VI.3 Interfacial Stability of Thin Film Hydrogen Sensors

Roland Pitts (Primary Contact), R. Davis Smith, II, Se-Hee Lee, Ed Tracy
National Renewable Energy Laboratory
1617 Cole Blvd.
Golden, CO 80401
Phone: (303) 384-6485; Fax: (303) 384-6655; E-mail: roland_pitts@nrel.gov

DOE Technology Development Manager: Patrick Davis
Phone: (202) 586-8061; Fax: (202) 586-9811; E-mail: Patrick.Davis@ee.doe.gov

Objectives

Assist DOE in the development of hydrogen safety sensors.

- Provide the technology to produce safe, reliable, sensitive, fast, lightweight, and inexpensive hydrogen safety sensors.
- Determine the factors limiting the lifetime and performance of thin film sensors in realistic environmental conditions.
- Extend the lifetime and functionality of thin film 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:

- 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

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 to environmental stresses and aging.
- Develop improved protective strategies, increasing lifetimes.

Accomplishments

- Tested optical sensor configurations that meet most DOE criteria for safety sensors.
- Extended sensor lifetimes by an additional year (>3 year lifetimes).
- Analyzed subtle compositional differences in protective coatings that result in dramatic changes in performance.
- Provided support for the bio-hydrogen production work by constructing large area sensor plates for semi-quantitative evaluation of hydrogen producing algae.
- Issued two technical publications and was awarded one U.S. patent.

Future Directions

- Investigate the fundamental behavior of the protective coatings in order to optimize their 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 a prototype sensor and control package for testing.

Introduction

The goal of this project is to develop safe, low cost, lightweight, reliable hydrogen sensors that can be used as safety sensors where hydrogen is used, stored, or transported. These sensors must be inexpensive enough to allow the use of multiple sensors on a hydrogen powered vehicle, and they must be sensitive and fast enough to provide early leak detection so that action can be taken before the explosive limit in air is reached. We have chosen to work on a fiber-optic sensor configuration that stands the best chance of meeting all or most of these goals. For transportation safety, we need (a) lightweight, (b) low-cost, (c) sensitive, (d) reliable, and (e) inherently-safe sensors that can alert operators or take automatic action in the event of a hydrogen leak. The fiber-optic approach is the only proposed sensor configuration that meets the criterion of being inherently safe. All other sensor configurations use electrical wiring and represent a possible ignition source in the presence of hydrogen.

DOE has proposed specific targets for transportation safety sensors. These are as follows:

- Measurement range: 0.1–10% H_2 in air
- Operating temperature: -30 to +80 °C
- Response time: <1 s
- Accuracy: 5%
- Gas environment: ambient air, 10 – 98% relative humidity range
- Lifetime: 5 y
- Selectivity from interference gases, such as hydrocarbons, is needed.

Our efforts for FY 2004 are focused on developing a better understanding of the service lifetime and performance issues that will enable the commercialization of thin film hydrogen sensors.

Approach

We use chromogenic materials as indicators of the presence of hydrogen. At concentrations above 0.02% hydrogen in air, these materials undergo optical changes, either changing color or changing the transmittance through the film as atomic hydrogen is incorporated. A number of materials exhibit such optical changes, including WO_3, NiO_x, V_2O_5, and an assortment of metal hydrides. Dissociation of hydrogen gas is accomplished on the surface of a thin catalyst top layer (e.g., Pd). Some of the atomic hydrogen diffuses rapidly through the catalyst and into the chromogenic layer, changing its optical properties. The optical changes can be read easily by a light beam, either by measuring transmission through the stack of thin films, or by measuring the reflectance off the catalyst layer. The optical thin films may be deposited on the end of a fiber-optic cable, as depicted in Figure 1. A beam of light is propagated down the cable, and the intensity of either the reflected beam or the transmitted beam is monitored to provide detection to hydrogen gas.

Research this year focused on using a protective coating to keep the Pd catalyst surface clean. Previous observations had shown that it was possible for a film to be deposited upon the Pd that could maintain it operational over time periods exceeding one year. However, the performance of these coatings was inconsistent in the ability to handle doses of pollutant gases. Work this year focused upon discovery of those parameters affecting the performance of the coating and methods to mitigate their influence.

Results

We have tested chromogenic hydrogen sensors under various conditions of temperature, relative humidity, and exposure to pollutant gases (CH_4, CO,

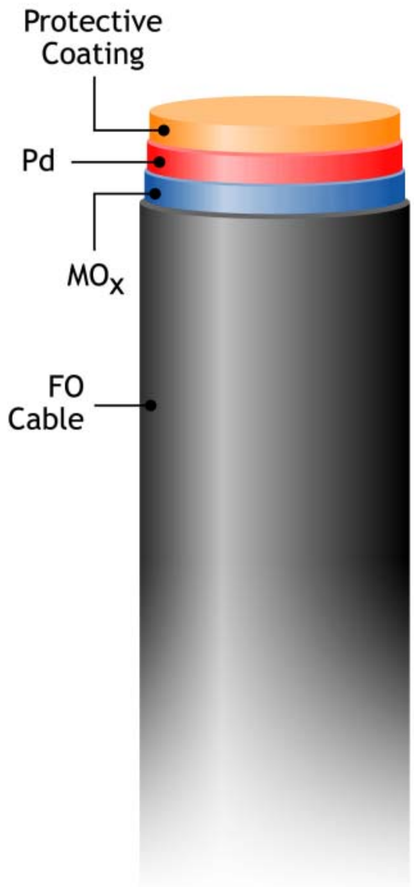

Figure 1. Schematic of Fiber Optic Cable with Chemochromic Hydrogen Sensor Deposited On End

and H_2S). After exposure to pollutants, the response of the sensors is temporarily affected, but they remain operational and recover over time. Most of the DOE target goals have been reached:

- Measurement range: 0.1–10% H_2 in air (**achieved**).
- Operating temperature: -20 – +80 °C (target is –30 °C on the low end).
- Response time: <1 s (**achieved**, except below –20 °C at the detection limit).
- Accuracy: 5% (these sensors are on/off in their current configuration, and may saturate prior to 10 % H_2 in air, depending upon composition).
- Gas environment: ambient air, 10 – 98% relative humidity range (**achieved**).
- Lifetime: 5 y (> 3 years)

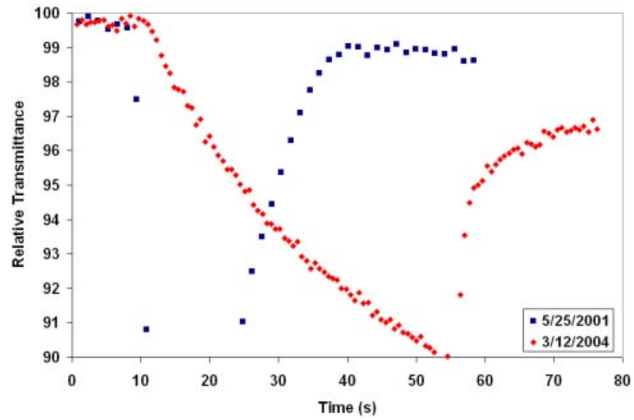

Figure 2. Response of Optical Hydrogen Sensor to the Lower Detection Limit of Hydrogen (0.1 %) After 3 Years, Compared to its Original Response After Fabrication

- Selectivity from interference gases, such as hydrocarbons, is needed (**achieved**).

Further, we have retested optical sensors that were fabricated in May 2001 and found they continue to be operational in sensing hydrogen at the lower detection limit of 0.1% H_2 in air. Response time has increased and the dynamic range of coloration has decreased, but the sensor itself is still functional. The response of a 3 year old sensor is plotted in Figure 2 and compared to its original performance.

Conclusions

Inherently safe, inexpensive optical sensors can be fabricated from chemochromic materials. Such sensors meet almost all of the targets set by DOE for safety sensors. The notable areas that fall short of the DOE targets are performance below -20 °C and lifetime. We believe that a relatively simple strategy of periodically increasing the pulsed power in the probe light beam will be sufficient to alleviate the degradative effects of encapsulation of the thin film sensor by ice at the lower temperatures. The sensors fabricated more than 3 years ago are still operational and will likely survive to the 5-year target.

Future work will focus on the mechanisms by which the protective films function and the secondary effects that appear to occur over long periods of time in the chemochromic layers. Optimization of the protective coatings, design of the control and sensing electronics, and enhancement of the performance at low temperatures are tasks that need to be addressed.

FY 2004 Publications/Presentations

1. R. Davis Smith, Se-Hee Lee, Ed Tracy, and J. R. Pitts, "Protective coatings for Pd-based hydrogen sensors", 228th ACS National Meeting, Philadelphia, PA, August 22-26, 2004.

2. R. Davis Smith, Se-Hee Lee, Ed Tracy, and J. R. Pitts, "Advances in Fiber Optic Hydrogen Sensor Technology", Eighth World Renewable Energy Congress August 28 - September 3, 2004, Denver, Colorado.

Special Recognitions & Awards/Patents Issued

1. Se-Hee Lee, Roland Pitts, Ed Tracy, and Ping Liu, "Palladium/Nickel-Tungsten Oxides anodic Double Layer Gasochromic Device," U.S. Patent #6,723,566 to Midwest Research Institute (4/20/04).