

Interfacial Stability of Thin Film Sensors

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Objectives

The goal of this project is to develop safe, low cost, lightweight, reliable hydrogen safety sensors that can be used wherever hydrogen is used, stored, or transported. Safety sensors need to satisfy the following requirements established by DOE:

- Measurement range: 0.1–10% H₂ in air
- Operating temperature: -30°C – +80°C
- Response time: <1 s
- Accuracy: 5%
- Gas environment: ambient air, 10–98% relative humidity (RH) range
- Lifetime: 5 years
- Selectivity from interference gases, such as hydrocarbons, is needed.

Technical Barriers

This project addresses the following technical barriers from the following sections of the Hydrogen, Fuel Cells and Infrastructure Technologies Program Multi-Year R,D&D Plan:

Hydrogen Safety

- A. Limited Historical Database for Components
- C. Validation of Historical Data
- D. Technical and Scientific Understanding of Systems Limits the Value of Protocols
- F. Liability Issues
- L. Expense of Data Collection and Maintenance
- M. Quality of Data

Hydrogen Delivery

- D. High Capital Cost of Pipelines

Fuel Cells

- B. Sensors

Technology Validation

- C. Hydrogen Refueling Infrastructure

Hydrogen Production

- E. Control and Safety

Approach

- Investigate the stability of thin films that undergo optical changes in the presence of hydrogen.
- Construct test articles of thin films and subject them to environmental stresses.
- Measure response of hydrogen sensing to environmental stresses and aging.
- Develop improved protective strategies.

Accomplishments

- Designed optical sensor configurations that meet most DOE criteria for safety sensors.
- Demonstrated sensor lifetimes in excess of 1 year.
- Measured response of test articles to thermal stresses (-20°C to +80°C) and relative humidity (0% to 100%).
- Analyzed subtle compositional differences in protective coatings that result in dramatic changes in performance.
- Supported NREL's photobiological hydrogen production project by constructing large area sensor plates for semi-quantitative evaluation of hydrogen-producing algae.

Future Directions

- Investigate the fundamental behavior of the protective coatings in order to optimize performance.
- Analyze the response of optical sensors coated with protective polymeric chemical vapor deposition (CVD) films when exposed to low temperature and high humidity environments.
- Design a control package for probing the status of the thin film optical sensors.
- Fabricate prototypes for testing.

Introduction

Public perception of the hazards of hydrogen fuel use, its production, and storage, as well as governmental regulation will require extensive safety precautions and codes to be in place before hydrogen can be incorporated into the energy infrastructure in a meaningful way. Currently, commercial hydrogen detectors are not useful for widespread use, particularly in transportation, because they are too bulky, expensive, and dangerous. Work sponsored by DOE has developed promising technologies for satisfying the future demands. Specific performance targets for safety sensors have been proposed:

- Measurement range: 0.1%–10% H₂ in air
- Operating temperature: -30°C – +80°C
- Response time: <1 s

- Accuracy: 5%
- Gas environment: ambient air, 10%–98% RH range
- Lifetime: 5 years
- Selectivity from interference gases, such as hydrocarbons, is needed.

Sensors that exhibit physical changes when exposed to hydrogen have been fabricated and tested, and they have the potential to provide inexpensive hydrogen detection. For example, there are thick film and thin film metallic sensors that exhibit conductivity changes when hydrogen adsorbs on the surface and is incorporated into the lattice. There are thin film sensors that are deposited as a part of a field-effect transistor, where accumulation of atomic hydrogen at the metal/insulator interface results in a

change of response from the circuit. Finally, there are chemochromic sensors, where reaction of thin films with hydrogen gas results in an optical change that can be sensed by a probe beam of light. All four of these configurations have the potential for degradation in their performance over time due either to mechanisms that are inherent in their construction, effects of their cyclic interaction with hydrogen, or contamination from impurities in the environments in which they will be used. Prior research to study these issues has ranked their importance to the various sensor concepts and has suggested the relevant mechanisms. This work has led, in turn, to methods of mitigating these factors. The research reported here addresses these issues and is directed toward substantially extending the lifetime and utility of these sensors, especially in the configuration that is based upon the optical response of the sensor materials. This concept appears to offer the greatest safety by design, and it would appear to meet cost goals.

Approach

All of the thin film safety sensor designs currently use a Pt group metal (usually Pd or an alloy) as the hydrogen dissociation catalyst. Atomic hydrogen is the species that causes a physical change in the sensing material, thereby providing a means to detect the presence of hydrogen. In the case of multiple layers of thin films forming the detection ensemble, the interfaces between layers, including the surface of the dissociation catalyst, control the response of the sensor. Changes in the interfaces most often result in degradation in the performance of the device. Consequently, our research and development activities deal mainly with the stability of the interfaces and the approach to the performance goals listed in the objectives.

Work this year concentrated upon understanding the performance of a protective coating, which in prior years had shown extraordinary promise to prolong the life of the Pd catalyst. The approach was to study the influence that various parameters (e.g., precursor purity, the details of the synthesis, and deposition techniques) played in the performance of the film. The objective was to optimize the performance of the coating and extend the lifetime of

the sensors past the one-year mark that had been accomplished in FY 2002.

A secondary effort was to characterize the performance of the sensors over an expanded range of temperatures and relative humidities. Specifically, the temperature range for characterization was extended to -30°C to $+80^{\circ}\text{C}$, and the relative humidity range was extended to 0% to 100%. The sensors were tested in the full target range of the DOE goals for safety sensors.

Results

The results of the studies on the synthesis and preparation of the protective coating for the sensor films were mixed. Replication of early results proved elusive, although it was shown that the performances of the protective coatings are sensitive to almost every aspect of the preparation. A great deal of analytical work has suggested why the results of this study were mixed and has pointed to the fact that additional fundamental work is needed to fully understand the functioning of these films and their sensitivity to the details of their preparation.

The performance of typical tungsten oxide sensor elements at various temperatures is illustrated in Figures 1 and 2. The data indicate that the tungsten oxide sensors operate reasonably well in a temperature range from 0°C to $+80^{\circ}\text{C}$. However, excursions to the upper temperature apparently result in irreversible changes in the WO_3 film that affect performance (Figure 1, 19°C after heating). This irreversible change does not constitute a fatal flaw in the design of these sensors, since the performance is

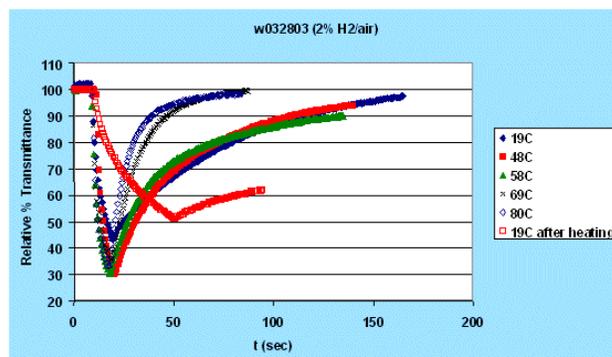


Figure 1. Optical Sensor Response to 2% Hydrogen in Synthetic Air at Temperatures from 19°C to 80°C

likely adequate (rather than optimum) after the material changes. At temperatures below 0°C, the performance of the sensors degrades rapidly (Figure 2). We think that it is likely that the formation of ice on the catalyst surface progressively covers the hydrogen dissociation sites. This inhibits both the response to hydrogen and recovery after exposure. At temperatures below -10°C, the response of the sensor may be degraded to the point where response is deemed unacceptable. There are two approaches to mitigate the problem of condensation and ice formation at these temperatures. One is to use a physical barrier to inhibit the diffusion of water through the coating, while allowing hydrogen to diffuse at a relatively high rate. The other is to periodically pulse the light source to such an intensity as to evaporate a substantial amount of the ice that fouls the Pd surface. Studies of these methods had to be deferred to another year.

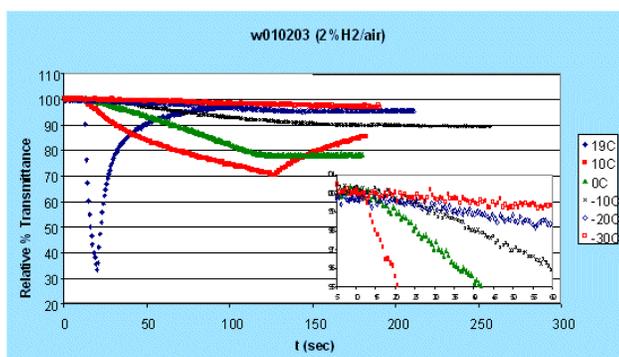


Figure 2. Optical Sensor Response to 2% Hydrogen in Synthetic Air at Temperatures Ranging from -30°C to 19°C

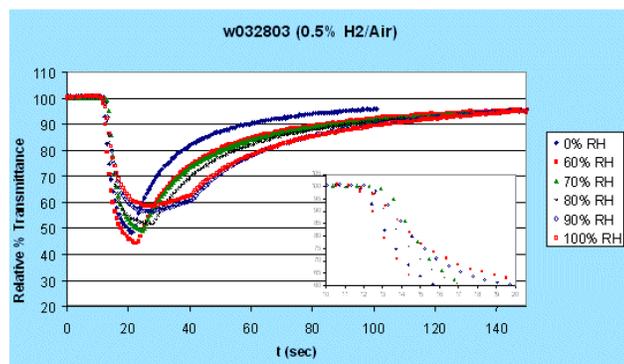


Figure 3. Response of a WO₃ Sensor to 0.5% Hydrogen in Air at Room Temperature and Various Relative Humidities

The response of a typical WO₃ based sensor to 0.5% hydrogen in air is shown in Figure 3. Increasing relative humidity slows the response of the sensors, which is observed by the change in slope of the curves in the inset. The inset is a magnification of the “knee” region of the curve showing more detail of the sensor response upon admission of hydrogen into the gas stream. Another observation is that increasing relative humidity decreases the depth of coloration at saturation. However, neither of these effects represents a fatal flaw in the operation of the devices as safety sensors. We believe that we can improve the performance of these sensors in high humidity by the application of polymeric thin films with surface properties designed to minimize the interaction with water vapor. Preliminary experiments with such films give a good indication that they will inhibit the ingress of water to the catalyst surface.

Conclusions

The performance of optical thin film sensors are represented in tabular form as follows:

- Measurement range: 0.02% – 10% H₂ in air
- Operating temperature: -20°C – +80°C
- Response time: <1 s
- Accuracy: needs to be determined
- Gas environment: ambient air, 0% – 100% RH range
- Lifetime: 1 year
- Interference resistant (e.g., all other gases)

Significant progress was made this year in understanding the sensitivity of our best protective coating to variations in the synthesis techniques. Furthermore, measurements of the response of the sensor under extremes of temperature and relative humidity have produced encouraging results. It appears that the major remaining criteria to meet, and the focus of future work in the area, is the durability of the sensor elements in realistic atmospheres.

FY2003 Publications/Presentations

1. R. D. Smith, P. Liu, S.-H. Lee, C. E. Tracy, and J. R. Pitts, "Low-Cost Fiber Optic Hydrogen Sensors," ABSTR PAP AM CHEM S 224: 171-FUEL Part 1, Aug. 18, 2002.

2. E. Ozkan, P. Liu, S.-H. Lee, C. E. Tracy, J. R. Pitts, and S. K. Deb, "Preparing Mesoporous Tungsten Oxide Thin Films Using Non-Ionic Surfactants as the Templates by Sol-Gel Deposition Process," *Solid State Ionics* (submitted).
3. S.-H. Lee, H. M. Cheong, M. J. Seong, P. Liu, C. E. Tracy, A. Mascarenhas, J. R. Pitts, and S. K. Deb, "Raman Spectroscopic Studies of Amorphous Vanadium Oxide Thin Films," *Solid State Ionics* (submitted).
4. E. Ozkan, S.-H. Lee, C. E. Tracy, F. Z. Tepehan, J. R. Pitts, and S. K. Deb, "Comparison of Electrochromic Amorphous and Crystalline Tungsten Oxide Films," *Solar Energy Materials and Solar Cells* (submitted).
5. P. Liu, S.-H. Lee, C. E. Tracy, J. A. Turner, J. R. Pitts, and S. K. Deb, "Electrochromic and Chemochromic Performance of Mesoporous Thin-Film Vanadium Oxide," *Solid State Ionics* (submitted).
6. J. R. Pitts, "Switchable Optical Materials Applications in Energy Conservation and Hydrogen Infrastructure," invited seminar, University of Texas at Arlington, Dept. of Chemistry and Biochemistry, Oct. 25, 2002.