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INTERFACIAL STABILITY OF THIN FILM FIBER-OPTIC HYDROGEN SENSORS

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Abstract

The goal of this research is to make available the technology to produce low-cost, lightweight, reliable, inherently safe hydrogen sensors for use as safety monitors wherever hydrogen is used, stored, or produced. Prior work has identified thin films that can be used as hydrogen detectors by measuring physical properties of those films and monitoring those characteristics that change in the presence of hydrogen. In all of the thin film sensors investigated to date, long term changes in the response to hydrogen after exposure to ambient air, or short-term changes in response after exposure to pollutants have been noted. The specific objective of this work is to study those mechanisms affecting the stability of the films with respect to these environmental factors and to use the knowledge gained from these studies to craft methods of mitigating those mechanisms. We have worked primarily with thin films that can be coated on the end of a fiber optic cable. This configuration meets the qualifications of being lightweight, potentially inexpensive, and inherently safe, since no electrical leads are employed in the monitored space. Since the use of palladium or its alloys as either the primary sensor material or as a catalyst layer appears to constitute the method of choice for such low cost hydrogen sensors, we have concentrated on studying the stability of the palladium surface with respect to the dissociation of hydrogen.

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 the DOE Hydrogen Program has developed promising technologies for satisfying the future demands. Specific performance targets for safety sensors have been proposed:

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

Sensors that exhibit physical changes when exposed to hydrogen have been fabricated and tested, and promise 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, a result of their cyclic interaction with hydrogen, or contamination from impurities in the environments in which they will be used. Prior research to study those issues has ranked their importance to the various sensor concepts and has at least suggested the relevant mechanisms, which point to methods of mitigating these factors. The research reported here addresses those 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 would appear to meet cost goals.

Background on Optical Sensors

The Fiber-Optic sensor consists of coatings at the end of an optical fiber that sense the presence of hydrogen in air. When the coating reacts with the hydrogen, its optical properties are changed. Light from a central electro-optic control unit is projected down the optical fiber where it is either reflected from the sensor coating back to central optical detector, or is transmitted to another fiber leading to the central optical detector.

A change in the reflected or transmitted intensity indicates the presence of hydrogen. The fiber-optic detector offers inherent safety by removing all electrical power from the test site, and it reduces signal-processing problems by minimizing electromagnetic interference. Critical detector performance requirements include high selectivity, response speed, and durability as well as potential for low-cost fabrication, meeting or exceeding most of the proposed criteria for safety sensors.

Fiber-optic sensors have been made in a variety of configurations, most using one or more thin films at the end of the cable. Butler (1991, 1994) suggested using a thin film of Pd as a mirror on the end of a fiber optic cable. Garcia (1996) and Mandelis (1998) describe a more sensitive (and much more complex) method of sensing hydrogen optically. They use a diode laser and beam splitters to illuminate reference flats in a gas flow chamber. One flat is coated with Pd, while the other is coated with Al. Reaction to hydrogen at concentrations above 0.2% in nitrogen is registered by the optical changes of the Pd film.

Ito (1984) originally proposed using the palladium-catalyzed reaction of amorphous tungsten oxide with hydrogen in a fiber-optic hydrogen detector. The reaction causes partial reduction of the tungsten oxide and introduces a strong optical-absorption band near 800 nm. The increase in absorption reduces the intensity of the light beam reflected by the coated optical fiber. We found this sensor design to be adequately sensitive, but too slow for the intended use.

A different sensor design using a surface-plasmon resonance (SPR) configuration was also evaluated (Raether, 1988 and Chadwick, 1993). Chemochromic materials, such as tungsten oxide and certain Lanthanide hydrides (Griessen, 1997) were used in thin film stacks on a sensor head at the end of an optical fiber (Benson, 1998). A layer of silver was deposited first, in which the surface plasmon was generated. The chemochromic layer was deposited upon the silver, followed by a thin layer of palladium, which acted as the hydrogen dissociation catalyst. When hydrogen comes in contact with the sensor head, small amounts of atomic hydrogen change the optical properties of the chemochromic layer. The SPR shifts in response to very subtle changes in the refractive index of the coating and is detected as a change in intensity of the reflected beam of light. This shift can be monitored to provide a faster response than was evident in the first tungsten oxide sensors.

Yet another variation of this sensor design uses a Pd coating on the sides of the fiber optic cable, after the jacketing material in a section of the fiber is removed (Tabib-Azar, 1999). In this configuration the Pd interacts with the evanescent field as the light beam propagates down the fiber via total internal reflection. When exposed to hydrogen, the complex index of refraction of the Pd film changes, affecting the transmission of light down the fiber. Detection of variations of light intensity at the end of the fiber signals changes in the Pd film due to the incorporation of hydrogen. This construction allows multiple sensors to be deposited along a single strand of fiber-optic cable. However, to allow this concept to identify the sensing station that has detected hydrogen, fiber optic Bragg gratings (FBGs) must be etched into the fiber at each station (Sutapun, 1999).

The individual gratings are tuned to specific wavelengths. Then, they are coated with Pd. Hydrogen incorporated into the Pd causes an expansion of the film that results in a stretch of the fiber and an alteration in the spacing of the FBG. The FBG acts as a strain gage and shows a linear response in the shift in Bragg wavelength with hydrogen concentration over a range from 0.3% to 1.8% hydrogen in nitrogen. Thus, multiplexed hydrogen sensors may be fabricated on a single fiber.

We have extended the concepts of Benson, et al., and have improved upon the chemochromic materials used as the sensing material under the Pd layer (Liu, 2002). Materials are now available that can be tailored in sensitivity and response to hydrogen. There is hope that they can be made at least semi quantitative in the measurement of the partial pressure of hydrogen over useful ranges up to 100% hydrogen.

Key Issues

There are four key issues to be satisfied by any hydrogen detector, if it is to gain wide acceptance for use within the hydrogen infrastructure (production, storage, transportation, and utilization).

- **Performance** – sensors must respond to the presence of hydrogen well before the explosive limit (4% H_2 in air) is reached. This requirement dictates that a premium is placed on detecting small quantities of hydrogen in the ambient atmosphere (goal is 0.1% or better). The sensor must also respond quickly (goal is 1 second or less), so that corrective action or evacuation can occur before the explosive limit is reached. Fast response times are also desired for diagnostic study of hydrogen transportation systems (vehicles, electrolyzers, storage containers, etc.).
- **Lifetime** – sensors must have a usable lifetime consistent with the application for which it is intended. For transportation applications that must be at least the time between scheduled maintenance (minimum 6 months), but the goal is 5 years. In this respect the sensor must be operational without cleaning, calibration, or replacements for a minimum of that period, while exposed to ambient conditions.
- **Reliability** – sensors must indicate the presence of hydrogen reliably. That is, they must perform to some specification, each and every time they are exposed to hydrogen over the lifetime of the sensor. Response must not drift outside acceptable limits over that lifetime. Functionality of the sensors should be easily verifiable, but there will be a low tolerance for false alarms. Sensors should be able to survive multiple excursions to hydrogen concentrations above the explosive limit without damage.
- **Cost** – sensors and their controllers must be reasonably priced, so that their inclusion within the hydrogen infrastructure can be ubiquitous. A worthy goal is \$5 per sensor and \$30 per controller, which should be able to handle 5 or more sensors. As long as performance, lifetime and reliability are not compromised, less expensive is better.

The common link in all of the hydrogen sensor concepts is that they all use Pd or one of its alloys as a catalyst. Molecular hydrogen dissociates on the catalyst surface, and atomic hydrogen diffuses rapidly through the film. Physical or optical changes in the catalyst film itself, or in adjacent films or interfaces, are used to detect the presence of hydrogen. All of the current sensor concepts share Pd or an alloy as the catalyst. Therefore, we have chosen to focus on stability issues related to ambient exposure of Pd and cyclic exposure of Pd to hydrogen.

Experimental

Thin films of the active layers of the optical sensors are fabricated by standard techniques of vacuum deposition. Thermal evaporation is carried out on a Varian Model 3118 evaporator. Sputtered films are prepared on a Leybold magnetron sputter coater, and plasma enhanced chemical vapor deposition is done on a Plasma Technology deposition system. Performance testing of the completed articles is carried out at the National Renewable Energy Laboratory (NREL). Analytical investigations of failed articles are carried out in the Device Characterization Laboratory at NREL.

The fiber-optic sensor test station consists of a gas flow manifold that can be switched automatically from gas mixtures containing hydrogen to air. The same computer that acquires optical spectra controls switching. The manifold delivers the test gas stream into a test chamber, constructed so that the dead volume is minimal (0.1 cm^3). In addition the chamber was constructed so that we could measure either spectral transmittance or reflectance. The spectrometer used for the optical measurements is an Ocean Optics S2000 spectrometer, measuring flux from 300 nm to 800 nm. Either fiber-optic tips or small glass slides coated with the active layers can be used as test articles. Glass slides are often used to simplify deposition and analysis after testing. The photos of this measurement system appear in Figs. 1 and 2.

Manifold and Test Station

Test Chamber

Figure 1. Fiber-Optic Sensor Test Station

Test Chamber, Transmission Mode

Gas Manifold

Figure 2. Transmission Mode and Gas Manifold Details

Analytical work on functional and failed specimens is carried out with an array of tools available in the Characterization Laboratories at NREL. These include optical microscopy with Nomarski phase contrast (Neophot 21), electron microscopy (JEOL JSM-5800 and JSM-6320), Auger electron spectroscopy (Physical Electronics 670 Auger Nanoprobe), and X-ray photoelectron spectroscopy (Physical Electronics 5600 ESCA System).

Results

The major issues focused upon during the experimental work for FY 2002 were protection of the palladium (Pd) catalyst films from airborne contaminants and characterization of the metal oxide-palladium interface. Additionally, tests were conducted to determine the response of the sensor at varying temperatures and relative humidities. For the latter work, we had to construct a new gas manifold and proportioner and an environmental chamber to allow control of gas and sensor temperature.

Protection of Pd Catalyst Layer

A number of strategies for protecting the Pd catalyst were investigated in fiscal year (FY) 2001, and these were reported in last year's annual report. The most effective of these were the application of novel coatings, which could offer effective protection to the hydrogen dissociation sites. Work continued in FY 2002 on the most effective of these strategies. Additionally, some work was undertaken to investigate the application of polymeric films that were applied via a chemical vapor deposition process.

Inorganic Coatings

The study of inorganic coatings was focused mainly on the coating strategy that was found to be most effective during FY 2001. Samples made during this period were continually tested and have survived to more than one year with some degradation in performance noted. An example of this performance is illustrated in Fig. 3.

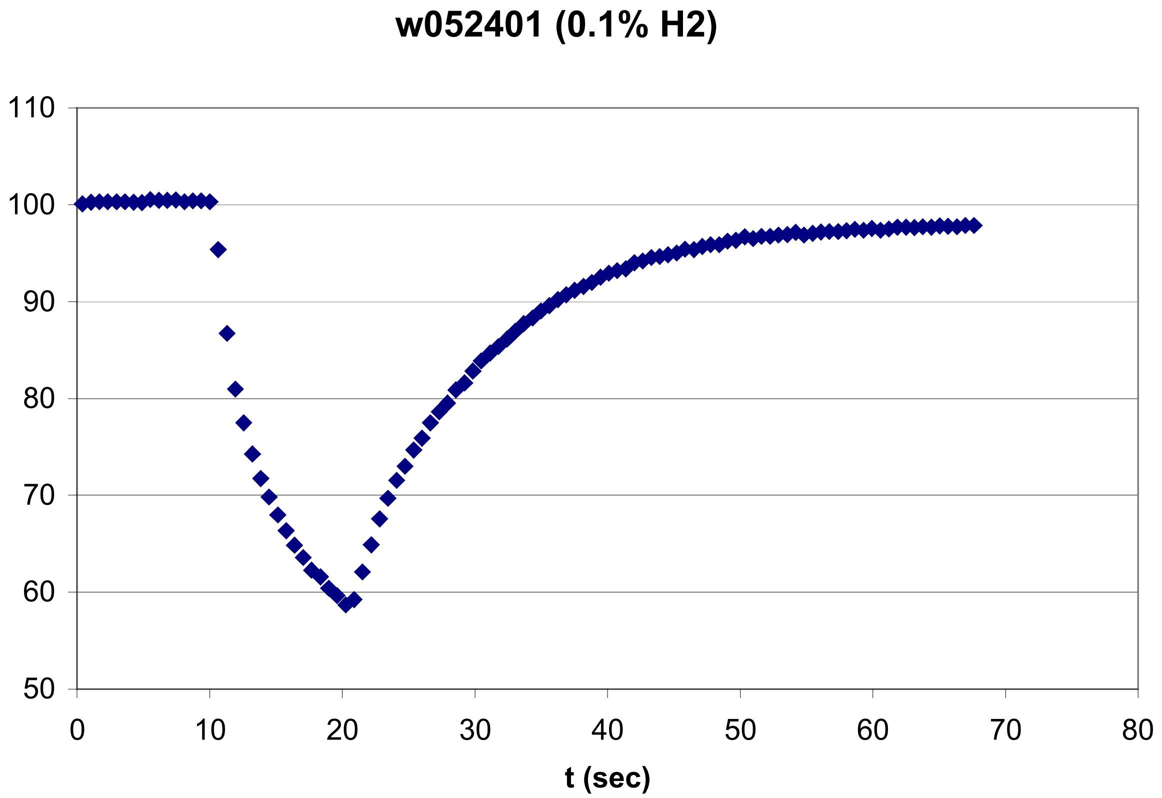

Figure 3. Response of WO3/Pd sensor with protective coating, after one year of aging in polluted atmospheres and cycling in hydrogen.

Organic Coatings

Interaction with representatives of GVD Corporation resulted in a short-term collaboration to test the efficacy of their proprietary polymer coatings. These coatings are deposited using a chemical vapor deposition technique, which results in a substantial amount of control of the film composition, density, and morphology. Additionally, the surface energy of the films can be designed by controlling their termination. This allows surfaces that exhibit a wide range of contact angle.

Sensor films were fabricated on microscope slides at NREL and then mailed to GVD for application of a variety of polymeric films. After coating, the films were returned to NREL for testing, and these films showed good resistance to pollutants in ambient air. Figure 4 illustrates the resistance to contamination of a sensor film over 2 months of testing. This represents a remarkable degree of protection for a polymer film and gives us an attractive avenue for exploration in the future, especially to control the ingress of water into the optically active elements of the sensor.

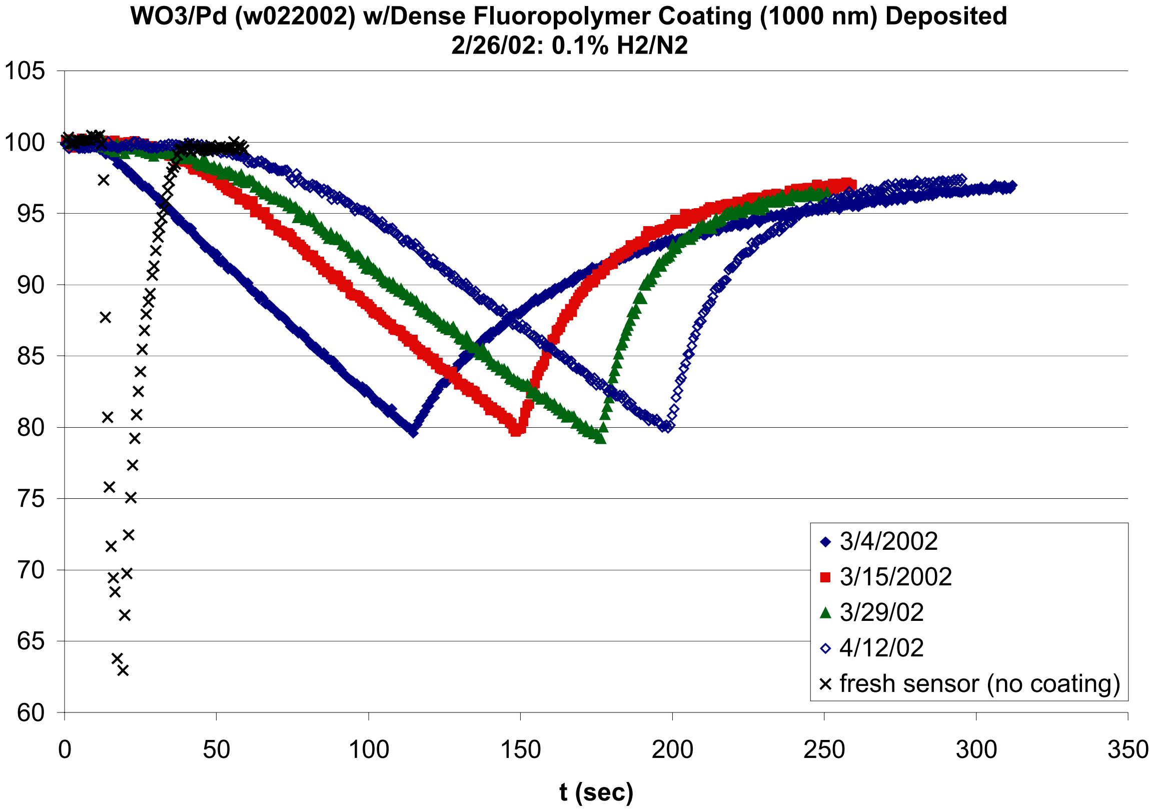

Figure 4. Response of sensor coated with GVD film after ambient exposure.

Sensor Response as a Function of Temperature

An environmental test chamber was constructed from an insulated cooler. The optical test fixture (Fig. 1) can be inserted into the environmental chamber and positioned on a block of aluminum metal. A dry ice slush or liquid nitrogen provides effective cooling of the chamber and the gas inlet lines. Heating tape on the gas inlet line and a proportional temperature controller allow us to control the gas temperature and thus the thin film temperature to within 0.1 °C. An illustration of this chamber and its functional elements are shown in Fig. 5.

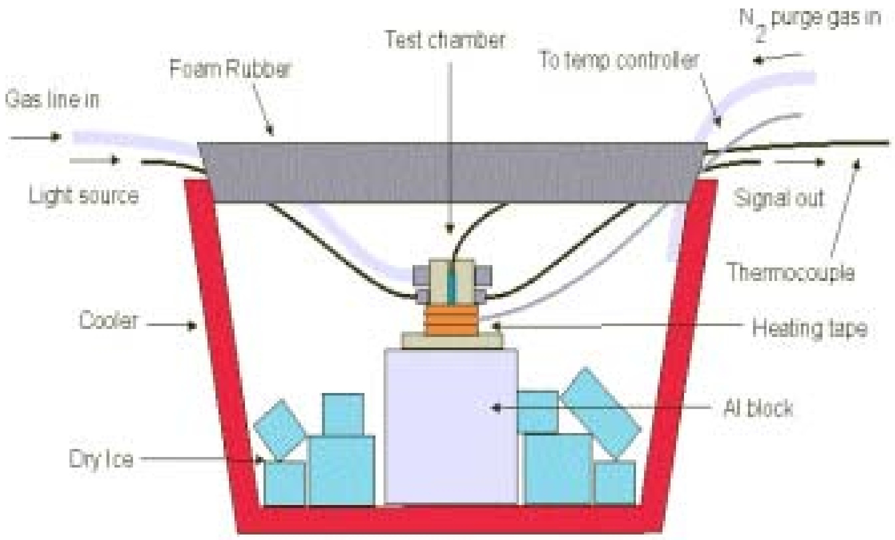

Figure 5. Illustration of the Environmental Test Chamber

Stabilized sensors were tested with variations in temperature and variations in relative humidity separately. Sensor response is illustrated in Figs. 6 and 7.

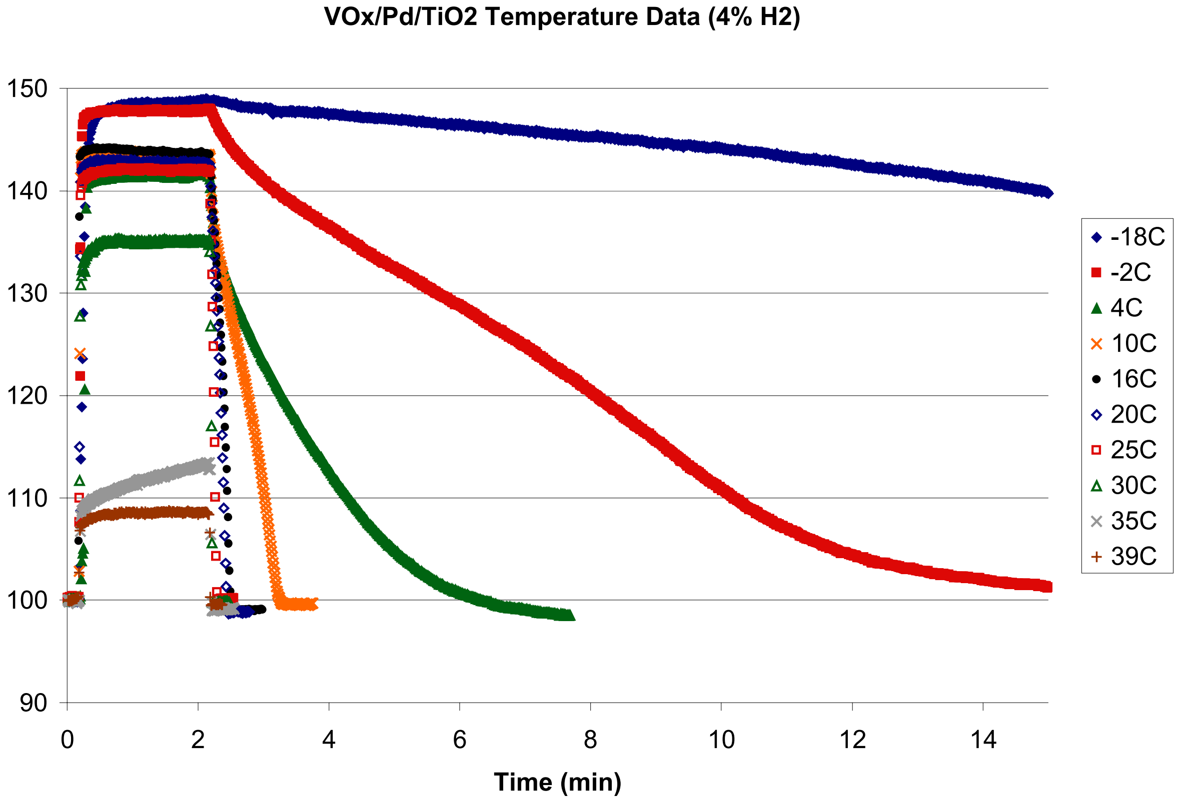

Figure 6. V_2O_5 sensor tested with 2% H_2 in air as a function of temperature.

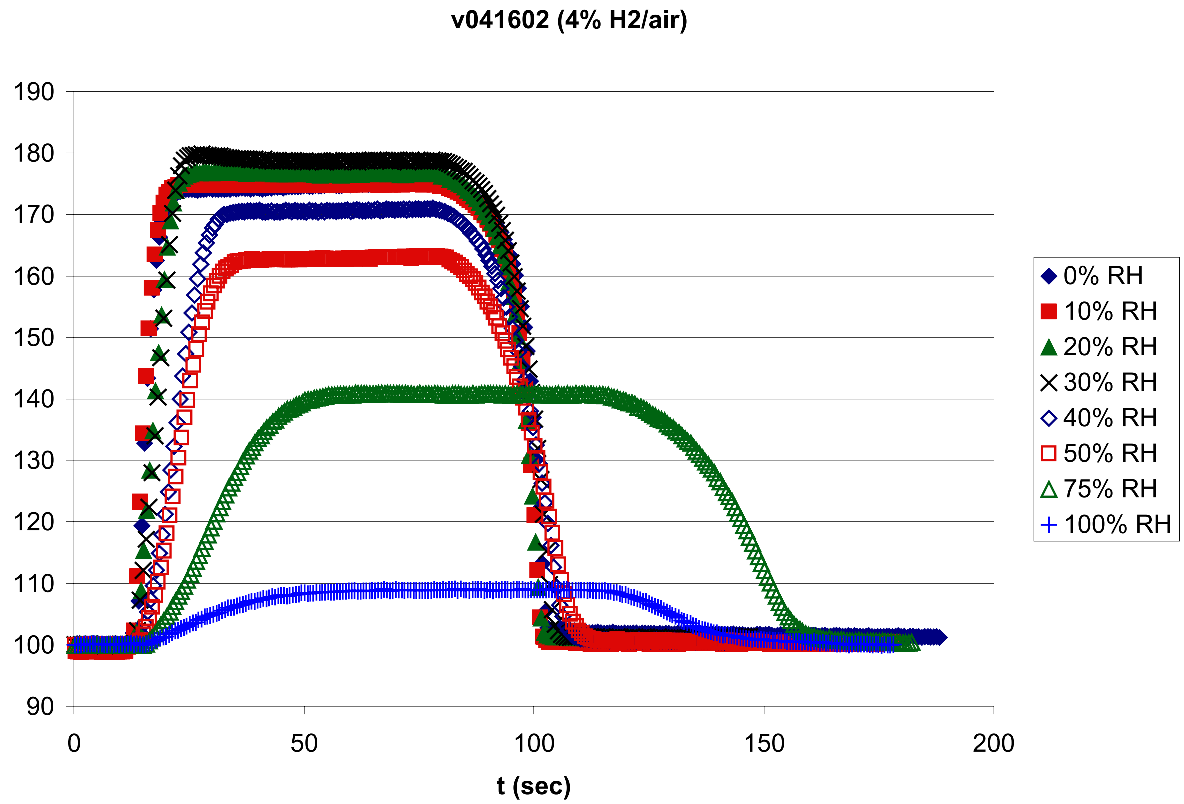

Figure 7. V_2O_5 sensor response to 4% H_2 in air as a function of relative humidity.

Materials Research

In addition to innovative coatings for the protection of the hydrogen dissociation catalyst, we have been investigating mesoporous metal oxides layers for enhanced performance of the sensor elements. Precursors are electrodeposited about a host molecule. Upon firing, the host is consumed and the precursor is decomposed into the metal oxide of choice. When this is done carefully, the inverse of the shape of the template is left, so that the metal oxide has a regular, defined structure of pores on the nanoscale (Liu, 2002-2).

Mesoporous Vanadium Oxide Sensor

In a Pd/V_2O_5 configuration, we have found that vanadium oxide undergoes an irreversible transformation from yellow to blue upon hydrogen insertion, while the formation of palladium hydrides gives rise to the net optical signal. The ability of vanadium oxide to act as a proton insertion host is found to be critical, however, for the proper functioning of the device. Our optical data for the palladium catalyzed mesoporous vanadium oxide device indicate a much faster kinetic response than that for evaporated vanadium oxide, which is commonly used. Figure 8 shows the optical response of a sensor based on a mesoporous vanadium oxide film. Upon exposure to

4% of hydrogen in nitrogen, the relative transmittance decreases quickly due to the coloration of vanadium oxide. In comparison, the relative transmittance normally increases first for a device based on evaporated vanadium oxide, due to the formation of palladium hydride. The extremely fast coloration of vanadium oxide effectively offsets that signal. Subsequent alternating exposure to 100% of hydrogen and air shows that the sensor is very stable, indicating that mesoporous vanadium oxide successfully functions as a fast hydrogen insertion host.

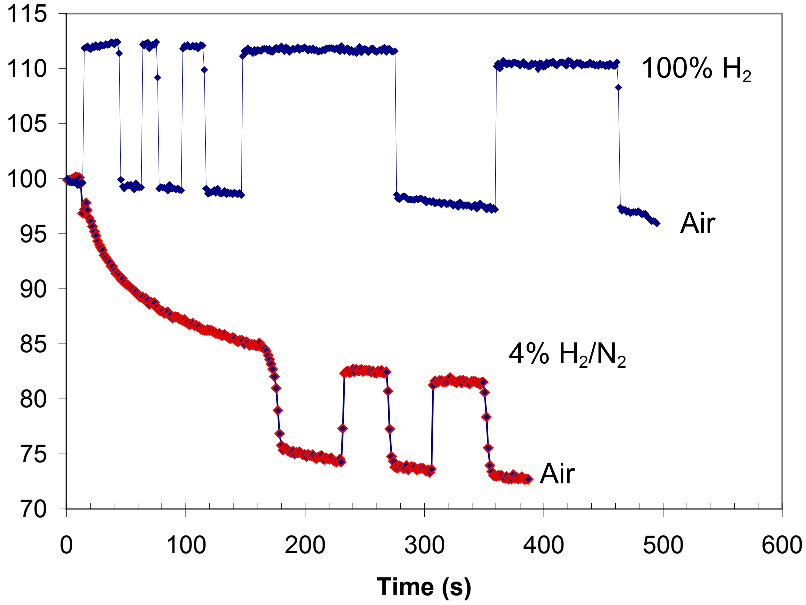

Figure 8. Optical response at 545 nm of a Pd/V_2O_5 sensor in which the vanadium oxide is an electrodeposited mesoporous film.

Mesoporous Tungsten Oxide Sensor

We have also demonstrated the suitability of an electrodeposited tungsten oxide as a chemochromic layer for hydrogen detection, providing a valuable alternative to vacuum deposition. Figure 9 shows the optical response of a Pd/WO_3 sensor to 0.1% hydrogen/nitrogen. The sensor exhibits a fast response that is comparable to that of an evaporated tungsten oxide-based sensor.

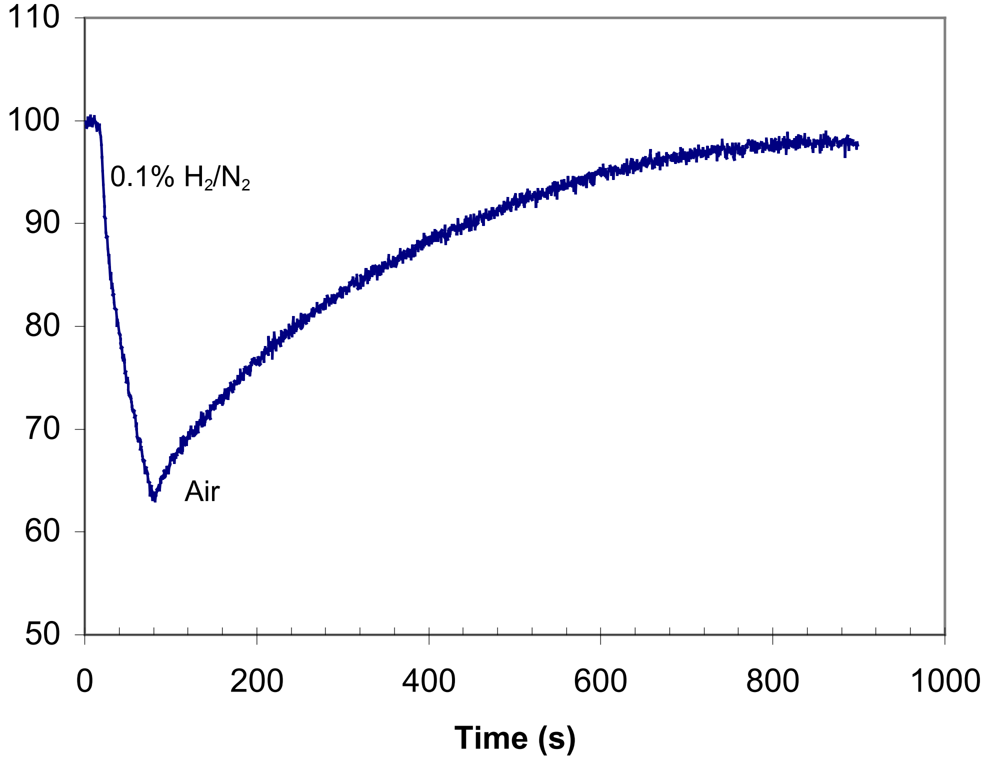

Figure 9. Optical response at 650 nm of a Pd/WO_3 sensor in which the tungsten oxide is an electrodeposited mesoporous film.

Summary and Conclusions

We have continued development and testing of fiber-optic, thin film hydrogen sensors designed to meet the criteria of safety sensors for the DOE Hydrogen, Fuel Cells, and Infrastructure Technologies Program. The primary goals of speed, sensitivity, weight, and inherent safety have been met. Work continues on functional lifetime and response to variations in temperature and relative humidity. Some sensor films have been demonstrated to be stable over 1 year.

An environmental chamber was constructed to test sensor films at various temperatures. In addition, a gas manifold with four mass flow controllers for proportioning gases and controlling relative humidity was constructed. Preliminary experiments indicate that both the speed and sensitivity of the sensor films vary with both temperature and relative humidity.

Future Work

Research this year has established that we have developed stable chemochromic materials and that we have effective means of protecting the Pd catalyst from contamination in ambient air. There are several issues that remain to be resolved in the future.

- The hydrogen dissociation catalyst be protected from trace contaminants in the air and from common pollutants found in the transportation environment for periods in excess of 1 year. Can this lifetime be extended?
- Can the sensor films be made to function in the range of –30 – +80 °C?
- Can the sensor films be made to function well above 50% relative humidity?
- What is the optimum thickness for all of the individual layers in these multi-layered, thin film devices, including the protective layers?

Work will continue to address these issues.

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