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INTERFACIAL STABILITY OF THIN FILM HYDROGEN SENSORS

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Abstract

The goal of this research is to make available the technology to produce low-cost, lightweight, reliable 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 very inexpensive, and inherently safe, since no electrical leads are employed in the monitored space. We have concentrated on studying the stability of the palladium surface with respect to the dissociation of hydrogen, since the use of palladium as either the primary sensor material or as a catalyst layer over the sensor materials appears to constitute the method of choice for such low-cost hydrogen sensors.

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. 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 of these sensors 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 will be 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 sites and reduces signal-processing problems by minimizing electromagnetic interference. Critical detector performance requirements (for all four configurations) include high selectivity, response speed, and durability as well as potential for low-cost fabrication.

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 of 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 Pd deposits 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. (1998), and have improved upon the chemochromic materials used as the sensing material under the Pd layer (Liu, et al., 2001). 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 met 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 (prefer detection limit of 0.5% or better). The sensor must also respond quickly (prefer response time of 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, prefer 1 year or more). In this respect the sensor must be operational with no active effort 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. 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 as a catalyst, because of its superior properties among the noble and semi-noble metals for dissociating and transporting hydrogen. Molecular hydrogen dissociates on the Pd surface, and atomic hydrogen diffuses rapidly through the film. Physical or optical changes in the Pd film itself, or in adjacent films or interfaces, are used to detect the presence of hydrogen. All of the current sensor concepts share Pd 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. Additional work reported here has focused upon the interface between the Pd layer and the optically active layers used for fiber optic sensors.

Experimental

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

The fiber-optic sensor test station consisted of a gas flow manifold that could be switched automatically from gas mixtures containing hydrogen to air. Switching was controlled by the same computer used to acquire optical spectra. The manifold delivered the test gas stream into a test chamber, constructed so that the dead volume was 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 was 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 could be used as test articles. Glass slides were often used to simplify deposition and analysis after testing. The details of this measurement system appear in Fig. 1 and Fig. 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 was carried out with an array of tools available in the Characterization Laboratories at NREL. These included 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 2001 were protection of the palladium (Pd) catalyst films from airborne contaminants and characterization of the metal oxide-palladium interface.

Protection of Pd Catalyst Layer

Several different strategies were investigated for extending the sensor lifetime by inhibition of Pd catalyst poisoning. These strategies included addition of alloying elements and deposition of various protective coatings.

Addition of Alloying Elements to Pd Catalyst

Experimental work on hydrogen separation membranes (Bryden, 1998) suggested that the use of Pd-Fe alloys might inhibit poisoning of the catalyst surface in ambient air. In addition, the Robust Hydrogen Sensor manufactured by DCH Technology makes use of a Pd-Ni alloy maintained above ambient temperature. For these reasons it was decided to fabricate sensors using the above-mentioned alloys in place of pure palladium and compare their response to sensors made with the original catalyst composition.

The sensor alloy films were prepared by vacuum co-evaporation. Compositions of the alloys were varied from approximately 5 to 20 percent Fe or Ni. The sensors were deposited on microscope slides and tested in the custom-made gas manifold using a 0.1% hydrogen/nitrogen mixture. The sensors using alloyed Pd films did not display additional resistance to poisoning at ambient temperature as compared with pure Pd at any of the alloy compositions used. Consequently, the work was discontinued in favor of an approach using protective coatings.

Protective Coatings for Inhibition of Pd Catalyst Poisoning

Several organic and inorganic coatings were tested for their ability to inhibit poisoning of the Pd catalyst.

Organic Coatings

Organic coatings investigated included colloidal Teflon and Nafion, as well as a dense, amorphous organic film. These coatings tended to deactivate the catalyst immediately upon deposition due to their organic nature or that of their precursors. They may occupy or block a significant portion of the Pd surface sites that would otherwise be available for the dissociation of hydrogen. Another type of film was therefore developed based on a mesostructurted Pd. This film created a nanoporous structure that prevented subsequent films from blocking active sites on the evaporated Pd. Sensors with this nanoporous coating overcoated with the dense, amorphous protective layer have shown increased resistance to poisoning for a period of over a month, as illustrated in Fig. 3.

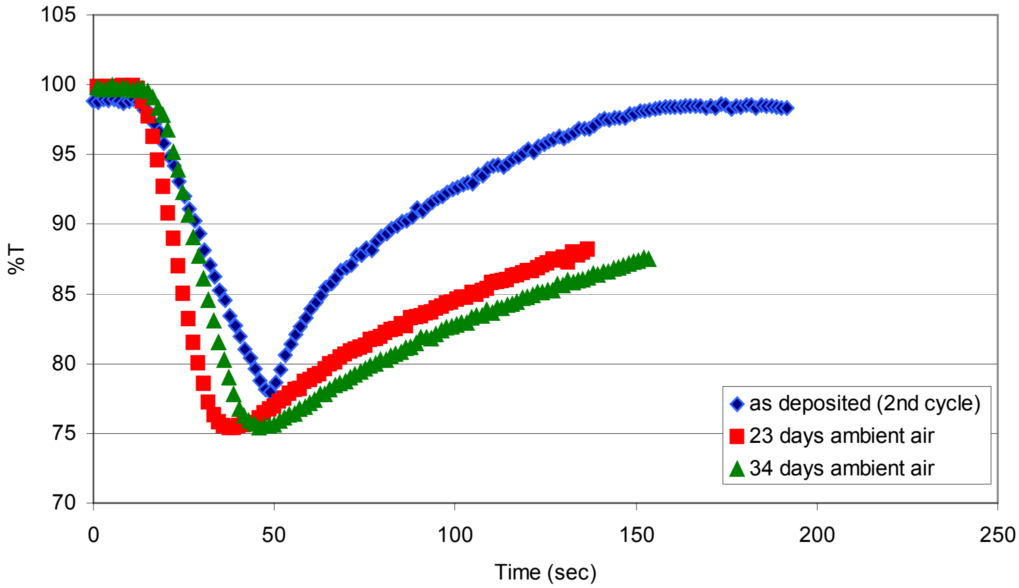

Figure 3. High sensitivity sensor response to 0.5% hydrogen after 34 days with "dense" protective coating

Inorganic Coatings

The study of inorganic coatings was focused mainly on the deposition of colloidal metal oxide films. Films of varying thickness were deposited by spin coating on freshly made and aged sensors. Sensors with the coating were functional for a period of approximately two weeks then started to degrade. Fresh sensors with activated coatings were still functional for periods exceeding one month, whereas a duplicate sensor with no protective coating degraded within a few days as shown in Figures 4 and 5. High durability sensors were completely degraded after periods exceeding 1 month. When coated with an activated metal oxide layer, the same sensors were partially rejuvenated. Figure 6 shows data for one of these sensors.

A possible theory for the observed behavior is that the relatively large pore size of the coating does not provide complete protection against airborne contaminants. However, the activated coating serves as a powerful catalyst to remove gaseous hydrocarbon species. The main source of contamination on the Pd active sites may be due to the formation of a chemisorbed methyl-Pd species (Albers, 1995). The activated coating removes the gaseous precursors before they can reach these sites. Previously contaminated sensors may be rejuvenated due to the migration of atoms on the Pd surface. When a methyl group migrates to the protective layer it is subsequently removed. After a certain time enough active sites on the Pd are again free to catalyze the hydrogen dissociation reaction.

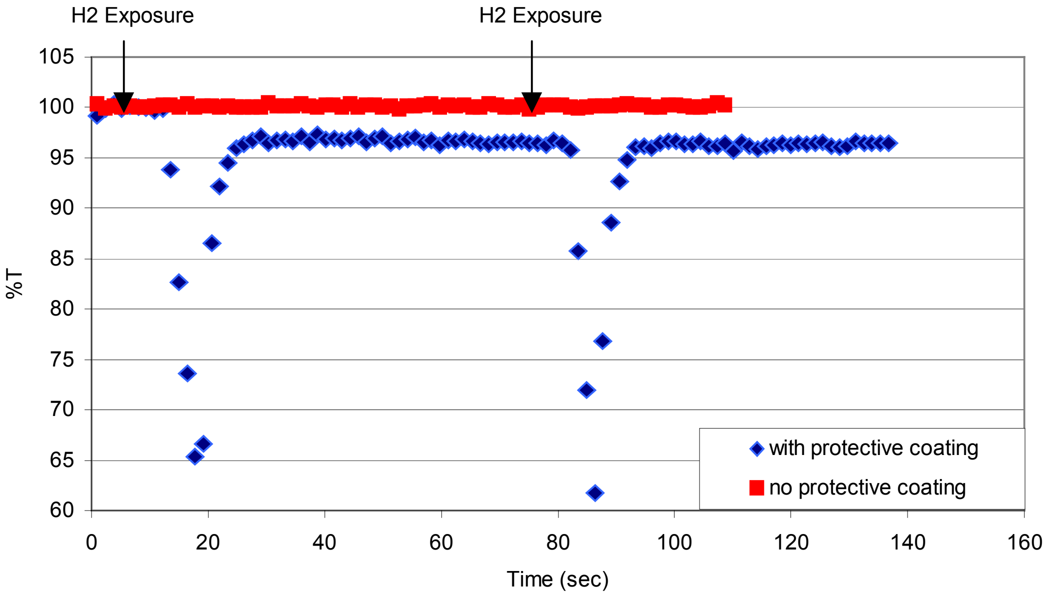

Figure 4. High sensitivity sensor response to 0.1% hydrogen after 10 Days with and without protective coating

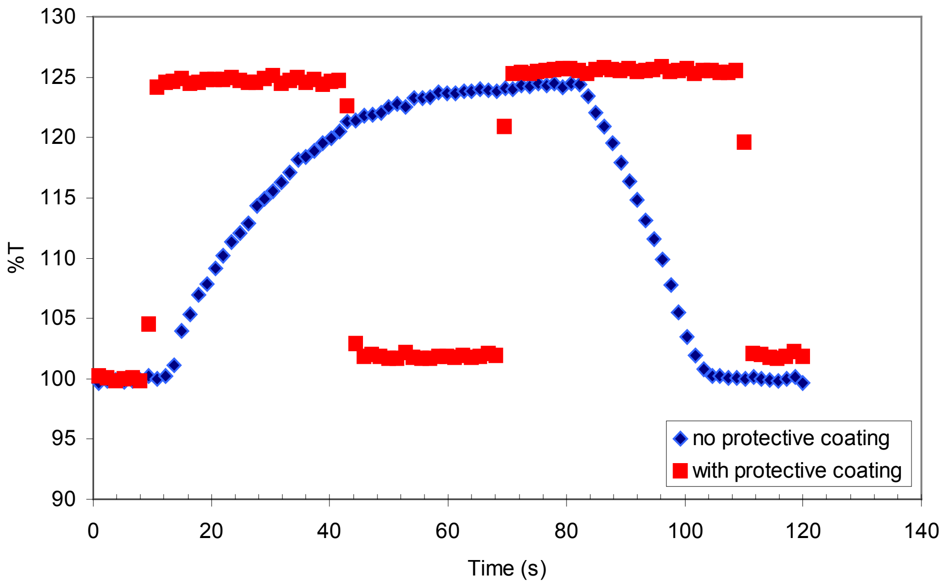

Figure 5. High durability sensor response to 4% hydrogen with/without protective coating (after 5 days ambient air exposure)

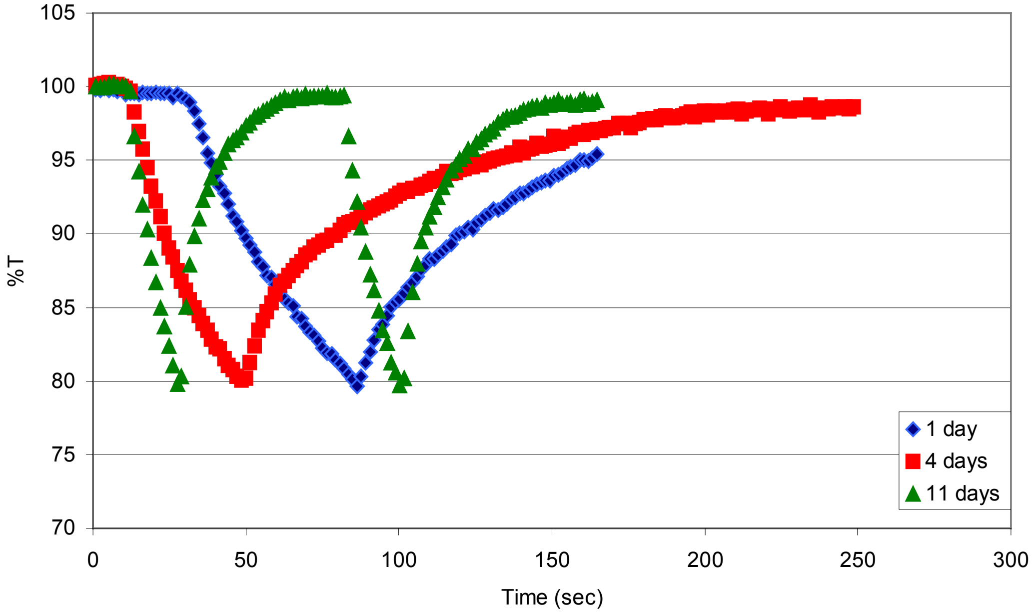

Figure 6. Regeneration of high sensitivity sensor exposed to 0.1% hydrogen: protective coating applied after 44 days

Characterization of the Metal Oxide/Pd Interface

Tests performed on aged sensors led to the conclusion that contamination of the catalyst active sites is primarily responsible for the observed degradation. In most cases once enough active sites are free on the Pd film the underlying metal oxide behaves normally even after a period of one year. To confirm this behavior further experiments were conducted on sensor films using AC impedance spectroscopy. A variety of sensor structures were developed that allowed us to examine the charge transfer process across the interface. In the simplest case, a sandwich structure of Pd/WO_3/ITO-glass (Indium Tin Oxide) was fabricated. Two different WO_3 layers were employed, with one of them showing improved response time to hydrogen. Preliminary data demonstrated that the faster sensor had a much smaller charge transfer resistance. This result indicated that for pristine sensors with a very active Pd catalytic layer the interface charge transfer process could be the rate-determining step during hydrogen insertion. Further measurements were performed on the two sensors to record their stability during storage. It was found that the charge transfer resistance became similar, while their chemochromic performance remained very different. One possibility is that the diffusion rate of proton in the tungsten oxide layer could be responsible for the difference. Efforts were then made to measure the diffusion coefficient of protons using AC impedance spectroscopy. At very low frequencies the impedance usually corresponded to the solid-state diffusion. Unfortunately, such a diffusion process was not observed with the sandwich structure employed in this study due to the apparent shorting of the device. The shorting was consistent with the fact that tungsten oxide is a semiconductor, which behaves like a conductor at very low frequencies. We attempted to insert a proton conductor between WO_3 and ITO to address this issue. However, the proton conductors investigated so far all have limited conductivities at room temperature. Consequently, the impedance spectra were dominated by the contribution from the proton electrolytes. We will continue to search for a suitable proton conductor that will allow us to determine the proton diffusion coefficient in tungsten oxide.

Summary and Conclusions

We have researched the issues regarding the interfacial stability of thin film, fiber-optic sensors. We have determined that the new chemochromic materials developed last year are extraordinarily stable and undergo no measurable changes in performance when stored in air over periods in excess of one year. This result implies that the interface between these materials and the Pd catalyst overlayer remains stable, and the fouling of the Pd surface itself is the primary mode of degradation of these sensors. Fouling of the active sites on the surface of the catalyst occurs rapidly (1 to 5 minutes) with deliberate exposure to contaminants like CO, CH_4, and H_2S. It occurs more slowly (1 to 2 weeks) in ambient air.

Codeposition of getter materials with the Pd was not successful in extending the lifetime of the sensor in air, although some protection to H_2S was noted. Assembling multi-layered thin films to provide protection to the active hydrogen dissociation sites by inhibiting access of pollutants to the Pd surface does offer a good measure of protection. We have sensors in test with these coatings that have been exposed to ambient air in excess of 1 month and still function as well as pristine, just-made sensors. These coating strategies appear to offer some protection from pollutants such as the H_2S as well.

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 a number of issues that remain to be resolved in the future.

- How long can the hydrogen dissociation catalyst be protected from trace contaminants in the air and from common pollutants found in the transportation environment?
- What is the response of these fiber-optic sensors over a useful range of temperatures (40°C to – 40°C)?
- What is the response of these sensors to concentrations of H_2 above the explosive limit, and can they be made quantitative?
- What is the optimum thickness for all of the individual layers in these multi-layered, thin film devices?

Work will continue to understand the behavior of the optical films and catalyst and resolve these issues.

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