IX.9 Hydrogen Optical Fiber Sensors

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Objectives

- Refine and optimize indicators and polymer materials for hydrogen detection in different optical guiding formats, including optrodes and waveguides as point sensors and optical fibers as distributed sensors.
- Optimize the sensor element fabrication techniques to develop a multi-channel sensor chip.
- Demonstrate the sensor's ability to achieve the required sensitivity with no oxygen or humidity dependence.
- Design and interface optical coupling techniques for waveguide and distributed optical fiber hydrogen sensors.
- Deliver a complete optoelectronic package for point and distributed hydrogen sensors.

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 (MYRDDP):

- **Delivery**: Barrier I. Hydrogen Leakage and Sensors (MYRDDP page 3.2-20: "Low cost hydrogen leak detector sensors are needed")
- **Storage**: Barrier H. Balance of Plant (BOP) Components (MYRDDP page 3.3-14: "Light-weight, cost-effective… components are needed…These include… sensors")
- **Manufacturing**: Barrier F. Low Levels of Quality Control and Inflexible Processes (MYRDDP page 3.5-11: "Leak detectors… are needed for assembly of fuel cell power plants.")
- **Technology Validation**: Barrier C. Lack of Hydrogen Refueling Infrastructure Performance and Availability Data (MYRDDP page 3.6-8: "… the challenge of providing safe systems including low-cost, durable sensors [is an] early market penetration barrier")

Contribution to Achievement of DOE Safety, Codes & Standards Milestones

This project will contribute to achievement of the following DOE milestones from the Hydrogen Safety/Leak Detection Technology section of the Hydrogen, Fuel Cells and Infrastructure Technologies Program Multi-Year Research, Development and Demonstration Plan:

- MYPP Milestone: Develop sensors meeting technical targets. (4Q, 2012)
- MYPP Milestone: Develop leak detection devices for pipeline systems. (4Q, 2015)

Accomplishments

This project was initiated on June 1st, 2008. Experimental work started by building on previous efforts in developing both the point sensor and distributed sensor formats. One of the major limitations that needed to be addressed was the activation step, during which the sensor films are heated to high temperatures (300-350°C). This heating step is needed to activate the catalyst precursor yielding a sensor matrix with a high degree of attenuation. In order to overcome this issue, we established collaboration with Raymat, Inc. to help in the development of heat tolerant, yet permeable, polymers for both applications: distributed optical fiber cladding, and high refractive index waveguide elements.

- Evaluated heat tolerant, low refractive index-matching polymers for fiber cladding applications. A hydrogen sensitive fiber cladding was fabricated and tested against various hydrogen concentrations down to 10% lower flammability limit (LFL). The cladding shelf-life aging was studied for ~9 months with good stability results.
- Evaluated heat tolerant, high refractive index polymers for waveguide applications. The hydrogen

sensitive waveguide approach had attenuation limitations, thus an attenuated total reflection (ATR) testing mode was used to achieve higher sensitivity through multiple optical paths. The cladding shelf-life aging was studied for ~6 months with satisfactory results.

- The optrode preparation scheme was optimized through the indicator solution infusion, reduction, and drying steps. The optrodes were tested against various hydrogen concentrations down to 10% LFL. Efforts in this project included optimization of the performance of previous optrodes in elevated humidity environments (>90% relative humidity). The reproducibility of the optrode fabrication, and the quality control of the resulting elements, will be targeted in the future work plan.
- Optical components were selected and the system design was outlined.

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Introduction

IOS is leveraging its unique capabilities and expertise in optical sensors to develop reliable and sensitive hydrogen leak detectors with a wide dynamic range. The primary focus was on the development of sensor formats for two distinct embodiments: point sensors and distributed sensors. Point sensors are those that detect and measure a gas at a single location. Multiple point sensors are frequently used to simulate distributed sensor coverage. Truly distributed sensors can be realized by fabricating optical fibers whose light-confining cladding is a hydrogen sensitive polymer. Using optoelectronic methods developed at IOS, the distributed sensor will not only be able to sense hydrogen along its entire length, but will also be able to indicate, along the fiber length, the location at which the hydrogen has been released.

Point sensors are being explored in two major formats. The first is in the form of "optrodes," where hydrogen indicator chemicals are deposited on a porous substrate. Optrode sensors can be completely passive, located at one end of an optical fiber, and probed by sending light through the optical fiber and observing the intensity of the reflected signal. This is especially attractive in situations where it is undesirable or difficult to introduce electrical devices. Optrodes can also be mounted directly between a light source and detector to achieve compact detection. The second type of point sensor will be in the form of an integrated optical waveguide. In this form, the sensor, optics, and electronics will all be located on a common chip, much as in semiconductor fabrication. In this latter example, the sensor chemistry could be incorporated either in a porous matrix or in a solid polymer, as long as the chemistry is compatible with processes for chip fabrication. In both configurations, the hydrogen sensor element can be integrated with humidity, oxygen, and temperature sensor elements to eliminate the possible interference of these factors on hydrogen sensitivity.

Approach

IOS has studied three formats for hydrogen sensors: porous glass substrates (optrodes), evanescent-field polymer-clad silica optical fiber sensors (distributed sensors), and integrated-optic chip sensors.

A comparative evaluation of the various sensor matrices has revealed that, overall, the porous glass sensors (optrodes) performed the best. Thus, these were chosen as the hydrogen indicator matrix that will be used in the final product prototype. The sensor prototype design has been outlined and optoelectronic components have been acquired. The optrode response time is quite rapid (time to reach 90% of full-scale, $T_{90} \approx 10$ seconds); software routines will be developed to provide a warning of 10% LFL concentrations in one second by analyzing sensor dynamic response.

Results

Distributed Optical Fiber Approach

Polymers with refractive indices lower than borosilicate glass were investigated for application as a distributed optical fiber cladding ($\eta < 1.43$). In this project, IOS has developed and demonstrated the world's first fully distributed hydrogen transducer: an optical fiber that responds to hydrogen over its entire length. Although the fiber sensor development task is now complete, a long-term study of the hydrogen fiber cladding material stability is being carried out.

In order to develop a successful optical fiber cladding, and lower the optical attenuation in the evanescent field region, we investigated various indicator doping levels. The heat activation step that is required to reduce the catalyst also increases the optical attenuation because it causes a coloration of the indicator cladding layer. The fiber was exposed to a 4/3/2/1/0.4% hydrogen ladder using air as the carrier gas; the results shown in Figure 1 represent the sensitivity of one meter exposed sensor fiber over this dynamic range.

Integrated Sensor Chip (Polymer Waveguide Approach)

Polymers with refractive indices higher than silica were investigated for application as a waveguide array ($\eta > 1.48$). In order to function as an optical waveguide to contain and guide the transmission of light through

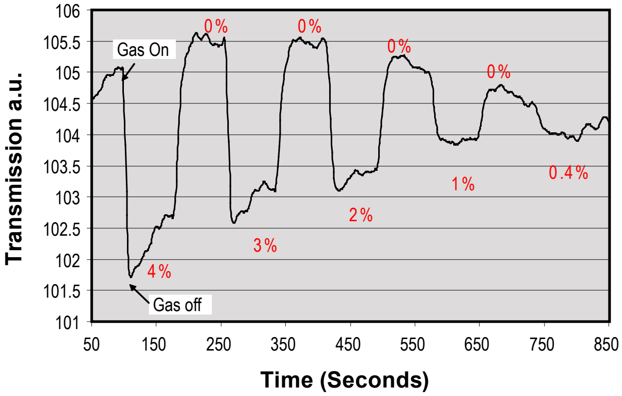

FIGURE 1. One Meter Hydrogen Sensor Fiber Response to Hydrogen Concentration "Ladder" in Dry Air

the structure, the refractive index of the guide must be higher than that of its surroundings. The high refractive index optical conductive polymer, IOS 146 (n=1.460), was evaluated for humidity interference, hydrogen sensitivity, and thickness dependence. A hydrogen colorimetric indicator was immobilized in IOS 146; the results showed promising sensor performance to LFL and 10% LFL levels of hydrogen in single-pass transmission mode (i.e., when the light signal measuring the optical absorbance change due to hydrogen exposure is passed through and perpendicular to the sensor film). We use this test mode for the initial screening and evaluation of all of our indicator chemistry formulations prior to incorporation into specific sensor formats. This particular combination of polymer and colorimetric indicator proved to be too high in absorbance (too dark) to be useful in waveguide mode (in which the light is guided longitudinally through a length of sensor material). While it is often desirable to pass the light through as much sensor material as possible in order to maximize exposure path length, in this case, since high optical attenuation prevents waveguide mode operation, we attempted a different route to light propagation in the sensor: an ATR mode. In true ATR, light is launched into the film through a prism at an angle such that a portion of the incident light traverses the film in multiple reflections until it is collected at the far end in the photodetector. The purpose of this method is to increase the exposed path length of the optical signal, thereby enhancing sensitivity beyond that which can be achieved in single-pass transmission mode. Unfortunately, even with two discrete reflections, the dark sensor film attenuated the optical signal below detection limits.

Using this technique, the light incidence angle θ was varied from 41˚ to 45˚ and the sample was challenged with hydrogen at the LFL at each setting. The incident angle 43˚ was used in sensitivity test measurements where the hydrogen sensor film was exposed to 4%, 0.5%, and 0.1% H_2 in air. Figure 2 represents the response of the sensor film in reflection mode when the hydrogen gas was introduced after a 60 second conditioning period. Both sensor response time and signal magnitude were improved in reflection mode over the performance achieved in single-pass transmission mode.

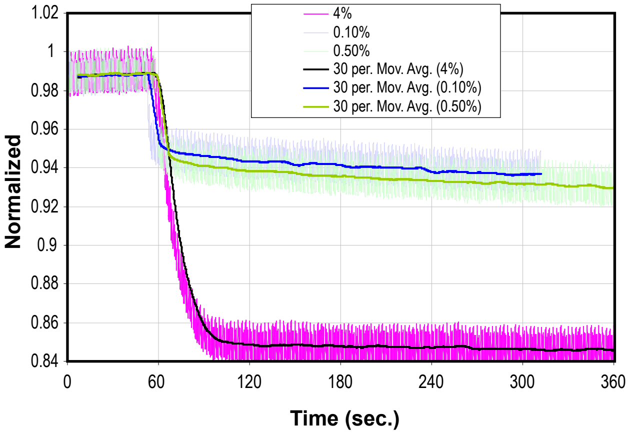

FIGURE 2. Reflection Measurements with Exposures at 4, 0.5, 0.1% Hydrogen

Integrated Sensor Cassette (Porous Glass Approach)

The steps for processing porous glass sensor substrates into hydrogen-sensing optrodes were refined and documented. Process steps include cleaning the raw substrates, and then etching and impregnating the glass matrix with IOS hydrogen indicator. Optrodes prepared under these procedures showed enhanced response (over earlier efforts) to hydrogen at 4, 3, 2, 1, and 0.4% cycled with air. Figure 3 shows the response performance of four optrodes; three were prepared within a single batch, while the fourth optrode was prepared in a second batch to verify process control. The data shows comparable response to hydrogen between batches; clearly variations (optrode-to-optrode) in response would need to be accounted for by signal processing in a practical system. The upward "jump" of the baseline (0% H_2) signals for two of the optrodes, indicating increased transmission after the first exposure to hydrogen, is irreversible. This implies that optrodes may need to be preconditioned at the manufacturing facility before deployment. Optimization in the optrode fabrication process was continued using 10 mm optrodes, with the goal of achieving reproducibility with <10% signal strength deviation (permissible) from the mean value.

Optrode substrates were studied for their response to 4% H_2 at various humidity levels to evaluate their applicability in different environments. The substrates were preconditioned for one hour at the desired humidity prior to hydrogen gas introduction. At room

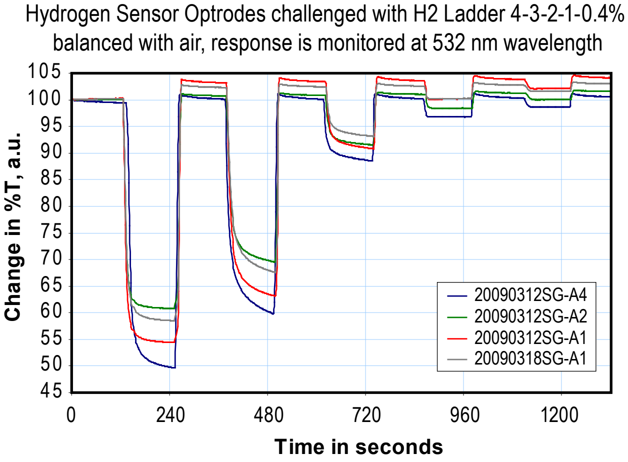

FIGURE 3. Response of Optimized Hydrogen Sensor Optrodes to Varying Hydrogen Concentrations in Dry Air

temperature, humidity levels were ramped up from 5% to 50% and 95% relative humidity. The uncoated optrodes appear suitable for use in environments ranging from "bone dry" to "tropical." However, to forestall unanticipated problems with aging in aggressive environments, we will also investigate the performance of optrodes with single- and dual-layer humidity barriers composed of polymeric coatings (e.g., Cyclic Olefinic Polymer 10%COC8007, and Soluble Perfluoro Polymer AF1600 6.0% in Fluorinert FC-770), and other hydrophobic materials

Optoelectronic Package

Sensor Hardware

We are designing a re-configurable stand-alone sensor module. The module schematic design is near completion. The unit will incorporate a microcontroller with digital signal processing capabilities and a built-in universal serial bus peripheral interface controller (USBPIC). Our research determined that the USBPIC 24 family by Microchip was most suitable, both for cost and architecture reasons.

The prototype will support four channels: signal, reference, temperature and humidity. The module's interface will include both USB and RS232 serial communication. The design is illustrated in Figure 4.

Optical receivers with dynamic range exceeding 80 dBs have been developed at IOS; similar principles will be utilized in the hydrogen sensor optoelectronic module once the optrode designs are finalized, and optrode cassette light attenuation and response are fully characterized. The architecture includes light emitting diode (LED) drivers, sensor inputs, a user interface consisting of a keyboard and a liquid crystal display (LCD), and communications interfaces. Later in development, we will examine a controller–area network, which is utilized in the vehicle industry, and wireless expansion options (consisting of either SYNAPSE, ANT, or Zigbee).

FIGURE 4. Illustration of the Hydrogen Sensor Prototype

Software

A dsPIC development board and C compiler were purchased and installed. Initial code building blocks were established for panel testing. Signal measurement and analysis goals previously acquired will be implemented using C code to take advantage of the microcontroller's extensive capabilities.

Modules for keyboard input, LCD output, alarm algorithms, environmental and aging compensation, and data logging will be implemented after completing the basic routines for controlling the hardware.

Conclusions and Future Directions

- Continue studying the optrode hydrogen sensor fabrication and process control.
- Study different humidity barriers to optimize the optrode's response in the presence of elevated humidity levels.
- Evaluate the lifetime of the chosen optrode hydrogen sensors.
- Design the optoelectronic interface into a compact sensor chip that will include the selected LED and photodiodes in a modular sensor package.
- Design and validate the data processing and algorithms.
- Explore commercial possibilities for the different hydrogen sensor embodiments.

FY 2009 Publications/Presentations

1. 2009 Annual Merit Review Proceedings, poster presented May 20, 2009.