# Characterization of a Selective, Zero Power Sensor for Distributed Sensing of H<sub>2</sub> in Energy Applications

Joseph R. Stetter<sup>1</sup>, V. Patel<sup>1</sup>, W. Buttner<sup>2</sup> and H. Wright,,<sup>23</sup>

<sup>1</sup> KWJ Engineering Inc. and Spec-Sensors LLC, 8430 Central Ave., Newark, CA 94560 USA,

<sup>2</sup> National Renewable Energy Laboratory, Golden CO 8040, USA

<sup>3</sup> Colorado School of Mines, Golden, CO 80401 USA

Corresponding Author: jrstetter@gmail.com

#### **Abstract**

The use of hydrogen as an energy source is increasing rapidly. There are safety concerns wherever  $H_2$  is made, used, and transported [pipelines and tanks] for both vehicle and stationary applications. Mobile and localized detectors are needed to meet safety codes and to enable a smooth rollout of  $H_2$  as an energy alternative. One impediment is a sensor that simultaneously has the combined features of small size, low cost for easy deployment in large numbers, low power to simplify fixed and mobile applications, and high performance including sensitivity, selectivity, fast response, stability and long lifetime. A new novel printed electrocatalytic amperometric gas sensor or AGS [1] with a circuit for monitoring  $H_2$  in air has been fabricated and evaluated for low level leak detection [0-1000 ppm  $H_2$  in air] and safety levels [alarms at 0.5%, 2.5%, and 4% in air]. The new  $H_2$  sensor is designed for manufacture [DFM] using scalable methods of "Printed Electronics" [PE] and is made on a template the size of an 8" wafer to enable volume low cost manufacture by leveraging PE and semiconductor fab infrastructure.

Key words: low cost, miniature, safety, Hydrogen, printed-sensor, characterization.

## Introduction

Hydrogen sensors are viewed as an enabling technology for the safe implementation of  $H_2$  as an alternative energy carrier. Cost is a factor that impedes the wide spread use of sensors, especially [4] in large operations and vehicular applications. Low-cost manufacturability with improved sensor selectivity can make distributed sensing possible. KWJ-Spec has collaborated with NREL who have an advanced  $H_2$  sensor characterization lab to measure sensor performance and provide data for determination of the sensor specifications and to evaluate future possible application success.

Characterization data [2,3] are obtained by measuring the sensor signal defined as the quantitative difference in sensor output when the target analyte is present and when absent in the matrix [here  $H_2$  in air]. We express this as: Signal =  $[S(H_2) - S(air)]$ .

Five categories of parameters are calculated when evaluating practical commercial gas sensors. Sensitivity, Selectivity, Speed of response, Stability, and Logistics [e.g., size, cost, power, lifetime, manufacturability, and application specific needs like consumables, maintenance, or certifications]. Sensitivity is

defined as the slope of the calibration curve determined by plotting the sensor signal vs gas concentration.  $S = d[Signal]/d[H_2]$  and in our case is reported as nA/ppm. From recorded sensor signals at various known concentrations in the range of interest, it is possible to quantify sensitivity-related parameters such as noise [ppm], limit of detection [LOD], linearity, precision, and accuracy. Selectivity is obtained by exposure to known concentrations of expected interfering gases and often quantified as the ratio of sensitivities [ppm H<sub>2</sub>/ppmGasX]. Speed of response is only obtained from the data if the sensor response is slower than the test chamber purge time. Stability of the signal [zero and sensitivity] is the drift or change over variables including time, temperature, pressure, RH, vibration, and/or gas matrix. Stability is derived from measurements of the calibration curve over the variables [time, T, P, RH].

The new sensor reported herein is fabricated using printed electronics (PE) and MEMS fabrication approaches wherein the sensors' critical elements are screen printed from nanocatalyst inks [1] and the sensors are assembled in a layer by layer process of additive and subtractive plastic conductive and nonconductive materials on a substrate the size of

an 8" wafer. This new sensor design and fab process successfully bridges the "cost-performance gap" for the sensor and most importantly allows a fully deployable solution.

### **Experimental**

The fully assembled H<sub>2</sub> AGS (below) actually produces a [few] nanoamps per ppm H<sub>2</sub> and is operated with a resistor or with a single OpAmp

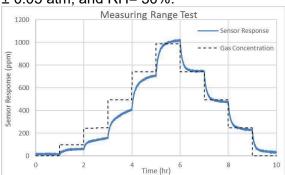


to convert the signal to an easily displayed and recorded voltage. The sensor is catalytic and has zero consumables. The sensor is intended to last decades in a workplace.

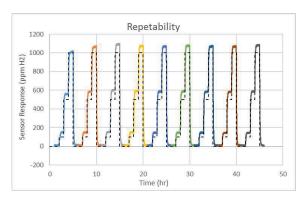
The signal is amplified by an inexpensive OpAmp that uses only about 600nA so the power dissipation [at 3V] of the entire system is about 1.8 uW. A small coin cell battery can power the device for nearly a decade. Characterization is performed in NREL's lab.

#### **Results and Discussion**

The output of the sensor was recorded under variable condition of P, T, RH, and at  $H_2$  concentrations in the relevant range. Initial data has been obtained to assess sensitivity, response time, and precision. These parameters are calculated from the data illustrated in figures below. First test results involved one-hour steps of 100, 250, 500, 750, and 1000 ppm of hydrogen air mixtures in an ascending and descending manner at  $T = 25^{\circ}C \pm 5^{\circ}C$ ;  $P = 1 \pm 0.05$  atm; and P = 50%.



A Short Term Stability/Repeatability Test was used to quantify sensor short-term drift, baseline drift, and the precision. The test was composed of 9 iterations of a 5 step sequence of air, 100 ppm H<sub>2</sub>, 500 ppm H<sub>2</sub>, 1000 ppm H<sub>2</sub>, air with no time delay between each repetition. This test was performed under similar T, P conditions to test above except the RH was about 5%.



In general, the gas concentration is given by:

$$Cx = \frac{1}{M} * (Vgas - Vref)$$
 [1]

Where the signal is the difference in mV between the circuit output with and without the gas present and M is a calibration constant. In practice, the sensor signals are temperature and pressure dependent. Additional tests have been performed and will be reported to quantify the T and P dependence of the signal so that compensation algorithms can be written. Also, less than 1 ppm interference was measured from RH or CO changes, two anticipated gases often can interfere with measurements. Additional data on sensor construction and performance will be available.

# **References and Acknowledgements**

We would like to acknowledge KWJ for providing the sensors and circuits and the NREL Sensor Laboratory for characterization resources and LANL for collaboration on sensor selection for characterizations. DOE FCTO is acknowledged for support provided through the Small Business Voucher Program to enable the partnership with the national laboratories.

- [1] M.T. Carter, J. R. Stetter, M. W. Findlay and V. Patel, "Printed Amperometric Gas Sensors," *Electrochem. Soc. Trans.* (2012) and <u>Stetter, et al., US</u> Patent 8795484 (Aug 5, 2014)
- [2] Joseph R. Stetter, Chapter 1, "Experimental Methods in Chemical Sensor and Sensor Array Evaluation and Development," in "Computational Methods for Sensor Materials Selection, M.A. Ryan, A.V. Shevade, C.J. Taylor, M.L.Homer, M. Blanco, and J. R. Stetter, editors, 2009, pp3-46. DOI 10.1007/978-0-387-73715-7-1
- [3] Joseph R. Stetter and Jing Li, in Modern Topics in Chemical Sensing: Chapter 4, "Amperometric Gas Sensors – A Review," Chemical Reviews, 108 (2), 2008, pp352.
- [4] Weidner, Buttner, and Bonato in "Summary Report for H2 Sensor Workshop" [JRC report EUR 28852 EN Dec.2017] H2 Safety sensors...