IX.15 Optically Read MEMS Hydrogen Sensor

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Projected End Date: Project continuation and direction determined annually by DOE

Objectives

- Develop sensing technology that achieves DOE research and development (R&D) targets for hydrogen safety sensors.
- Characterization of response time, recovery time, sensitivity and accuracy within the operating temperature range.
- Demonstrate sensor performance and compliance with safety goals.
- Establish partnership to develop pre-commercial sensor prototype.

Technical Barriers

The project addresses the following technical barriers from the Hydrogen Safety section (3.8.4) of the Fuel Cell Technologies Program Multi-Year Research, Development and Demonstration Plan (October 2007):

(D) Liability Issues

(E) Variation in Standard Practice of Safety Assessments for Components and Energy Systems

Technical Targets

The long-term project objective is to achieve commercialization and regulatory acceptance of fiber-reinforced polymer pipeline technology for hydrogen transmission and distribution. Accordingly, the project tasks address the challenges associated with meeting the DOE hydrogen delivery performance and cost targets for 2017:

- Measurement Range: 0.1%-10%
- Operating Temperature: -30 to 80°C
- Response Time: under one second
- Accuracy: 5% of full-scale
- Gas environment: ambient air, 10%-98% relative humidity range
- Lifetime: 10 years
- Resistant to interferents (e.g., hydrocarbons)

Accomplishments

- Developed new highly porous nanoparticle palladium-coated microcantilever sensor arrays.
- Developed a new wet chemical Pd film deposition technique on Ag/Cr coated cantilever sensors using a galvanic $PdCl_2$ exchange reaction.
- Demonstrated that large sensor surface area in comparison with film volume leads to very fast sensor response and recovery times.
- Completed selectivity, sensitivity, response and recovery time and regeneration analyses of the nanoporous Pd coated sensors and demonstrated excellent response characteristics.
- Demonstrated excellent stability, repeatability and life measurements that have been observed during more than a year of operation.
- Fabricated first field portable instrument to demonstrate operational performance of the Pd based sensors.
- Identified sensor commercialization partners and are negotiating commercialization agreements.

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Introduction

Utilization of hydrogen as a transportation fuel requires comprehensive safety management during its storage, handling and use. Although safety-by-design and passive mitigation systems are the preferred methods for safety management, it is vitally important to develop technologies that can detect hydrogen releases and alert to system failures. The DOE Fuel Cell Program's Hydrogen Safety sub-program recognizes the need to develop and commercialize hydrogen sensors that provide the appropriate response time and the sensitivity and accuracy necessary for use in safety applications, thereby reducing risk and helping to establish public confidence in the hydrogen infrastructure.

This project addresses the above needs by developing, proving and commercializing a hydrogen detection device based on nanostructured thin film palladium microcantilever arrays. This hydrogen sensor has been shown to provide major performance improvements over existing and other recently developed sensors. The overall objective is to develop sensor technology that achieves DOE R&D targets for hydrogen safety sensors at lower cost and with the potential for wide-area hydrogen gas detection.

Approach

Microcantilever-based chemical sensors were first seriously explored as a trace gas sensing technology in 1990s with the first reported use of Pd coated microcantilevers for sensing H_2 occurring in 2000. Adsorption of a gas onto a thin film surface can cause large changes in stress and consequent bending of a thin cantilever structure. This bending response can be sensitively detected using piezoresistive, capacitive and optical techniques such that sub part-per-billion (ppb) sensitivities are achievable. Microcantilever-based chemical sensors have been shown to have high sensitivity, wide dynamic range and fast response times. Optically read microcantilever sensors are particularly advantageous in the presence of combustible or explosive gases and vapors (e.g. H_2) due the possibility of vapor ignition when using heated or electrically operated sensors. Other advantages of this sensing technique include very low power consumption, and their potential use in distributed wide area sensor networks allowing multiple low cost chemical sensors to be located at storage or processing facilities (e.g. in the H_2 fuel economy) or on H_2-powered or transportation vehicles [1].

One of the most challenging aspects of detecting and quantifying the amount of a low concentration gas or vapor in the environment is the effect of potential interferents on the gas sensor response. Interferents can lead to false positive responses or suppressed responses to the gas being detected. One approach to overcoming this problem is the use of a multiplexed sensor array, with each sensor having a distinct sensitivity response to the gas or vapor of interest and any potential interferents. A much simpler approach is to use a single sensor, or small array of sensors, to sense a single gas species, as the computational processing of the array responses is much less intensive than for the multiplexed sensor array. The single sensor mode of operation is feasible if a coating can be found that responds primarily to the gas species of interest with minimal response to any potential interferents. Palladium has previously been used as a sensing medium in a number of sensor technologies due to its strong and reasonably unique response to H_2. The possibility of using Pd-coated microcantilever sensors to detect H_2 leaks has been examined in several previous studies. The issue with most previous thin film Pd studies, and all of the previous microcantilever-based work, is that the sensor response and recovery times are far longer than acceptable for most applications; response times for these microcantilever-based H_2 sensor studies varied from a few minutes to as long as 1 hour. The long response and recovery times are attributed to the long diffusion time for elemental hydrogen to diffuse into and out of the palladium film to form palladium hydride.

Our approach is to use a new nanostructured Pd/Ag alloy that we developed specifically for the hydrogen sensing application. Microcantilever sensors coated with this alloy have fast, near ideal response characteristics when monitoring low concentration H_2 gas. In particular, the response and recovery times measured with these sensors are far shorter (<10 s) than those reported in all previous microcantilever-based H_2 sensor studies. The development work performed to optimize the performance of our sensor consisted of efforts to increase the sensitivity and dynamic range, to minimize the response and recovery times, to improve its resistance to interferents, and to increase its accuracy, repeatability and lifetime. We are presently working on the development of a prototype that can be performance-evaluated by third parties and adapting the sensor system for use in wide-area sensing.

Results

We conducted sensitivity and performance measurements of the Pd-Ag functionalized, optically read microcantilever using a benchtop setup consisting of the microcantilever in a gas flow cell, an optical readout system, a flow control valve and sample loop, and a LabVIEW®-based data acquisition system. The threshold and dynamic range test results revealed a lower-limit-detection of 0.01% (100 ppm) H_2 in argon, with three orders of magnitude dynamic range. Response and recovery times for 4% H_2 in argon were <3 s and <10 s, respectively. Over an eight-month period the sensor accuracy and repeatability remained constant within ±2%, indicating that the projected operational lifetime of this early version of the sensor could be as long as several years. Measurements of sensor specificity to common impurities and carrier gases (CO_2, CH_4, H_2O, N_2, He, CO) showed that in all cases, the responses from the interferents were an order of magnitude or more smaller than that observed for H_2 at similar concentrations (see Figure 1). This degree of discrimination against interfering species will be adequate in all but the most demanding applications.

As illustrated in Table 1, in laboratory tests completed to date, we demonstrated that our microcantilever-based H_2 sensors meet all but the most stringent requirements for automotive sensing applications.

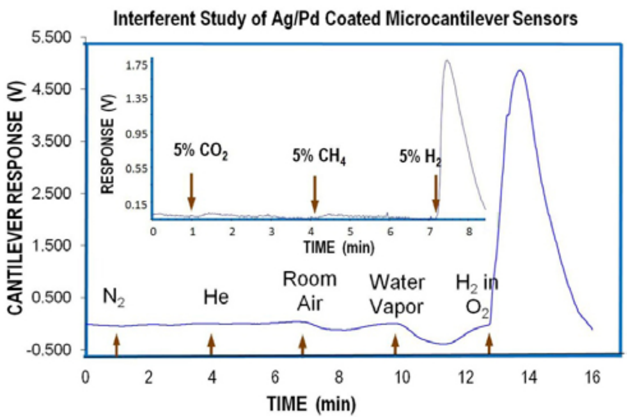

FIGURE 1. Response of our palladium coated sensors to several potential interferents, including CO_2, CH_4, N_2, He, room air and saturated water vapor (25°C). The sensor response to the interferents was an order of magnitude or more smaller than that observed for H_2 at similar concentrations.

Conclusions and Future Directions

We have demonstrated that Pd-Ag functionalized, optically read microcantilever H_2 sensors have nearly ideal attributes required for distributed low cost sensing of hydrogen leaks in many applications. These include high sensitivity, wide dynamic range, adequate response and recovery times and repeatable response. These sensors have been operating in a laboratory environment for more than a year without noticeable changes in sensitivity, specificity and response and recovery times. Work is also progressing on the development of low-cost portable detector prototypes that can be used to validate the expected performance of this potentially lower cost, better performing sensing technique. To this end, we have developed and done preliminary performance studies on two generations of portable instrumentation with encouraging results. We plan to report on these studies at a later date.

In the next project year we plan to:

- Improve H_2 sensor response in several areas:
  - Faster response/recovery times: shorten recovery from 3-10 s to <1 sec.
  - Improve specificity by reducing response to water vapor.
  - Continue studies on potential interferents such as CO, EtOH, CH_4, H_2S.
  - Perform studies on multi-component mixtures.
- File patents applications on techniques, methods, coatings, applications.
- Finalize commercialization partnership agreements.

TABLE 1. ORNL microcantilever-based H_2 sensor meets all requirements for stationary and automotive applications and possibly exceeds performance of other recent sensors.

	Performance Requirement*	ORNL Measured Performance	Competitor #1 (IOS)	Competitor #2 (LANL)
Sensitivity Range	< 0.1% to > 4%	0.01 – 10%	0.2 – 10%	0.1% - 2%
Survivability Limit	100%	Linear response to 100% H_2	unknown	unknown
Response Time	Automotive: < 3 sec Stationary: < 30 sec	1-3 sec	> 5 sec	3 – 8 sec; figures show much longer response times
Recovery Time	Automotive: < 3 sec Stationary: < 30 sec	3-10 sec	> 5 sec	3 – 8 sec; figures show much longer recovery times
Temperature Range	Automotive: -40°C to +125°C Stationary: -20°C to +50°C	Yes	Yes	Yes
Pressure Range	Automotive: 62-107 kPa Stationary: 80-110 kPa	Yes	Yes	Yes
Ambient Relative Humidity Range	Automotive: 0 – 95% Stationary: 20 – 80%	0-100% - little response to changes in humidity	significant response to changes in humidity	unknown
Interferent Resistance	No false positive responses	Excellent	poor – H_2S, CO, CH_4	unknown
Power Consumption	< 1 Watt	0.2-0.5 Watt	0.5 watt	5-10 watt
Operating Temperature	Room temperature	room temperature	room temperature	535°C
Lifetime	Automotive: 6,000 hr Stationary: > 5 years	Demonstrated > 12 months	unknown	2000 hours; Response times much longer at longer times
Accuracy and Repeatability	Automotive: 5-10% Stationary: 10%	> +/- 5%	> +/- 5%	+/- 10%

*See L. Boon-Brett et al., "Identifying performance gaps in hydrogen safety sensor technology for automotive and stationary applications," *Int. J. Hydrogen Energy*, **35**, 373-384 (2010).
LANL - Los Alamos National Laboratory

- Complete fabrication and preliminary testing of a field portable instrument.
- Implement commercialization plan with commercial partner.
- Begin tech transfer to commercialization partner for preproduction prototype development.
- Manage preproduction instrument fabrication at commercialization partner facilities.
- Test pre-commercialization prototype at National Renewable Energy Laboratory Hydrogen Sensor Laboratory.

FY 2010 Publications/Presentations

1. "Distributed optical microsensors for hydrogen leak detection and related applications," S.R. Hunter, J.R. Patton, M.J. Sepaniak, P.G. Datskos and D.B. Smith, published in Proceedings of SPIE: Volume 7693, Unattended Ground, Sea and Air Sensor Technologies and Applications XII, Orlando, Florida, 5–9 April 2010.

2. "Rapid response microsensor for hydrogen detection using nanostructured palladium films," S.R. Hunter, J.R. Patton, M.J. Sepaniak, P.G. Datskos and D.B. Smith, Sensors & Actuators: A Physical (2010), *in press*.

3. 2010 DOE Hydrogen Program Annual Merit Review – Washington, D.C. – June 9, 2010, Presentation SCS018.

References

1. L. Boon-Brett et al., "Identifying performance gaps in hydrogen safety sensor technology for automotive and stationary applications," Int. J. Hydrogen Energy, 35, 373-384 (2010).