Optically Read MEMS Hydrogen Sensor

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Project ID #: SCS018

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Overview

Timeline
- Start: Late FY 2007
- Finish: Project continuation & direction determined annually by DOE

Budget
- Project funding profile
  - FY 2007: $125k
  - FY 2008: $300k
  - FY 2009: $200k*

*Project moved to VT for 1 year

Barriers
- D. Liability Issues
- E. Variation in Standard Practice of Safety Assessments for Components and Energy Systems
  Technical Targets on next slide

Partners & Collaborators
- University of Tennessee
- Advanced Catalyst Systems
- Agiltron, Inc.
- United Protective Technologies
Overview

- **Technical Targets**
  - H₂ concentration measurement range: 0.1%-10%
  - Operating temperature: -30 to 80°C
  - Response time: less than one second
  - Accuracy: 5% of full scale
  - Gas environment: ambient air, 10-98% relative humidity range
  - Lifetime: 10 years
  - Interference resistant (e.g., hydrocarbons)
Relevance - Objectives

**Project goal:** Develop optics-based sensing technology that achieves DOE R&D targets for hydrogen safety sensors.

<table>
<thead>
<tr>
<th>Month-Year</th>
<th>Milestones</th>
</tr>
</thead>
<tbody>
<tr>
<td>May 2009</td>
<td>Milestone: Complete characterization of response time, recovery time, sensitivity and accuracy within the operating temperature range <em>(100% complete)</em></td>
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<tr>
<td>Jul 2009</td>
<td>Milestone: Establish commercialization partnership <em>(75% complete)</em></td>
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<tr>
<td>Sep 2009</td>
<td>Milestone: Demonstrate sensor performance and compliance with safety goals <em>(75% complete)</em></td>
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Technical Highlights

FY 2009

- Functionalized Polymer-Film Microcantilever Arrays (MCA)
  - Work performed in collaboration with University of Tennessee, Department of Chemistry
  - Fabricated and tested MCA coated with composite films of select polymers
    - Cantilevers are responsive to $\text{H}_2$ but minimally responsive to chemical interferents
    - Reversible cantilever responses to all chemicals in air sample
    - MCA provided patterned response for each chemical; pattern recognition software enabled quantification of each chemical present in the air sample
    - Determined best performing phases with respect to ability to discriminate against $\text{CO}_2$, water vapor, methane
  - Completed selectivity, sensitivity and regeneration analyses of the functionalized polymer-film cantilevers
  - We now have a prototype MCA sensing device that provides qualitative and quantitative information on $\text{H}_2$ present in air sampling
Technical Highlights

FY 2010

- 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
  - 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 – excellent response characteristics
  - Excellent stability, repeatability and life measurements have been observed during more than a year of operation
  - First field portable instrument fabricated to demonstrate operational performance of the Pd based sensors
  - Sensor commercialization partners identified and agreements in progress
Technical Approach –
Microcantilever Hydrogen Detection

Functionalized (blue layer) micro-cantilever bending in response to changes in surface stress induced by adsorption of a gas or vapor

Probe laser beam is reflected off the surface of the cantilever sensor and the amount of bending is recorded by a position sensitive photodetector (PSD).

Cantilever sensor is located within a flow cell to control sensor exposure to calibrated H₂ and potential interferent gas streams.
Testing Hydrogen Sensors –
Microcantilever sensor lab bench system

Lab bench setup for the H₂ sensitivity and potential interferent measurements
Sensor Material Development - Functionalized multi-cantilever arrays

We use commercially available microcantilever arrays which are differentially functionalized with materials that potentially interact with H₂ to produce a bending response.

Schematic of cantilevers coated with different thin films to invoke an array of response to H₂ and potential interferents.
Wet chemical galvanic PdCl$_2$ exchange reaction with thin silver/chromium sputtered film leads to very nanoporous textured Pd metal surfaces.

Conjectured to lead to fast response and recovery times.

Microcantilever sensor coated with an H$_2$ sensing nanostructured Pd thin film.
Technical Accomplishments –
Low threshold and wide dynamic range response

Representative sensitivity measurements using Pd/Ag coated microcantilever H₂ sensors.
- Detection threshold – 0.01% H₂
- Dynamic range – > 3 orders of magnitude
Sensor response to a 4% H₂/Ar gas mixture after the microcantilever had been passivated by flowing the various carrier gases through the flow cell

Technical Accomplishments –

Fast sensor response and recovery

Fast Response (< 3 sec) and recovery (< 10 sec) in simulated air

Sensor response to a 4% H₂/Ar gas mixture after the microcantilever had been passivated by flowing the various carrier gases through the flow cell.
Technical Accomplishments –
Excellent specificity to common impurities and carrier gases

Nanostructured Pd coated cantilever shows negligible response to most potential interferents

Differences in temporal response and signal magnitude allow discrimination between more significant interfering species
High sample-to-sample repeatability of the sensor bending response in a simulated H$_2$/air environment

Single microcantilever response to a 4% H$_2$/Ar-O$_2$ mixture over an 8 month period
Technical Accomplishments –

First Field portable instrument

First field portable prototype sensor hardware incorporating the same features as the benchtop apparatus but on a much reduced scale. This unit is operated by a standard laptop computer.

The unit is fabricated on a 4” optical breadboard.
Coated arrays of cantilever sensors have been used in arrays and combined with pattern recognition algorithms to obtain quantitative estimates for $\text{H}_2$ and various potential interferents for enhanced selectivity.
Results – Cantilever array measurements and neural network give accurate estimates for H$_2$ and CO$_2$

Experiment to demonstrate the ability of an artificial neural network (ANN) algorithm to predict component mixtures of multiple species

- Two component mixture comprised of varying concentrations of H$_2$ and CO$_2$
- Experiments were performed using arrays of silicon microcantilevers coated successively with nanostructured metal coatings.
- The graph shows the ability of the ANN to accurately predict the relative concentration of the two components
Collaborations

Partners:

– University of Tennessee - Improved H₂ sensor response
  • Faster response/recovery times – now around 3-10 sec – reduce to ~ 1 sec
  • Improved specificity – reduced water vapor response
  • Further studies of potential interferents – CO, EtOH, CH₄, other hydrocarbons
  • Multi-component mixture studies
– IP and patent filings – techniques, methods, coatings, applications
– Agiltron - Commercialization partnership agreements finalized

Technology Transfer:

– Agiltron collaboration
  • Tech transfer to commercialization partner for preproduction prototype development
  • Manage preproduction instrument fabrication at commercialization partner facilities

Agiltron’s existing low cost microcantilever based infrared camera optical readout circuitry can easily be modified to interrogate an array of microcantilever chemical sensors

Microcantilever based infrared camera operation
Future Work

FY 2010

- **Improved H₂ sensor response**
  - Faster response/recovery times – now around 3-10 sec – reduce to ~ 1 sec
  - Improved specificity – reduced water vapor response
  - Further studies of potential interferents – CO, EtOH, CH₄, other hydrocarbons
  - Multi-component mixture studies

- **IP and patent filings – techniques, methods, coatings, applications**

- **Commercialization partnership agreements finalized**

FY 2011

- **Finish fabrication and preliminary testing of field portable instrument**

- **Implement commercialization plan with commercial partner**
  - Tech transfer to commercialization partner for preproduction prototype development
  - Manage preproduction instrument fabrication at commercialization partner facilities

- **Test pre-commercialization prototype testing at NREL Hydrogen Sensor Laboratory**
  - Short-term repeatability test
  - H₂ mixtures in air
  - Temperature and Relative Humidity
  - Response and recovery kinetics
  - Linearity/dynamic range test
  - Atmospheric pressure sensitivity
  - Long term stability
  - Interferent testing
Summary Table – Measured Performance

Present microcantilever based H₂ sensors meet all but the most stringent requirements for automotive applications

<table>
<thead>
<tr>
<th>Performance Requirement*</th>
<th>Measured Performance</th>
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<tbody>
<tr>
<td>Sensitivity Range</td>
<td>&lt; 0.1% to &gt; 4%</td>
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<tr>
<td></td>
<td>0.01 – 4%</td>
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<tr>
<td>Survivability Limit</td>
<td>100%</td>
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<tr>
<td></td>
<td>Linear response to 100% H₂</td>
</tr>
<tr>
<td>Response Time</td>
<td>Automotive: &lt; 3 sec</td>
</tr>
<tr>
<td></td>
<td>Stationary: &lt; 30 sec</td>
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<tr>
<td></td>
<td>~ 3-5 sec</td>
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<tr>
<td>Recovery Time</td>
<td>Automotive: &lt; 3 sec</td>
</tr>
<tr>
<td></td>
<td>Stationary: &lt; 30 sec</td>
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<tr>
<td></td>
<td>~ 10-20 sec</td>
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<tr>
<td>Temperature Range</td>
<td>Automotive: -40°C to +125°C</td>
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<tr>
<td></td>
<td>Stationary: -20°C to +50°C</td>
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<tr>
<td></td>
<td>Yes</td>
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<tr>
<td>Pressure Range</td>
<td>Automotive: 62-107 kPa</td>
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<tr>
<td></td>
<td>Stationary: 80-110 kPa</td>
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<tr>
<td></td>
<td>Yes</td>
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<tr>
<td>Ambient Relative Humidity Range</td>
<td>Automotive: 0 – 95%</td>
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<tr>
<td></td>
<td>Stationary: 20 – 80%</td>
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<tr>
<td></td>
<td>0-100%</td>
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<tr>
<td>Interferent Resistance</td>
<td>No false positive responses</td>
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<tr>
<td></td>
<td>Excellent</td>
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<tr>
<td>Power Consumption</td>
<td>&lt; 1 Watt</td>
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<tr>
<td></td>
<td>0.5-1 Watt</td>
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<tr>
<td>Lifetime</td>
<td>Automotive: 6,000 hr</td>
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<tr>
<td></td>
<td>Stationary: &gt; 5 years</td>
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<tr>
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<td>Demonstrated &gt; 9 months</td>
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<td>Accuracy and Repeatability</td>
<td>Automotive: 5-10%</td>
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<td>Stationary: 10%</td>
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<td>&gt; +/- 5%</td>
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Project Summary

Relevance:

Commercialize optical technology that achieves DOE R&D targets for hydrogen safety sensors

Approach:

Develop and characterize an optically based, cost effective hydrogen sensor that can be used in distributed hydrogen leak sensing applications

Technical Accomplishments and Progress:

Demonstrated that optically read microcantilever based sensors meet all the H₂ sensor performance and life operating requirements

Technology Transfer/Collaboration:

Active partnership with the University of Tennessee. New partnerships with Agiltron, Advanced Catalyst Systems and UPT – publications, patents, preproduction prototype development.

Proposed Future Research and Development:

Improved H₂ sensor response and interferent selectivity. Portable preproduction instrumentation development for competitive benchmarking at NREL.