VII.4 Hydrogen Optical Fiber Sensors

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Contract Number: DE-FG36-06GO86057

Project Start Date: May 01, 2006
Project End Date: April 30, 2008

Objectives

- Reduce or eliminate interferences from humidity and oxygen exhibited by virtually all current optically-based hydrogen detectors.
- Demonstrate a compact hydrogen detector capable of distributed area detection.

Technical Barriers

This project addresses the following technical barriers from the Hydrogen Safety section of the Hydrogen, Fuel Cells and Infrastructure Technologies Program Multi-Year Research, Development and Demonstration Plan:

(A) Limited Historical Database
(B) Proprietary Data
(D) Liability Issues
(F) Safety is Not Always Treated as a Continuous Process
(G) Expense of Data Collection and Maintenance
(H) Lack of Hydrogen Knowledge by Authorities Having Jurisdiction

Accomplishments

- Developed polymeric coating that dramatically improves resistance to humidity and oxygen interference for porous glass sensor substrates.
- Polymer coated sensor responds to 1% H_2/air in relative humidity ranges 0-95% meeting DOE sensitivity/cross sensitivity target for indoor safety.
- Hydrogen chemistry modified and immobilized in polymer with properties suitable for fabrication of enhanced polymeric waveguide sensor.
- Multiplexed fiber optic test unit developed incorporating low cost energy efficient light emitting diode (LED) light sources forming the basis of a compact hydrogen sensor detector system.

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Introduction

The hazards associated with using a combustible gas, such as hydrogen, for fuel purposes can be reduced with sensor technology that can monitor the gas supply and warn in the event of a release. An optical sensor technology in which the electrical power is maintained out of the hydrogen environment offers the most inherently safe design. A limiting factor is that the number of sensors required scales with the supply size, and hence multiple sensors are needed to provide adequate coverage. With optical sensors, multiple locations distributed over an area can be monitored using fiber optic lines connected to a central data acquisition unit in an intrinsically safe location. To be commercially viable, the safety sensor technology should be low-cost, sensitive, and reliable, and should maintain operation in non-laboratory environments. The fiber optic sensors being developed in this project address these commercial matters also.

Intelligent Optical Systems (IOS) has developed a proprietary chemical formulation that changes color in the presence of hydrogen [1]. The formulation is readily immobilized in an optical platform that can be used either in intrinsically safe remote fiber optic sensor networks, or in compact (hand held or wall-mountable) sensor units. The underlying sensor mechanism builds on recognized color changing hydrogen sensors that use a palladium (Pd) catalyst paired with tungsten oxide (WO_3). The IOS sensor, however, is uniquely manufacturable, being homogeneously produced using inexpensive solution phase techniques rather than heterogeneously produced using vacuum or electrodeposition. The primary objective of this research is to reduce or eliminate the interference, caused by humidity and oxygen, exhibited by virtually all current metal catalyst based hydrogen detectors. This project has allowed IOS to formulate our sensor chemistry in robust homogenous substrates amenable to encapsulation by barrier coatings. In doing so, IOS has shown that low-cost, sensitive, and intrinsically explosion-proof optical sensor platforms can be developed to facilitate the adoption of a safe hydrogen economy.

Approach

IOS's sensor formulation was originally infused into a porous glass substrate. Commercial-off-the-shelf glasses often exhibit properties, such as high oxygen permeability and hydrophilicity, which are less than optimal for palladium-catalyzed hydrogen sensing. Two strategies are being investigated to reduce or eliminate the interference caused by humidity and oxygen. One strategy is to coat the porous glass sensor with a hydrophobic and oxygen impermeable polymer barrier so that the sensor operates from 0-95% relative humidity (RH). The second strategy is to immobilize the sensor chemistry in a water-resistant polymer, instead of porous glass. Both strategies involve the use of advanced polymers and as a result, IOS has formulated, applied, and evaluated numerous polymer materials and combinations of polymers during the course of this project.

We have also developed a compact multi-channel hydrogen detection unit that can be used with both glass and polymer sensor substrates. The unit consists of a proprietary optoelectronic and software system that uses low cost LEDs and solid state photodetectors. The system is designed to be used in a multiplexed format allowing up to eight sensors to be monitored simultaneously in real time using fiber optic cables. Using this system, numerous sensor samples have been tested with varying hydrogen concentrations and relative humidities in a test system that incorporates a calibrated gas delivery and mixing apparatus.

Results

We have observed that no single polymer performs adequately as a barrier at elevated humidity (e.g., 95% RH), but we can combine two layers of differing polymers to get the characteristics we desire. The polymers are first dissolved in solvent and then the solutions are imbibed in the porous glass sensor, one at a time, with a solvent evaporation step between. Our results show that interference from humidity and oxygen can be greatly reduced using this novel polymer composite as a barrier coating.

The performance of uncoated porous glass sensors is represented in Figure 1. The data shows that the sensor response diminishes at elevated humidity, such that no response is recorded at 95% RH, independent of the presence of oxygen. Much work has been focused on reducing or eliminating this interference. The performance of a representative porous glass sensor coated with the novel polymer composite is shown in Figure 2. This data shows that the sensor continues to respond to H_2 at 95% RH when oxygen is present in the environment; i.e., our coating significantly reduces the interference effects of both humidity and oxygen. This dramatic improvement indicates that additional work on this polymer system can further improve the signal-to-noise ratio of this prototype sensor, yielding an easily distinguishable response to 1% hydrogen in an environment containing oxygen. It should be noted that artifacts in the response data graphs induced by our gas mixing setup cause the appearance of drift and signal fluctuation. The source of these artifacts has been identified and will be eliminated in future work.

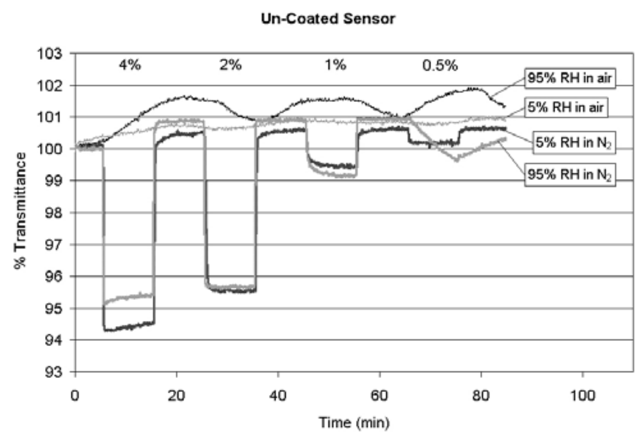

FIGURE 1. Effect of relative humidity and environment on un-coated sensors response to hydrogen cycling 4, 2, 1, 0.5% measured as sample transmittance. Uncoated sensor shows no response to hydrogen at 95% RH.

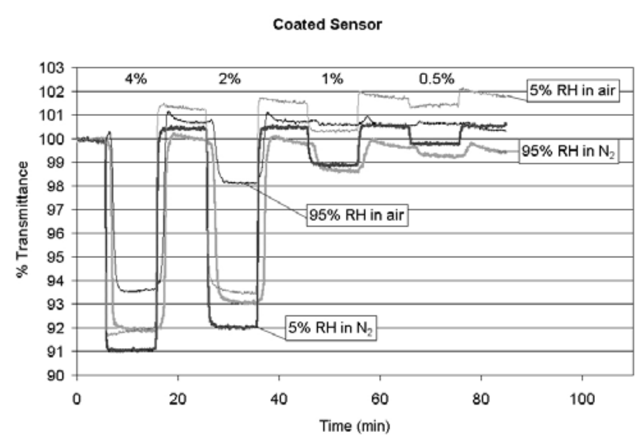

FIGURE 2. Effect of relative humidity and environment on coated sensors response to hydrogen cycling 4, 2, 1, 0.5% measured as sample transmittance.

A second key component of this year's research and development was to immobilize the sensor chemistry in a water-resistant polymer. The goal of this work was to show that our colorimetric formulations can be used in fiber optic cladding based sensors or in integrated optic polymer waveguide sensor platforms. We have successfully developed a homogeneous hydrogen sensitive polymer that has optical properties amenable to cladding or waveguide design. A thin film of this material (ca. 40 microns thick) has exceptional sensitivity to hydrogen as shown in Figure 3. The sensitivity of this material degrades slowly with time and our initial formulation is also humidity dependent, but we anticipate a one year minimum lifetime. Further work is needed to chemically modify the polymer matrix to increase sensor lifetime and reduce interference from water vapor. Further work will also allow the material to be fashioned into a fiber cladding or waveguide format resulting in several orders of magnitude greater sensitivity. This magnitude of enhanced sensitivity is anticipated to yield a much longer lifetime and reduced interference effects from oxygen or water vapor.

A prototype multi-channel fiber optic detection unit developed this year is shown in Figure 4. A 9-volt source powers the proprietary electronics that are designed to be used in a portable multiplexed format allowing up to eight sensors to be monitored simultaneously using fiber optic cables. The unit is controlled by a personal computer using software written in Labview®. The software includes an easy-to-use graphical user interface illustrated in the Figure 4 inset. Data is streamed to the computer via a RS-232 serial interface. This unit is a first-generation device that can be used to monitor several sensors in different locations simultaneously. This unit can be upgraded into a more sophisticated detection device including, but not limited to, a smaller footprint, battery power, and lock-in detection. Such a device would be suitable for use in a real-world multipoint hydrogen detection system.

Conclusions and Future Directions

- Polymeric barrier developed.
- Sensor relative humidity range 0-95%.
- Detection of 25% lower flammability limit with +/-10% accuracy shown.
- Polymer immobilized sensor developed.
- Multiplexed fiber optic sensor monitoring unit developed.
- Fiber-cladding sensor to be developed.
- Multichannel integrated optic sensor to be developed.
- Second-generation optoelectronic module to be developed.

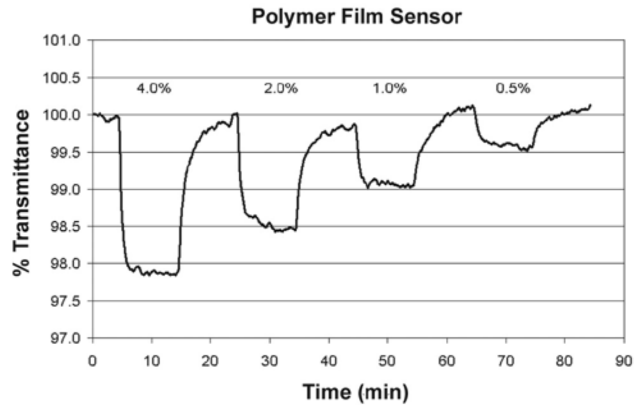

FIGURE 3. Polymer sensor response to hydrogen cycling 4, 2, 1, 0.5% measured as sample transmittance.

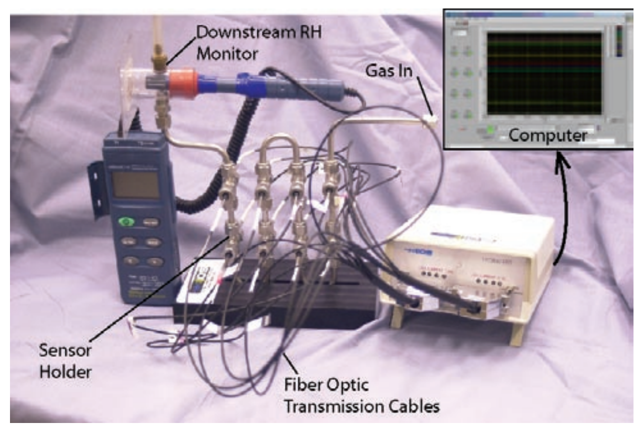

FIGURE 4. Multichannel prototype controlled by PC using easy-to-use graphical interface (inset).

FY 2007 Publications/Presentations

1. Quarterly #3 report, submitted 3/7/07.
2. Quarterly #4 report, submitted 6/13/07.
3. Steven R. Cordero and Robert A. Lieberman, 2007, "IOS Sensor Technology," DOE Hydrogen Sensor Workshop, Washington, D.C.
4. Steven R. Cordero and Robert A. Lieberman, 2007, "Hydrogen Optical Fiber Sensors," DOE Hydrogen Program Annual Merit Review, Crystal City, VA.

References

1. Edgar A. Mendoza and Anil Menon, "Hydrogen Sensor Apparatus and Method of Fabrication," US Patent 6535658, March 2003.