sensor response, which was obtained as the average of two measurements for identical test gas concentrations; one measurement was from the ascending sequence data, the other was obtained from the descending sequence data. The error bars indicate that under these test conditions, O2-Sensor1 can resolve changes in oxygen concentration to within approximately 0.075 vol% O<sub>2</sub>, corresponding to a diluent LDL of 0.36 vol%, which is essentially the typical alarm level for hydrogen. O2-Sensor2 has a resolution of approximately 0.15 vol% O<sub>2</sub>, corresponding to a diluent LDL of 0.71 vol%. Assuming that the LDL provides sufficient accuracy, O2-Sensor1 would be barely adequate for hydrogen safety applications. This LDL determination was based solely on short-term drift noise under the regulated conditions employed in these tests, and ignores other potentially more significant factors

that contribute to uncertainty in oxygen sensor measurements, such as drift induced by aging or fluctuations in environmental parameters.

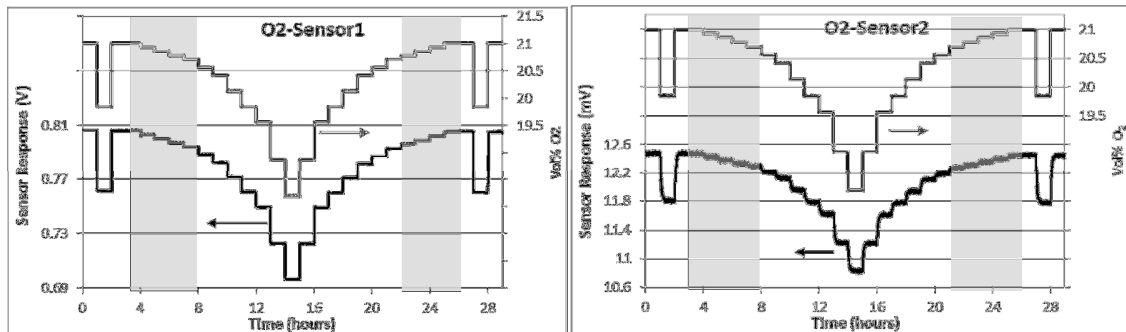


Figure 2: The Low Range Test: Response of O2-Sensor1 (left) and the O2-Sensor2 (right) to various air/helium mixtures exposed in discrete 1-h steps. Specific helium concentrations included an initial sequence of 0.0, 5.5, and 0.0 vol% He. The sensors were then exposed to 0.0 to 13.5 vol% He in ascending and descending concentrations, followed by a repeat of the initial exposure sequence. The highlighted area was evaluated separately to assess the impacts of sensor drift and noise on analytical performance.

Long-term sensor drift was also observed, as indicated by the systematic difference between the actual oxygen concentration (indicated by the dotted lines in Figure 4) and the oxygen calculated per the calibration curves (indicated by the solid lines in Figure 4). A 2-point calibration curve was used, so the shift in the measured oxygen level in air occurred because of sensor drift, and was apparent throughout the test range. The long-term sensor drift was considerably greater than the short-term drift and corresponded to an apparent change in oxygen concentration of +0.05 and +0.25 vol% O<sub>2</sub> for O2-Sensor1 and O2-Sensor2, respectively. This drift had near-negligible practical impact on oxygen measurement accuracy. However, in this case, the sensor drift was positive relative to the calibration data, corresponding to apparent oxygen levels in undiluted air increasing from 21.0 to 21.05 and 21.25 vol%, respectively, for O2-Sensor and O2-Sensor2. Using Eq. 1, this positive swing would be calculated as an apparent “negative” concentration for the diluent, specifically -0.24 vol% and -1.19 vol%, respectively, for O2-Sensor and O2-Sensor2. Of course, a negative diluent concentration would be interpreted by the end user as 0 vol%. However, a positive sensor drift could result in a false negative because additional diluent (e.g., hydrogen) would be required to reach the alarm set point. It is again emphasized that these tests were performed under highly controlled conditions with T, P, RH, and gas environment rigorously regulated. Such controlled environments will be unlikely in real-world deployments, and as discussed in the next sections, the impacts of variations of environmental parameters can be quite significant, especially when the oxygen sensor is used to determine diluent concentrations.

For comparison, a TC sensor was deployed with the oxygen sensors during the low range test; the dynamic range of the TC sensor was approximately 0 to 13.5 vol% He, and thus would electronically saturate when exposed to helium concentrations beyond this range, such as those used in the extended range test. Data are shown in Figure 5. This sensor was marketed for hydrogen, but is sensitive to helium as well. Thus, the TC sensor responds directly to either hydrogen or helium. However, unlike the oxygen sensor, whose response would be invariant with different diluents, the TC sensor would need to be calibrated to the analyte of interest. The TC sensor had a resolution and LDL of 0.05 vol% H<sub>2</sub>. For helium, the resolution and LDL of the sensor would be approximately 0.07 vol% He. In contrast with the oxygen sensor, the TC sensor did not show any short-term drift such as that which plagued the oxygen sensor as shown in Figure 3.

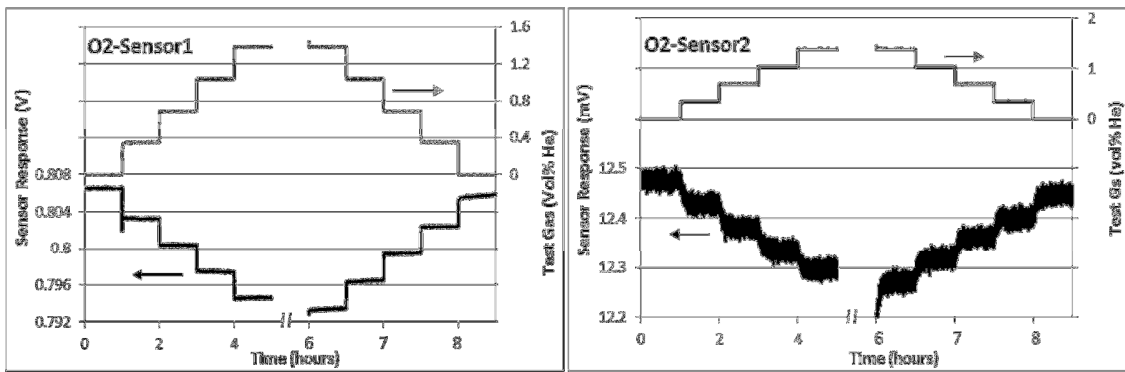


Figure 3: An expanded view of the data presented in Figure 2 (highlighted areas) showing the response of O2-Sensor1 (left) and O2-Sensor2 (right) to air/helium mixtures exposed in discrete 1-h steps. The diluent concentration (vol% He) is also plotted.

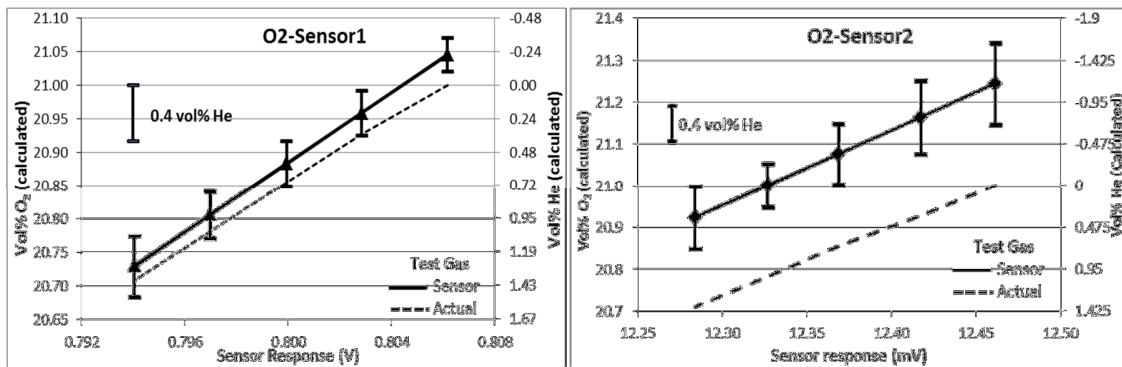


Figure 4: Oxygen concentrations calculated from the calibration curves (—) compared to the actual test gas concentration (---). The left ordinate is the actual oxygen concentration; the right ordinate is the corresponding diluent concentration (e.g., vol% He). The sensor response was taken as the average sensor final indication for the ascending and descending exposures. The error bars represent the calculated oxygen concentration corresponding to  $\pm 3$  times the standard deviation (corresponding to the LDL) of the average sensor final indication.

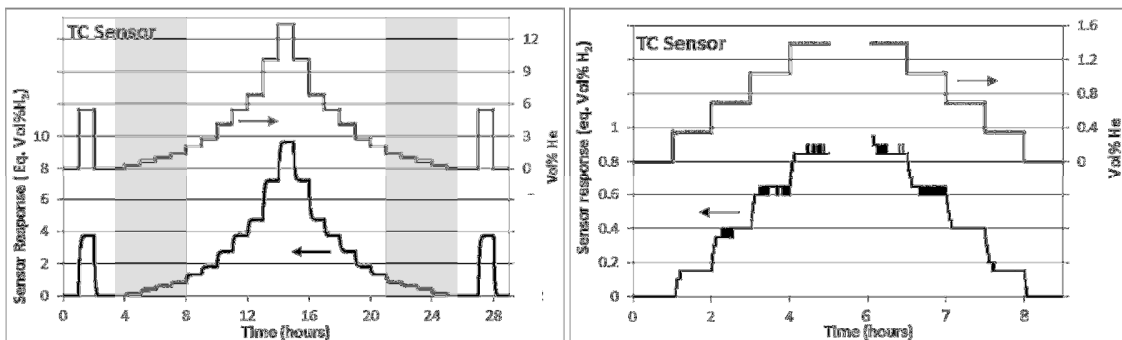


Figure 5: Response of the TC sensor to air/helium mixtures identical to that of Figure 2. The highlight area was expanded (right) to illustrate the short-term stability of the TC sensor relative to the oxygen sensor response shown in Figure 3.

### 3.2 Impacts of Environmental Parameters (P and T)

Many sensor platforms will be impacted by changes in environmental parameters such as T, P, and RH. Such fluctuations will be encountered in real deployments. To assess these impacts, the sensors were subjected to a 5-step exposure sequence with specific nominal gas compositions of 0.0, 0.69, 2.76, 5.48, and 0.0 vol% He in air. The T dependence study was performed at 5°C, 25°C, and 40°C with a fixed dry RH (<5%) and the pressure set to 1 bar. To review the P effect, the sequence was performed at 0.8 bar, 1.0 bar, and 1.2 bar with the RH and T set to 45% and 25°C, respectively. Humidity effects will be covered in a separate paper.

### 3.2.1 Pressure Dependence of the Oxygen Sensor

The sensors were evaluated at  $P$  of 0.8, 1.0, and 1.2 bar. The results for O2-Sensor1 are shown in Figure 6. Each test sequence was performed with identical vol%  $O_2$  profiles. The oxygen sensor response is, however, controlled by the partial pressure of oxygen ( $P_{O_2}$ ) and not the vol%. The relationship between vol% and partial pressure for a component is a scaling factor defined by the total pressure (e.g.,  $\text{vol}\%_i/100 * P_{\text{total}} = P_i$ ). To obtain the vol%  $O_2$ , the sensor response should be divided by the ambient  $P$ , as illustrated in Figure 6 (right). This of course requires the simultaneous measurement of the ambient  $P$  followed by scaling the sensor response to determine vol%  $O_2$ , which can then be used to calculate the diluent concentration. If uncompensated, a barometric  $P$  change of only 0.02 bar would induce a sensor response equivalent to a diluent concentration of 8 vol%. The oxygen sensor response, uncompensated for  $P$  fluctuations, would accurately provide  $P_{O_2}$  determinations (Figure 7). Conversely, the TC sensor responds directly to vol% of the diluent (Figure 8). Figure 8 also shows a comparison of the apparent diluent concentration (vol% He) based on the uncompensated signals from the oxygen and TC sensors. The  $P_{O_2}$  dependency of the oxygen sensors can have serious ramifications for determination of diluents in closed systems or systems with restricted venting, as discussed in the next section.

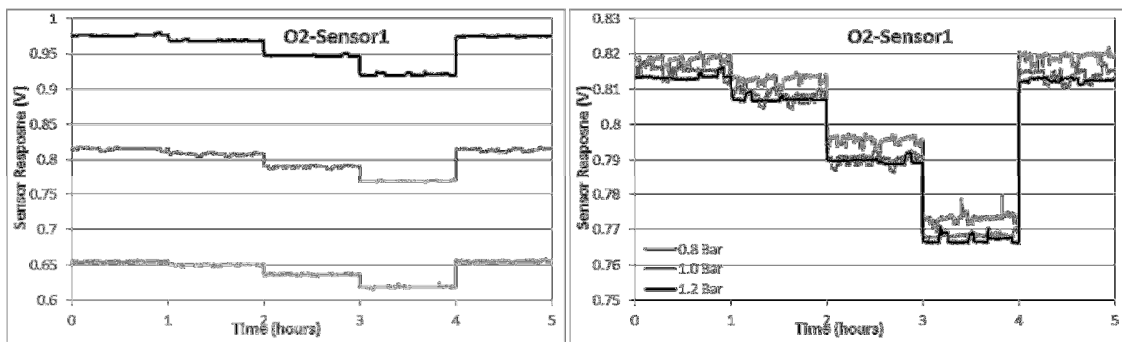


Figure 6: P dependence of the oxygen sensor. (Left): Sensor responses for identical vol%  $O_2$  profiles but at different total  $P$ . (Right): The sensor response compensated for different test  $P$ .

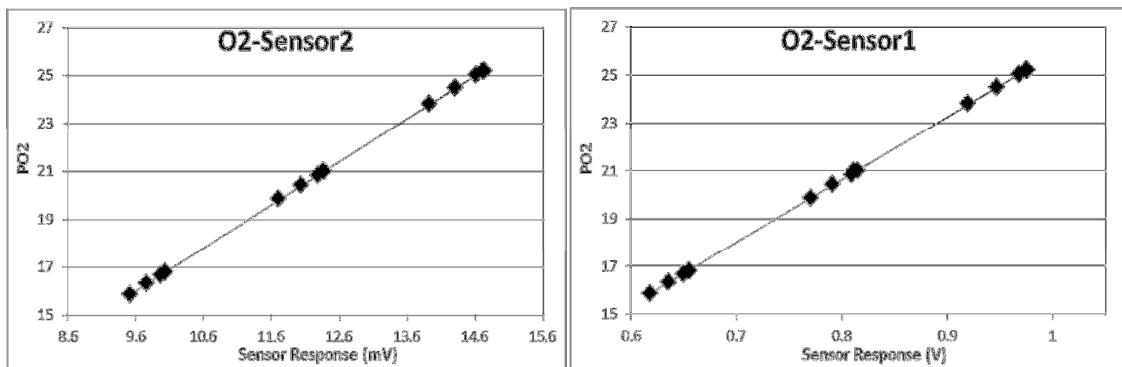


Figure 7: Dependence of the oxygen sensor on  $P_{O_2}$



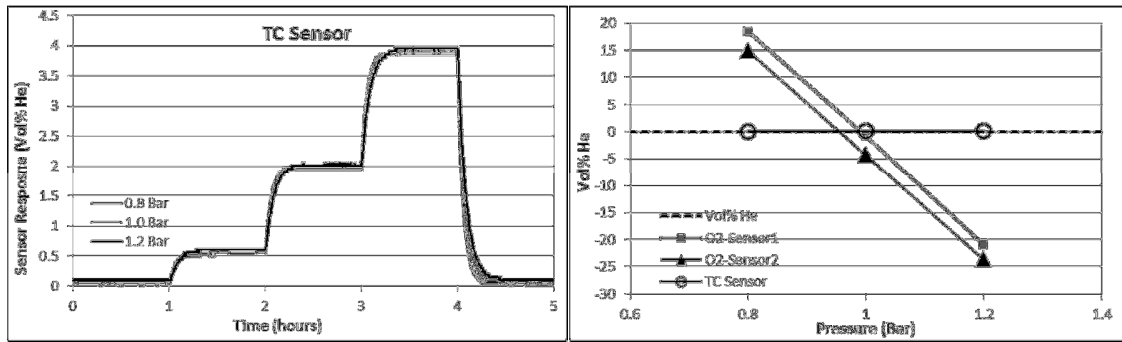


Figure 8: (Left) P dependence of the TC sensor. (Right) The apparent diluent concentration (vol% He) obtained from the output of the TC sensor (○), O2-Sensor1 (■) and O2-Sensor2 (▲) compared to the actual diluent concentration (---).

### Section 3.2.2 Performance of the Oxygen Sensors in Enclosed Environments

Hydrogen sensors are often placed in closed environments, which can include protective enclosures that isolate a system from the surrounding environment. For example, a hydrogen dispenser may have internal pneumatic controls, metering systems, compressors, and other elements. The enclosure protects the internal elements from the ambient environment and provides a degree of protection to the operator. An automobile passenger or trunk compartment could also be considered an enclosure. Because many enclosures are small and confined, slow internal hydrogen releases can quickly lead to hazardous situations. For example, less than 4 grams of hydrogen uniformly distributed within a 1-m<sup>3</sup> enclosure would exceed the lower flammability limit. A leak rate of 1 mg/sec would exceed this level in approximately 1 h. The oxygen sensor may not be able to respond to hydrogen releases in closed environments, even at very high concentrations. The insensitivity of the oxygen sensors to diluent releases in closed environments is a direct manifestation of the P<sub>O<sub>2</sub></sub> dependence of the sensor response. A release

into a closed system may change the vol% of oxygen, but the P<sub>O<sub>2</sub></sub> will remain unaffected. This behavior and its effect on the oxygen sensor response are shown in Figure 9. In region A of Figure 9, the sensors were deployed in an air atmosphere (e.g., 21 vol% oxygen) at a system P of 0.8 bar. Thus P<sub>O<sub>2</sub></sub> was 0.168 bar. The vent of the test chamber was closed (Region B), and the chamber was pressurized with helium to 1 bar. At this point, flow into and out of the chamber was stopped and the helium concentration remained fixed at 20 vol%. As a result of the helium pressurization, the oxygen concentration in the chamber decreased from 21.0 to 16.8 vol%, but P<sub>O<sub>2</sub></sub> remained at 0.168 bar. Even though the helium level was 20 vol%, the oxygen sensor did not respond. Alternatively, a response was readily seen on the TC sensor as the helium entered the sensor test chamber, although the output electronically saturated when the helium level exceeded 13.5 vol%. In region C of Figure 9, the test chamber was maintained at a P of 1 bar while the helium/air mixture in the chamber was purged with air. As the helium was displaced, P<sub>O<sub>2</sub></sub> increased and the oxygen sensor responded quantitatively to the change in P<sub>O<sub>2</sub></sub>. Although the oxygen sensor did not respond to changes in vol% O<sub>2</sub>, the TC sensor was able to directly measure the vol% He (or hydrogen) during the pressurization of the chamber by helium, the P hold step, and the subsequent purge by air, limited only by the dynamic range of the sensor. Oxygen sensors cannot therefore be used to measure hydrogen or other diluent levels in closed environments (or environments with restricted venting); the use of this approach in vehicle passenger compartments, per the GTR recommendation, must be discouraged.

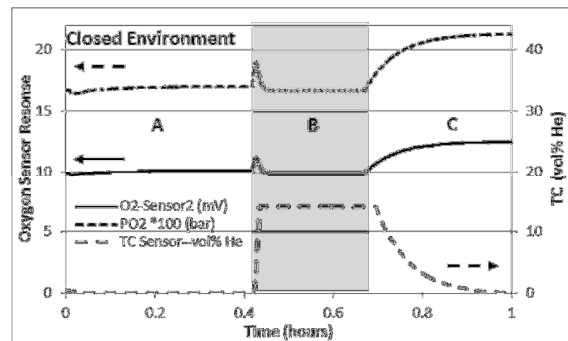


Figure 9: Behavior of the oxygen sensor and TC sensor in a closed environment. Vol% O<sub>2</sub> was calculated using Eq. 3 and converted to P<sub>O<sub>2</sub></sub>. Vol% He was calculated per the equation in Figure 7. Region A: The sensors were deployed in the sensor test chamber containing air at 0.8 bar (21 vol% O<sub>2</sub>, P<sub>O<sub>2</sub></sub>= 0.168). Region B: The vent was sealed and the chamber was pressurized to 1 bar using helium. Region C: The sensor chamber was purged with air. The oxygen sensor responded only to the increased P<sub>O<sub>2</sub></sub>.

### 3.2.3 Temperature Dependence of the Oxygen Sensor

The T range of most oxygen sensors is limited to approximately 0 to 40°C, because of restrictions imposed by an aqueous electrolyte that may freeze at the low limit and evaporate at higher T. TC sensors, which are solid-state devices, have a much broader range, operating well below -20°C and above 80°C. The data shown in Figure 10 are restricted to the T range set by the oxygen sensor. The impacts of T can be complicated. T can affect diffusion rates through the membrane, the partition between the bulk gas phase and the diffusion membrane, and the rate of the chemical reactions at the sensor electrodes. The potential complexity of the oxygen sensor dependence is exemplified by the two systems used here. O2-Sensor2 shows a positive T coefficient, and has increased sensitivity as the T increases. O2-Sensor1 shows the opposite, having attenuated sensitivity as T increases. Throughout the range studied, the T-induced variations of the sensor response in air corresponded to an apparent diluent concentration of up to 8 vol%. In contrast, the TC sensor exhibits near negligible T impacts in this range (Figure 11). Figure 11 also shows provides a comparison of the apparent diluent concentration (vol% He) based on the uncompensated signals from the oxygen and TC sensors.

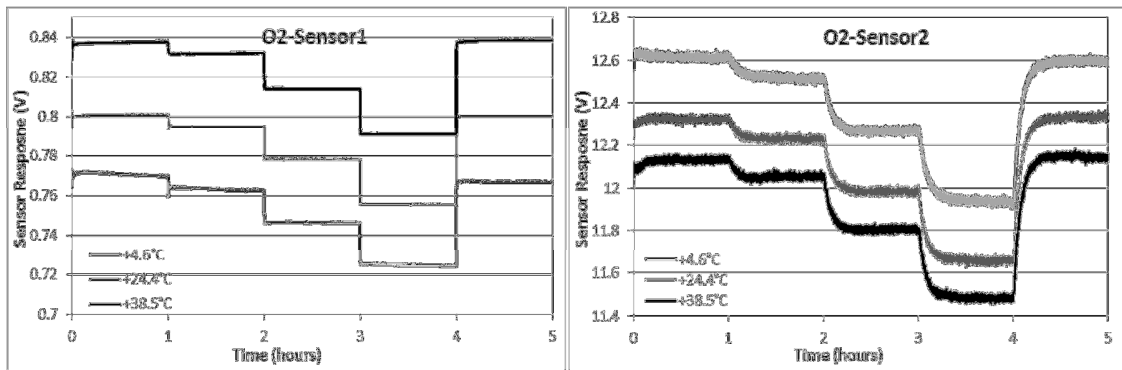


Figure 10: T dependence of O2-Sensor1 and O2-Sensor2.

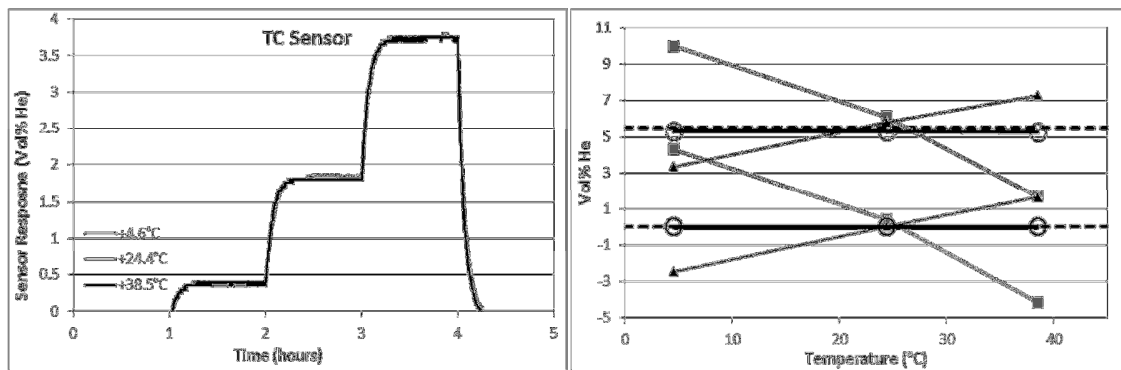


Figure 11: (Left) T dependence of the TC sensor. (Right) comparison of the apparent diluent concentration as obtained from outputs of the TC sensor (○), O2-Sensor1 (■) and O2-Sensor2 (▲) compared to the actual concentration (---).

## 4.0 Conclusions

Hydrogen determination via oxygen monitoring is fundamentally an indirect approach. This paper provided a brief assessment of some shortcomings associated with using oxygen sensors to determine hydrogen concentration. A more complete assessment is being prepared. Although cited in the GTR as a potentially viable method to verify fuel system integrity in a hydrogen-powered vehicle [8], the oxygen sensor is fundamentally inappropriate for hydrogen measurements in enclosed environments such as passenger compartments. Although oxygen sensors are quite specific to oxygen, this will not be true for

the diluent gas, and, in fact, the identity of the diluent(s) in real-world applications will be unknown without additional information. This ambiguity contributes to the measurement uncertainty. In controlled releases, this ambiguity can be alleviated by experimental design, but would persist in any real-world deployment. The lack of selectivity in a monitor can lead to false alarms, which are not only a nuisance, but can be costly [13]. The lack of selectivity is not necessarily the most critical shortcoming of this approach. The oxygen sensor works well to measure moderate changes in oxygen concentration; a typical application is to ensure that ambient oxygen levels are safe. For example, the U.S. Occupational Safety and Health Administration requires a minimum oxygen concentration of 19.5 vol% in confined spaces [14], which can be readily differentiated by most commercial oxygen sensors relative to ambient levels of 20.9 vol%. However, determining small changes in oxygen levels is more problematic, especially over extended periods without periodic recalibration. Even in the short term, fluctuations in ambient parameters adversely impact the sensor signal, which for hydrogen monitoring can lead to either false positives or false negatives. Because oxygen represents approximately 21% of the typical composition of air, the accuracy of hydrogen measurements is nearly a factor of 5 lower than the ability of the oxygen sensor to differentiate between oxygen levels. The oxygen sensor does not have the analytical resolution or environmental stability to reliably quantify low levels of hydrogen that are critical for safety monitors. Calibration errors, sensor drifts, and impacts of environmental parameters further degrade their ability to accurately quantify the diluent concentration. Because of a sacrificial anode, most commercial oxygen sensors have operational lifetimes of 1 year or less; the lifetime of the TC sensor is considerably longer. Table 1 provides a comparison of critical performance parameters between the TC and oxygen sensor for hydrogen monitoring applications. Only in ease of calibration and the ability to substitute helium for hydrogen without recalibration does the oxygen sensor exhibit slightly better characteristics than the TC sensor. In all other major metrics, the TC is equivalent or superior to the oxygen sensor.

Table 1: Comparison of performance metrics for the TC and oxygen sensor for hydrogen monitoring applications

<b>Metric</b>	<b>O2 Sensor</b>	<b>TC Sensor</b>
DEPLOYMENT		
COTS	Yes	Yes
Low cost	Yes	Yes
OPERATIONAL		
low power	yes	yes
life	<b>&lt; 1 year</b>	<b>&gt;&gt; 1 year</b>
ANALYTICAL		
He & H2 detection	yes	yes
Selectivity	non-selective	<b>moderate</b>
Environmental impacts		
T	Strong	<b>negligible</b>
T range	poor	<b>broad</b>
P	Strong	<b>negligible</b>
RH	Moderate	<b>negligible</b>
LDL	poor	<b>good</b>
Resolution	moderate	<b>good</b>
Stability (drift)	poor to moderate	<b>moderate to good</b>
Range	broad	<b>broad</b>

This approach should be discouraged. In addition to significant ambiguity in measurement accuracy, especially at concentrations germane to hydrogen safety, the use of this approach in controlled release studies may lead to broader and possibly inappropriate use by other stakeholders in the hydrogen community, especially for safety applications. It is also not necessary. The oxygen sensor is an excellent technology for the direct determination of ambient oxygen concentrations, but this not necessarily true for measuring diluent levels. Alternative sensor platforms are available that meet or exceed the performance metrics of oxygen sensor when used for hydrogen detection. One platform, the TC sensor, was used as a comparative technology in this evaluation. The TC sensor is amenable to hydrogen and helium detection,

and would be the technology of choice for modeling studies that use helium as well as hydrogen. Other hydrogen sensor platform types would also be appropriate for general hydrogen safety applications [15].

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