VERY LOW-COST VISUAL AND WIRELESS SENSORS FOR EFFECTIVE HYDROGEN GAS LEAK DETECTION

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ABSTRACT

Element One, Inc., Boulder, CO is developing novel hydrogen gas leak indicators to improve the safety and maintenance operations of hydrogen production and chemical processing facilities and hydrogen fueling stations. These technologies can be used to make visual gas leak indicators such as paints, decals, and conformal plastic films, as well as RF sensors for wireless networks. The primary advantage of the Element One hydrogen gas indicators is their low cost and easy deployment which allows them to be used ubiquitously at each and every potential hydrogen leak site. They have the potential to convert safety problems into routine maintenance problems, thereby improving overall safety and decreasing operational costs.

1.0 INTRODUCTION

Hydrogen and other gases are stored and used in vast quantities for industrial applications. In any gas production, distribution, or utilization system, primary leak detectors and alarms are required. For reliability, the leak detectors in such a system must be particularly robust and must be hard-wired to an alarm/response unit. Because of these reliability requirements, primary leak detectors are expensive and costly to install and are used sparingly. What is needed is an affordable way to ensure that leaked gases do not go undetected. Element One is in the process of developing *low-cost sensors* as auxiliary safety devices [1]. Low cost sensors are not intended to replace primary leak detectors, but may provide a cost-effective auxiliary function that adds to the overall safety of the operation. Low cost gas indicators may augment primary gas leak detectors in many applications. They may be valuable in non-critical situations where gas leaks are not large enough to require an emergency system shutdown; but are nevertheless large enough to require repair during maintenance operations. In effect, a low cost indicator may warn of a leak while it is still small enough to be treated as a routine maintenance problem rather than as a safety problem that requires system shutdown.

The indicators typically consist of a thin film coating or a pigment of a transition metal oxide such as tungsten or molybdenum oxide, along with a catalyst such as platinum or palladium. The oxide is partially reduced in the presence of hydrogen (H_2) in concentrations as low as 300 parts per million and changes from transparent to a dark color. The change is fast and easily seen from a distance. For reversible indicators, the color change is reversed spontaneously in air when the source of H_2 gas is removed. A number of possible implementations have been successfully demonstrated in the laboratory including hydrogen indicating paints, tape, decals, coatings for storage tanks and wireless electronic sensors. These and other implementations may find use in vehicles, stationary appliances, piping, refueling stations and in closed spaces such as maintenance and residential garages for hydrogen-fueled vehicles.

2.0 VISUAL HYDROGEN INDICATORS

2.1 Reversible (WO_3) based indicator coatings

Tungsten trioxide (WO_3) is a well known chemochromic material – meaning that it undergoes color changes when it reacts with certain materials such as hydrogen. These color changes accompany a change in the oxidation state of some of the tungsten ions in the normally transparent crystalline WO_3. There are several proposed mechanisms for the coloration, but the most widely accepted is the intervalence transfer model [2] where partial reduction of the WO_3 replaces some of the W^{6+} ions with

W^{5+} ions. Because of the high dielectric constant of WO_3, a free electron in the vicinity of a W^{5+} ion is trapped in a polarization field around the W^{5+} ion. This kind of trapped electron is called a small polaron and exhibits quantized optical absorption similar to those of orbiting electrons in a simple atom. However, the interaction of the electron with the thermal vibrations of the WO_3 lattice spreads the optical transitions into a broad absorption band that peaks near 800 nm and extends into the red portion of the visible spectrum. Consequently, the partially reduced WO_3 appears blue.

Initial research at Element One was focused on reversible indicators using WO_3, and this material was eventually adapted for use in resistive electronic sensors as described in one of the following sections. However, it was found that a different material which reacts irreversibly with hydrogen would prove to be more useful for visual detection.

2.2 Irreversible (MoO_3) based indicator coatings

Molybdenum trioxide (MoO_3) is also a well known chemochromic material and the reaction with hydrogen is similar to that of WO_3, but its use in applications such as "smart windows" was limited due to the fact that it would tend to color irreversibly. This was actually found to be an advantage for visual leak detection according to several industrial collaborators. In addition to the essentially permanent color change, thin films and coatings using MoO_3 display a "dosimeter" type effect which can be partially quantified. Fig. 1 shows the cumulative effect of coloration with hydrogen exposure for a MoO_3 based coating approximately 100 μm thick, where the scale is in millimoles of H_2 per cm^2.

Figure 1- Color calibration of MoO_3 based "smart paint" as a function of hydrogen exposure.

2.3 Applications

This type of indicator has already found use in both research and industry. Fig. 2 is an example of a related coating specifically designed for aqueous environments, used for detecting H_2 in a biochemical application [3]. Figs.3a and 3b show the coating impregnated on a cloth substrate for leak detection in high temperature pipeline environments, before and after H_2 exposure.

Figure 2 - MoO_3 based coating used as a hydrogen detector for biochemical experiments.

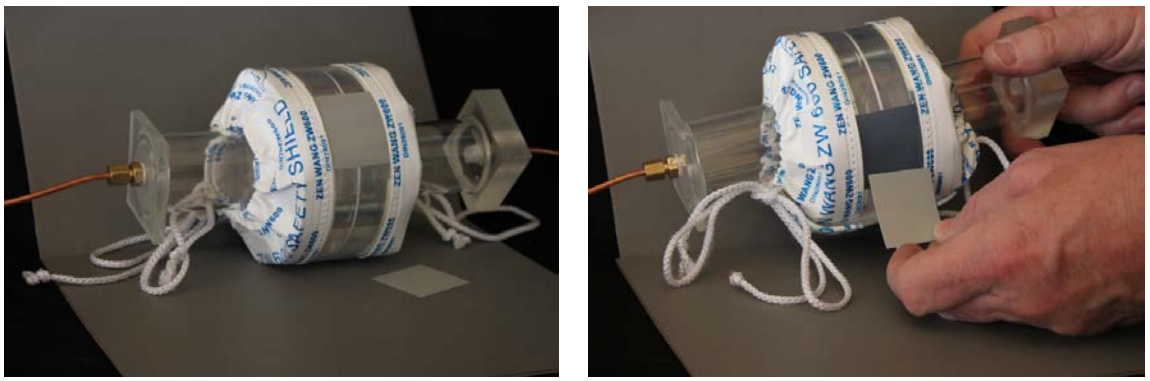

Figure 3 - MoO_3 based coating used as a flange shroud for detecting hydrogen pipeline leaks before (left) and after (right) exposure.

3.0 WIRELESS HYDROGEN SENSORS

3.1 Radio Frequency Identification (RFID)

The use of RFID sensors for purposes of inventory tracking or temperature measurement is already prevalent in modern industry. The same concept can be applied to leak detection. A standard RFID tag consists of an integrated circuit and an antenna, which allows remote monitoring of the signal of interest. Element One is developing resistive H_2 sensors which when coupled with existing technology can serve as low cost, wireless gas detector arrays. These sensors are based on the same materials as the previously described visual indicators. In the case of WO_3 the resistivity change upon reaction with hydrogen is several orders of magnitude more pronounced than the optical change. Thin film sensors made from WO_3 therefore provide hydrogen detectors that are very sensitive as well as being inexpensive to produce.

3.2 Sensor configuration

The sensor films are deposited by thermal evaporation. The substrates are glass/indium tin oxide with overlying inter-digitated electrodes of a conducting material such as gold. A typical sensor stack consists of WO_3 with a very thin, discontinuous layer of palladium (Pd) on top, along with some type of protective coating such as polytetrafluoroethylene (PTFE). The PTFE helps to retard catalyst poisoning of the Pd by airborne contaminants and also partially protects against water damage. Fig. 4 shows a sensor substrate with dimensions 0.5 by 1 cm.

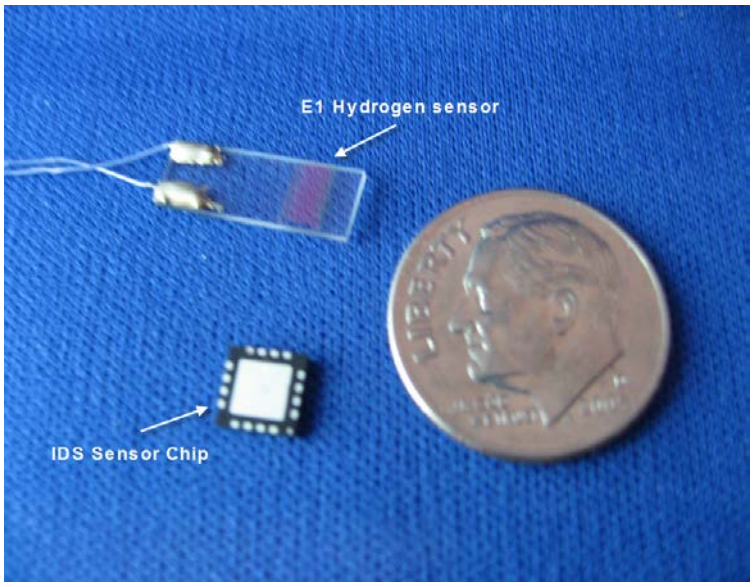

Figure 4 - WO_3 based resistive sensor on glass/ITO substrate.

3.3 Sensor response

The WO_3 has an intrinsically high resistance on the order of 150 MΩ or greater. Upon hydrogen exposure the resistance drops rapidly, with a time constant of approximately 20 seconds when tested in a 1% hydrogen/air mixture. Fig. 5 is a plot of time constant for the sensor as a function of H_2 concentration.

Although the PTFE coating is somewhat effective at protecting the sensor element in aqueous environments, more recent experiments have utilized a silicone based coating which is also more temperature resistant. Fig. 6 shows response curves for the sensor with and without silicone encapsulation, tested in both 1% H_2/air and 10% H_2. Fig. 7 is the encapsulated sensor response when submerged in H_2 saturated water.

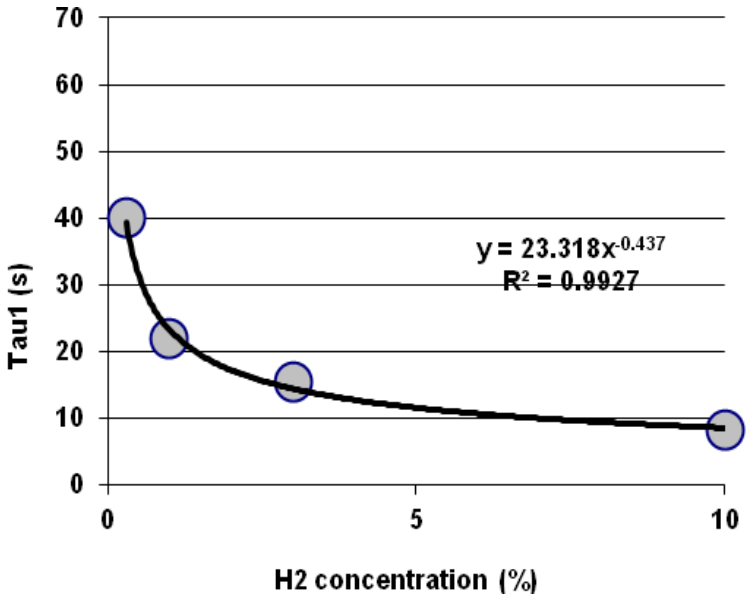

Figure 5 - Time constant versus H_2 concentration for WO_3 based resistive sensor.

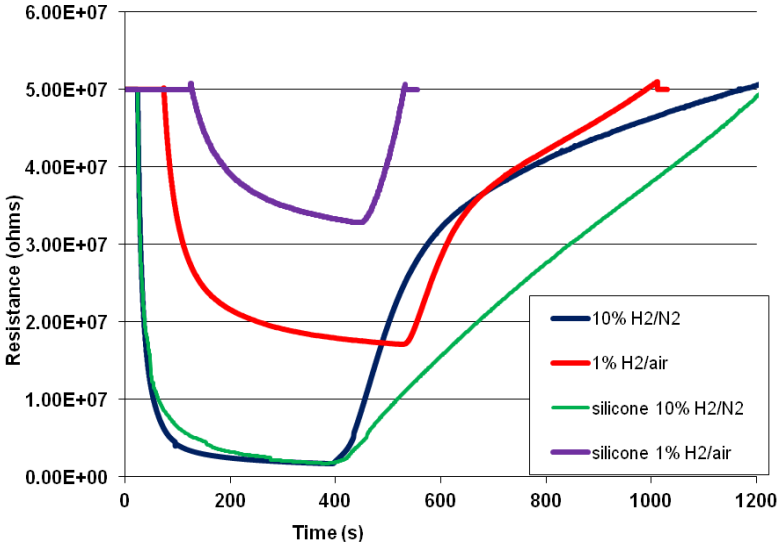

Figure 6 - Response curves for WO_3 based resistive sensor with and without silicone encapsulation as a function of H_2 concentration.

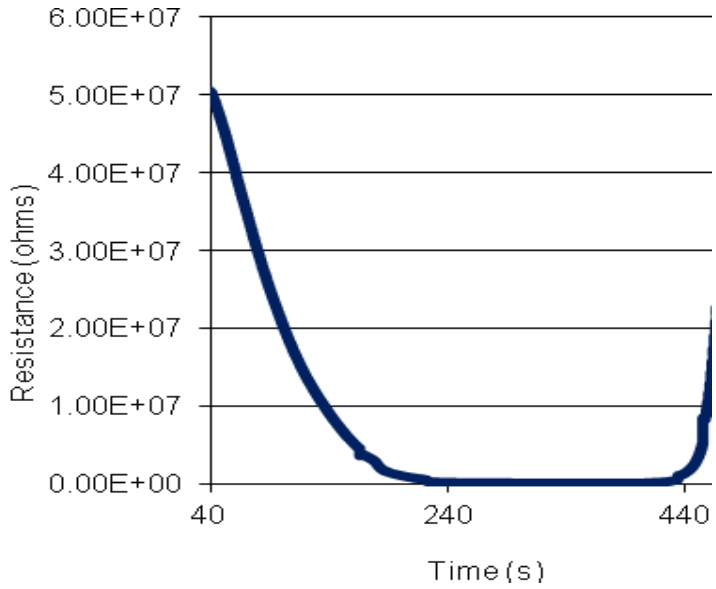

Figure 7 - Response curve for WO_3 based resistive sensor immersed in H_2 saturated water.

4.0 VISUAL THIN FILM HYDROGEN SENSORS

Element One's thin film sensors also dramatically change color in the presence of hydrogen. Figure 8 is an example of the recordings of the visual indicators' responses to flowing hydrogen/air gas mixtures at room temperature. The optical transmittance through the sample was measured continuously using an optical spectrophotometer. When the gas mixture was introduced into the sample holder the optical transmittance decreased exponentially. When the flow of hydrogen was replaced by a flow of air, the transmittance of these reversible (tungsten oxide) indicator films increased back to their original value.

We have found that such dynamic response curves are accurately fit by a bi-exponential function.[1] Each response curve has two characteristic time constants; one for the initial fast response in hydrogen and another for the slower, later response to hydrogen. By fitting the measured data to such analytic functions, we can characterize the response with a few kinetic parameters: the two time constants and the maximum decrease in transmittance (which depends upon film thickness).

[1] http://paulbourke.net/miscellaneous/functions/

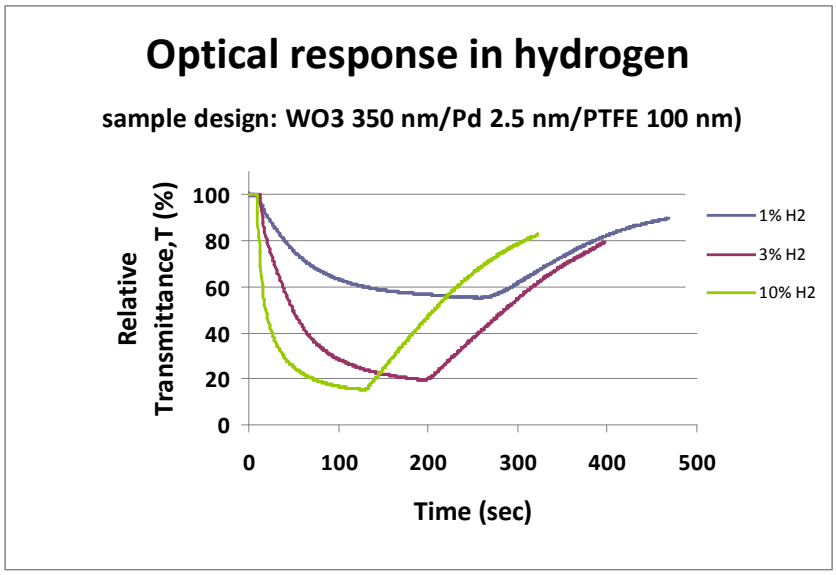

Figure 8 - Decrease in optical transmittance in different H_2 concentrations followed by recovery in air.

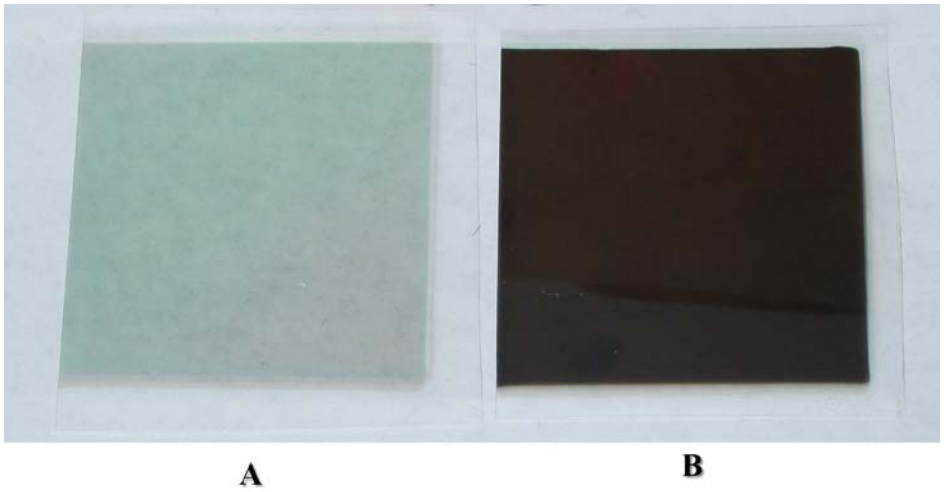

Figure 9 - Vacuum deposited visual indicators on clear plastic: A- unexposed; B- hydrogen-exposed

Figure 9 shows a side-by-side comparison of an unexposed, A, and a hydrogen-exposed, B, thin film visual indicator. Both indicators were vacuum deposited together and both consist of a 350 nm thick molybdenum oxide layer, a 1 nm thick layer of palladium catalyst, and is covered by a protective 100 nm layer of polytetrafluoroethylene. The optical transmittance (400-700 nm) of this un-exposed film is 70% and the transmittance of this hydrogen–exposed film is 24%.

Figure 10 shows how the speed of the hydrogen response increases with increasing hydrogen concentration and with increased palladium thickness. Note that the vertical axis is the dominant, initial faster ***time constant***; so lower values on the curve correspond to faster response.

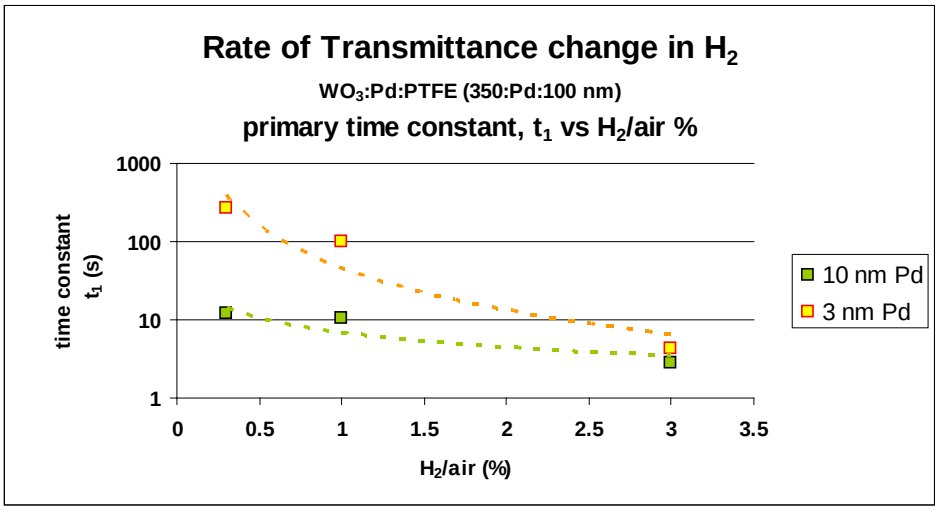

Figure 10 - Rate of change in optical transmittance as a function of H_2 concentration for WO_3:Pd:PTFE thin film samples.

Figure 11 shows an example of how the ultimate decrease in optical transmittance (how dark the indicator becomes) changes as a function of hydrogen concentration and catalyst thickness.

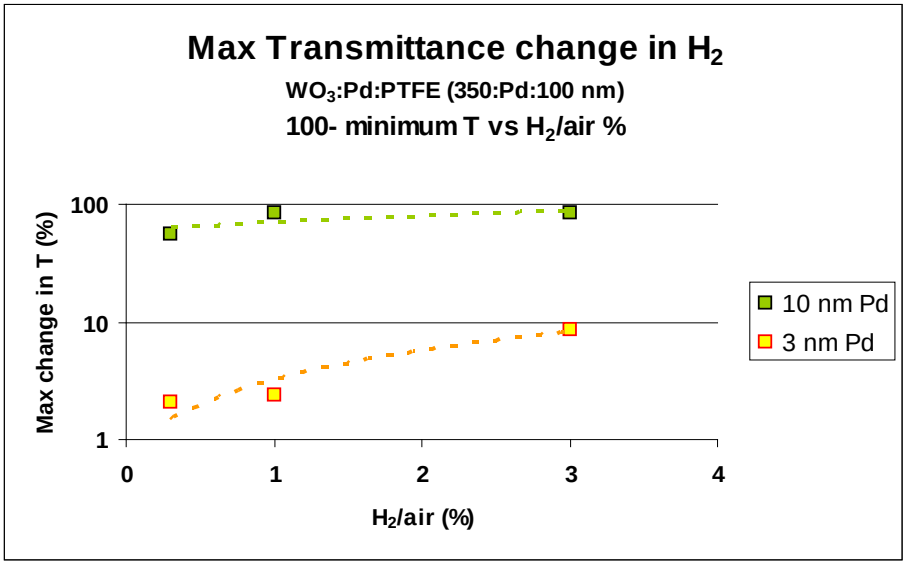

Figure 11 - The maximum change in optical transmittance when exposed to hydrogen/air mixtures.

We must also address the effect that atmospheric contaminants will have on the performance of the hydrogen indicators and sensors. The catalyst in our thin-film coatings and sensors is particularly susceptible to "poisoning" by gases that strongly adsorb to its surface. Perhaps the most well-known catalyst poison is hydrogen sulfide which is present in most industrial and transportation environments – even in household environments where it tarnishes the family silver.

A sample of the reversible indicator coating was exposed to a gas mixture of 10 ppm hydrogen sulfide in nitrogen for about one hour and then tested for its response to hydrogen. Figure 12 shows the response of this sample before and after the exposure to hydrogen sulfide. Notice that the response to hydrogen is little changed; but the recovery in air is greatly slowed.

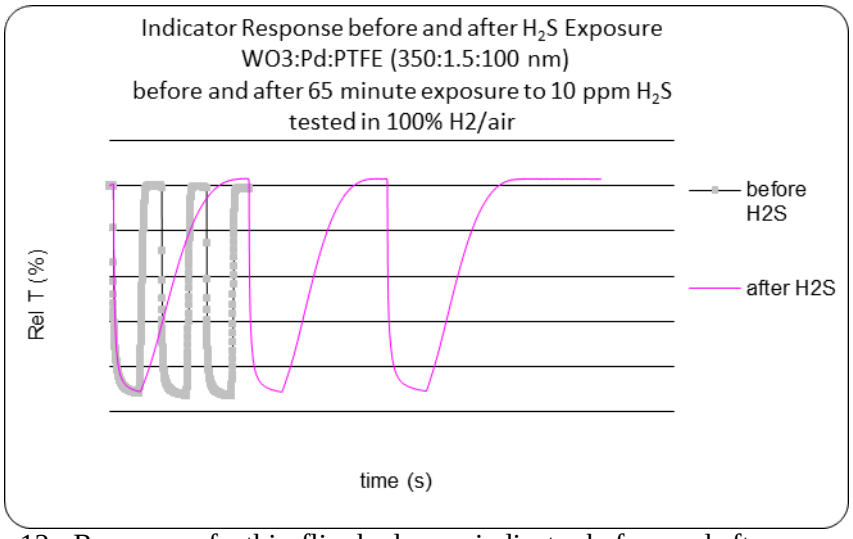

Figure 12 - Response of a thin-flim hydrogen indicator before and after exposure to H_2S

Tungsten oxide is a well-known oxidizing catalyst. Perhaps the reversible indicator's normally fast recovery is aided by the oxidative catalytic effect of the tungsten oxide and the hydrogen sulfide is poisoning that effect. In any case, the thin-film sensor's response to hydrogen appears to be fairly resistant to the worst of catalyst poisons even without the benefit of a protective encapsulant.

The thin film electronic sensors are based on the same chemistry as the visual indicators and can use much of the same film stack design principles. A thin-film electronic sensor was fabricated on ITO-coated glass so that both optical and electrical responses could be measured in the same sample simultaneously. Figure 13 shows how the optical transmittance and electrical resistance change together.

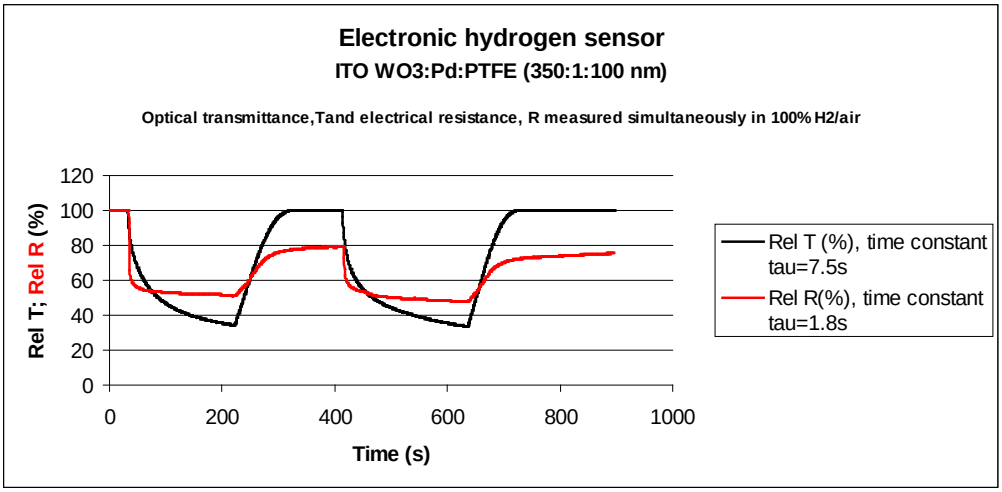

Figure 13 - Simultaneous recording of optical and electrical response of a thin-film hydrogen indicator/sensor

Figure 14 shows a portion of these same data with the optical transmittance plotted against the electrical resistance showing the one-to-one linear correlation between these two properties over much; but not all of the range of response.

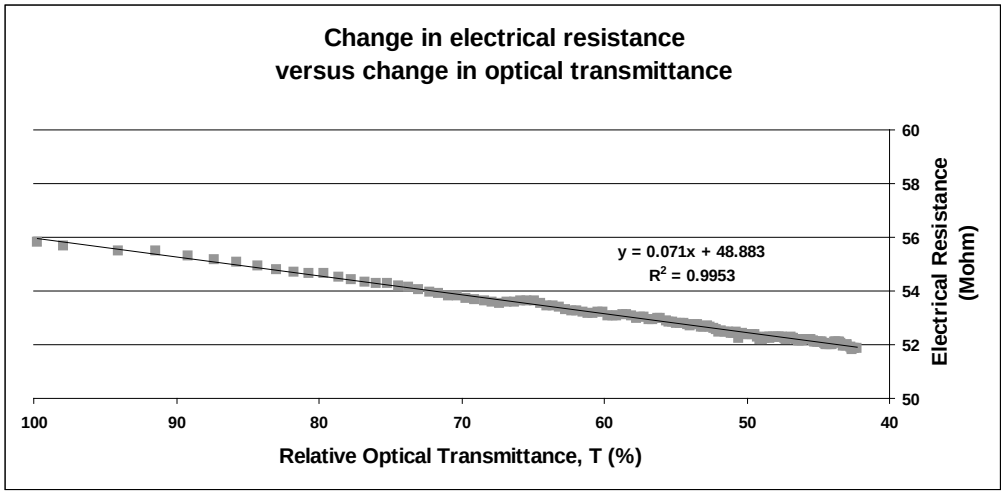

Figure 14 - Electrical resistance and optical transmittance during exposure to 100% hydrogen (data from figure 13).

An encapsulant is essential for the practical application of the thin-film visual indicator and the electrical sensors. The encapsulant must be resistant to environmental assaults; but also be permeable to the gases involved in the indicators and sensors: hydrogen (for response) and oxygen (for recovery of the reversible version). Fortunately, we found a suitable choice for encapsulant material in the silicone polymers. Table 1 compares the gas permeability of a number of types of polymers. The silicones stand out for their high hydrogen and oxygen permeability.

Polymer	Gas Permeability at 25°C, [cm³ (STP) mil]/(100 in²/day · atm)				Moisture Vapor Transmission
	N_2	O_2	CO_2	H_2	90% RH, 37°C, (g mil/100 in² · day) **
Parylene N	7.7	39	214	540	1.5
Parylene C	1.0	7.2	7.7	110	0.21
Parylene D	4.5	32	13	240	0.25
Epoxides	4	5 - 10	8	110	1.79 - 2.38
Silicones	—	50,000	300,000	45,000	4.4 - 7.9
Urethanes	80	200	3,000	—	2.4 - 8.7

Table 1 - Gas permeability of various types of polymers.

We have tested the silicone polymer encapsulant option. Figure 15 shows a comparison of the response speed of the thin-film electronic sensors with and without a 100 micron protective encapsulation of a silicone polymer. The vertical scale is the reciprocal of the time constant. Note that there is very little loss of response speed due to the silicone encapsulant.

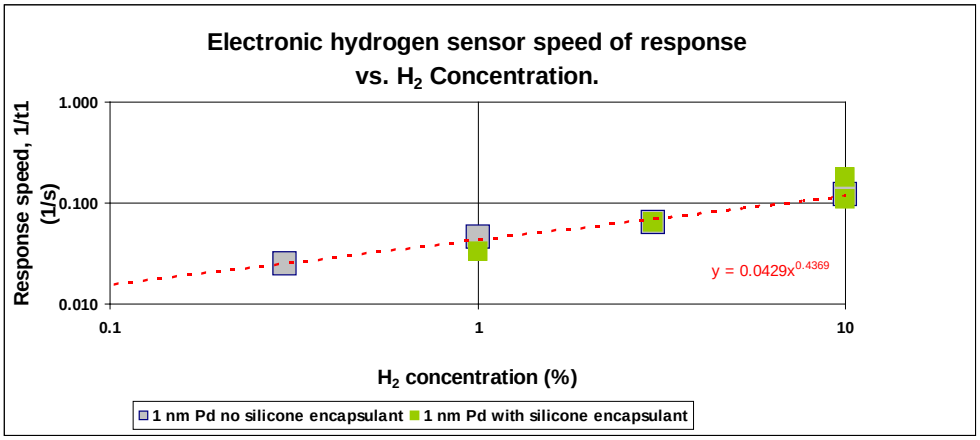

Figure 15 - Response speed of electronic hydrogen sensors with and without silicone encapsulant coatings.

Both the change in electrical resistance and the maximum change in resistance are little affected by the addition of the silicone encapsulant as shown in Figure 16.

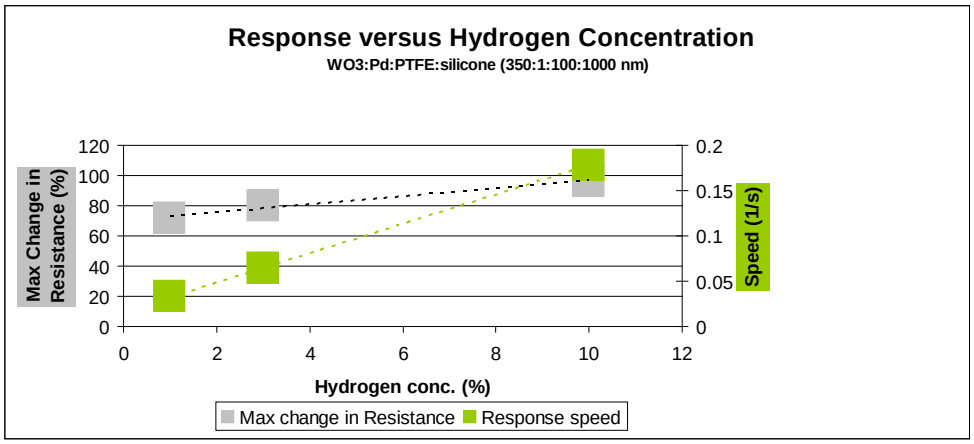

Figure 16 - Electronic sensor with silicone encapsulant - response speed and maximum change in resistance in hydrogen.

One of the most pervasive environmental hazards for a hydrogen indicator or sensor is water. We tested the silicone encapsulated electronic sensor after immersion in water and saw no adverse effect. We then tested the hydrogen sensor in hydrogen-saturated water and showed that it worked well to detect the dissolved gaseous hydrogen in the water (see Figure 17).

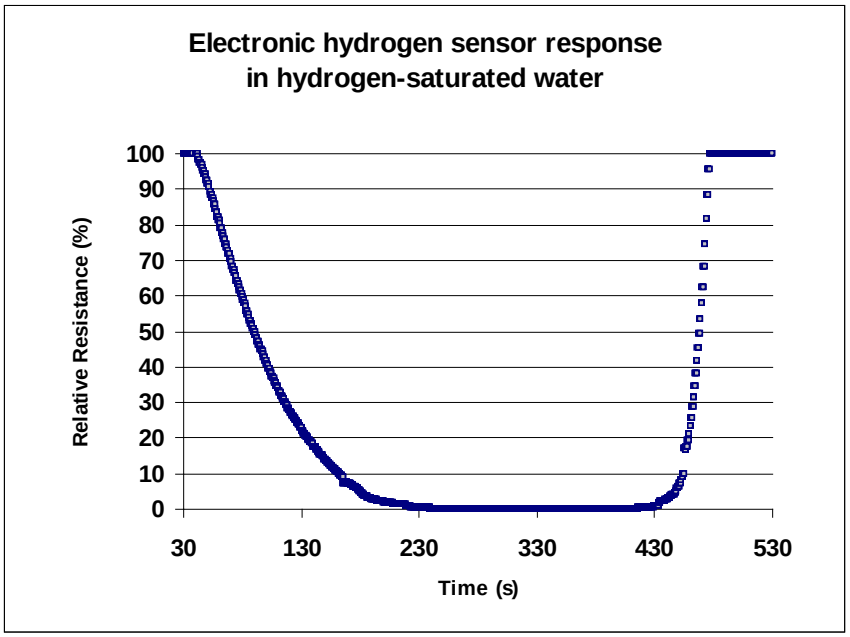

Figure 17 - Response of thin film electronic hydrogen sensor in hydrogen-saturated water.

The successful detection of hydrogen in water suggested testing the sensor's ability to detect hydrogen in other liquid media. Figure 11 shows the response of the hydrogen sensor in hydrogen-saturated mineral oil. The noise in the data is caused by stirring of the oil which is necessary to get the dissolved hydrogen to the sensor. Apparently, the dissolved hydrogen does not diffuse very rapidly in the mineral oil.

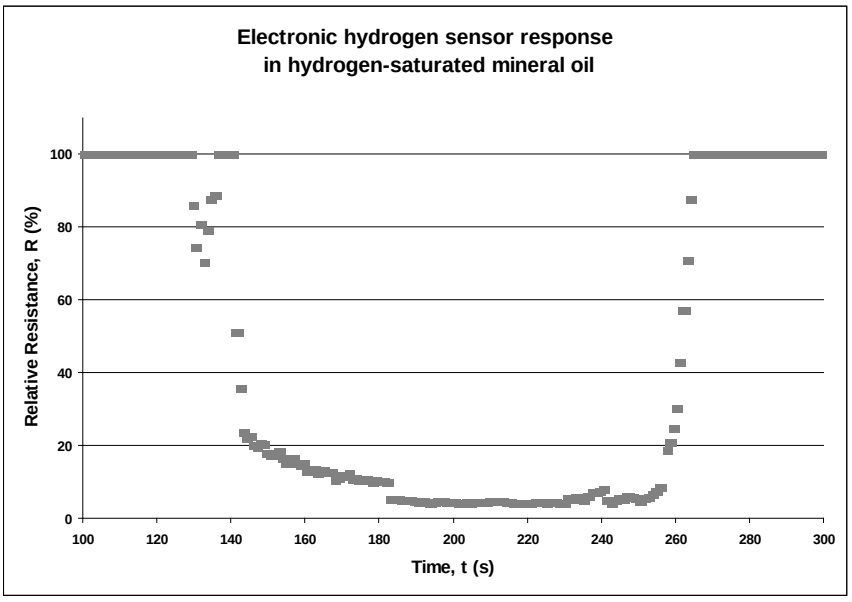

Figure 18 - Response of a silicone encapsulated thin-film electronic hydrogen sensor to hydrogen in hydrogen-saturated mineral oil.

5.0 INDICATORS/SENSORS FOR OTHER GASES

The majority of the work done so far has been on sensors for hydrogen detection. Current research at Element One is now directed toward other industrial gases, including both visual indicators and resistive sensors for hydrogen sulphide (H2S), visual indicator coatings for chlorine (Cl2) and ammonia (NH3) and acid-base indicator coatings. This is work in progress; however, it is hoped that testing will produce results suitable for publication in the near future.

6.0 CONCLUSION

At Element One, visual indicators and resistive sensors for detecting gaseous hydrogen have been developed and characterized. These thin film coatings and paints are suitable for indicating the presence of hydrogen at concentrations well below safe limits. New silicone based protective coatings help prevent catalyst poisoning and allow the use of both types of device in liquid environments.

Experimental results to date show that very low-cost hydrogen indicators and thin film sensors can be produced cheaply enough to be abundantly applied in close proximity to all potential leak sites where they will reliably detect leaks while still a maintenance problem and before they become a safety issue. Additional testing is needed on sensors with the silicone encapsulant coatings to determine the effectiveness of the PTFE/silicone combination on preventing ***long term*** degradation from environmental contaminants.

We have a design concept for the automatic temperature compensation of the electronic thin-film sensors; but have yet to evaluate its effectiveness. We have yet to characterize the performance of the prototype sensors over a broad temperature range.

Our sensors are simple in their electronic behavior. They are merely variable resistors and as such should be easily adapted to existing commercial wired and wireless sensor electronics. We have yet to select and work with an established sensor electronics manufacturer to integrate our sensors into a complete package.

6.0 REFERENCES

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2. Deb, S.K., Opportunities and Challenges in Science and Technology of WO_3 for Electrochromic and Related Applications, *Solar Energy Materials and Solar Cells*, **92**, 2008, pp. 245-258.
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