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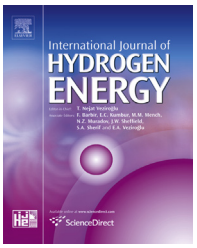

# An assessment on the quantification of hydrogen releases through oxygen displacement using oxygen sensors

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ABSTRACT

Gas sensors that respond directly to hydrogen are typically used to detect and quantify unintended hydrogen releases. However, alternative means to quantify or mitigate hydrogen releases are sometimes proposed. One recently explored approach has been to use oxygen sensors. This method is based on the assumption that a hydrogen release will displace oxygen, which can be quantified using oxygen sensors. The use of oxygen sensors to monitor ambient hydrogen concentration has drawbacks, which are explored in the current study. It was shown that this approach may not have adequate accuracy for safety applications and may give misleading results under certain conditions for other applications. Despite its shortcomings, the Global Technical Regulation (GTR) for Hydrogen and Fuel Cell Vehicles has explicitly endorsed this method to verify hydrogen vehicles' fuel system integrity. Experimental evaluations designed to impartially assess the ability of oxygen and hydrogen sensors to reliably measure hydrogen concentration changes are presented. Specific limitations on the use of oxygen sensors for hydrogen measurements are identified and alternative sensor technologies that meet the requirements for several applications, including those of the GTR, are proposed.



## Introduction

The U.S. Department of Energy (DOE) Fuel Cell Technologies Office has taken the lead to support the development and deployment of hydrogen as an alternative energy source in the United States [1]. It supports DOE's mission to ensure the United States' security and prosperity by addressing energy and environmental challenges through transformative science and technology solutions [2]. Similarly, the European Commission identified the potential of hydrogen and fuel cells in the 2011 Technologies Map [3]. Hydrogen infrastructure must be developed safely if hydrogen is to be used successfully as a fuel. One element of a hydrogen safety system is the

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use of sensors to detect unexpected hydrogen releases. Sensor test facilities were independently established by the European Joint Research Centre (JRC) at the Institute for Energy and Transport [4] and by DOE at the National Renewable Energy Laboratory (NREL) [5] to ensure that hydrogen sensors are available to meet the needs of the hydrogen infrastructure and to educate the hydrogen community on the proper use of hydrogen sensors. These laboratories have ongoing collaborative sensor research programs formalized by a Memorandum of Agreement.

Hydrogen releases are typically detected using sensors that respond directly to hydrogen. However, one emerging approach to detection of hydrogen releases is to use oxygen sensors to measure changes in ambient oxygen levels and then equate this change to a change in the hydrogen level [6–8]. This approach has been explicitly endorsed by the Global Technical Regulation (GTR) for hydrogen-fueled vehicles [Section II.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)"] [9]. Some studies that used oxygen sensors for hydrogen monitoring were for controlled releases and not as safety monitors deployed for extended times to detect unexpected releases. In controlled releases, helium is sometimes used as a surrogate for hydrogen. This paper presents the results of an investigation performed under the auspices of the NREL-JRC Memorandum of Agreement to impartially assess the use of oxygen sensors for monitoring hydrogen releases.

Typically, the electrochemical oxygen sensor, also known as the *galvanic oxygen sensor*, was selected for this application. In this paper *oxygen sensor* refers to the galvanic oxygen sensor. The use of oxygen sensors for hydrogen determination has apparent advantages. As a mature technology, they are commercially available from various manufacturers and have some impressive performance specifications that include a broad linear detection range for oxygen and reported response times of less than 1 s for some models and modes of operation. They are quite specific to oxygen. The oxygen sensor will indicate a decreased oxygen level as 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 surrogate without recalibration. The oxygen sensor is extremely simple to use, and 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. Calibration is performed using ambient air (20.9 vol% $O_2$) and an inert gas (e.g., nitrogen).

However, the use of oxygen sensors to determine hydrogen has tangible limitations that can adversely impact their reliability for most hydrogen applications. This paper discusses these limitations. It is concluded that oxygen sensors should not be used to monitor hydrogen. It is demonstrated that the endorsement in the GTR of the use of oxygen sensors to measure in-vehicle releases of hydrogen is inappropriate. Even in controlled investigations, including those using helium, the oxygen sensor is not the platform of choice. An alternative technology is proposed that meets or exceeds the performance of oxygen sensors for hydrogen monitoring for all critical applications.

## Experimental

### Sensor selection

Two commercial electrochemical oxygen sensor models ("O2-Sensor1" and "O2-Sensor2") were used in this study. Both were operated according to the manufacturers' recommendations. O2-Sensor2 was operated without additional circuitry. O2-Sensor1 was interfaced to commercial control circuitry specifically designed for this sensor. The signals from both sensors were logged by a data acquisition system. A thermal conductivity (TC) sensor marketed for hydrogen detection was used as a control. The TC sensor is amenable to both hydrogen and helium detection [10]. The TC sensor was factory-calibrated for hydrogen with an output corresponding to equivalent vol% $H_2$, but in-house calibration readily converted the response to vol% He. The range of the TC sensor used in this study is 0–10 vol% $H_2$, which is adequate for safety applications [11]. Due to lower sensitivity, the helium range of the sensor is approximately 0–14.2 vol% He.

### Sensor test protocols

Sensor evaluations were performed in either the NREL [5] or JRC [4] sensor test apparatus, which were developed 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 control of gas parameters with multiple precision digital mass flow controllers operating in parallel. Certified probes monitor test conditions ($T$, $P$, RH, and flow). Both apparatus utilize data acquisition systems (DAQ) based upon LabVIEW and National Instruments hardware. The apparatus were cross-validated through round-robin testing of various sensor technologies [12].

The three sensors were simultaneously deployed in the sensor test apparatus. Test gas mixtures were generated from gas cylinders of synthetic air (certified to 21.0 ± 1.5 vol % $O_2$ with a nitrogen balance) and ultra-high purity helium. For this study, air was considered to be 21 vol% $O_2$ in nitrogen, which closely approximates the typical ambient oxygen concentration of 20.9 vol%. Standard test conditions were:

Temperature ($T$): 25.0 ± 2 °C
Pressure ($P$): 1.0 ± 0.05 bar
Relative humidity (RH): <5% RH
Gas flow rate: 1000 standard cubic centimeters per minute

Conditions were varied to investigate the impacts of environmental parameters on sensor response (SR).

Sensor exposures were performed in discrete steps of fixed oxygen concentrations. The test gas composition was generated by the dynamic mixing of air and helium with the respective flow rates regulated by mass flow controllers. The DAQ continuously logged the signals from the chemical sensors and environmental probes at a nominal rate of 1 data point per second and stored them in an electronic data file.

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