

NOVEL WIDE-AREA HYDROGEN SENSING TECHNOLOGY

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ABSTRACT

Element One, Inc. is developing novel indicators for hydrogen gas for applications as a complement to conventional electronic hydrogen sensors, or as a low-cost alternative in situations where an electronic signal is not needed. The indicator consists of a thin film coating or a pigment of a transition metal oxide such as tungsten oxide or molybdenum oxide with a catalyst such as platinum or palladium. The oxide is partially reduced in the presence of hydrogen in concentrations as low as 300 parts per million and changes from transparent to a dark color. The color change is fast and easily seen from a distance. In air, the color change reverses quickly when the source of hydrogen gas is removed in the case of tungsten oxide or is nearly irreversible in the case of molybdenum oxide. A number of possible implementations have been successfully demonstrated in the laboratory including hydrogen indicating paints, tape, cautionary decals, and coatings for hydrogen storage tanks. 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. The partially reduced transition metal oxide becomes semi conductive and increases its electrical conductivity by several orders of magnitude when exposed to hydrogen. The integration of this electrical resistance sensor with an RFID tag may extend the ability of these sensors to record and transmit a history of the presence or absence of leaked hydrogen over long distances. Over long periods of exposure to the atmosphere, the indicator's response may slow due to catalyst degradation. Our current emphasis is on controlling this degradation. The kinetics of the visual indicators is being investigated along with their durability in collaboration with the NASA Kennedy Space Center.

KEYWORDS: Hydrogen, sensor, detector, visual indicator, thin film, coating, tungsten oxide, molybdenum oxide

1.0 INTRODUCTION

Large quantities of hydrogen gas are used in numerous industries, and wherever hydrogen gas is used, detection of leaks is important. Most hydrogen gas detectors currently in use are electronic, so that they can trigger safety devices such as shutoff valves and alarms. However, there are many situations where a visual indicator of a hydrogen leak may be sufficient, or where such an indicator could be a useful complement to electronic leak detectors.

In this paper we describe a set of visual hydrogen gas indicators [1] now under development and show some potential applications. We have measured the kinetics of these developmental hydrogen gas indicators and are attempting to understand the mechanisms involved to assist in the development of durable indicators.

A visual indication of hydrogen gas may be helpful in several situations:

- To detect and remedy a gas leak when it is not an immediate safety concern (e.g., during construction and maintenance);
- To complement electronic sensors which may have responded to hydrogen gas presence over a large area (e.g., locating the specific source of a leak after detection by conventional sensors or routine inspections);
- To detect and locate a hydrogen leak too small for conventional electronic detectors that may not be sensitive enough or present, but nevertheless the leak must be detected and located; and,

- To provide reassurance in areas where a leak is unlikely to be a safety concern, but where the signaled *absence of a leak* could ease the concerns of a gas user (e.g., on the refueling door and fittings of a hydrogen vehicle or on the refueling nozzle of a dispensing station), facilitating public acceptance and allaying fears of hydrogen fuel.

2.0 POSSIBLE APPLICATIONS AND PROTOTYPICAL DESIGNS

Element One's visual hydrogen gas indicators use thin films or suitably sized particles of a transition metal oxide, such as tungsten oxide which changes color reversibly in air or molybdenum oxide which yields a color change that is not reversible under normal ambient conditions. Non-reversible indicators may be used in conjunction with a reversible indicator to provide current as well as historical information about leaking hydrogen.

A very thin coating of platinum or palladium is applied to the metal oxide to catalyze its reaction with hydrogen. A typical thin film indicator consists of a transparent polymer substrate, a 500 nm thick layer of tungsten oxide, a 3 nm layer of palladium catalyst, and a 100 nm thick protective coating of poly-tetrafluoroethylene (PTFE). The tungsten oxide layer is nano-porous. The semitransparent catalyst layer is discontinuous, consisting of nano-scale islands on top of the metal oxide. The very thin PTFE partially protects the catalyst from poisoning by atmospheric pollutants. It also tends to stabilize the thin film stack against abrasion by providing a low friction surface. All of the layers are deposited by thermal vaporization in vacuum.

Nano-particles of tungsten oxide are made commercially by gas-phase plasma reaction in vacuum and are subsequently coated with a partial layer of platinum or palladium catalyst by conventional chemical techniques [2]. These nano-particles are typically 50 nm in diameter and can be used as pigments in indicator paints and inks. Recent work has indicated that reagent grade metal oxide powder in the range of 10-100 μm particle size may also be used to achieve suitable pigments for use in specialty coatings or indicating paints.

Element One's thin film indicators also change resistance dramatically and may be used to provide an electrical indication of hydrogen gas. They may be incorporated into a Radio Frequency Identification Device (RFID) to achieve a low cost, remotely monitorable sensor. Such RFID tags could be deployed to create a low cost network. With such RFID indicators, it becomes possible to monitor many points for leaking hydrogen by placing such tags in close proximity to potential leak sites. Such a network could monitor a wide area for leaking hydrogen, even where it is not detectable by conventional wide area combustible gas sensors.

Below are two examples of how the visual indicator could be used to detect leaks:

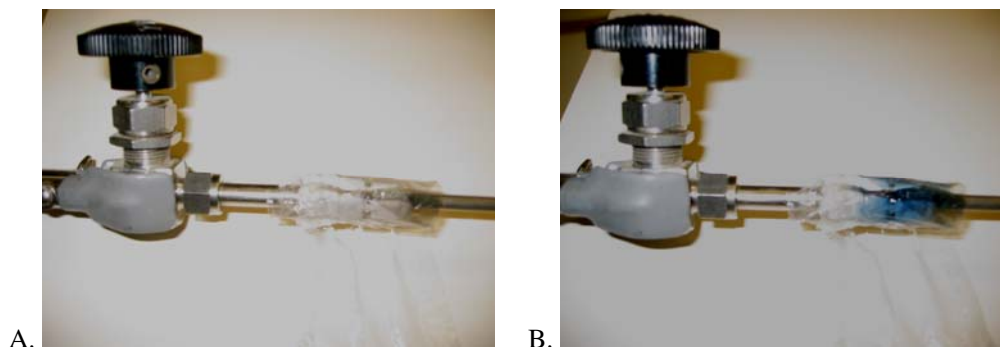


Figure 1. Hydrogen indicator thin film $\text{WO}_3\text{:Pd}$ coated stretch film wrapped around a leaky coupling: A (before) and B (after) admitting forming gas (10%)

H₂ in N₂). The dark coloration of the plastic film in B is the bright blue indicator.



Figure 2. A low-pressure cylinder wrapped with thin film WO₃:Pd coated indicator "shrink wrap" film. A (before) and B (after) admitting low pressure forming gas to the cylinder. The cylinder has an intentional 57 micron hole near the laser pointer spot on B. Notice the darker indicator pattern in B that developed within a few seconds of pressurizing the cylinder.

3.0 REACTION MECHANISMS

Tungsten and molybdenum tri-oxides (WO₃ and MoO₃) are well known chromogenic materials – meaning that they undergo color changes under various circumstances. These color changes result from a change in the oxidation state of some of the metal ions in the normally transparent crystalline oxide. Partial reduction of the oxide replaces some of the 6+ metal ions with +5 ions. Because of the high dielectric constant of the crystalline oxide, a free electron in the vicinity of a +5 ion is trapped in a polarization field around the ion. This kind of trapped electron is called a 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 oxide lattice spreads the optical transitions into a broad absorption band that peaks in the near infrared and extends into the red portion of the visible spectrum. Consequently, the partially reduced oxide turns from white to blue to black.

Crystalline WO₃ and MoO₃ can be partially reduced by heating in a non-oxidizing atmosphere, electrochemically in a cell configuration, or by chemical reaction with a reducing agent such as lithium or hydrogen. Thin films of WO₃ have been used in various applications. In electrochromic windows the WO₃ film is reversibly darkened by applying a small voltage across a multi-layer thin film electrochemical cell made up of the WO₃, a solid electrolyte and a counter-electrode layer all of which are applied to the window glass in a vacuum deposited multi-layer coating [2]. In a similar application, "gasochromic" windows can be dimmed by reversibly introducing hydrogen gas into the sealed gap between glass panes of a sealed insulating glass window [3]. A thin coating of WO₃ and platinum or palladium turns dark in the hydrogen gas. WO₃ thin films have also been used in various designs of hydrogen gas detectors including the authors' designs for a fiber-optic hydrogen detector [4], a bio-hydrogen screening device [5], and a detector for hydrogen gas dissolved in welded metal [6]. In each of these designs, a catalyst is applied to the thin film WO₃ to increase its reaction rate with

hydrogen gas. The molybdenum oxide has found fewer applications because it is more difficult to reverse its reduction. However, for some hydrogen detection applications this irreversibility is advantageous.

4.0 RESPONSE KINETICS

Different applications for the indicator will have different requirements for both speed and durability. Response kinetics and their changes over the useful life of the indicator are keys to meeting the performance requirements in any application and an improved understanding of the basic kinetics of response is an important aspect of their development. We have concentrated on the tungsten oxide based indicators because of their wider range of applications; but the chemistry of the molybdenum oxide and the response of indicators based on it are expected to be similar.

Dynamic measurements were made of changes in optical absorption of prototype indicators under exposures to different concentrations of hydrogen gas mixtures. By analyzing the response curves in detail and fitting them to mechanistic models, we have improved our understanding and gained useful guidance for our product development. The basic measurement is a recording of the optical transmittance of a test coupon as it is exposed to hydrogen. Figure 3 shows two views of the apparatus.

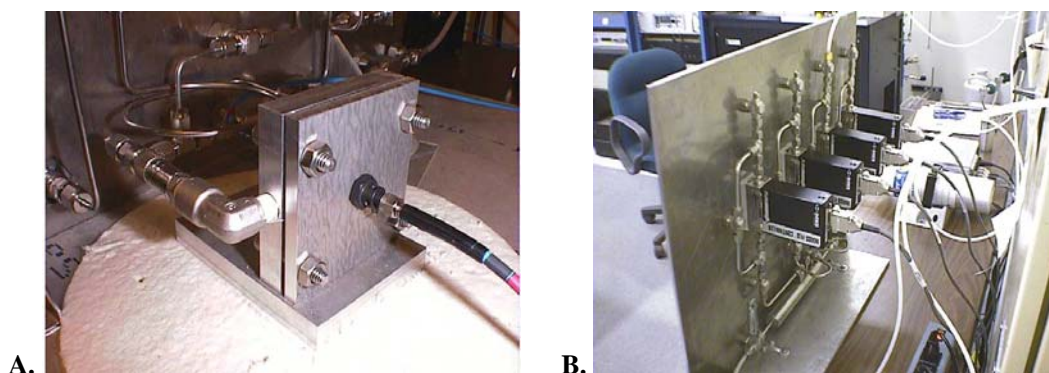


Figure 3. A, Sample holder with gas lines and optical fibers: B, gas manifold with mass-flow controllers

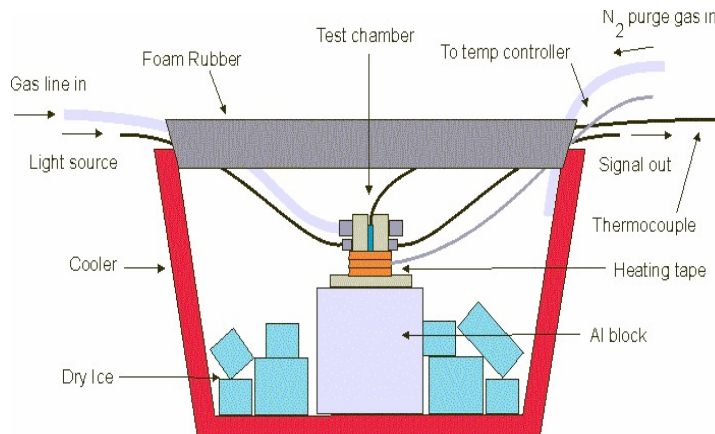


Figure 3a. Schematic of experimental setup.

A schematic of the experimental setup is shown in Figure 3a, above. The sample is housed in a simple fixture that clamps it between a backing plate and an o-ring sealed chamber of less than one cubic centimeter volume. The premixed gas mixture is fed through the chamber from a manifold of mass-flow controllers. Each of the controllers controls the flow of a different gas from the bank of compressed gas cylinders so that we may supply the desired mixture to the sample chamber reproducibly. The temperature is set with an Omega temperature controller that is accurate to 1 degree. Higher temps are achieved using heating tape; lower temps by placing the sample chamber in an insulated container and cooling with dry ice. The temp controller/heating tape is also used for the lower temps. The time constant of the instrumental component was not measured, but all data is consistent. All measurements were made at 150 sccm flow rate of both hydrogen and purge gas. The sample chamber is only ~ 1cc in volume.

The optical transmittance is measured with a spectrometer that is capable of measuring and recording the full spectrum from about 500 nm to 1100 nm each fraction of a second repeatedly throughout the exposure period. The light source is directed to the sample by an optical fiber and the transmitted beam is collected by another optical fiber connected to the optical spectrometer. Because the optical absorption spectrum of the sample is so broad and changes primarily in amplitude rather than in spectral detail, it is sufficient to make dynamic measurements at a single wavelength. We typically use 840 nm as the measurement wavelength because this is near the peak of the absorption band and is the peak wavelength of a convenient diode infrared laser light source (Fig. 4).

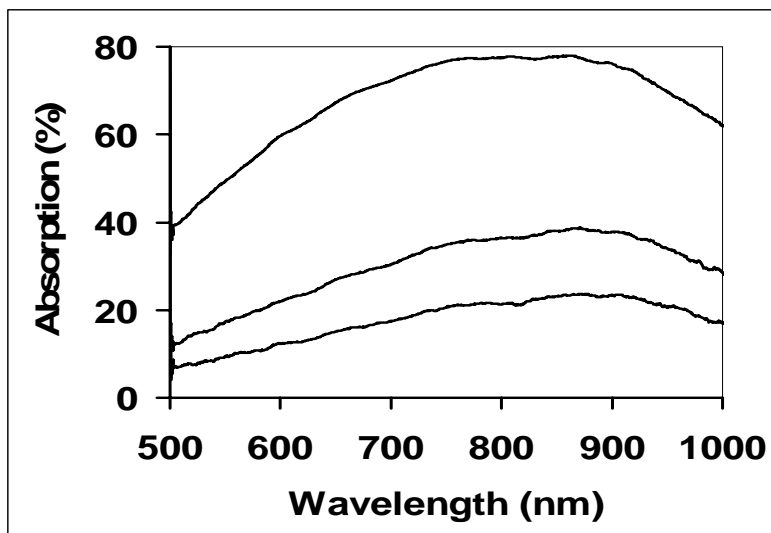


Figure 4. Optical absorption of a WO_3 indicator film at intervals during brief exposure to hydrogen.

Figure 5 shows a typical recording of transmittance vs. time for a nano-particle $\text{WO}_3\text{:Pt}$ powder dispersed on a filter paper.

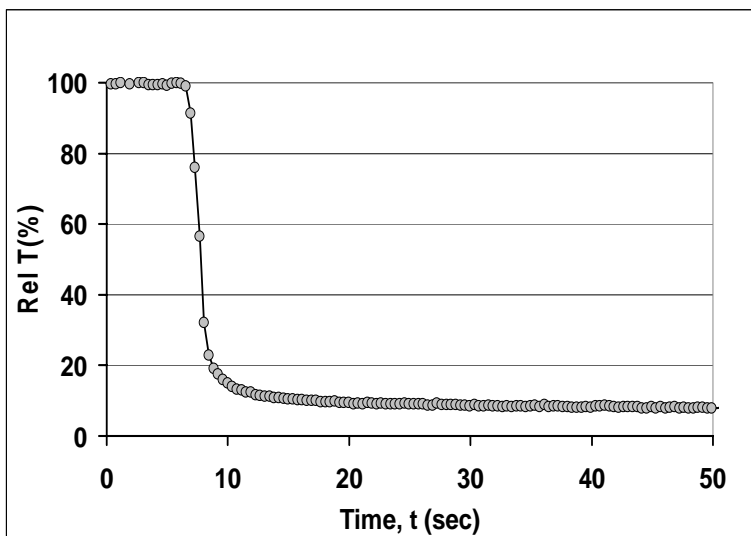


Figure 5. Transmittance of a nano-powder $\text{WO}_3\text{:Pt}$ dispersed on a filter paper and exposed to 0.5% H_2/N_2 mixture

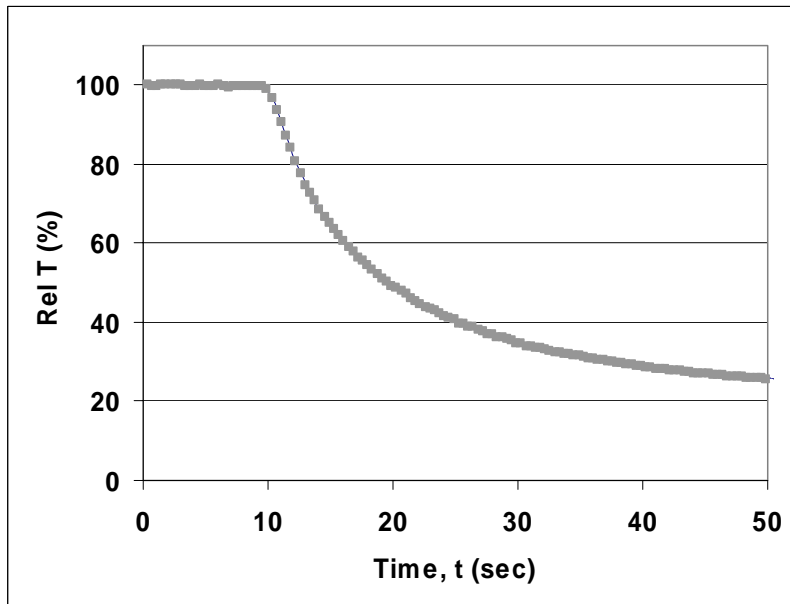
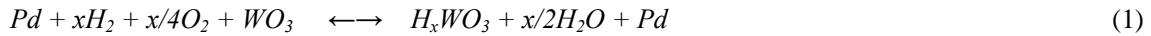


Figure 6. Transmittance of a $\text{MoO}_3\text{:Pt}$ powder pigment dispersed on a filter paper and exposed to 0.5% H_2/N_2 mixture

The transmittance of the sample decreases as the sample becomes more deeply colored. The rate of change in the transmittance reflects the rate of chemical reaction occurring in the oxide.

The tungsten oxide chemical reaction in a hydrogen/air mixture can be represented as:



From the simple nature of the chemical reaction the rate is expected to be first-order and the response is expected to exhibit an exponential shape as indeed it does. The recording may be fit to an exponential function to determine a characteristic time constant for the reaction. The simplest fitting function is:

$$T(t) = T_0 + A_1 \exp(-(t-t_0)/\tau) \quad (2)$$

Where the time constant, τ , is the time it takes for the transmittance to change by $1/e=1/2.718=0.37$ of the total maximum change in transmittance. The time constant for the powder sample in Figure 6 is 0.78 seconds. The maximum change in transmittance is dependent on the thickness of the WO_3 layer in the indicator as well as the concentration of the hydrogen in the gas mixture.

However most of our indicators have a somewhat more complex response. Figure 7 shows another indicator response measurement that is better fit by a combination of two different exponential functions:

$$T(t) = T_0 + A_1 \exp(-(t-t_0)/\tau_1) + A_2 \exp(-(t-t_0)/\tau_2) \quad (3)$$

This type of response function is characteristic of two parallel first-order reactions – a faster reaction and a slower reaction.

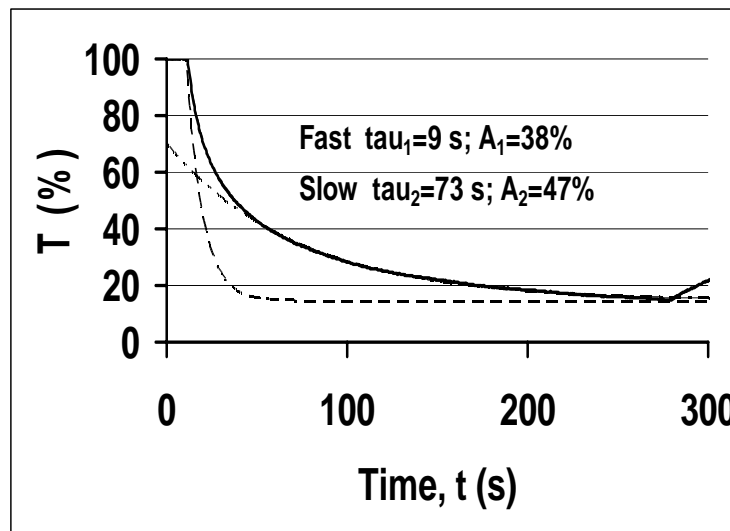


Figure 7. Response of a thin film WO_3 :Pd indicator to 0.5% H_2/N_2 showing both fast and slow components

We speculate that two different reaction rates occur because there are two different kinds of sites where the hydrogen actually reacts with the WO_3 . The hydrogen gas first reacts with the catalyst where it is dissociated into atomic hydrogen. This atomic hydrogen may diffuse *through* the catalyst to the catalyst/ WO_3 interface and react there or it may diffuse *over the surface* of the catalyst and react at the edge of the catalyst island where the free surface of the catalyst meets the free surface of the WO_3 . These two different kinds of reaction sites would be expected to have significantly different reaction kinetics.

As is to be expected from the simple chemical reactions, the speed of reaction increases with hydrogen concentration (e.g. the time constant *decreases*). Figure 8 shows the measured time constant as a function of hydrogen concentration. The speed of response is proportional to the square root of the hydrogen concentration as would be expected from the hydrogen molecule dissociation step in the reaction (Eq. 1).

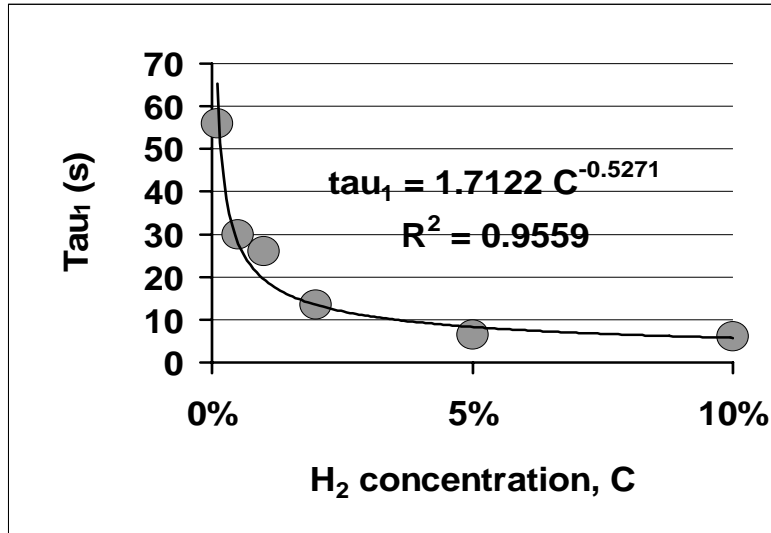


Figure 8. The speed of WO₃:Pd response is proportional to the square root of hydrogen concentration.

The response slows as the hydrogen concentration is decreased exhibiting a lower response limit of about 300 ppm H₂ in air as shown in Figure 9.

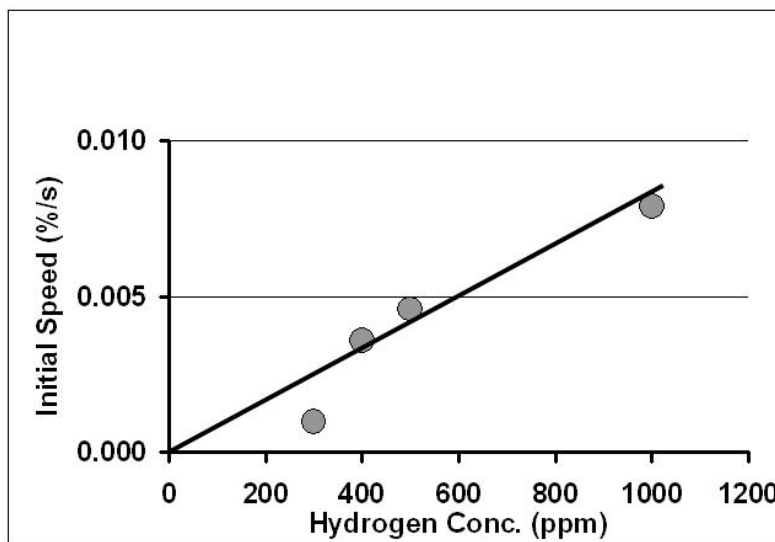


Figure 9. The thin film WO₃:Pd indicators show a response limit near 300 ppm H₂ in air

The reaction rate also increases with temperature as would be expected. Figure 10 shows that the temperature dependence changes at around 15°C - the dependence changing more rapidly at lower temperatures than at higher temperatures.

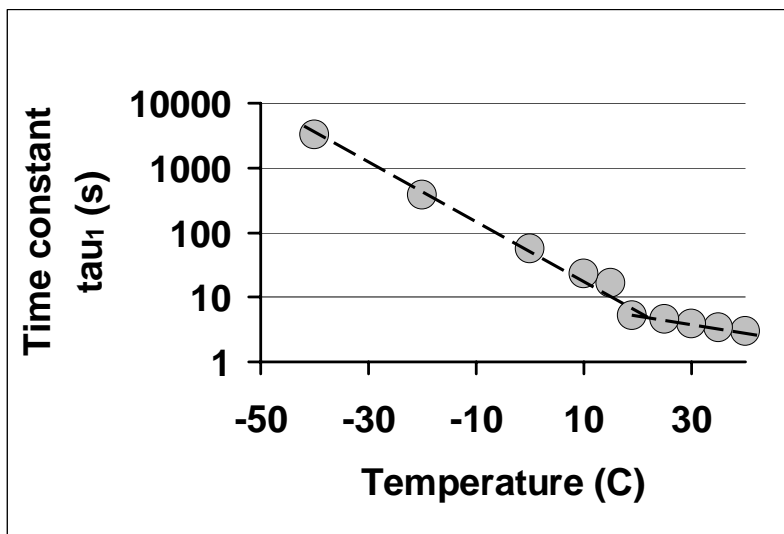


Figure 10. Temperature dependence of $\text{WO}_3\text{:Pd}$ response

If we plot these same data on a log scale versus reciprocal temperature (Figure 11) we can see that the two segments of temperature dependence show two different thermal activation energies – a higher energy barrier for the reaction at temperatures below 15°C and a lower barrier above 15°C. The change may be due to the presence of a layer of water on the surface of the indicator at temperatures below the dew point. The water forms as a result of the reaction (Eq. 1) and may retard the further reaction of the hydrogen by competing for reaction sites on the catalyst surface and also by favoring the back reaction.

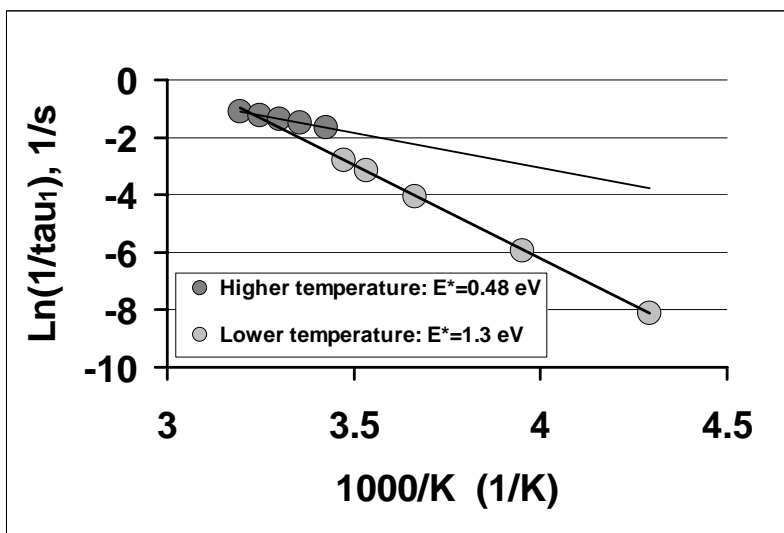


Figure 11. Arrhenius plot of $\text{WO}_3\text{:Pd}$ response speed and temperature

If an indicator is stored in sealed packaging (such as a resealable polypropylene bag), the response changes very little over time, or not at all. However, if an indicator is exposed to the environment for a long period of time, its response slows significantly. This slowing is, at least in part, due to contamination by chemicals in the environment that adsorb strongly to the catalyst and block subsequent hydrogen reactions. Chemicals that are known to be particularly troublesome are sulfur bearing compounds such as H_2S , mercaptans and thiols, some hydrocarbons, and CO. The very thin PTFE top layer of our indicators helps to retard such contamination, but does so imperfectly. Thicker protective layers and more dense protective layers applied by chemical vapor deposition slow the rate of contamination more, but also slow the indicator response.

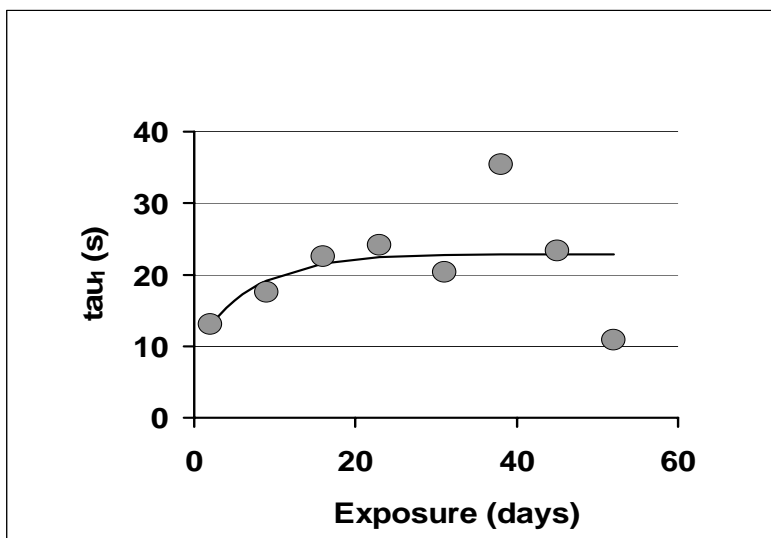


Figure 12. Changing WO_3 :Pd response speed during exposure to laboratory air (tested in 0.5% H_2/N_2)

Figure 12 shows the trend of a thin film indicator's time constant over several weeks during which it was exposed to the laboratory air. There is a significant and variable change in the response time constant. Sometimes the variability can be associated with the changes in the chemicals being used in adjacent laboratory spaces. For example, a sudden increase in time constant was noted when a fellow chemist used thiols in a fume hood within our laboratory (see the data points at days 38 and 52). The time constant increased by more than 50 % over a couple of days and then paradoxically recovered to a faster response within a couple of weeks. This kind of behavior is probably due to the reversible catalyst contamination by the errant thiol vapors.

The indicator paints are significantly different from the thin film indicators. Prototype indicator paints require a trade-off between protection from environmental contamination and sensitivity to hydrogen. The polymer of the paint must exclude contaminants while admitting the hydrogen for reaction with the pigment particles embedded in it. The early prototype indicator paints show much reduced speed of response to hydrogen and require further refinement. Figure 13 shows the response of prototype paints to 10% H_2/N_2 .

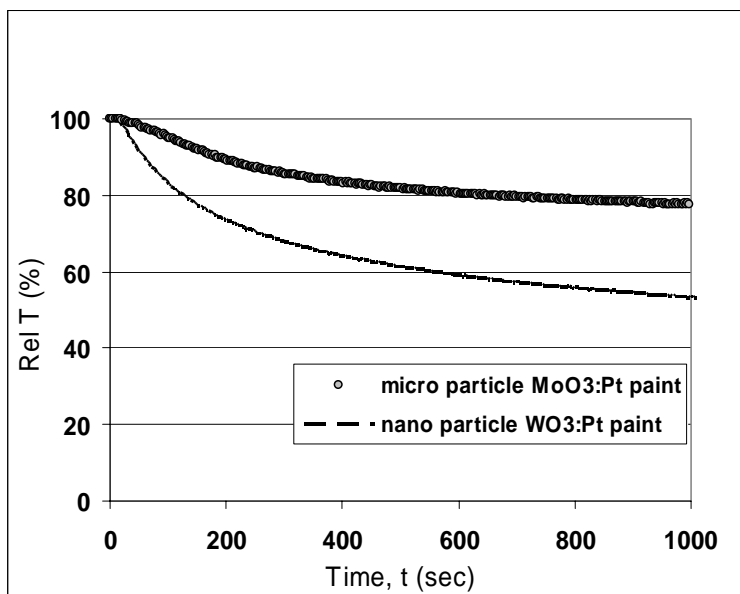


Figure 13. Response of prototype indicator paints to 10% H₂/N₂.

5.0 ONGOING R&D

Prototype thin film indicators on transparent plastic substrates appear to be suitable for wrapping and “shrink wrapping” applications without much further improvement. These applications do not require long term exposure to the environment because the sensitive coating is on the *inside* of the wrap and is mostly protected from the environment. Other indicator applications requiring long term exposure to the environment require better protection against contaminants.

In collaboration with development partners and NASA KSC we are developing various forms of indicators that can retain their speed and sensitivity after long periods of exposure to the environment. We are focusing on the development of improved protective coatings that remain highly permeable to hydrogen. These coatings include chemical vapor deposited polymer coatings for the thin film indicators and for the pigment particles themselves as well as the development of paint formulations that can provide the necessary environmental protection to the imbedded pigment particles. The most recent paint formulation using nano-particle WO₃:Pt in a water-based PVA paint shows a time constant of 40 seconds in 10% H₂/N₂ whereas the bare pigment powder has a time constant of 0.78 seconds in 0.5% H₂/N₂. More work is required to optimize these paint formulations.

5.1 Developing hydrogen leak detectors for NASA

Element One is working with NASA to evaluate our indicators for use in detecting leaks during launch operations. The initial stage of this work is concentrating on the durability of our leak indicators in the harsh environment of the Kennedy Space Center. Significant progress has been made toward development of hydrogen gas indicators for a number of the identified NASA KSC safety applications. Of particular utility to NASA is the irreversible indicator chemistry based on platinum-catalyzed molybdenum oxide. During their fuelling operations personnel are excluded from areas prone to hydrogen leaks. The irreversible hydrogen leak indicators may help to identify where leaks have occurred during the fuelling operation and thereby facilitate maintenance and repairs. Chemical vapor deposited PTFE protective coatings for the thin film hydrogen indicators and special water-based PVA paint formulations are undergoing environmental exposure testing at the seacoast KSC Corrosion Test Site. Repeated environmental exposure and testing of these samples should help us to identify the best

combination of material, thickness and density needed to assure indicator durability in the KSC environment.

6.0 CONCLUSIONS

Prototype visual indicators of gaseous hydrogen have been developed and characterized. Thin film tungsten oxide and molybdenum oxide coatings on transparent polymers are suitable for indicating the presence of hydrogen at concentrations well below safe limits. Fine powder pigments of tungsten oxide or molybdenum oxide with small amounts of added platinum catalyst have been used as the basis for sensitive hydrogen indicator paints. In applications where the indicator need not be exposed to the environment for many days, the response of some of these indicators is fast and reliable. However, the present developmental indicators become slower if they are exposed to the environment for long periods of time. The rate of slowing depends upon the nature of the environment as well as the design of the indicator. Chemical vapor deposited PTFE films and special paint formulations show promise for providing the necessary protection to make these indicators useful for long term applications in demanding environments. We are working with NASA to improve the durability of the indicators.

REFERENCES

1. Hoagland, W., *Hydrogen gas indicator system*, US Patent 6,895,805, May 24, 2005.
2. See Sage Electrochromics, Inc. at <http://www.sage-ec.com>
3. Lee, S., Hyeonsik, M., Cheong, P. L., Smith, R. D., Tracy, C. E., et al., Gasochromic mechanism in a-WO₃ thin films based on Raman spectroscopic studies, *J. Applied Physics*, V 88, No. 5, September 1, 2000, pp. 3076-3078.
4. Benson, D. K., Bechinger, C. and Tracy, C. E. *Fiber optic device for sensing the presence of a gas*, US Patent 5,708,735, January 13, 1998.
5. Seibert, M., Benson, D. K., and Flynn, T. M., *System for Rapid Biohydrogen Phenotype Screening of Microorganisms Using a Chemochromic Sensor*, US Patent 6,448,068, September 10, 2002.
6. Smith, R. D., Benson, D. K., et al, The determination of hydrogen distribution in high-strength steel weldments part 2: opto-electronic diffusible hydrogen sensor, American Welding Society, <http://files.aws.org/wj/supplement/SmithPart2-05-01.pdf>.