Hydrogen Optical Fiber Sensors

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Intelligent Optical Systems, Inc.
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Project ID#
SAP2

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Overview

Timeline
• Start - May 01, 2006
• Finish - April 30, 2007
• 90% complete

Budget
• Total project funding
  – DOE - $495K
  – Contractor- $124K
• Total funding in FY06
  – $236K
• Funding for FY07
  – $383K

Safety Sensor Development
• Hydrogen Program Barriers Addressed
  1. Expense of data collection and maintenance
  2. Liability issues
  3. Safety is not always treated as a continuing process

• Sensor Performance Targets
  1. Measurement range: 0.1%-10%
  2. Gas environment: ambient air, 10%-98% RH range
  3. Interference resistant (e.g. moisture, hydrocarbons)
## Technical Objectives

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| **Overall**    | • Reduce or eliminate interferences from humidity and oxygen exhibited by virtually all current optically-based hydrogen detectors  
                  • Establish and fully characterize a compact hydrogen detector |
| **FY2006**     | • Transfer existing indicator chemistry from commercial to in-house porous glass substrate and improve indicator performance  
                  • Transfer indicator chemistry from porous glass substrate to polymeric substrate  
                  • Establish ppm-level response to hydrogen in one or more candidate substrates |
| **FY2007**     | • Establish good hydrogen sensitivity, response time, and sensor performance with little or no response to moisture and oxygen  
                  • Develop compact multi-channel detector/test system |
Technical Approach: Optical Detection of Hydrogen

• Colorimetric Detection
  – Immobilize hydrogen-sensitive indicator in optically transparent medium
  – Indicator mixture changes color in presence of hydrogen
  – Transmitted light intensity depends on hydrogen concentration

• Optical Formats
  » “Optrode:” Indicator immobilized in point sensors mounted on fiber tip. Sensors can be located far from electronics.
  » Integrated Optic: Indicator embedded in waveguides on optical chip. Multiple channels improve performance.
  » Distributed: Indicator coated on entire fiber. Wide area can be covered with a single cable.
Technical Plan

Task 1.0 Acquire reagents and substrate materials
- Maintain workflow

Task 2.0 Formulate porous glass sensors from silicate and/or silicone reagents
- Devise new indicator-immobilization techniques
- Synthesize and characterize thin porous glass films

Task 3.0 Evaluate hydrogen diffusion in polymer materials
- Evaluate polymers and copolymers for oxygen and humidity barriers
- Rank-order polymer materials tested

Task 4.0 Evaluate various techniques to produce thin-film and/or slab sensors from advanced polymers
- Survey waveguide fabrication methods
- Develop waveguide-based sensor with enhanced optical performance

Task 5.0 Evaluate sensor response to hydrogen under inert conditions
- Measure baseline hydrogen response and sensitivity of candidate sensors
- Measure response to hydrogen in the absence of water and oxygen
- Select preferred operating wavelengths

Task 6.0 Evaluate sensor performance and resistance to moisture and oxygen
- Select best material for use in a waveguide-based hydrogen sensor
- Test under operational conditions
- Establish preliminary design of integrated optic waveguide-based hydrogen sensor

Task 7.0 Incorporate new sensors in compact hydrogen detector and test system
- Combine proprietary optoelectronic and software subsystems
- Demonstrate a portable hydrogen detector unit

Task 8.0 Project management and reporting
- Document progress and provide deliverables

100% complete

100% complete

90% complete

90% complete

95% complete

90% complete

80% complete

90% complete
Technical Accomplishments

1. Porous glass sensor optimized
   -- Polymer coating provides resistance to humidity
   -- Commercial glass selected as most stable

2. Hydrogen chemistry modified and embedded in optical grade polymer
   -- Provides even greater resistance to humidity
   -- Properties suitable for fabrication of integrated optic sensor

3. Multiplexed fiber optic test unit developed
   -- Incorporates low cost energy efficient LED light sources
   -- Basis for compact hydrogen sensor detector system

These three accomplishments all contribute to the Hydrogen, Fuel Cells, and Infrastructure Technologies Program’s need for reliable, intrinsically safe, accurate, and cost-effective hydrogen detectors.

All FY06 Objectives have been met.
Potential Long-Term Humidity Effects
(above 90% RH uncoated glass substrate fails)

- Repeated exposure to 5% hydrogen in air at 90% RH results in loss of sensor response
- Primary cause: Humidity-fouling of porous glass substrate
Porous Glass Sensor Response

--- Inert Environment

- 0.1 % hydrogen detected with excellent signal-to-noise ratio
- Projected sensitivity <100 ppm
Optimized Porous Glass Substrates

Sensor with barrier coating developed in project (blue line above) has:
- More stable response (consistent peak-to-peak values)
- Faster equilibration in 80% RH environment
Water Resistant Polymeric Substrate

- Optical grade polymer supports hydrogen indicator chemistry
- No observable interference from O₂ or humidity
- Chemistry shows good sensitivity over range of H₂ concentrations
**IOS Hydrogen Sensor Test Facility**

- **Mass flow controllers**
- **Electronic switching valve**
- **COTS fiber optic spectrophotometer**
- **Gas delivery line**
- **Flow cell**
- **Humidity monitoring**
- **Humidity generation**

**Fully automated test equipment:**
- Computerized mass flow controllers for gas mixing
- Online humidity measurement
- Detailed test protocols established
Multichannel Optoelectronic System

Fiber optic multi-sensor analyzer
a) Proprietary optoelectronics
   - High sensitivity and stability
   - Suitable for fiber optic or integrated optic readout
b) PC-enabled graphical user interface
c) Simultaneous data acquisition for 8 sensor channels
Future Work

FY 2007
-- Develop and characterize polymer waveguides
-- Finish optoelectronic system development
-- Test response to hydrogen, oxygen, and humidity

Final milestone: Create and characterize an optical hydrogen sensor with improved humidity and oxygen resistance

FY 2008 (Proposed)
-- Test sensor longevity and response to potential “interferants”
-- Fabricate multichannel waveguide chips
-- Develop advanced signal acquisition and processing
-- Miniaturize optoelectronic system
IOS Optical Waveguide Technology

Step 1: Fiber coupled waveguide **film**

- Light travels horizontally through sensor film
  - Path length increases by 2-3 orders of magnitude
  - Sensitivity increases

- Hydrogen enters through top of film
  - Diffusion length unaffected
  - Sensor response time stays the same
IOS Optical Waveguide Technology

Step 2: Fiber coupled waveguide channel

- Light confined in two dimensions
  - Horizontal launch preserves path length increase
  - Side confinement improves light throughput
  - Multiple channels can share same chip

- Hydrogen enters through top and sides of film
  - Average diffusion length shortens
  - Sensor response time improves
Summary

Relevance:
• Reliable, cost-effective hydrogen safety sensors are required for generation, storage, transport, and (eventually) home safety applications

Approach:
• Optical sensors based on indicator chemistry can be designed for high performance and low cost

Technical Accomplishments:
• Developed barrier coating for moisture resistance
• Improved indicator chemistry performance
• Embedded Indicator chemistry in optical grade polymer
• Hydrophobic material suitable for waveguide fabrication

Proposed Future Work:
• Fabricate hydrogen sensitive waveguides
• Analyze longevity, specificity, and moisture response
• Package system and include final corrections for temperature and humidity

Final Goal:
• A miniaturized sensor using multiple channels on a single optical chip will achieve an extremely high probability of detecting dangerous hydrogen levels and an extremely low false alarm rate
## Target Summary

### Hydrogen Safety Sensor Targets

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<tr>
<th>Metrics</th>
<th>2008 System Target</th>
<th>FY 06 Results</th>
<th>FY 07 Results</th>
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<tbody>
<tr>
<td>Dynamic range</td>
<td>0-100%</td>
<td>0-5%</td>
<td>0-10%</td>
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<tr>
<td>Response time</td>
<td>1 sec</td>
<td>3-50 s</td>
<td>1-10 s</td>
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<tr>
<td>Accuracy (noise)</td>
<td>+/- 10% signal</td>
<td>+/- 10% signal</td>
<td>+/- 10% signal</td>
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<tr>
<td>1% hydrogen detection in ambient atm</td>
<td>Yes</td>
<td>Yes</td>
<td>Yes</td>
</tr>
<tr>
<td>Possible interferences</td>
<td>none</td>
<td>T, Humidity, CO</td>
<td>CO</td>
</tr>
</tbody>
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