Safe Detector System for Hydrogen Leaks

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Intelligent Optical Systems, Inc.
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Project ID #
scsp_03_lieberman

Overview

Time Line

- Start –June 2007
- Finish- May 2010
- 50% Complete

MYPP Barriers/Targets

- **Delivery**: Barrier I. Hydrogen Leakage and Sensors
- **Storage**: Barrier H. Balance of Plant (BOP) Components
- **Safety:** Targets
- (Also: **Fuel Cells**, **Manufacturing**, and **Tech. Validation**)

Budget

- Current Project funding: $1,230,000
  - DOE... $984,000
  - IOS… $246,000
- Funding received in FY07: $383,000

Partners

- Dr. Gerald Voecks – Advisor
- Dr. Angelo A. Lamola – Consultant
- Mr. Gerald Cole – Consultant
- Jadoo Power – Customer/Commercialization
- Intelligent Optical Systems, Inc.– Program Lead

Project Goal:

- Develop optical waveguide hydrogen sensor technology
- Produce manufacturable prototype single-point sensors
- Investigate cable-based sensors for wide-area protection

Technical Objectives:

Overall	♦ Integrate IOS' proprietary hydrogen indicator chemistry into a complete optoelectronics package with well-defined sensing characteristics and a known end-use market ♦ Identify different formulations and physical embodiments of the sensor to meet requirements for specific markets, such as fuel-cell powered passenger vehicles, hydrogen refueling stations, hydrogen generation facilities. and semiconductor manufacturing
CY 07/08	♦ Transfer indicator chemistry from porous glass substrate to polymeric substrate ♦ Establish response to low levels of hydrogen in one or more candidate substrates ♦ 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
CY08/09	♦ Finalize indicator chemistry immobilization into porous glass optrodes; reduce or eliminate sensitivity to moisture and oxygen with polymeric barrier coating ♦ Develop sensor polymers for two distinct embodiments: point sensors and distributed sensors ♦ Optimize integrated optic sensor composition and fabrication ♦ Design and fabricate optoelectronic interface for integrated optic sensors ♦ Demonstrate feasibility of making intrinsically hydrogen sensitive fibers for distributed sensing

Relevance

Barriers Addressed

- **Delivery:** Barrier I. Hydrogen Leakage and Sensors (MYPP page 3.2-20: "Low cost hydrogen leak detector sensors are needed")
- **Storage:** Barrier H. Balance of Plant (BOP) Components (MYPP 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 (MYPP 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 (MYPP page 3.6-8: "…the challenge of providing safe systems including low-cost, durable sensors [is an] early market penetration barrier")

Source: "DOE Hydrogen, Fuel Cells and Infrastructure Technology Multiyear Research, Development and Demonstration Plan" (MYPP), 2007 edition. http://www1.eere.energy.gov/hydrogenandfuelcells/mypp/

Relevance

Performance Targets

- Intermediate Specifications (4Q 2010):
  - Range: 0 – 100% H_2
  - Sensitivity : (min) 0.1%H_2 - 4% of reading
  - Environment: Ambient air, 5-95%RH, and 0-55ºC range.
  - Interference resistant (e.g: moisture, hydrocarbons, oxygen)
- Applications:
  - Vehicular safety
  - Home/garage safety
  - Safety in distribution/production facilities
  - Leak detection

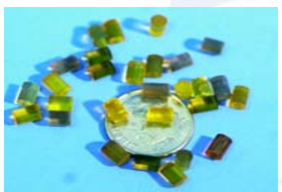
Relevance

Technical Approach: Optical Waveguide Hydrogen Sensing

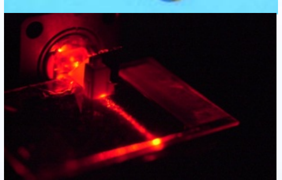
Colorimetric Detection

- Immobilize hydrogen-sensitive indicator in polymeric, optically transparent medium
- Indicator/polymer matrix changes color in presence of H_2
- Intensity of light transmitted through matrix depends upon hydrogen concentration

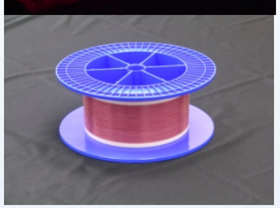
Optical Sensor Formats



Optrode: Indicator immobilized in point sensors mounted on tips of optical fiber. Sensors can be located far from electronics.



Integrated Optic Waveguide: Indicator imbedded in waveguides fabricated on optical chip. Multiple channels improve performance.



Distributed Sensing Fiber: Indicator coated on entire length of sensing fiber. Wide and continuous coverage with a single cable.

Approach

FY 08-09 Technical Tasks

100% complete — **Task 1: Investigate Designs, Materials, and Indicators for Improved Hydrogen Sensors**
- Identify FY-07 Optrodes performance and weakness.
- Acquire additional material, and indicators

100% complete — **Task 2: Optimize, Fabricate, and Test Improved Hydrogen-Sensing Optrodes**
- Investigate new versus old moisture barriers
- Test optrodes for higher levels of humidity, finalize fabrication techniques

65% complete — **Task 3: Optimize, Design, Fabricate, and Test Multi-Channel Integrated Optical Waveguide Sensor Chip**
- Select components for waveguide sensor testing and set-up
- Dual vs. single layer waveguide sensor array testing for hydrogen response at different %RH

65% complete — **Task 4: Design and Integrate Optoelectronic Interface to Waveguide Sensor Chip**
- Combine proprietary optoelectronic and software systems
- Evaluate the optical coupling structures, test and record data

25% complete — **Task 5: Test and Characterize Packaged Multi-Channel Integrated Waveguide Hydrogen Sensor**
- Test for sensitivity and response time, cross interference, temperature and humidity dependence

80% complete — **Task 6: Investigate, Design, Fabricate, and Evaluate Prototype Distributed Hydrogen-Sensing Fiber**
- Survey, select, and optimize the fiber cladding sensor formulation
- Test Hydrogen fiber for sensitivity and cross-interferences

75% complete — **Task 7: Perform Hydrogen Sensor Market Study under DOE Guidance**
- Perform a hydrogen sensor market study, focusing on current and future needs for sensors in production, control, and safety applications

90% complete — **Task 8: Continue FY07 Investigation of Irreversible Chemistry for Hydrogen Sensing**
- Optimize chemistry capability
- Develop into the form of an aerosol that can be applied similar to a spray paint or lacquer coating.

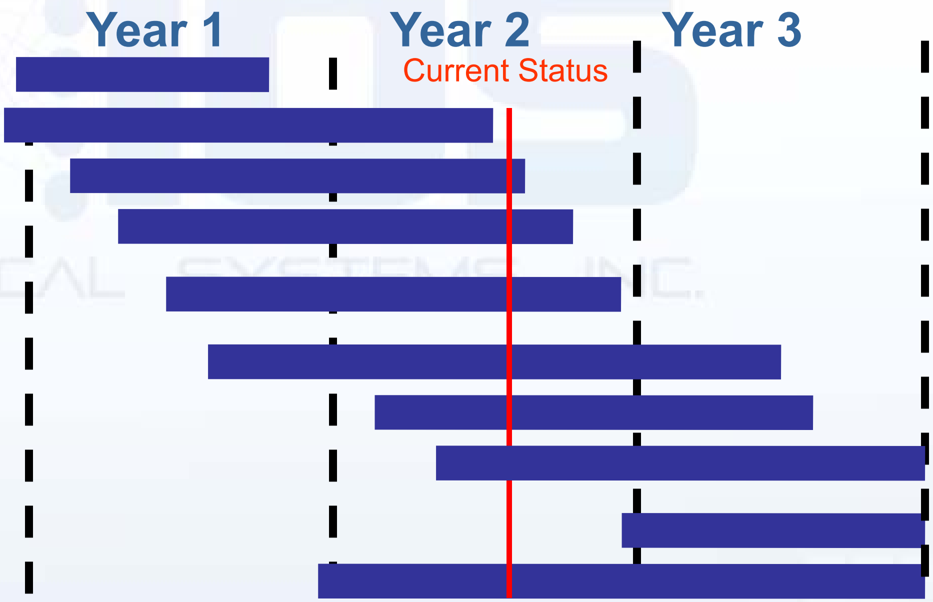
35% complete — **Task 9: Project Management and Reporting**
- Document progress and provide deliverables

Approach

Project Plan: FY08 –FY10

- Identify critical sensor applications that mitigate hydrogen liability issues
- Research and develop reliable hydrogen sensors that fit these applications
- Engineer and commercialize cost-effective hydrogen detection systems

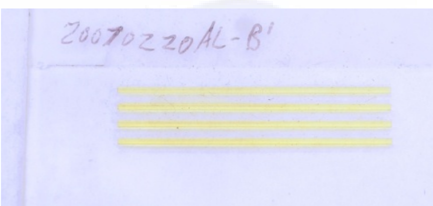
- Define hydrogen indicator chemistry
- Evaluate the sensor matrices
- Validate the sensor response
- Validate the sensor cross-interferences
- Develop integrated optic point sensor design
- Refine point sensor format based on market needs
- Optimize and refine optoelectronic system
- Develop hydrogen sensor fiber for cable-based system
- System installation and beta-site testing
- Establish commercial market and partnerships

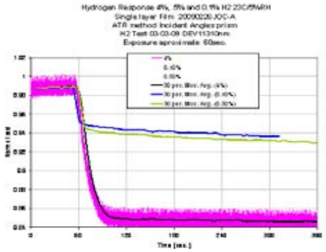


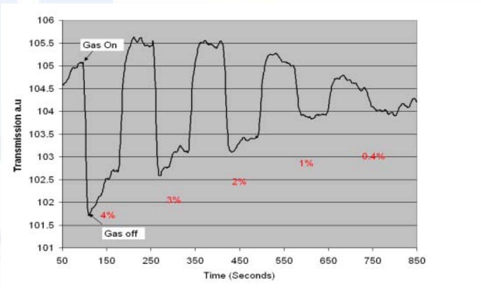
Approach | Future Work

Technical Accomplishments

1. **Porous glass sensor optrode development finalized**
   - ✓ Tested various optrode compositions and confirmed optimum performance with optrodes bearing proprietary coating # 070626
   - ✓ Confirmed coating produces best humidity resistance in 0.5 - 4% hydrogen range
2. **Hydrogen sensitive optical polymer films and waveguides fabricated**
   - ✓ Better performance than optrodes towards humidity and oxygen interference
   - ✓ Integrated optic chips fabricated and being optimized
   - ✓ Feasibility of hydrogen sensor fiber fabrication shown







3. **Optoelectronic interface designed**
   - ✓ Incorporates low cost energy efficient LED light sources and photodiode devices
   - ✓ Basis for compact hydrogen system; can address multiple sensor channels
   - ✓ First-generation signal acquisition board fabricated

These accomplishments all contribute to the development of reliable, cost-effective hydrogen detectors to improve safety and mitigate liability for hydrogen infrastructure and vehicles

Technical Accomplishments	Relevance

Sensor Material Development

- Optimization of optrode chemistry:
  - Maximize hydrogen response using formal "Design of Experiment" techniques to vary composition of chemically sensitive material embedded in porous glass
  - Minimize humidity interference by applying moisture-barrier coatings
- Testing of optrodes:
  1. Imbibe porous glass with indicator mixture; apply moisture barrier coating.
  2. Mount optrodes in test cell for transillumination
  3. Measure intensity while varying hydrogen concentration and %RH

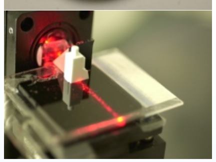
- Optimization of polymers for use in waveguides:
  - Maximize hydrogen response using "Design of Experiment" techniques to vary composition of chemically sensitive material and polymer composition
  - Minimize humidity response by judicious choice of polymer materials
- Testing of waveguide polymers
  1. Spin-cast thin film of candidate polymer composition on glass slide.
  2. Mount films in test cell for illumination perpendicular to film.
  3. Measure intensity while varying hydrogen concentration and %RH

Approach

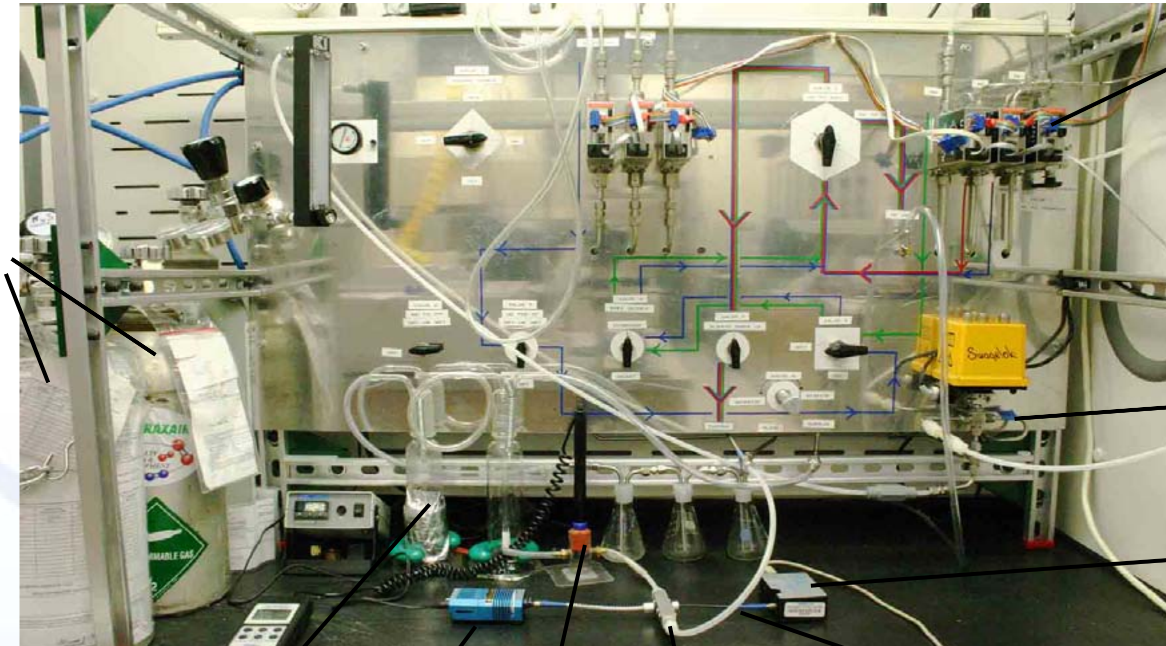
Testing Hydrogen Sensors and Sensor Materials

Fiber Test Cell

Waveguide Light Launch



H_2, air, and other test gases



Mass flow controllers

Electronic switching valve

Fiber optic spectrophotometer

Humidity generation

Light Source

Humidity monitoring

Optrode Test cell

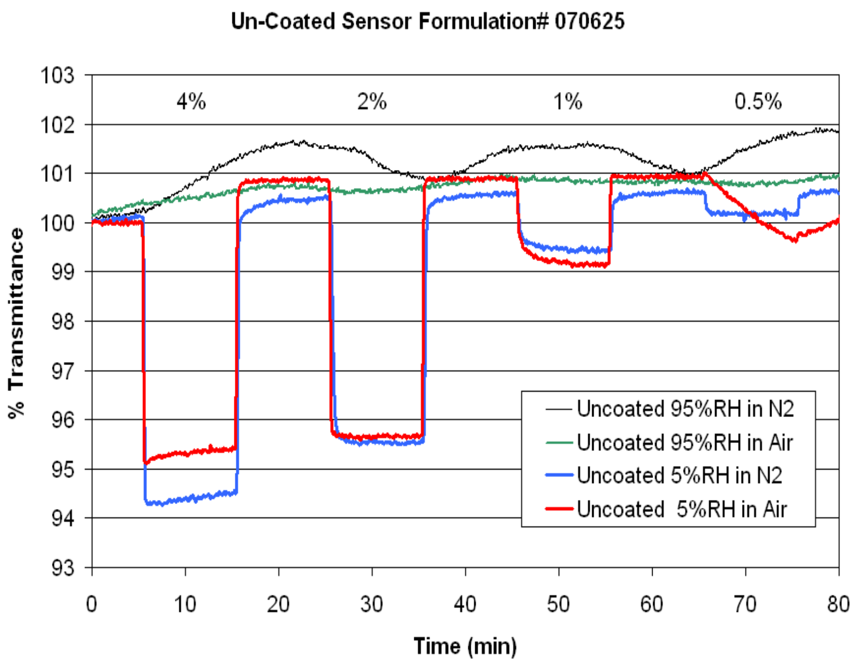
Gas delivery line

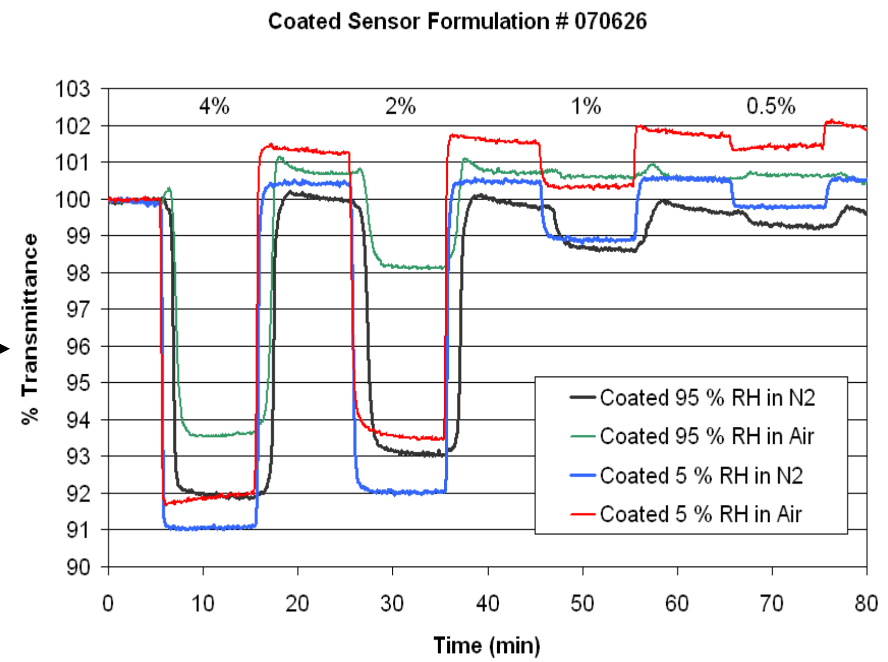
<u>CY 2008-2009 Accomplishments:</u>

- Comprehensive Hydrogen Safety Plan developed, approved, and implemented
- Film test cell redesigned and upgraded
- Integrated optic waveguide test cell constructed
- Fiber test cell constructed

Technical Accomplishments

Porous Glass Optrodes Optimized





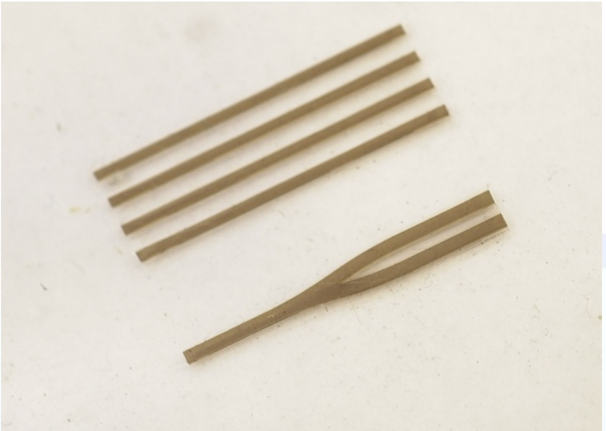
Sensor with newly developed barrier coating has:

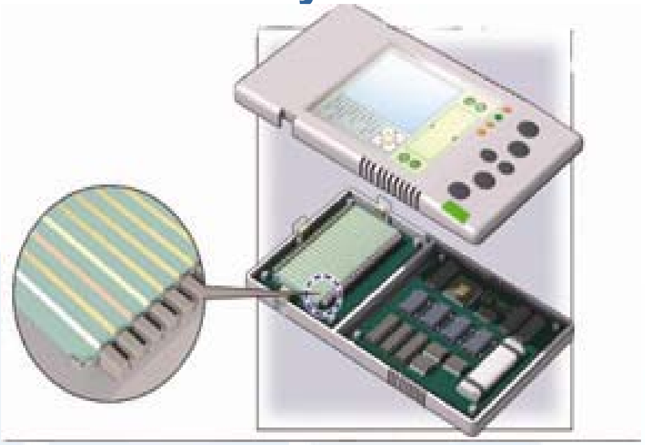
- More stable response (consistent peak-to-peak values)
- Faster equilibration in 95% RH flow

Technical Accomplishments

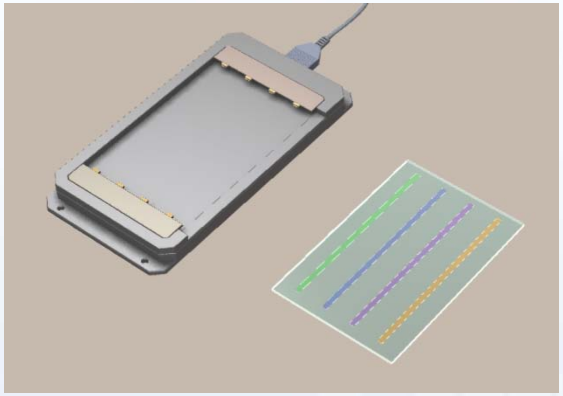
Integrated Optic Sensors For Single-Point Sensing

Approach: The sensor element is a low-cost optical chip composed of polymer lightguide cores specifically manufactured to be chemically sensitive





Hand-Held Point Sensor



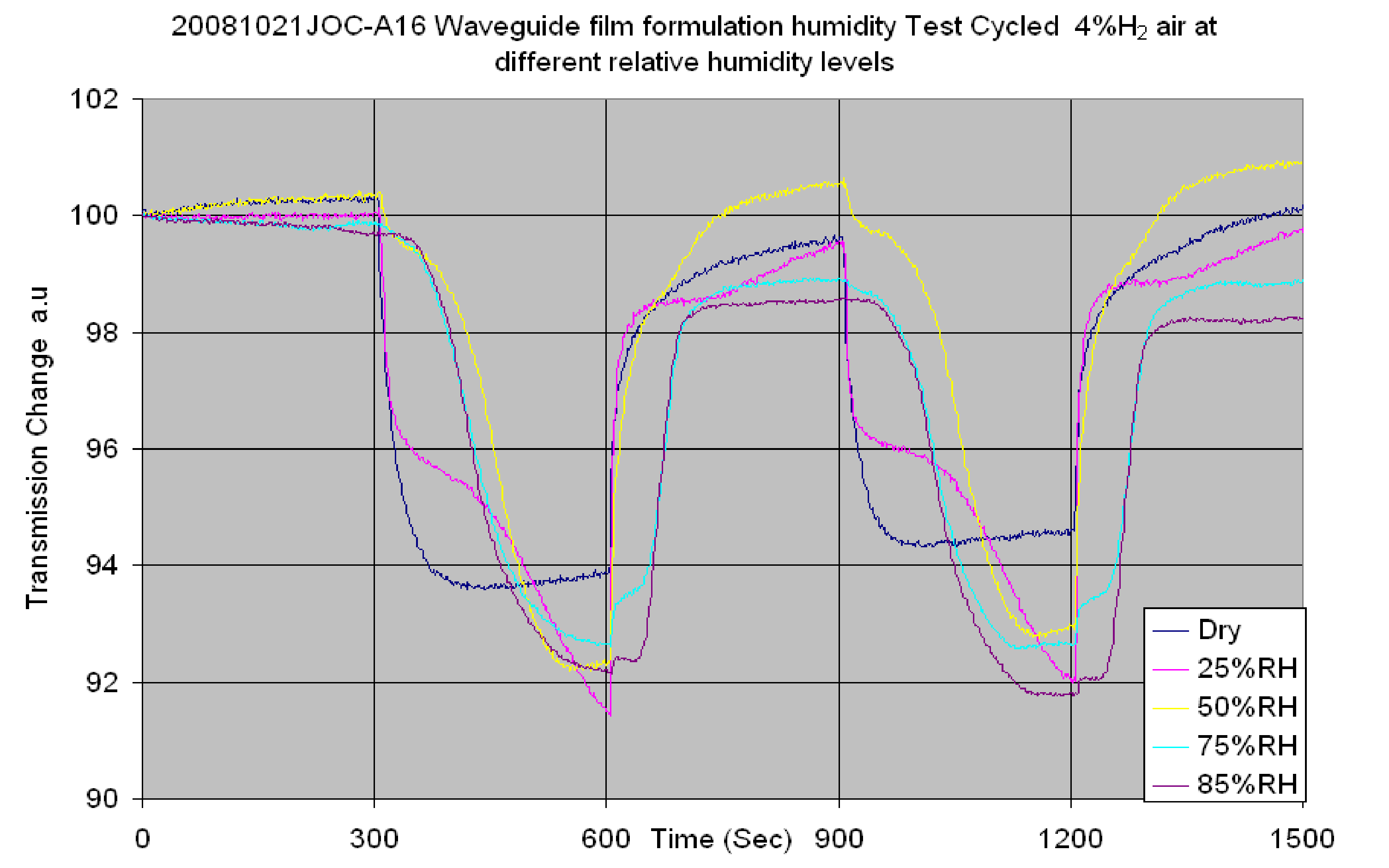
Fiber-Accessed Point Sensor

Advantages:

- Reliable
- Intrinsically safe
- Cost effective for vehicles, single rooms
- Multiple waveguides eliminate chemical interference

Approach

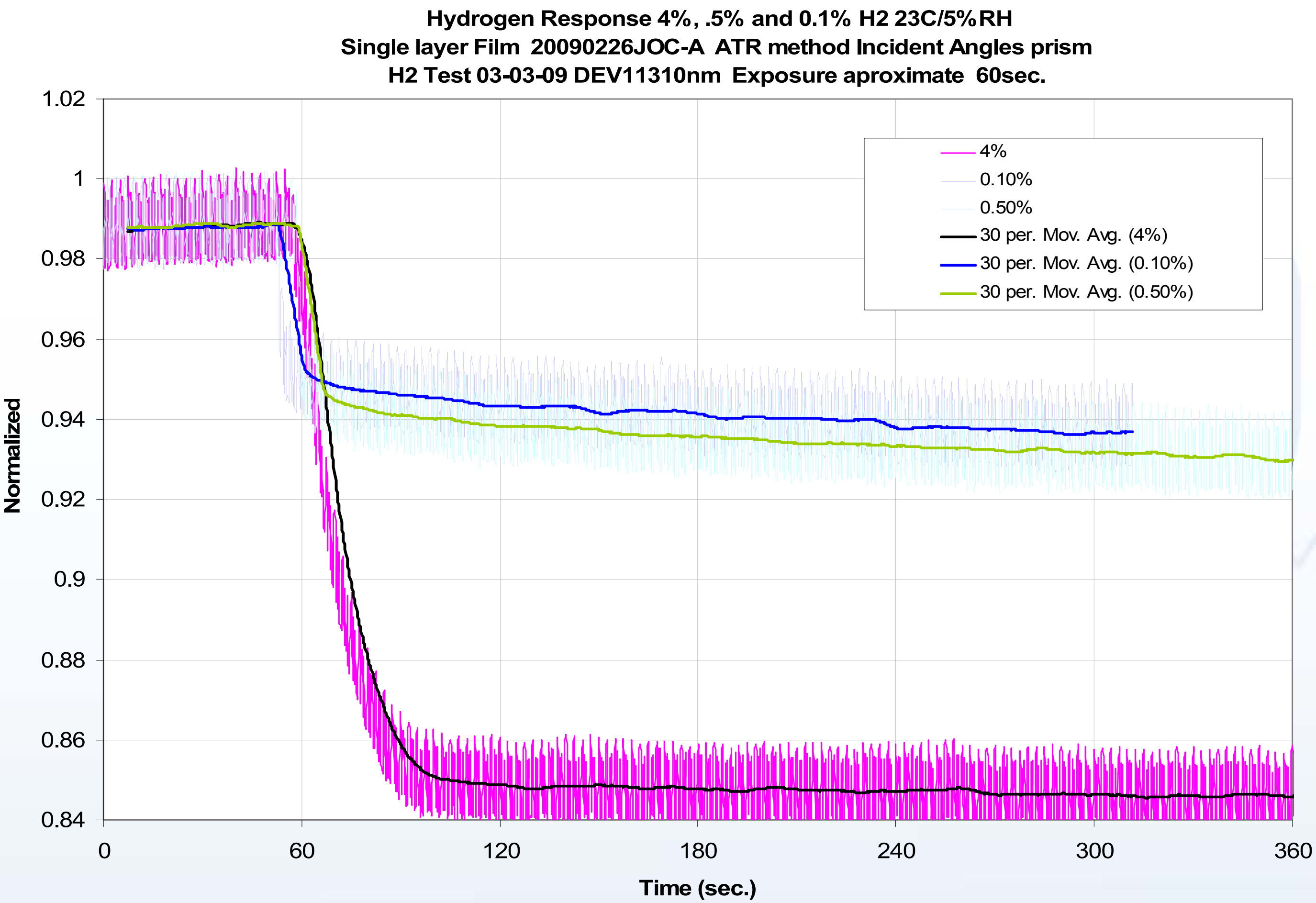
Polymer Film Tests – Optical Waveguide Core Material



High refractive index materials for optical waveguide cores

Technical Accomplishments

Integrated Optic Sensor Response



- Response Time:

t_{90}(sec): 20 at 4%H_2

t_{90}(sec): 10 at 0.1%H_2

- Sensitivity:

LFL(4%H2) - 10%LFL

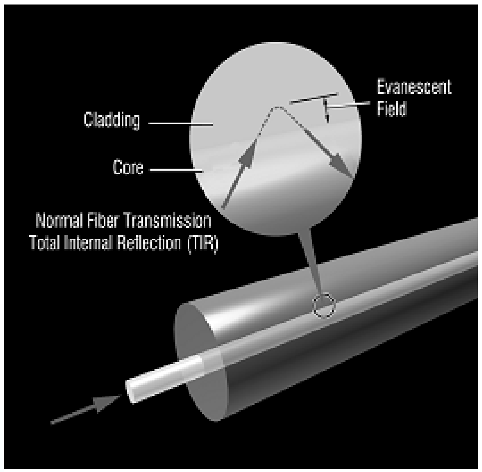
- Range:

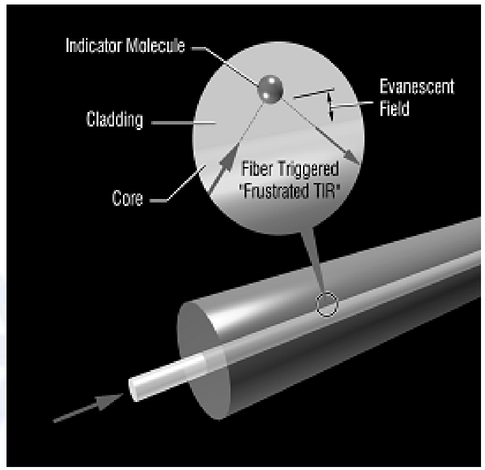
0-100%H_2

Technical Accomplishments

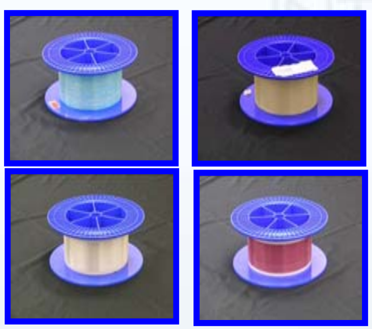
Intrinsic Optical Fiber Sensors for Broad-Area Sensing

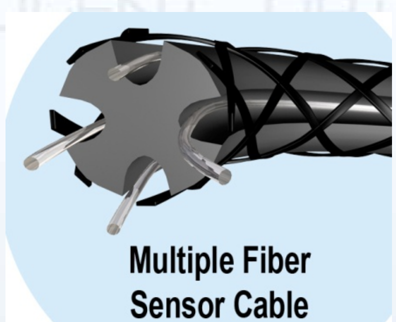
Approach: The cable *is* the sensor – composed of fibers specifically manufactured to make their entire lengths chemically sensitive.

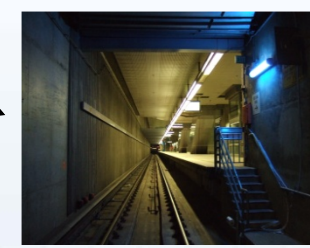




Advantages:
- ➢Wide range coverage
- ➢Intrinsically safe
- ➢Highly sensitive
- ➢High spatial resolution
- ➢Cost-effective for large installations
- ➢ Multiple waveguides eliminate chemical interference

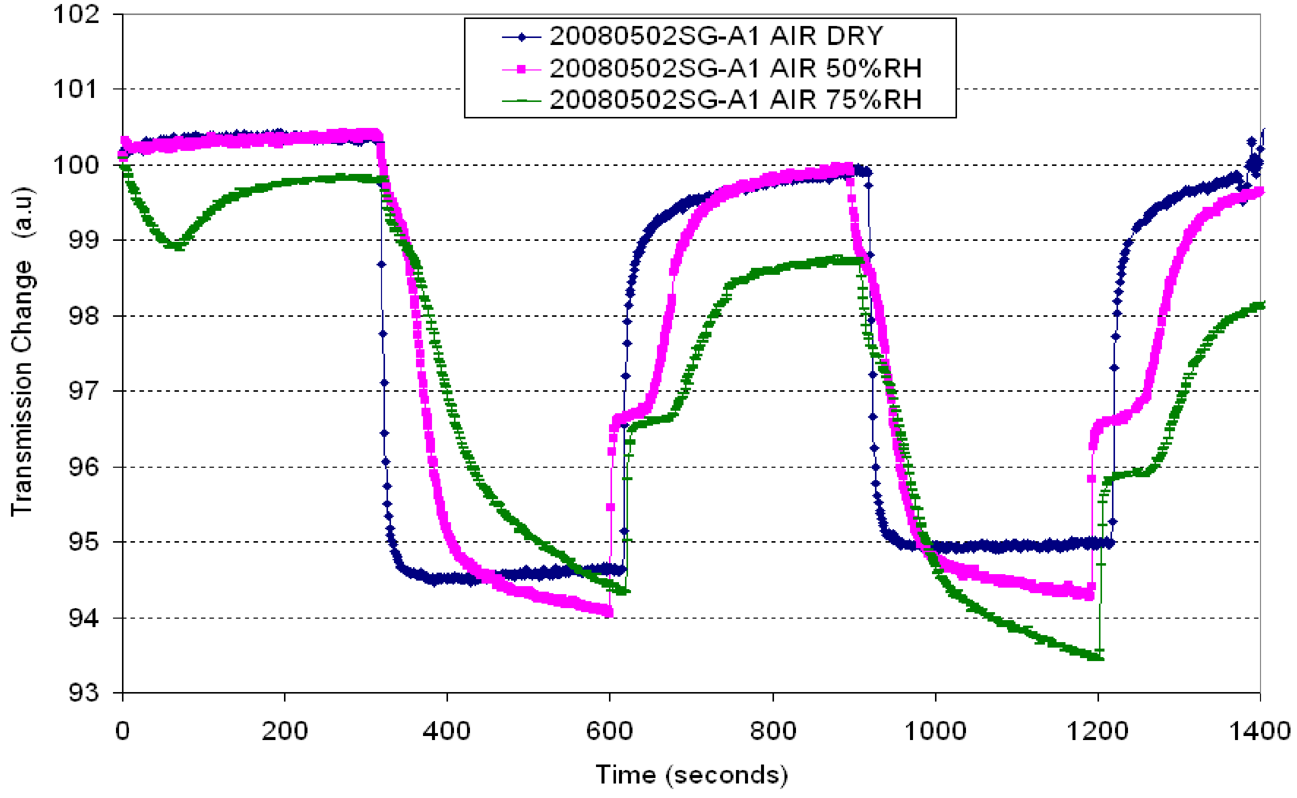






Approach

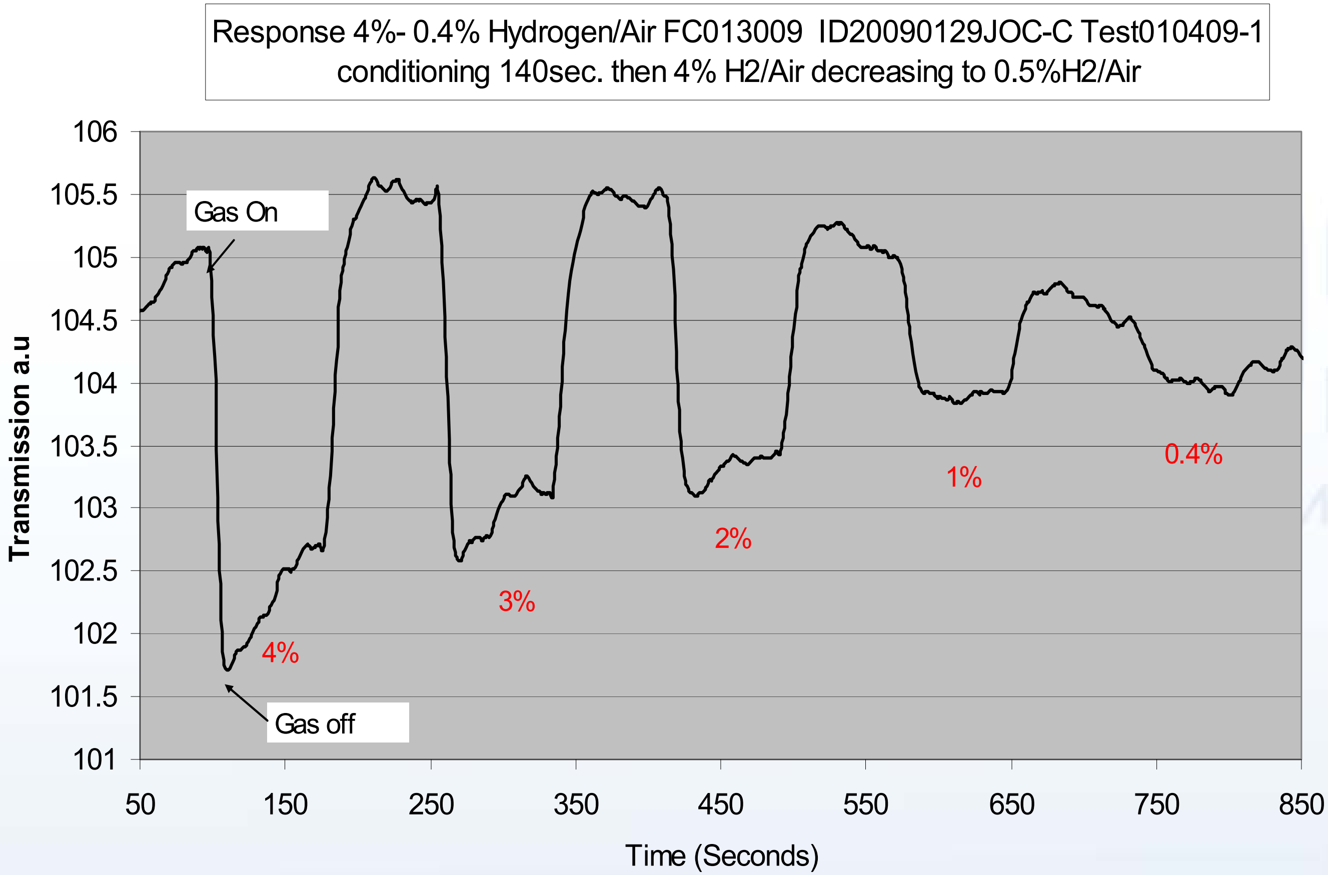
Polymer Film Tests –
Optical Fiber Cladding Materials



Low refractive index materials for optical fiber claddings

Technical Accomplishments

First ("Handmade") Intrinsic Optical Fiber Sensor for Hydrogen



- Response Time:

  t_{90}(sec): 8 at 4%H_2

  t_{90}(sec): 10 at 1%H_2

- Sensitivity:

  LFL(4%H2) - 10%LFL

- Range:

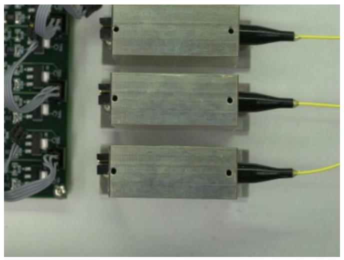
  0-100%H_2

- Segment Length:

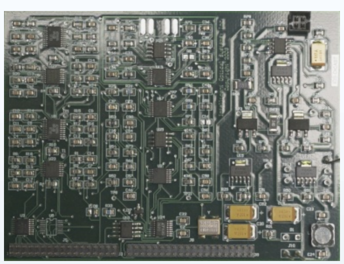
  1 meter tested

Technical Accomplishments

Self-Referenced Optoelectronic System



- ♦ Dual wavelength illumination
  - “Signal” wavelength: Large color dependence on hydrogen concentration
  - “Reference” wavelength: Small color dependence on hydrogen concentration
- ♦ Low-background photodiode detection
- ♦ Onboard signal processing
  - Can process signal and reference data from multiple channels simultaneously
  - Software will combine signals from different waveguide types to minimize false alarms



Technical Accomplishments

Collaborations/Acknowledgements

- Dr. Gerald Voecks – Advisor
  - Fuel cell applications and commercialization
- Dr. Angelo A. Lamola – Consultant
  - Photochemistry/indicators
- Mr. Gerald Cole – Consultant
  - Sensor design and hydrogen power market studies
- Jadoo Power
  - Customer/commercialization partner

Planned Activities for Next Calendar Year

- **Integrated Optic Sensor Finalization and Testing**
  - Polymer/indicator mixture optimization to provide maximum hydrogen response
  - Moisture barrier development for integrated optic format
  - Development of "reference waveguide" materials (e.g. humidity, temperature)
  - Integrated sensor chip finalization and beta-site testing
- **Distributed Fiber Sensor Studies**
  - Development of distributed-fiber responding to low hydrogen levels
  - Optical modeling of fiber response; experimental verification of model
  - Optimization of distributed fiber sensor performance to meet specifications
- **System Integration & Testing**
  - Optical module miniaturization to reduce cost and ruggedize system
  - Optoelectronic subsystem optimization to reduce cost
  - Software "customization" to provide reliable information in a user-friendly format
  - System-level laboratory testing to optimize software and hardware
  - Beta site testing & evaluation

Future Work

INTELLIGENT OPTICAL SYSTEMS, INC.

DOE Hydrogen Program

Summary

Relevance:

- Reliable, cost-effective hydrogen sensors are needed for the Delivery, Storage, Manufacturing, Fuel Cell, and Safety Key Activities of the DOE Hydrogen Program. Applications range from garage and passenger compartment safety to leak detection in production facilities and refueling stations.

Approach:

- High performance, low cost optical sensors based on indicator chemistry can meet projected needs
  - Integrated optic sensors and optrodes are ideal for single-point or multiple-point detection
  - Fiber optic cable sensors are ideal for large-scale facility monitoring, flange/seal integrity verification, etc.

Technical Accomplishments:

- Improved indicator chemistry performance (wider humidity range, more sensitive, more stable)
- Developed optically sensitive polymers for two different optical detection platforms
- Integrated sensor chemistry into a compact prototype optoelectronic package
- Improved universal sensor test facility; developed new protocols and Safety Plan
- Tested first hydrogen sensitive optical fiber, proving feasibility of developing distributed sensors

Collaborations:

- Consultants/Advisor: Gerald Voecks, Jerald Cole, Angelo Lamola
- Customer/Commercialization Partner: Jadoo Power
- Subcontractors: Polymer material, waveguide fabrication equipment, fiber manufacturing

Proposed Future Work :

- Finalize integrated optoelectronic point sensor design and construct final sensor units for testing
- Analyze point sensor longevity, specificity, and environmental effects
- Develop optical fibers for distributed sensor cables