LOW-COST FIBER OPTIC HYDROGEN SENSORS

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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. This paper reports the progress made on the development of a low-cost fiber-optic hydrogen sensor (FOHS) intended to meet the safety requirements of a hydrogen-fueled passenger vehicle.

The FOHS consists of a hydrogen sensitive coating at the end of an optical fiber. When the coating reacts with 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 the 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 FOHS 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 include high selectivity, response speed, and durability as well as potential for low-cost fabrication.

Summary of Prior Work. Initial experiments were conducted using a "simple" sensor configuration, essentially a palladium/metal oxide (Pd/MO_x) reflective fiber optic sensor. The principal material used as the hydrogen sensitive coating was tungsten (VI) oxide or WO_3 (1). A thin over-layer of Pd dissociates the hydrogen molecules into atomic hydrogen, which then readily diffuses into the metal oxide causing the optical change. This sensor design was found to be adequate for hydrogen detection, but too slow for safety applications, with a response time of approximately 30 seconds (2). However, the response time was adequate for the use of the "simple sensor" as a detector of diffusible hydrogen from welded steel (3-5). A surface-plasmon resonance (SPR) sensor was also designed and evaluated. The principle behind SPR is based on light adsorption in a thin metal layer causing oscillation of free electrons, or surface plasmons; hydrogen adsorption by an underlying metal oxide layer causes a change in its refractive index and a subsequent resonant wavelength shift, which is then measured. The response time of the SPR sensors was found to be on the order of 5 seconds. However, the SPR shift was found to be sensitive to changes in relative humidity, causing a false positive signal (2). Alternate materials such as transition metal hydrides were then investigated for their suitability as sensor materials. These materials were subsequently found to be unstable in ambient air. Lattice expansion of the metal hydride during hydrogen absorption also caused delamination of the sensor films at higher concentrations.

Another factor in the unsuitability of these prior sensor designs was degradation of performance, attributable to poisoning of the Pd surface by airborne contaminants. This phenomenon was observed in all types of sensors studied since each design used a thin film of Pd as a hydrogen dissociation catalyst. Research was therefore redirected towards the development of new sensor materials that displayed superior properties in terms of response time and durability.

Experimental

Thin films were fabricated by standard techniques of vacuum deposition. Thermal evaporation was carried out on a Varian Model 3118 evaporator. The working pressure was less than 1×10^{-5} torr and the metal oxide deposition rates were controlled at 0.1 to 0.5 nm/s. The palladium layer was deposited on top of the oxide at a rate of 0.1 nm/s. Plasma enhanced chemical vapor deposition (PECVD) of organic thin films was performed using an RF-powered 13.5 MHz Plasma Technology CVD system. Glass microscope slides were used as substrates to simplify deposition and analysis. The films were deposited at room temperature.

The fiber-optic sensor test station consisted of a gas flow manifold connected to a fiber optic photodiode-array Ocean Optics 2000 Spectrometer. 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 measurements could be made in either spectral transmittance or reflectance. The data were acquired by a modified LabView software program, which also controlled the alternative switching of gases. Hydrogen/nitrogen mixtures with different concentrations of hydrogen were used to evaluate the response of the sensors and synthetic air (20% oxygen, balance nitrogen) was used for recovery to their initial optical state.

Results and Discussion

Several new types of materials were developed to improve sensor performance. Each has certain advantages as explained below.

Water Doped WO_3. A modification of WO_3 using water vapor as a dopant resulted in a porous sensor material with improved response time. In addition to improving the rate of hydrogen transport due to the higher water content, water doping also produces microstructural changes in the film resulting in increased porosity. Sensors using this material are sensitive down to hydrogen concentrations of approximately 200 parts per million (ppm) and display an extremely rapid initial response to hydrogen as shown in Figure 1.

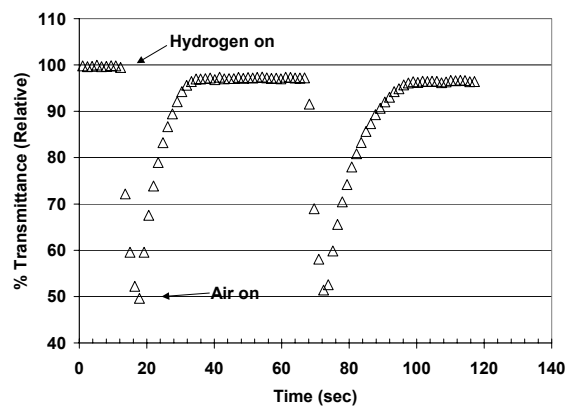

Figure 1. Optical response of Pd/WO_3 sensor to 0.1% hydrogen.

Vanadium Oxide. A new sensor design with vanadium oxide (VO_x) as the sub-layer was also developed. This sensor design utilizes the Pd/PdH_x transition to generate the optical signal, i.e. the optical properties of the Pd itself are changed upon exposure to H_2. The sensor is responsive down to approximately 0.5 percent hydrogen, and is stable even in the presence of pure hydrogen gas, whereas an unprotected Pd thin film will crack and delaminate at hydrogen concentrations above 4 percent. Representative data for the Pd/VO_x sensor is presented in Figure 2.

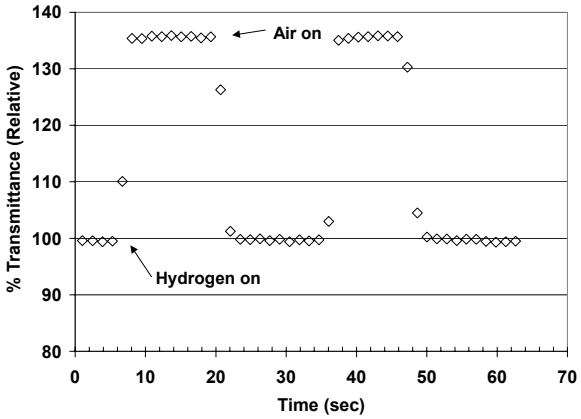

Figure 2. Optical response of Pd/VO_x sensor to 4% hydrogen.

The following mechanism has been established to explain the stability of the Pd/VO_x sensor: hydrogen is dissociated on the surface of palladium and hydrogen atoms diffuse to the interface between palladium and vanadium oxide. Vanadium oxide is reduced with the insertion of protons. During the first exposure, vanadium oxide undergoes an irreversible optical change after which the proton insertion becomes fully reversible while the color remains unchanged. At the same time, the palladium layer gives rise to an optical response due to the formation of the hydride. A high average vanadium oxidation state enhances the absorption of hydrogen in two aspects: a low chemical potential that results in a high thermodynamic driving force, and a large capacity to react with hydrogen due to the great amount of vanadium (V) species that can be reduced. The presence of a vanadium oxide layer that is capable of accepting hydrogen without optical modulation allows the palladium hydride layer to be stable over repeated hydrogen exposures at concentrations higher than 4%.

Materials for Protection of Pd Catalyst. Experiments were conducted with the new sensor materials to determine their susceptibility to selected airborne contaminants. Exposure to CO, CH_4 and H_2S was found to have a detrimental effect on sensor performance. In addition, prolonged exposure to ambient air for periods of longer than 2 days caused similar degradation. It was therefore decided to investigate ways of protecting the Pd surface from these contaminant species.

The main goals were to identify the compounds in ambient air responsible for poisoning of the Pd catalyst. A search of the literature revealed the distinct possibility that airborne hydrocarbons produced from incomplete combustion were forming a Pd-CH_3 complex on the metal surface and deactivating it towards hydrogen dissociation (6). It was decided to attempt the development of surface coatings to protect Pd from these compounds, and if possible to extend the sensor operational lifetime to 6 months. A further priority was to maintain a fast response time for the sensors.

"Dense" Organic Coating. Various coatings were investigated for protection of the Pd catalyst. These included a "dense" organic coating as well as an "active" inorganic coating. The "dense" organic coating consists of a proprietary material that has shown promise for protection of the Pd catalyst layer, essentially acting as a filtration membrane for airborne contaminants. As shown in Figure 3 an unprotected Pd/WO_3 sensor is completely unresponsive after exposure to 10 ppm H_2S, whereas a sensor with the "dense" coating still responds to hydrogen.

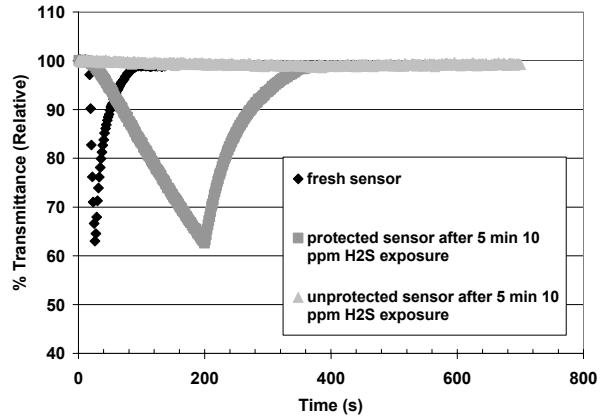

Figure 3. Optical response of Pd/WO_3 sensor with "dense" organic coating exposed to 10 ppm H_2S.

"Active" Inorganic Coating. Of the coatings studied the "active" coating (using a different proprietary material) offered the best protection. Deposition by spin coating produced a thick porous film that did not impede the diffusion of hydrogen or oxygen to the underlying films. Sensors with this "active" coating were protected for approximately two weeks before degrading, whereas unprotected sensors degraded in 1-2 days. Subsequent experiments have shown that the properties of the material in the "active" coating can be used to prevent hydrocarbons from reaching the Pd surface, thus preventing formation of the Pd-CH_3 complex and poisoning of the hydrogen dissociation sites. Sensor operational lifetimes have been extended to over 9 months. In addition, fouled sensors can be partially regenerated by application of the coating.

Figure 4 shows the optical response of a Pd/WO_3 sensor after 10 days ambient air exposure, with and without the coating. The unprotected sensor is totally inert to 0.1 percent hydrogen, but the coated sensor is still active. Figure 5 shows similar data for a Pd/VO_x type sensor after 5 days. The unprotected sensor is compromised but the coated sensor still maintains a fast response. Figure 6 shows a fouled sensor coated then monitored over a period of 65 days. After approximately 9 days the response is approaching that of a fresh sensor.

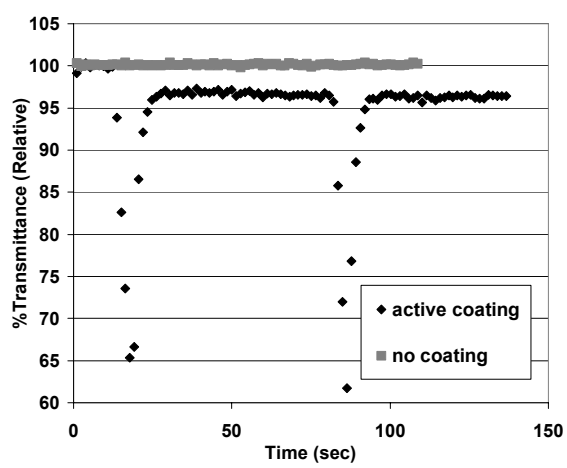

Figure 4. Optical response of Pd/WO_3 sensors tested in 0.1% hydrogen after 10 days ambient air exposure.

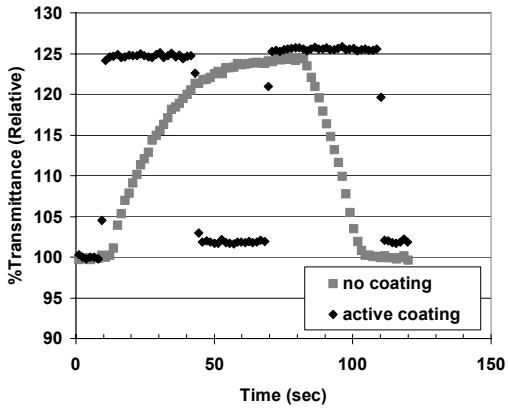

Figure 5. Optical response of Pd/VO_x sensor tested in 4% hydrogen after 5 days ambient air exposure.

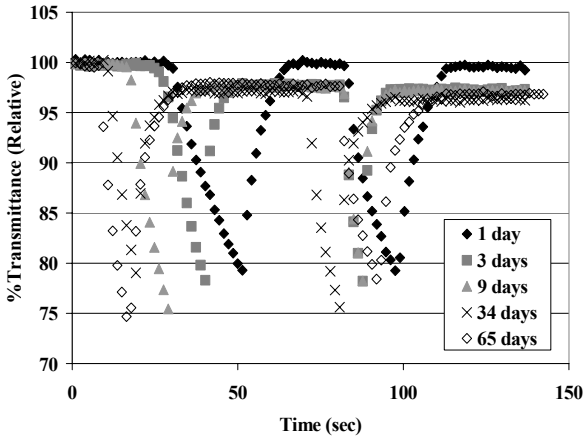

Figure 6. Optical response of fouled Pd/WO_3 sensor with "active" coating, tested in 0.1% hydrogen.

Prototype FOHS. A prototype of the FOHS suitable for field-testing has also been developed. Various designs have been evaluated and the most promising is a sensor that operates in transmittance mode using plastic collimating lenses. One possible design is presented in Figure 7, and optical data generated with a Pd/WO_3 sensor using this design is presented in Figure 8.

Assuming that the prototype sensor will behave similarly to the laboratory samples, the next logical step is to test the sensor under field conditions. Cost management and other factors will of course need to be taken into account if large-scale manufacturing is planned, but the additional elements of collimating lenses are estimated to only raise the cost per sensor to approximately $25.

Conclusion

New, superior materials have been developed for thin film optical hydrogen sensors. Sensors using these materials display fast response times, high sensitivity and resistance to degradation caused by airborne contaminants. A minimum of further work is needed to bring the prototype sensors to the field-testing stage.

In conclusion, the work described here has taken the FOHS technology to the point where a working sensor is achievable. Further issues will undoubtedly need to be addressed as they arise,

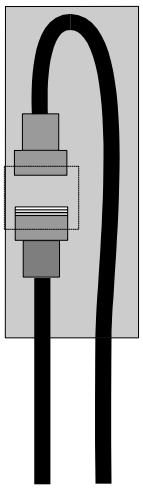

Figure 7. A possible design for the FOHS using collimating lenses.

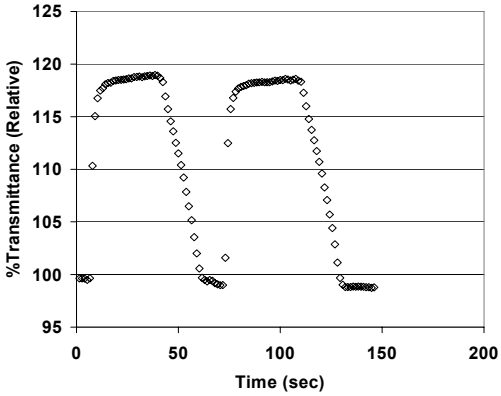

Figure 8. Optical response of prototype Pd/VO_x sensor in 4% hydrogen.

but the research performed at NREL has laid the groundwork for producing a low-cost fiber optic hydrogen sensor ready to meet the safety needs of a growing hydrogen economy.

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