INTERFACIAL STABILITY OF THIN FILM HYDROGEN SENSORS

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Abstract

The real and perceived hazards of hydrogen fuel use, its production, and storage require extensive safety precautions and codes to be put in place before any serious movement can be made towards a hydrogen based energy future. Currently, commercial hydrogen detectors are not useful for widespread use, particularly in transportation, because they are too bulky, expensive, and dangerous. Recent work sponsored by the DOE Hydrogen Program has developed promising technologies for satisfying the future demands. Sensors that exhibit physical or optical 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 a conductivity change 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. Research to study those issues in order to rank their importance to the various sensor concepts, to determine the relevant mechanisms, and to mitigate these factors is reported here.

Introduction

The ability to detect hydrogen gas leaks economically and with inherent safety is an important technology that could facilitate commercial acceptance of hydrogen fuel in various applications. In particular, hydrogen-fueled passenger vehicles will require hydrogen leak detectors to signal the activation of safety devices such as shutoff valves, ventilating fans, and alarms. Such detectors may be required in several locations within a vehicle—wherever a leak could pose a safety hazard. It is therefore important that the detectors be very economical. This paper reports on progress in the development of low-cost hydrogen detectors intended to meet the needs of a hydrogen-fueled passenger vehicle and then treats stability issues in optical sensors specifically.

There are four candidate sensor configurations that look particularly attractive for the transportation applications. These are termed the HFET, the Thick Film, and the Thin Film, and the Fiber-Optic sensors. The HFET construction uses a thin film of Pd as the metal contact controlling the device. The presence of hydrogen results in the migration of atomic hydrogen to the interface between the metal film and the insulator, which results in a change in the output of the device that is scaled to the hydrogen concentration. The Thick Film device uses thick film Pd alloy paste to form a four resistor network (Wheatstone bridge) on a ceramic substrate. Two opposed resistors are covered to isolate them from the ambient atmosphere. The exposure of the uncovered resistors to hydrogen results in a change in resistivity of the thick film material and a shift in the balance point of the bridge, which can be scaled to the hydrogen concentration. The thin film device is equivalent in design to the thick film, only much thinner films (typically vacuum deposited) are used as the resistors.

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, all using one or more thin films coating 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.

Key Issues

There are a series of key issues for 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 performance issues related to fiber-optic sensors (response time, reliability, and lifetime).

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. Thick film sensors were prepared either at Oak Ridge National Laboratory or at DuPont by the thermal decomposition of metalorganic pastes.

Performance testing of the completed articles was carried out at the National Renewable Energy Laboratory (NREL) or at DCH Technology (Valencia, CA). Analytical investigations of failed articles were carried out in the Device Characterization Laboratory at NREL.

The experimental set-up for testing of thick film components is detailed by the photographs in Fig. 1. The apparatus consists of a cylindrical Plexiglas test enclosure, a regulated power supply, and a Kiethley electrometer to measure imbalances in the Wheatstone bridge. A typical experiment would consist of balancing the bridge under an ambient flow of synthetic air (dry). Airflow is turned off, then a hydrogen in nitrogen mixture is admitted into the test enclosure. Changes in the resistivity of the exposed Pd resistors upon admission of the hydrogen mixtures were then measured as an offset in the voltage across the bridge.
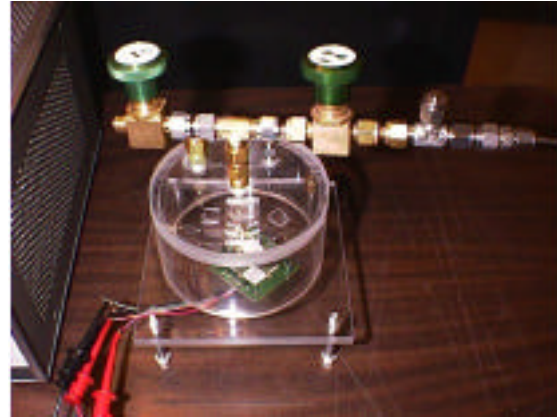
Figure 1. Test Apparatus for Thick Film Hydrogen Sensors.

For the fiber-optic sensor test station, we constructed a gas flow manifold that could be switched automatically from gas mixtures containing hydrogen to air. Switching is controlled by the same computer used to acquire optical spectra. The manifold fed 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. 2 and Fig. 3.
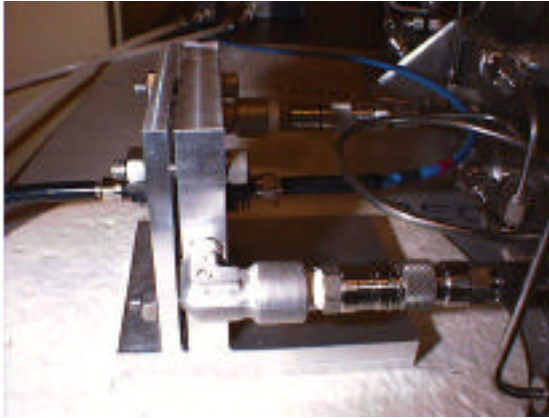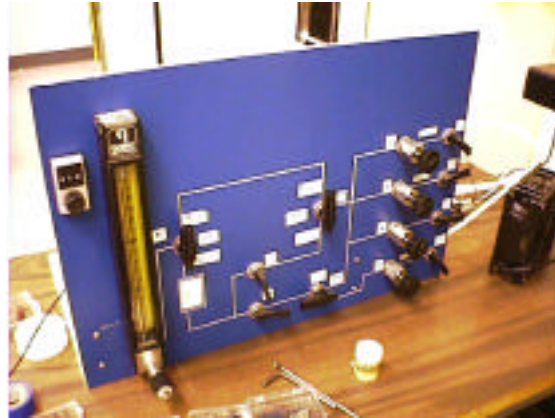

Manifold and Test Station
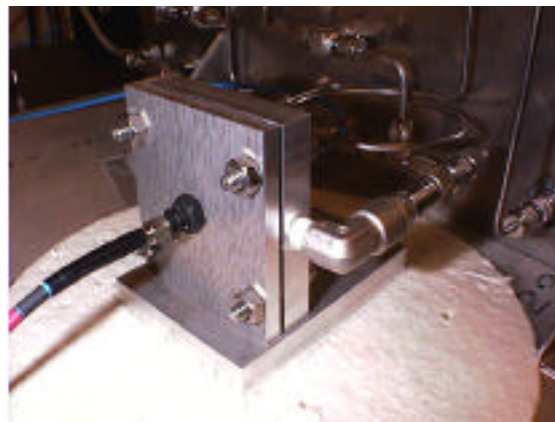
Test Chamber

Figure 2. Fiber-Optic Sensor Test Station

Test Chamber, Transmission Mode   Gas Manifold

Figure 3. 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

Research activities covered in this report were conducted in the second half of FY 1999 and the first half of FY 2000. These activities consisted of diagnostics and analysis of state-of-the art sensor materials. We quickly determined that the prior optical sensor configurations were unstable to repeated exposures to hydrogen. Signal response was slow, recovery was slow, and repeatability in response was poor. Furthermore, exposure of these sensors to concentrations greater that 2% hydrogen in nitrogen resulted in permanent damage to the Pd catalyst. Adhesion of the hydride sensor materials (YH_2 and GdH_2) to both glass substrates and polymer fiber faces was poor. Cyclic exposure to hydrogen resulted in severe cracking of the thin films and eventual delamination of the entire structure from the substrate material. New, improved materials were needed.

Work on the resistive sensor elements has shown that these sensors exhibit a decrease in response time after extended periods in air with no hydrogen, or may show no response for low concentrations of hydrogen in air. It is possible to restore the performance of these sensors by exposing them to hydrogen concentrations exceeding 2% in air for periods in excess of 2 h. There appears to be a surface reaction that inhibits the dissociation of the hydrogen molecule on the surface, or its propagation into the film.

Having determined the most important issues for durability and reliability in the field for the current sensor concepts, it appears that the relevant issues, broken down by sensor type are:

Optical Thin Films
- Primary issue is durability and repeatability of response for the chemochromic layers at ambient exposure conditions.
- Stability of the hydrogen dissociation catalyst (Pd) to cyclic exposures to hydrogen.
- Fouling of the catalyst due to impurities and pollutants in or reaction with the air.

Thick Film and Thin Film Resistive
- Stability of the Pd films after long (days) exposures in ambient air.
- Stability of the films to repeated exposures to hydrogen, or excessive concentration of hydrogen once.
- Fouling of the film surface due to impurities and pollutants in or reaction with the air.

Thin Film Electronic
- Fouling of the film (Pd) surface due to impurities and pollutants in or reaction with the air.

We believe that we have a fundamental understanding of the first two issues for optical thin films and proceeded with work to mitigate those issues. We also worked on the issue of fouling of the Pd surface by pollutants and have proposals for methods of mitigation.

Three new material configurations were created to solve the problems associated with the previous optical sensors. A high sensitivity configuration exhibits superior performance properties. It displays the best sensitivity and response times of any material evaluated to date, at least down to hydrogen concentrations of 200 ppm. Typical response curves are shown in Fig. 4, and we have measured response times of 15 seconds at concentrations of 0.1%. While its high sensitivity and fast response time make this the best candidate as a safety device in such applications as transportation, further work is needed to address stability issues. However, it would function very well for applications where a new sensor is required for each test. The material is already the leading candidate for these applications, such as the detection of diffusible hydrogen in welds (Smith, 2000).

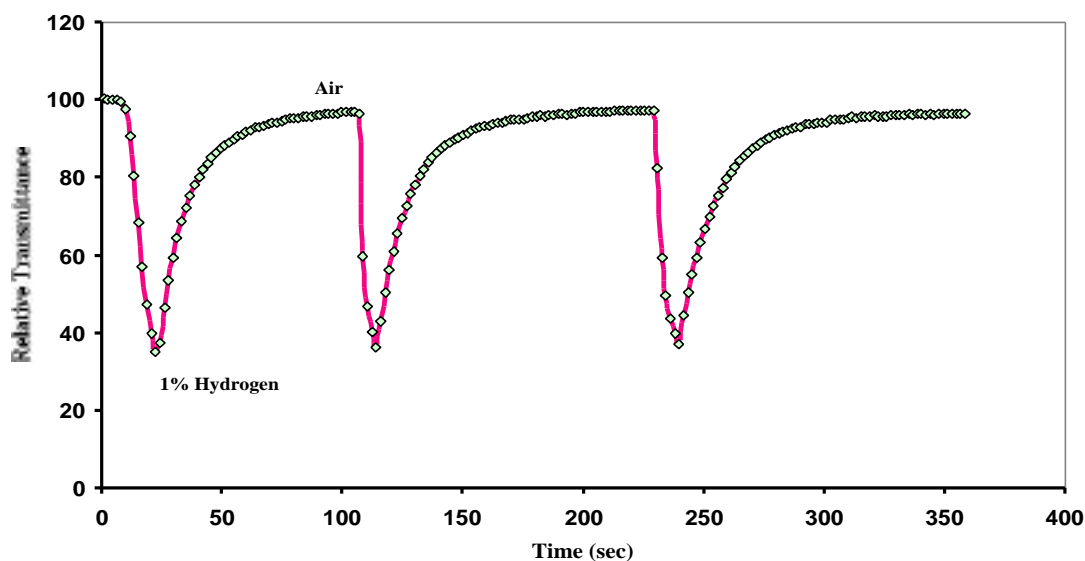## High Sensitivity Film Exposed to 1% Hydrogen
(02/10/00)

Figure 4. Cyclic Response of High Sensitivity Film to 1% Hydrogen in Nitrogen

The other two materials provide much enhanced performance (not quite as good as the high sensitivity material) and much enhanced reliability and lifetime. Examples of the performance over extended periods of time and many cycles of coloration and bleaching are shown in Fig. 5 (for Type 1 durable sensor) and in Fig. 6 (for a Type 2 durable sensor). Both of these films become more transparent with the addition of hydrogen and color as the hydrogen is removed. Some irreversible changes occur in the optical properties of the films with the first few cycles of hydrogen, but they remain stable thereafter. Both films become stable in response after a few cycles; however, long term drift in baseline is noted. This drift is the subject of further study.
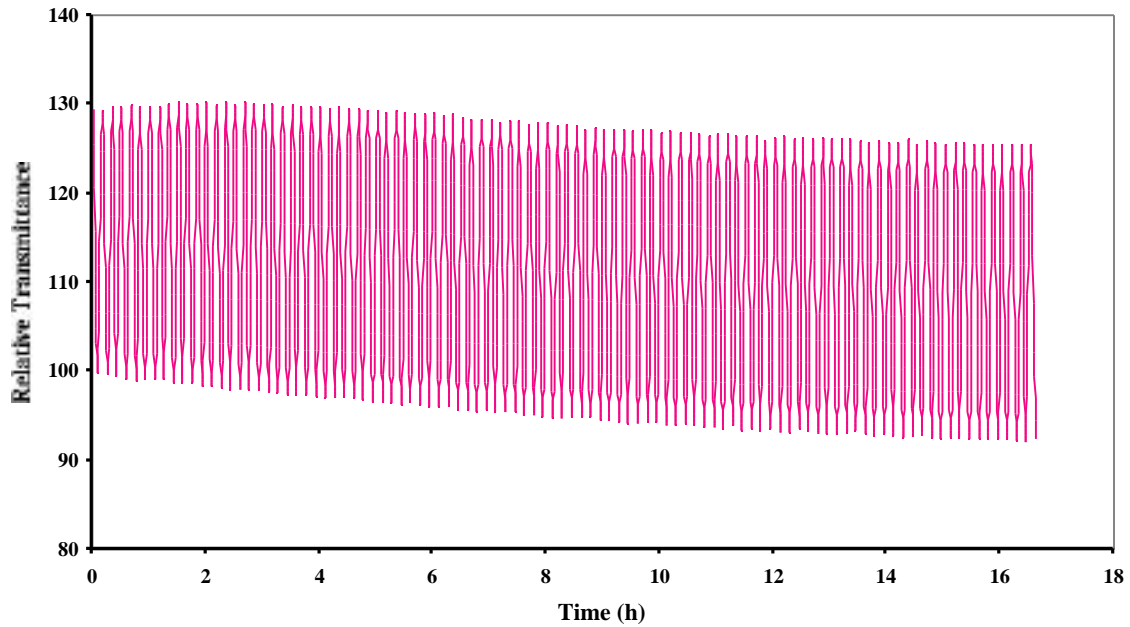
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Durable Sensor Type 1, Cycled in 4% Hydrogen
1/29/00

Figure 5. Type 1 Sensor Cycled Between 4% Hydrogen and Synthetic Air.

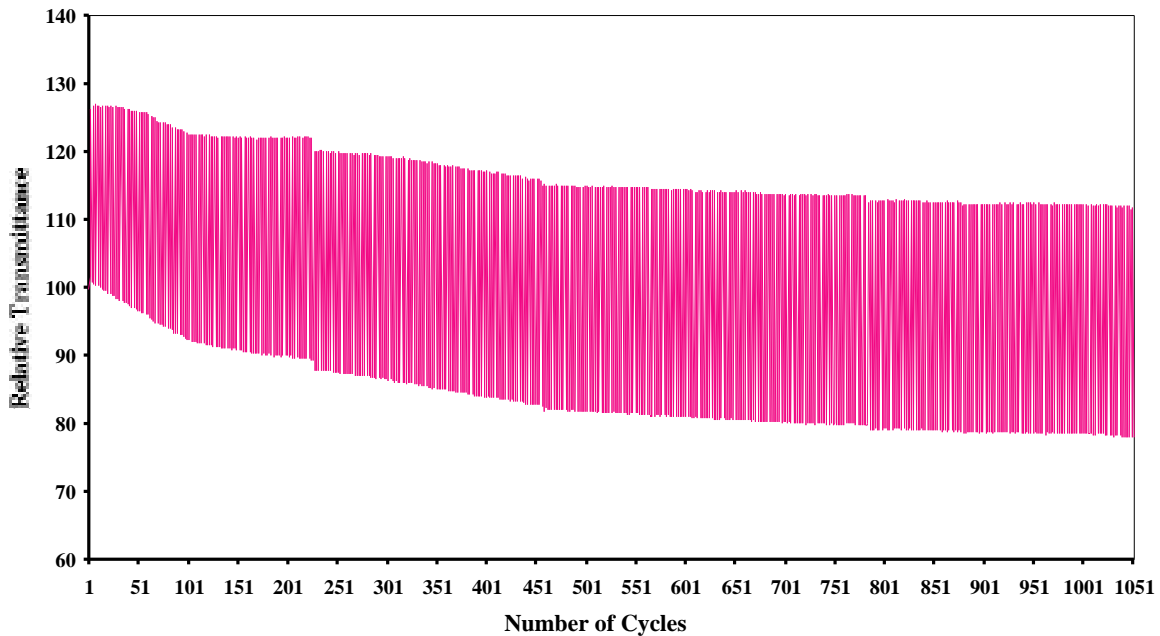## Durable Sensor Type 2, Cycled in 4% Hydrogen
2/13/00

Figure 6. Type 2 Sensor Cycled Between 4% Hydrogen and Synthetic Air.

During the testing of these sensor elements, we observed that exposure to ambient versus synthetic air (even for relatively short periods of time) caused a loss of sensitivity. However, after a few cycles of exposure to hydrogen, sensitivity returned. We speculate that the active Pd surface sites involved in the dissociation of the hydrogen molecule become covered with contaminant species, such as hydrocarbons. These species occlude those sites from participation in the dissociation reaction and inhibit hydrogen transfer into and out of the films. Evidence obtained from X-ray Photoelectron Spectroscopy (XPS) and Auger Electron Spectroscopy (AES) support this speculation. Air exposure of the clean Pd surface results in the buildup of a monolayer of carbon bearing compounds. These compounds are easily removed by light ion bombardment or by less destructive techniques ex situ.

In order to study more carefully the role of contamination in air, we did a number of controlled experiments, where small concentrations of contaminant gases were allowed into the test chamber during a testing sequence. In this way we could examine the deterioration of the signal and see whether it would recover or would remain desensitized. In Fig. 7 the response of a Type 1 sensor is presented before and after exposure to carbon monoxide (CO). The contaminant dosing significantly slowed the response and recovery of the sensor.
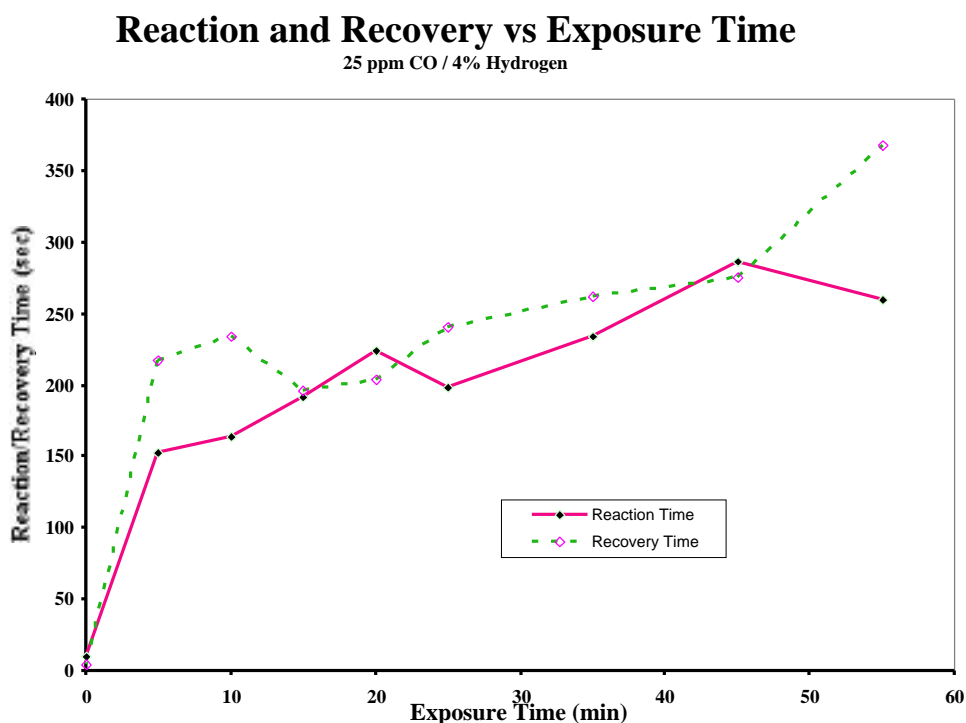
Reaction and Recovery vs Exposure Time
25 ppm CO / 4% Hydrogen

Figure 7. Effect of CO Adsorbed on Sensor Surface.

Similar experiments were performed using methane (CH_4) and hydrogen sulfide (H_2S) as the contaminant gases. Similar results were obtained, except the magnitude of the effect on the sensor varied dramatically for each contaminant gas. Figure 8 illustrates the effect from CH_4, and Fig. 9 illustrates the effect from H_2S.

Response and Recovery Time vs Exposure Time
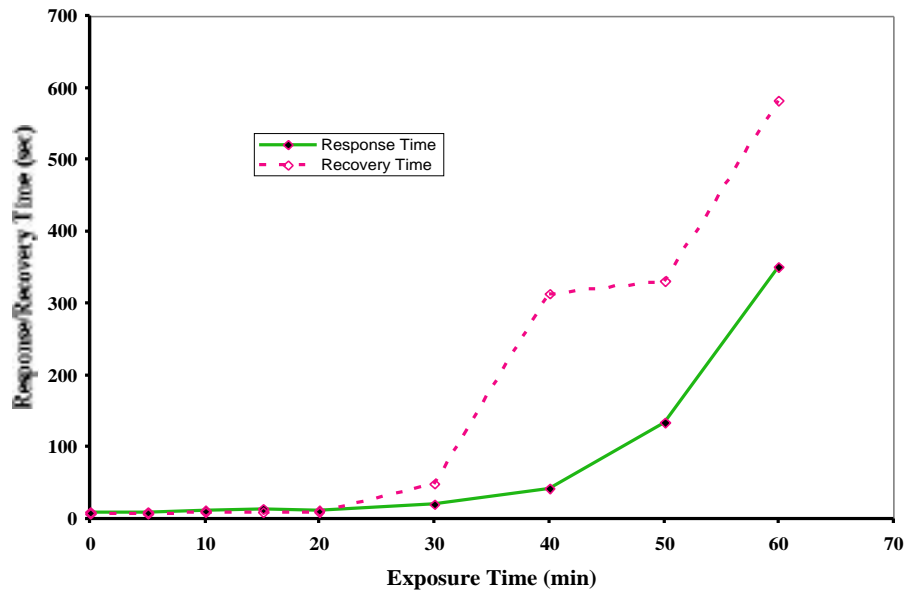
100 ppm CH4 / 4% Hydrogen

Figure 8. Effect of CH$_4$ Adsorption on Sensor Surface.
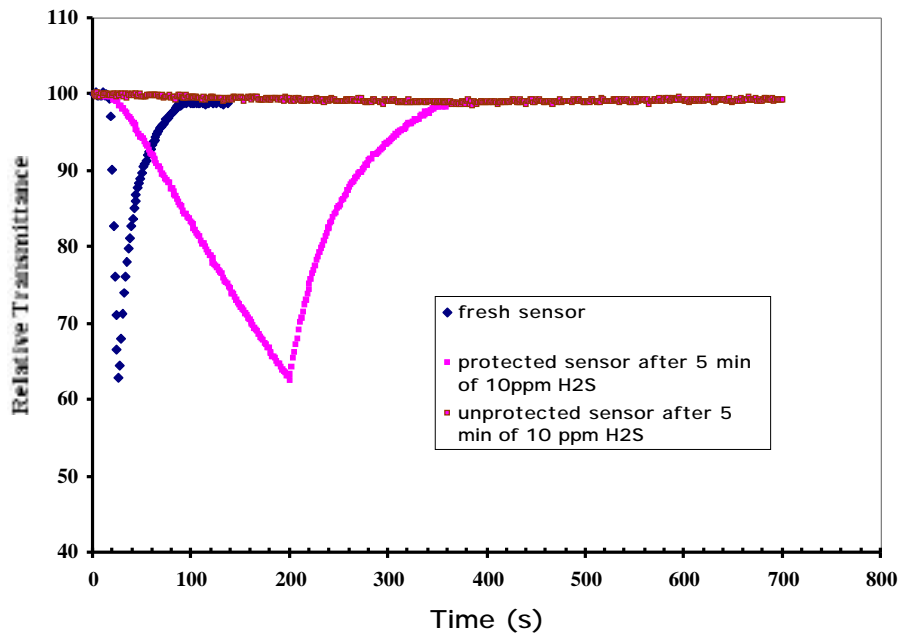

Figure 9. Effect of H$_2$S Adsorbed on Sensor Surface.

Both CH_4 and CO physisorb to the surface of the Pd so as to block the active sites for H_2 dissociation, as evidenced by the fact that the optical response of the sensor is significantly slowed by exposure to either of these gases. However, the sensor response is never killed, and exposing the sensor films to synthetic air for several hours is sufficient to restore the original response of the sensor. This indicates that the adsorption is weak enough to allow the pollutant molecules to exchange with N_2 and O_2 and diffuse away from the surface. The H_2S adsorption is very different.   As is evident in Fig. 9, this molecule adsorbs onto the Pd surface and can completely block all of the active surface sites for the H_2 dissociation in 5 minutes. There is no recovery in clean air without extra measures to clean the H_2S off the surface. We conclude that the H_2S is chemisorbed to the Pd surface. This conclusion is consistent with much literature in the binding of sulfur bearing compounds to noble and semi-noble metal surfaces.

It is clear that for these sensors to survive for any significant period in ambient atmospheres contaminated with automobile or industrial emissions, the Pd surface must be protected in some way to prevent it from losing sensitivity. A simple option is to encase the sensor head within a canister of activated carbon. This is represented in a sketch of the sensor head package and electronic control unit in Fig. 10. Activated carbon is an efficient way to absorb polar molecules, thus removing most of the contaminants before they can approach the clean Pd surface. Less expensive and more effective means are needed for keeping the Pd surface active for H_2 dissociation.
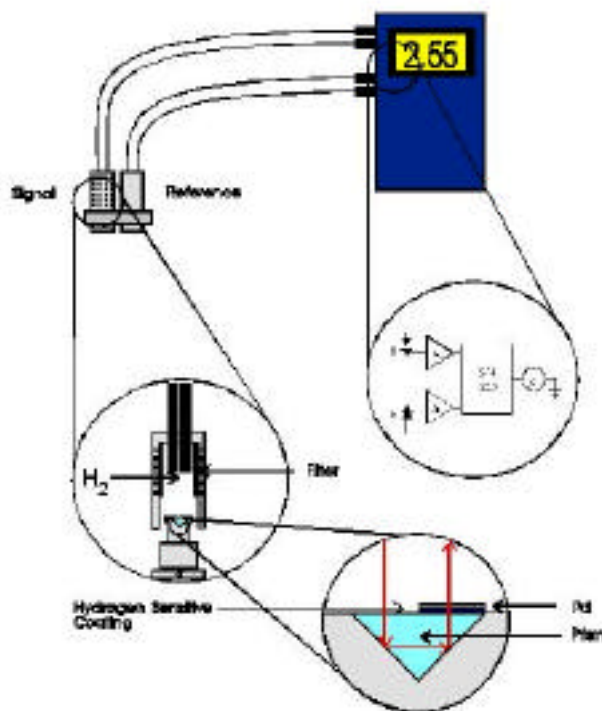

Figure 10. Schematic of Encased Sensor, Transmission Mode.

A final observation about the active Pd surface is that some experimental evidence obtained recently, as well as some investigations reported in the literature (Huang, 1999), suggest that at least of monolayer of PdO_x forms after extended inactive periods in air (natural or synthetic). It may be that this oxide monolayer is responsible for the loss in sensitivity observed in sensors that have been stored in air for extended periods of time. It has been noted that this loss of sensitivity is not permanent and sensor performance can be restored by exposure to H_2. This phenomena needs to be investigated thoroughly in the coming year.

Summary and Conclusions

We have researched the issues regarding performance and durability of thick film, thin film, and fiber-optic sensors. For the fiber-optic sensors that used metal hydrides for the detection of hydrogen, we found adhesion problems during cyclic exposure to hydrogen, most likely related to the expansion and contraction of the metal hydrides. Lifetimes of these sensors did not exceed 10 cycles. For the surface plasmon based sensors, we found that the response time was slow and that the repeatability of signal upon cyclic exposure was poor. Therefore, we concentrated most of the work on issues related to the metal oxide based sensors.

New optical materials have been developed that show great promise for the fiber-optic sensor development. One material has demonstrated high sensitivity and a response time of less than 1 second. Unfortunately, its sensitivity decreases with time over periods of storage of about 1 month. Other materials have shown good sensitivity and cyclic stability to over 1000 cycles. Long term stability of these sensors is now dependent upon the properties of the hydrogen dissociation catalyst (Pd).

Common air pollutants found in exhaust streams of current internal combustion engines seriously affect the palladium catalyst material. In particular, CO and CH_4 adsorb on the surface and restrict access to hydrogen dissociation sites. This adsorption appears to be weak and reversible when the sensor is exposed for extended periods in synthetic air. The effect observed with exposure to H_2S is much more dramatic. Exposure to 10 ppm H_2S for 5 minutes is sufficient to completely kill the sensor for the detection of hydrogen. This effect is not reversible after exposure to synthetic air, indicating that the H_2S has chemisorbed to the surface.

Finally, we have indications that residence times longer than one day in air (even synthetic) can significantly slow the response of the thick film, thin film, and the fiber-optic sensors. Subsequent exposure to hydrogen for periods up to 2 hours allows the sensors to recover their original performance. We suspect that a surface or near subsurface oxide is the basis of this effect. This will be a topic of continued research.

Future Work

Research this year has led to the development of some improved sensor materials. However, there are important questions remaining about the material performance for applications in the hydrogen infrastructure.

- Can the hydrogen dissociation catalyst be protected from common pollutants found in the transportation environment?
- Does the surface of the dissociation catalyst react with atmospheric oxygen, and, if so, can the surface be modified to mitigate the slow response that has been attributed to this reaction?
- Can the multi-layered thin film be stabilized for concentrations of hydrogen in air exceeding the lower explosive limit?

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

Acknowledgements

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