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Title: Leak Detection and H2 Sensor Development

Author(s): Brosha, Eric L.

Intended for: Report

# Leak Detection and $H_2$ Sensor Development

**Low-cost, durable, and reliable Hydrogen safety sensor for vehicle, stationary, and infrastructure applications**

**Primary Industry:** Production/Delivery

**Overview (Technology History):**

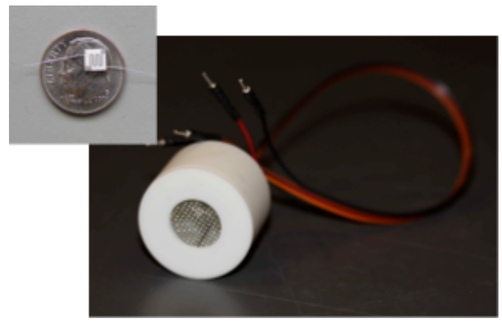
- Los Alamos National Laboratory (LANL) and Lawrence Livermore National Laboratory (LLNL)
- A new zirconia, electrochemical-based sensor technology is being transitioned out of the laboratory and into an advanced testing phase for vehicular and stationary $H_2$ safety applications.

**Applications:**
Can be used for on-vehicle leak detection, refueling, and for production and storage hydrogen safety applications.

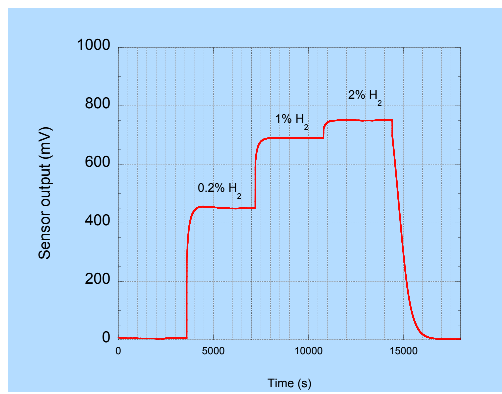
**Capabilities:**

- Achieves desired infrastructure and vehicular targets for minimum detection threshold of 1% $H_2$ in air (10,000 ppm ) and response time of ≤1 min
- Measures hydrogen in the range 0.04 - 4% with an accuracy of ± 1%
- Achieves Response Time: <1 min at 1% and <1 sec at 4% with sensor recovery <1 min
- Provides wide operating ambient temperature range -40°C to 60°C
- Shows minimal cross-sensitivity to common gas interferences such as $CO_2$, CO, and $CH_4$ and is insensitive to changes in the ambient humidity and barometric pressure

**Graphic:**



*Packaged Electrochemical $H_2$ Safety Sensor (above) and NREL rapid survey test, $H_2$ infiltration into fixed volume enclosure at 70% R.H. followed chamber purge (below).*




**Description:**

Hydrogen sensors are increasingly important for existing as well as emerging energy applications where hydrogen acts as a versatile energy carrier. For human safety and to ensure infrastructure reliability, sensors are needed to monitor hydrogen gas, which, when mixed with air, is flammable in the range of 4-75 vol%. In safety applications, sensors are required for detecting unintentional release or leaks. The availability of low-cost, reliable hydrogen safety sensors will encourage wider acceptance of hydrogen as a clean and sustainable energy carrier. Industry consensus is that there is a need for inexpensive, low-power, and compact sensors with long-term stability, minimal cross-sensitivity, and fast response.

LANL and LLNL, with FCT and Hydrogen Codes and

**Benefits:**

Cost Savings
Provides a low-cost and durable $H_2$ safety sensor for vehicle and infrastructure applications. Long lifetime, inexpensive manufacturing costs, and reduced calibration needs translate into an economical platform.

Durability
Sensor design is a derivative of the automotive Lambda sensor; robust ceramic design offers potential for OEM-desired 5-year operation without re-calibration.

Flexibility
Provides a low power, compact fit sensor package with a direct voltage read-out, circumventing the need for any additional conditioning circuitry.

Standards funding, are working together to develop and test inexpensive, zirconia-based, electrochemical (mixed-potential) sensors for $H_2$ detection in air. Mixed potential sensors are a class of electrochemical devices that develop a voltage in response to the difference in the electro-catalytic properties of the electrodes and the resulting difference in the rates of the redox reactions of various gaseous species at each electrode/electrolyte/gas interface. They are a derivative of the hugely successful and ubiquitous automotive Lambda sensor, which has been used since 1976 to maintain stoichiometric air/fuel ratio in IC engine vehicles with catalytic converters to limit emissions . Although zirconia-based mixed potential sensors for other applications have been investigated in various laboratories for several decades, issues centered on signal stability and device-to-device reproducibility have kept them out of the commercial mainstream.

Work in the fundamental understanding of the mixed potential phenomena at LANL and LLNL has led to new materials, methods, and designs for this important class of sensor. Our unique sensor designs facilitate a reproducible device response resulting from stable electrochemical interfaces. In addition, higher mixed potential signals result since gas diffusion is through the less catalytically active electrolyte than the electrode.

The sensor has shown desirable characteristics with respect to response time, stability and resistance to aging, and degradation due to thermal cycling. LANL and LLNL are now working to demonstrate the technology in $H_2$ applications and enable commercialization through cost-conscious, reproducible manufacturing methods. Cross-validation and eventual field-testing of advanced prototypes is now being undertaken with other DOE labs and commercial parties.

**Associated Parties:**

**Technology Partner(s)**

ESL ElectroScience, Inc.
416 East Church Road
King of Prussia, PA 19406-2625
Phone (610)-272-8000

Custom Sensor Solutions, Inc.
11786 N. Dragoon Springs Drive
Oro Valley, AZ 85737
Phone: (520) 544-7523
Email: wpenrose@customsensorsolutions.com

BJR Sensors, LLC.
37920 Flanders Dr.
Solon, OH 44139-6724

Contact Information:
Eric Brosha
Los Alamos National Laboratory
MS D429, P.O Box 1663
Los Alamos, NM 87545
Phone: (505) 665-4008
E-mail: brosha@lanl.gov
Website: www.lanl.gov

Robert S. Glass
Lawrence Livermore National Laboratory
L-103, P.O. Box 808, 7000 E. Ave.
Livermore, CA 94550
E-mail: glass3@llnl.gov

Phone: (440) 591-9766
Website: www.bjrsensors.com

Website: www.llnl.gov

**Status Information:**

| Year: | Status: | Comments: |
|---|---|---|
| **2012** | **Emerging** | **2012 Status: A $H_2$ safety sensor technology has been developed on an advanced sensor platform. A packaged, advanced prototype was fabricated using commercial ceramic sensor manufacturing methods and materials that can achieve a stable baseline signal, high sensitivity to $H_2$ with minimal humidity interference and response to variations in barometric pressure, exceptional low-level sensitivity, and high signal-to-noise. In addition to the sensor element, support electronics have also been identified, developed, and tested in 2011 and 2012. Device-to-device response reproducibility has been demonstrated. An industrial partner has performed a cost analysis and cost estimates are in line with a modern automotive lambda sensor. Multiple sets of sensors have been tested by the DOE's National Renewable Energy Laboratory (NREL) in a specialized test stand for evaluating and performance benchmarking of $H_2$ sensing technologies. Device technology has advanced from a naked sensor element suitable for laboratory R&D to a much more advanced state nearing field-testing capability.** |

**Description:**

**Also Known As:**
Controlled-interface, mixed potential electrochemical sensor based on yttria-stabilized zirconia (YSZ) electrolyte.

**Technical Description:**
Mixed potential sensors are a class of electrochemical devices that develop an open-circuit electromotive force due to the difference in the kinetics of the redox reactions of various gaseous species at each electrode/electrolyte/gas interface, referred to as the triple phase boundary (TPB). Therefore, these sensors have been considered for the sensing of various reducible or oxidizable gas species in the presence of oxygen. Based on this principle, a unique sensor design was developed by LANL and LLNL. The uniqueness of this sensor derives from minimizing heterogeneous catalysis (detrimental to sensor response) by avoiding gas diffusion through a catalytically active material and minimizing diffusion path to the TPB. Unlike the conventional design of these devices that use a dense solid electrolyte and porous thin film electrodes (similar to the current state-of-the-art zirconia-based sensors and fuel cells), the design of this sensor uses dense electrodes and porous electrolytes. Such a sensor design facilitates a stable and reproducible device response, since dense electrode morphologies are easy to reproduce and are significantly more stable than the conventional porous morphologies. Moreover, these sensors develop higher mixed potentials since the gas diffusion is through the less catalytically active electrolyte than the electrode. Lastly, the choice of electrodes is primarily based on their $O_2$ reduction kinetics and catalytic properties vis-à-vis the target gas of interest.

**References:**

**Source List:**

LANL Technology Transfer home: www.lanl.gov/orgs/tt

U.S. Patents no.s 6,605,202; 6,656,336; 7,214,333; and 7,264,700.

**Remarks:**

**History:**

LANL and LLNL partnered in 2008 and began to develop a new class of $H_2$ safety sensor as part of the DOE's Hydrogen Safety, Codes and Standards Program. Prior to 2008, LLNL had identified a suitable electrode material for a mixed potential, electrochemical hydrogen sensing application that exhibited high sensitivity to $H_2$, but with only low interference from interferences such as moisture, $CO_2$ , and methane that can lead to baseline instability and false positives. Since 2001, LANL has obtained 6 patents resulting from work aimed at the design of YSZ-based mixed potential sensors that are stable and reproducible with high sensitivity to target gas species. Concurrently, LLNL has received four patents on solid-state electrochemical sensors based on YSZ electrolytes. These patents include design and methods of manufacture that preserve crucial, electrochemical sensor attributes. In DOE-funded work from 2008 to the present, the Labs have conducted the necessary scientific investigations and entered into collaborations with industry to use this combined expertise to lead the development of a new $H_2$ safety sensor technology.

**General Comments:**

The salient features of the $H_2$ sensor prototype developed by LANL and LLNL are (a) rugged, (b) low power consumption potential, (c) compactness to fit into critical areas of application, (d) simple operation, (e) fast response, (f) a direct voltage read-out circumventing the need for complicated signal processing, and (g) a low cost sensor platform conducive to commercialization using common ceramic manufacturing methods.

**Markets and Economics:**

**Comments:**

Optional