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A Survey and Analysis of Commercially Available Hydrogen Sensors

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SUMMARY

The performance requirements for hydrogen detection in aerospace applications often exceed those of more traditional applications. In order to ascertain the applicability of existing hydrogen sensors to aerospace applications, a survey has been conducted of commercially available point-contact hydrogen sensors, and their operation has been analyzed. The operation of the majority of commercial hydrogen sensors falls into four main categories: catalytic combustion, electrochemical, and semiconducting oxide sensors and thermal conductivity detectors. The physical mechanism involved in hydrogen detection for each main category is discussed in detail. From an understanding of the detection mechanism, each category of sensor is evaluated for use in a variety of space and propulsion environments. In order to meet the needs of aerospace applications, the development of point-contact hydrogen sensors that are based on concepts beyond those used in commercial sensors is necessary.

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INTRODUCTION

The detection of hydrogen leaks in aerospace applications, especially those involving hydrogen fuel propulsion systems, is of extreme importance for reliability, safety, and economic reasons. The performance requirements for the sensor depend greatly on the application. Parameters such as sensitivity, ambient atmosphere, temperature, response time, and size, weight, and power restrictions vary considerably from application to application. The required sensor sensitivity may range from the detection of trace amounts of hydrogen (on the order of parts per million (ppm)) to levels near the lower explosive limit, or LEL, (4% H_2 in air) and even to concentrations of 100%. The ambient atmosphere surrounding the sensor may be helium, nitrogen (N_2), air, or even a vacuum. The temperature range may also vary considerably: Gas emerging from a liquid hydrogen line or into a space environment may be at cryogenic temperatures, whereas in other applications the gas is at room temperature. The response time required also depends on the application. A several-second response time may be adequate if the hydrogen concentration does not change rapidly, but in situations where the hydrogen concentration may quickly become hazardous, rapid response times are necessary. Size, weight, and power consumption may be a factor, depending on the leak location: In storage locations with sufficient room and power supply, a mass spectrometer may be an ideal way to monitor the hydrogen level. However, for applications involving remote or confined locations or on space vehicles, compact sensors with limited size and power requirements are preferred. Therefore, the conditions under which hydrogen sensors must function vary greatly in aerospace applications. A sensor that works well in one application may not be adequate in another.

An example of the range of conditions in which a hydrogen sensor must function in aerospace applications that illustrates the lack of a "universal" sensor is the hazardous gas detection system (HGDS) for the Space Shuttle (ref. 1 and personal communication from W. Helms). This system is used to prevent an explosive situation associated with the launch of the Space Shuttle orbiter. In order to detect an explosive situation, sensor sensitivity to 4% H_2 (LEL) in air is mandatory, but further sensitivity is necessary to warn of potentially hazardous situations. A "red flag" warning is set off at a hydrogen concentration of 2%, or 50% LEL. The sensor must continue to be operable even after exposure to hydrogen concentrations as high as 100%, such as would be encountered directly at the leak location.

The hydrogen concentration must be determined in several different environments. An array of 60 catalytic combustion sensors monitor leaks at near room temperature in air above all flanges in the main propulsion system. However, as discussed later, these sensors are inoperative in oxygen-deficient regions purged with helium (He), such as the umbilical cavities associated with liquid hydrogen lines. The temperature of the leaking gas in these cavities ranges from cryogenic at the leak location to room temperature farther from the leak. A totally different type of leak detection technique from the catalytic combustion sensor is necessary for monitoring gas concentration in these regions. The technique presently used is monitoring the hydrogen concentration with a mass spectrometer. The detection limit of this system is 200 ppm hydrogen over a range of 1 to 50 000 ppm. However, leak detection using a mass spectrometer in this application faces a number of problems. A mass spectrometer used in these regions must sample gas remotely through a pumping system connected to a number of sampling tubes. This decreases the speed of response owing to the travel time for the gas to reach the mass spectrometer. The leak detection is also complicated by the insulation covering the liquid hydrogen lines: The location where hydrogen leaves through the insulation and interacts with the sampling tubes may not be where the leak originates. Further, these lines must be disconnected shortly before launch, so that for a time hydrogen leaks are not monitored. Alternatively, detection of gas generated from leaks in the liquid hydrogen lines might be facilitated by a series of point-contact sensors placed inside the insulation or even on the surface of the supply lines if a suitable point-contact sensor could be found. Therefore, the varying environment on the Space Shuttle while on the launch pad means that the leak detection solutions that operate well in one part of the launch pad are problematic in another and each approach faces its own complications.

Motivated by leaks occurring in liquid hydrogen lines supplying the Space Shuttle main engine, NASA Lewis has been investigating the availability, method of operation, and range of application of point-contact hydrogen sensors. The emphasis on point-contact sensors is due to their small size, low power consumption, and versatility. The focus of the program thus far addresses not only the Space Shuttle applications but aerospace applications in general. Therefore, the properties of these sensors should be investigated throughout the environments present in the broad range of applications discussed previously. These include a hydrogen gas concentration from the parts-per-million range to 100%; an ambient atmosphere surrounding the sensor consisting of helium, nitrogen, air, or vacuum; and hydrogen gas temperatures from liquid hydrogen temperature to room temperature. Other factors to consider include response time, power consumption, and size limitations.

This report presents the results of a recently conducted survey of commercially available point-contact hydrogen sensors. This survey was not meant to be an analysis of all available commercial sensors but rather a discussion of the major types of point-contact sensor technology.

It was concluded that none of the sensors can meet all the needs of aerospace applications. The major limitations of catalytic combustion sensors are their need for oxygen and limited detection range. Electrochemical sensors have many favorable properties, but their temperature limitations and dependence on liquids are significant drawbacks. Semiconducting oxide sensors are limited in their detection range and need a stable temperature and oxygen concentration. The thermal conductivity detectors, which generally have a slower response time than the other techniques, have difficulty detecting hydrogen in helium. Although each of these sensors may perform well in a given environment, no single system is operable throughout the varied environments that are necessary in aerospace applications. In particular, operating a commercial point-contact hydrogen sensor in a low-temperature, helium-purged environment is not feasible. An example of the size, weight, and power requirements is given for each sensor category in appendix A. Appendix B shows which sensors are usable in a few limited applications.

PREVIOUS REVIEWS

Three broad surveys of standard hydrogen leak detection techniques have previously been performed. In 1970, Rosen et al. (ref. 2) reviewed the technology of hydrogen leak and fire detection with an emphasis on hydrogen safety. A variety of techniques were discussed and the results of on-site visitations to hydrogen users were included in this publication. In 1981, Lai (ref. 3) contacted a number of hydrogen detector suppliers that he located, in part, by using Best's Safety Directory and the Thomas Register, 1980. A number of hydrogen detection methods were presented and evaluated for use in secondary containment vessels for nuclear reactors. In 1989, Madzsar (ref. 4) reviewed a number of leak detection techniques for use in hydrogen-oxygen engines, including bubble tests, mass spectroscopic techniques, and optical and solid-state detectors. The applications included leak detection in acceptance, between-flight, test-stand, and flight testing. The concept of miniaturized sensors in various locations about a test stand was noted in this work. Other reviews have discussed experimental hydrogen sensors or the operation of a specific type of hydrogen sensor. (See, e.g., refs. 5 and 6.)

The applicability and limitations of commercially available point-contact hydrogen sensors in aerospace applications have not been discussed in the literature. This paper addresses that topic in detail.

METHOD

Three sources were consulted in order to find commercial suppliers of hydrogen sensors (refs. 7 to 9). Considerable overlap was noted between the three sources. A small number of companies that were not in these sources were contacted if recommended by other companies. Because the interest of this survey was point-contact sensors, companies specializing in mass spectrometry or optical systems, for example, either were not contacted or are not part of the discussion that follows. Approximately 55 companies were contacted. Of these, 43 produced sensors that could be used for hydrogen gas detection and 28 sent information on their sensors. Some companies produced more than one type of sensor that could be used for hydrogen detection.

Discussions with company representatives and reading product information identified four major types of hydrogen sensors: catalytic combustion sensors (14 sources), electrochemical sensors (14 sources), semiconducting oxide sensors (9 sources), and thermal conductivity detectors (5 sources). All other sensor types that were encountered are listed in the category "miscellaneous" (1 source). The mechanism of hydrogen detection is explained for each major category from product information and, preferably, reviewed journal literature.

SENSOR TYPES, OPERATION, AND CHARACTERISTICS

Catalytic Combustion Gas Sensor

Catalytic combustion sensors are effectively calorimeters. They are based upon the principle that the reaction of a combustible gas (e.g., hydrogen) on the surface of the sensor in the presence of oxygen releases heat. The sensors must have a minimum oxygen concentration available, at least 15 to 16%, to promote combustion (ref. 10).

The basic configuration of the sensing element, often referred to as a "pellistor," is shown in figure 1. It consists of a platinum (Pt) wire that serves as a heater and as a resistance thermometer. The Pt wire is covered with an alumina bead (≈1 mm in diameter) that is coated with a catalyst. An identical bead with the catalyst deactivated is used as a reference. Both sensors are placed in a Wheatstone bridge, and the output is monitored. The catalyst is used to decrease the reaction temperature that is necessary to completely oxidize the gas. However, the usual reaction temperature even with the catalyst is above 500 °C.

The catalyst material varies, with palladium (Pd)-based catalysts being the most common. The catalyst is placed on high-porosity alumina beads to increase the coated surface area and the number of active sites. Additives are combined with Pd or Pt to optimize the performance of the catalyst and to prevent deactivation through sintering or exposure to catalyst inhibitors and poisons (refs. 11 and 12).

The heat generated by the combustion of the gas on the catalytically active surface is proportional to the amount of gas and its heat of combustion. The heat is conducted through the alumina bead to the Pt wire. The heat flux generates changes in the Pt wire resistance that can be converted into a signal to give the concentration of a given gas.

The detector may be operated in an isothermal or nonisothermal mode (ref. 12). The nonisothermal mode is more common. The heat flux raises the temperature at the resistor and thus changes its resistance and the voltage drop across the resistor. This voltage change is correlated with the amount of combustible gas.

Firth et al. (ref. 13) have investigated the response of a catalytic combustion sensor that was operated in the nonisothermal mode. The voltage output was linearly proportional to the gas concentration in the range investigated near the LEL. Combustion of any of a large number of gases (including carbon monoxide (CO)) can cause a signal; thus, the selectivity to hydrogen of this sensor is poor. There is a general agreement in the voltage at LEL for all gases, assuming the same detector geometry and the same coefficient for gas diffusion migrating to the sensor surface. Although these conditions are not strictly met for all combustible gases, this work illustrates both the utility of this sensor for combustible gas detection near the LEL and the importance of gas migration to the detector surface.

The gas arriving at the sensor may be drawn in with an aspirator or a pump, or it may diffuse to the sensor. In both cases the catalytic bead is shielded from the environment by a flame arrestor. The flame arrestor, which is common to all combustible gas detectors operating at high temperature, is a stainless steel screen with a grid size smaller than the minimum quenching distance of a flame (on the order of 0.06 cm) and keeps the heated sensor from serving as an ignition source (ref. 3). Diffusion through the flame arrestor is the major factor in the sensor response time, which ranges from 5 to 30 sec to reach 90% static signal.

The sensitivity of this sensor is limited by the detection mechanism. The lower sensitivity is limited by the measurement of resistance changes for Pt wire, which means lower detection limits of combustible gas near 100 ppm (ref. 12). For hydrogen concentrations above the LEL, it is experimently observed that the output signal decreases and at higher hyrdogen concentrations the sensing element may burn out. Thus, this sensor is not usable for higher hydrogen concentrations.

Electrochemical Sensor

The operating principle for an electrochemical cell, which can be used as a gas sensor, is discussed in references 14 and 15. The cell may have two or three electrodes, depending on the purpose of the cell and the behavior of the electrodes. The following discussion concentrates on two-electrode systems to illustrate the concepts involved and the limitations of the technique. Components of a two-electrode electrochemical cell include a working (or sensing) electrode and a counter electrode that is connected through an electrolyte. The sensing electrode and the counter electrode form a complete circuit through the electrolyte, allowing charge to flow through the cell.

For hydrogen interacting at a Pt sensing electrode, the reaction that takes place is

$$H_2 \rightarrow 2H^+ + 2e^- \tag{1}$$

At the Pt counter electrode an oxidation reaction takes place:

$$O_2 + 4H^+ + 4e^- \rightarrow 2H_2O \tag{2}$$

These reactions produce a current between the sensing electrode and the counter electrode that depends on the hydrogen partial pressure (ref. 16).

The general design of most electrochemical gas-sensing cells is similar. Selectivity for a particular gas is achieved by controlling such parameters as electrode catalyst, electrolyte, membrane material, and biasing of the electrodes. The design and operation of CO sensors are very similar to those of hydrogen sensors and will generally be discussed interchangeably.

In gas-sensing applications a chemical reaction occurs at the surface of the sensing electrode. The reaction involves the gas to be sensed, the sensing electrode, and the electrolyte. The sensing electrode usually consists of a catalyst, such as Pt black or a Pt black alloy, that is interdispersed in a porous Teflon-based binder which is supported by a metal screen (refs. 17 to 22). The operation of a common electrode in liquid electrolytes, the Teflon-bonded diffusion electrode, relies on the porosity and thus surface area of the electrode, intimate contact between the electrode and the electrolyte, and acceptable diffusion coefficients and reaction rates (ref. 23).

The electrolyte, whether solid or liquid, must conduct current from the sensing electrode to the counter electrode. A number of electrolytes are used. Sulfuric acid in the 2 to 4 molar range is often used as a liquid electrolyte (refs. 16 to 21 and 24) for gases like CO and hydrogen and was the most often cited electrolyte in this survey. Variations in humidity can affect the electrolyte and thus the behavior of the sensor by changing the viscosity of the electrolyte as well as its volume (refs. 16 and 19).

Solid electrolytes, such as Nafion or hydrogen uranyl phosphate (HUP), which are used as electrolytes in some commercial sensors, are conductors of protons (hydrogen ions) (refs. 22, 24, and 25). Solid electrolytes have a number of advantages over liquid electrolytes, including increased sensor stability due to the stability of the electrolyte and the electrode/electrolyte interfaces, flexibility in design, and ability to produce compact sensors (refs. 17, 22, and 24 to 30). Although this approach eliminates the need for using corrosive solutions as electrolytes, hydration of these polymers is necessary for their operation (refs. 26 and 31).

There are two principal methods of operating these cells: potentiometric and amperometric. In a potentiometric cell an equilibrium state is established between the sensing electrode and the counter electrode. In this state no current flows and cell output is the measured potential across the sensing electrode and the counter electrode. This potential is a logarithmic function of the ratio of the hydrogen partial pressures across the electrodes and is often given by the Nernst equation (refs. 14, 15, and 30). Sensor operation in this mode depends on the dynamics of the electrode reactions. A schematic representation of a potentiometric cell is shown in figure 2 for a solid electrolyte.

In the amperometric mode of operation hydrogen gas enters the cell through a hydrogen-permeable membrane and reacts at the sensing electrode, generating a current between the sensing electrode and the counter electrode that is proportional to the hydrogen partial pressure. A representative schematic of a two-electrode amperometric sensor is shown in figure 3. By proper selection of the sensing electrode potential, a particular reaction may be preferentially driven at the sensing electrode. This allows the sensor to be selective to a given type of gas and eliminates the cross-sensitivity of hydrogen sensors to other gases, especially oxygen (O_2) (refs. 20 and 32). However, this technique does not completely eliminate cross-sensitivities. As noted previously, sensors sensitive to hydrogen are also sensitive to CO and vice versa (refs. 17, 19, 22, and 32).

Gas diffusion into the amperometric cell is usually controlled so that all the gas that reaches the catalytic surface of the sensing electrode is reacted. Under these conditions the current produced will be proportional not only to the reactant gas concentration but also to the diffusion coefficient of gas to the reactive sites on the electrode surface (ref. 23). Gas diffusion may be controlled in several ways, which usually include diffusion of the gas through a membrane (refs. 20, 24, and 33). A small pumping system may be used to regulate gas flow across the membrane. However, the presence of a pump complicates the system response and increases the amount of power that is needed to drive the sensor (ref. 19). Gas diffusion may occur through a membrane (ref. 32), through a capillary with a membrane (ref. 34), or through a diffusion chamber with a membrane (ref. 26). A prefilter to eliminate interfering gases may also be included in the system before the gas contacts the membrane (refs. 22 and 35).

The fact that electrochemical systems rely on chemical reactions and often diffusion for their operation implies dependence of the sensor on temperature (refs. 16, 19, and 22), and thus temperature control is a concern. These sensors are generally operated at room temperature. Operation at temperatures significantly higher or lower than room temperature leads to alterations in electrolyte properties. At higher temperatures, dehydration for hydrated solid electrolytes or boiling for liquid electrolytes becomes significant; at lower temperatures, freezing of liquid constituents eliminates electrolyte operation.

There are a number of advantages to electrochemical sensors: They include room-temperature sensing with little power consumption, a high degree of selectivity and sensitivity, low cost, and the possibility of decreasing sensor size with solid electrolytes. Disadvantages include the fact that liquid electrolytes may leak, thus changing sensor properties as well as releasing corrosive liquid. Further, the electrolyte concentration may vary with humidity, and solid electrolytes generally require hydration on a periodic basis.

Semiconducting Oxide Sensors

Semiconducting oxides were suggested for use as combustible gas detectors by Seiyama et al. (refs. 35 and 36) and developed by Taguchi (ref. 37). Doped tin dioxide (SnO_2), an n-type semiconductor, is the most widely used and most completely characterized system although other systems containing mixed oxides have been marketed. The mechanism by which CO or combustible gases are detected by these semiconducting oxides involves surface reactions with chemisorbed oxygen (refs. 12 and 38 to 47). The type of reaction depends on whether bulk or surface effects are controlling sensor resistance and the degree of sintering of the material. For commercial systems in which grain boundary resistance dominates the semiconductor resistance, the common theoretical explanation is as follows.

Chemisorbed oxygen on the semiconductor surface extracts conduction electrons from the near-surface region of the grains. This extraction does not significantly affect the resistivity of the bulk of the semiconductor, in which electrons are abundant. However, near the grain boundaries the electrons must pass from one grain to another through the field created by the depletion of the near-surface electrons. This field traps free electrons, creates a potential barrier that impedes the electron flow, and increases the resistance of the material. The magnitude of this effect depends on the amount and type of oxygen on the surface. When CO or combustible gases such as hydrogen are exposed to the surface of SnO_2 at elevated temperatures, the gases are oxidized and, depending on the temperature, leave the surface. This leaves oxygen-deficient states at the SnO_2 surface. The amount of oxygen available to affect the electron flow is decreased and the resistance decreases. This mechanism is shown in figure 4 for the behavior of CO on a SnO_2 grain boundary (ref. 38).

The resistance change is nonlinear and depends on the partial pressure of the reducing gas, such as hydrogen, as well as on the ambient oxygen partial pressure. Although this sensor is operable in a range of hydrogen/oxygen concentrations, the presence of some ambient oxygen is essential for its operation (ref. 39). Large hydrogen concentrations would saturate the semiconductor surface at a certain level, leaving it insensitive to increases in hydrogen concentration. Because the sensor will react with a wide range of reducing gases, this sensor is not selective to a particular gas. Further, effects of humidity on the resistance have also been noted (refs. 13, 40, 41, and 46).

The behavior of the sensor is also temperature dependent for a variety of reasons. These include temperature dependence of the type oxygen ion adsorbed and adsorbed water loss occurring with increasing temperature (ref. 46). The temperature must be high enough for the reactive gas to oxidize and be removed from the semiconductor surface and yet not so high as to limit the time the reactive gas spends on the semiconductor surface and thus prevent oxidation from taking place. Thus, the operating temperature for this type of sensor is limited to 200 to 500 °C (ref. 40). The semiconductor surface is often modified by a catalyst, such as Pd or Pt to assist in oxidizing the gas. Attempts have been made to improve the sensitivity and selectivity of SnO_2 with controlled processing conditions, various additives, multisensor schemes, or thermal cycling (refs. 43, 45, and 47 to 56).

Advantages of the semiconducting oxide sensors of the SnO_2 type include their simplicity of design, small size, high sensitivity, fast response time, and low cost. Disadvantages include a lack of selectivity, the need for a constant background oxygen concentration, saturation at higher hydrogen concentrations, long-term drift, and nonlinear response. Further, temperature control is necessary because the response of this sensor is temperature dependent.

Thermal Conductivity Detectors

A thermal conductivity detector senses gas composition by comparing the conductivity of a sample gas with that of either a flowing or stationary reference gas. The thermal conductivity of a gas is measured by monitoring the temperature of a heated element in a cell. A heated filament or thermistor is used as a source of heat and is placed in an isothermal chamber. The heater filaments are commonly made of tungsten (W), tungsten-rhenium (W-Re), or nickel-iron (Ni-Fe) with possibly a gold plating (refs. 57 and 58) and are usually operated between 100 and 200 °C; the thermistors are used at temperatures near 100 °C and below. Although thermistor elements are more sensitive than wire filaments because of their significantly greater temperature coefficients of resistance, they are also more susceptible to noise (ref. 59).

The heat is dissipated from the heated element to the surrounding environment. The majority of the heat Q for a resistive system with current I and resistance R is dissipated through conduction:

$$Q = \frac{I^2R}{J} = \lambda G \frac{dT}{dx} \tag{3}$$

where J = 4.19 W/cal is the Joules equivalent, λ is the thermal conductivity of the gas in the cell, G is the cell factor, which depends on the cell geometry, and dT/dx is the thermal gradient between the heater element and the surrounding cell walls (ref. 57).

The cell geometry can play a significant role in the response curve of a thermal conductivity detector (refs. 57 and 58). The temperature of the heater element for a given geometry and heat flux also depends on the thermal conductivity of the gas carrying the heat away and on the temperature of the surrounding walls (ref. 59). Given a constant wall temperature, cell geometry, and heat input, changes in the thermal conductivity of the gas can be detected by the temperature of the heated element.

Although the dominant heat loss mechanism is conduction, other factors, such as the gas flow in the cell, affect the accuracy of the gas thermal conductivity measured (refs. 57 and 60 to 62).

Two cells are necessary for thermal conductivity measurements to be used as accurate gas sensors. The cells and heated elements are identical except that one cell is exposed to a sample gas while the other is exposed to a reference gas. The sample gas may be the same as the reference gas except for the addition of an impurity, or it could be a different gas altogether. The reference gas may be flowing or enclosed in a sealed chamber.

The heated element in the sample cell and the heated element in the reference cell are part of a Wheatstone bridge. Changes in sample gas thermal conductivity yield a change in the resistance of the sample gas heated element. This resistance change produces a signal that can be correlated to the amount of change in the sample gas thermal conductivity. The response is nonlinear with concentration in part because changes in the conductivity of a gas with the addition of an impurity are not linear even for a binary gas mixture (ref. 57).

The ability to detect changes in the thermal conductivity of a sample gas due to a change in gas composition or the introduction of an impurity strongly depends on the difference in thermal conductivity between the reference gas and the sample gas. Thermal conductivity detectors are normally used as gas sensors in binary gas applications where the gases and their thermal conductivities are known (ref. 63).

The thermal conductivities of several gases of interest as a function of temperature are shown in figure 5 (ref. 64). The thermal conductivity of hydrogen is approximately seven times greater than that of nitrogen throughout the temperature range. This means that the addition of hydrogen to a nitrogen stream is detectable. This is the basis for using the thermal conductivity detector as a hydrogen leak detector. The sensitivity of this system, if the necessary parameters are properly controlled, for hydrogen in nitrogen is on the order of 1.0×10^{-5} cm^3/sec for a flowing stream and on the order of 100 ppm H_2 concentration. The response time varies but is on the order of tens of seconds for a 90% static signal. Detecting hydrogen in an helium stream, however, would be difficult because of their nearly equal thermal conductivities.

The major advantage of this approach is that the sensor is measuring a property of the gas and not relying upon the disassociation of the gas for its measurement. The disadvantages include its dependency on a number of parameters, notably temperature and gas flow control, for accuracy. The system strongly depends on a known impurity gas having a different thermal conductivity than that of the reference. The response time and the size of the complete system are also of concern.

Miscellaneous

Manufacturers were located who produce sensors that do not fall into the preceding categories. One company that was contacted is beginning to produce sensors that are based on planar semiconductor technology. The sensor involves several thin-film layers that are composed of a metal, often an oxide, and then a semiconductor. The operating principle for these metal-oxide-semiconductor sensors, or MOS, is significantly diferent from that for the semiconducting oxide sensors discussed previously. This type of sensor for hydrogen detection is still generally an experimental sensor about which an enormous amount of literature has been published. An upcoming paper is planned that will discuss the experimental sensors in detail, and this topic is deferred until then. An interested reader is referred to references 5 and 6 and references therein.

DISCUSSION

Each hydrogen detection technique that was described in the preceding section operates well for a limited range of applications. The question that will be addressed in this discussion is the effectiveness of these techniques in aerospace applications. Specifically, to which range of aerospace applications will the sensor be applicable? As stated in the introduction the operating conditions present in aerospace applications span a wide range of parameters. It is not feasible to discuss here the specific operating conditions for all possible applications. However, it is possible to discuss the gas environment of the sensor and the sensor response in a broad way without referring to the specific application.

The set of parameters related to the gas environment of the sensor are hydrogen concentration, ambient atmosphere surrounding the sensor, and temperature of the gas impinging on the sensor. The hydrogen concentration may vary from trace amounts of gas to 100% H_2. The ambient atmosphere surrounding the sensor may be air, nitrogen or helium purges, a vacuum, or mixtures of these gases from vacuum to at least atmospheric pressure. The gas temperature, which may be time dependent, can range from liquid hydrogen temperatures to room temperature and above.

The set of parameters related to sensor response are its ability to detect hydrogen in a given environment and at a given concentration level, sensor response time, and the sensor power requirement, weight, and size. Of these, the most important attributes of any sensor are the first two: its ability to operate in a particular environment and to give a meaningful signal in a period of time useful to the user. The discussion will center on whether the sensor is operational in a finite amount of time to changes in hydrogen concentration in the broad range of gas conditions outlined previously.

An example of the size, weight, and power requirements is given for each sensor category in appendix A. In appendix B, specific values for the condition of the gas are chosen and the corresponding sensor response is evaluated. These values are meant to be figures of merit illustrating the applicability of each sensor. Cross-sensitivities for each sensor have been noted in the preceding section and will affect the sensor performance in applications beyond those to be discussed.

Catalytic Combustion Sensors

The catalytic combustion sensor is operational in air at room temperature down to 100 ppm in sensitivity. Operation at high hydrogen concentrations leads to sensor burnout. At least 16% O_2 is necessary for its operation; therefore, it will not function in either of the pure gas ambients or in a vacuum.

Low-temperature operation may be complicated by several factors. The gas must diffuse through a flame arrestor and diffusion is a temperature-dependent process. As cryogenic gas gets close to the heated pellistors, it will warm and react at the surface of the catalyst, producing a signal. However, there is a question as to whether the migration of cryogenic gases through the flame arrestor will be sufficiently rapid at low temperatures to track changes in hydrogen concentration in a responsive manner. Associated with this potential problem is condensation, for example, of water on the flame arrestor, which will further decrease diffusion to the sensing element. Heating the flame arrestor may eliminate the diffusion and condensation questions as long as this can be done without turning the flame arrestor itself into a spark source. Thermal shock of the component materials should also be considered in all these sensors for applications from room temperature to cryogenic temperatures.

The power requirements for this system are a significant concern and will worsen as the sensor is exposed to cold gas. Improved catalysts may allow a lower gas combustion temperature for this sensor with smaller power requirements. This also would decrease the concern of having a 500 °C element near explosive hydrogen sources. Protective coverings and conduits make this sensor safe in such applications. However, they can increase the mass of the system to the point where one is not dealing with a point sensor. This leaves the use of the sensor questionable in applications where sensor size and weight are concerns.

Electrochemical Sensors

Electrochemical sensors are operational and sensitive from the low parts-per-million range to 100% H_2 in air and other gases at room temperature. The sensors have low power requirements and can be made lightweight. Electrochemical sensors were chosen by Stetter et al. (ref. 65) to meet the low power and safety requirements of methane detection in coal mine applications.

Electrochemical sensors involve some type of liquid in contact with an electrode or a diffusion medium. Thus, the sensor as constructed cannot be operated in a vacuum because of the instability of the liquid. Cryogenic temperature operation is also out of the question because the liquid, whether the electrolyte or water, involved with the sensor will freeze. Many of these sensors depend for operation on control of gas diffusion through a membrane. Exposure of the membrane to cryogenic or time-varying temperatures will greatly affect the gas diffusion and make the sensor unreliable. The inability of parts of the sensor to withstand thermal cycling will also be a limitation. For solid electrolytes, heating the electrochemical sensor and periodically rehydrating the electrolyte may allow electrochemical sensors to work at lower temperatures. Such an approach could make these sensors operational at cryogenic temperatures with a significant increase in size, weight, and power consumption.

Semiconducting Oxide Sensors

Semiconducting oxide sensors are operational and sensitive in air at room temperature. Their dependence on surface effects in an environment with a minimum oxygen concentration means that operation in helium, nitrogen, or vacuum or in high concentrations of hydrogen is not possible. Modification with other catalysts may make operating this sensor in these environments feasible.

Low-temperature operation would result in a signal when the gas makes contact with the heated semiconductor. However, problems associated with low-temperature operation of this system parallel those of the catalytic combustion sensor and include the effect of low temperature on the diffusion mechanisms involved in gas migration to the semiconductor surface, increases in the power necessary to heat the sensor to operational temperatures, the safety concerns associated with the presence of high-temperature elements near explosive sources, and thermal shock on the sensor components. Improved catalysts may allow a decrease in the sensor temperature for gas oxidation, but other processes that are involved with the detection mechanism, such as desorption of the reaction products, are thermally activated and require a minimum temperature.

Thermal Conductivity Detectors

The principle behind the operation of thermal conductivity detectors is operational from 100 ppm to 100% H_2 in most of the considered applications. This technique assumes an equilibrium condition between the heat source and its surroundings. A thermal gradient between a heated source and its surroundings may be established even at cryogenic temperatures. Monitoring changes in that thermal gradient can be used to determine if there are changes in the thermal conductivity of the gas. However, even at room temperature, care must be used in quantitative interpretations of the gas concentration with this technique. The signal produced upon the introduction of hydrogen is very dependent on the ambient gas and may be affected by the flow rate. In a helium ambient the sensitivity and reliability of the sensor will be poor.

Another difficulty with this sensor in some applications is the response time. At room temperature the time for equilibrium and a signal to be established is on the order of 30 sec. At lower temperatures this time may be impractically long. At low, time-varying temperatures it is unknown whether the signal of commercially developed thermal conductivity analyzers will be able to keep up with a varying hydrogen concentration. A miniaturized version of this sensor with only a small amount of heating necessary to stabilize the surroundings of the sensor may have possibilities in cryogenic applications. This is the only system of those discussed in this report that a manufacturer suggested would work in cryogenic applications. A low-temperature (70 to 300 K) thermal conductivity measurement apparatus is discussed in reference 66 that uses a transient rather than a steady-state technique.

CONCLUSIONS

The type, mechanism of operation, and aerospace applications of commercially available hydrogen sensors have been discussed. The major categories include the catalytic combustion gas sensor, the electrochemical sensor, the semiconducting oxide sensor, and the thermal conductivity detector. These sensors are generally sensitive and operational in air at room temperature. The catalytic combustion and semiconducting oxide sensors are limited in their operation to atmospheres with oxygen present; operation of thermal conductivity detectors is disrupted in a helium ambient. Low-temperature and vacuum-ambient operation will likely disrupt most of the sensors except for the thermal conductivity detectors. No system has been found to be reliable and operational in all the environments examined, and no system was operational in a low-temperature, helium-ambient application. These results are visualized for specific conditions in appendix B. The sensors may be modified to make them operational in a given application; for example, providing an oxygen source to a catalytic combustion sensor or semiconducting oxide sensor in a helium ambient. However, the more modifications made to the sensors, the more complicated their operation becomes and the less like point-contact sensors they are in structure. In order to meet the needs of aerospace applications, further development of point-contact hydrogen sensors beyond those commercially available is necessary.

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APPENDIX A

SENSOR CONFIGURATIONS

This appendix presents an example of the size, weight, and power requirements of each type of hydrogen sensor studied. The example will emphasize smaller sensor packages to illustrate the use of the sensor as a point-contact sensor.

Catalytic Combustion Gas Sensor

A representative example of a commercial version of this type of sensor has the following properties: The input power is 1.5 W at 24 V dc with an output signal of 4 to 20 mA linear with hydrogen concentration. The catalytic beads themselves are relatively small, but the flame arrestor housing with transmitter increases the size of a smaller system to 3.8 cm in diameter by 6.4 cm in height, weighing 0.45 kg. A larger system measures 8.9 by 10.2 by 17.8 cm including the protective housing. The suggested ambient temperature range for the system is −40 to 80 °C. Operation at high temperature also leads to a shorter detector life for these sensors especially in higher hydrogen concentration environments.

Electrochemical Sensor

The sensing element for the majority of commercial electrochemical sensors includes liquid for electrolysis (liquid electrolytes) or humidification purposes (solid electrolytes). The dimensions of a small electrochemical sensor element are typically 2.8 cm in diameter by 3.2 cm in height, weighing 30 g. A flame arrestor and a sensor housing would increase the size considerably depending on the housing configuration. The power consumption for this type of sensor is on the order of 0.6 W. Sensitivities on the order of parts per million are achievable with a response time on the order of several seconds. The suggested ambient temperature range of the cell is from 0 to 45 °C with a relative humidity range of at least 30 to 80%.

Semiconducting Oxide Sensor

A typical configuration of a SnO_2 sensor includes a sensing element inside a flame arrestor. Gas diffuses through the flame arrestor, where it comes in contact with the sintered or thin-film SnO_2 element. The sensor element with housing is as small as 0.76 mm in diameter by 1.25 cm in height. Heat is supplied by a resistive heating coil (usually precious metal), and the temperature is monitored. The power input is near 0.66 W. Sensitivities to hydrogen range from the low parts per million to near the LEL with the response time on the order of seconds.

Thermal Conductivity Detectors

The specifications for one thermal conductivity sensor system are as follows: The current necessary to drive the temperature element in nitrogen varies with the type of element: from 0.6 to 5.2 W for a heated filament and near 0.1 W for the thermistor element. The corresponding input current varies from 200 to 500 mA for the heated filament and is 6 mA for the thermistor. The size of the thermal conductivity cells (temperature element and chamber) varies, with the smallest system from this manufacturer (chromatography applications) having the dimensions 4.4 by 3.8 by 1.7 cm and a gas volume of 0.02 ml. This configuration has a flowthrough reference source, but systems are available with a reference gas (He, H_2, or N_2) sealed in the reference chamber. The response time of these complete systems is less than 30 sec for a 90% static signal.

APPENDIX B

SENSOR APPLICABILITY

This appendix evaluates the applicability of the hydrogen sensors discussed in this report with specific parameters for the condition of the gas surrounding the sensor and the sensor response. These parameters are meant to examine representative points of interest throughout the range of applications.

The parameters for the condition of the gas surrounding the sensor are as follows:

(1) Hydrogen concentration

- (a) 200 ppm H_2
- (b) 2% H_2
- (c) 100% H_2

(2) Atmosphere

- (a) Air
- (b) Nitrogen (pure)
- (c) Helium (pure)
- (d) Vacuum

(3) Temperature

- (a) 273 K
- (b) 77 K (liquid nitrogen temperature)

The hydrogen concentration spans the range from sensitive applications to explosive conditions. Specific values of hydrogen concentration include the parts-per-million range in air, 50% LEL in air, and 100% H_2 for the case where hydrogen is directly flowing on the sensor. "Atmosphere" denotes the ambient atmosphere into which hydrogen is injected and lists the atmospheres discussed in the introduction. "Temperature" denotes the temperature of the gas to be sensed. The liquid nitrogen temperature, 77 K, was chosen as one extreme to represent the case of cryogenic liquid hydrogen leaking from a line and impinging on the sensor at a constant temperature. Temperatures lower than the liquid nitrogen temperature would liquify the ambient gases in both the nitrogen and air examples; such a case would then reduce to the detection of hydrogen in a liquid, which is beyond the scope of this paper.

The sensor response to these conditions may greatly depend on the manufacturer and such factors as signal conditioning and sensor history. Nonetheless, some general patterns may be suggested. The operational responses will be grouped into three categories that cover a broad range of sensor behavior:

(1) Detection

- (a) Detects (+)
- (b) Inoperative (−)

(2) Response time

- (a) Less than 3 sec (+)
- (b) Less than 45 sec (0)
- (c) Greater than 45 sec (−)

(3) Power requirements

- (a) <1 W (+)
- (b) >1 W (−)

"Detection" refers to whether the presence of the hydrogen in these conditions results in a sensor response that can be reproducibly correlated to a hydrogen concentration or if the sensor is inoperative. "Response time" refers to the time it takes to achieve a 90% static signal after a change in hydrogen concentration. "Power requirements" refers to the power necessary to drive the sensor in the given conditions. The less power required, the less of a chance of accidental ignition if a wire is exposed. The value of 1 W was arbitrarily chosen as a power limit for safety considerations and based loosely on the power limit chosen by Stetter et al. (ref. 65) for mine applications of 0.3 W.

In table I, each of the sensor types, catalytic combustion, electrochemical, semiconducting oxide, and thermal conductivity, is evaluated for three sets of operational conditions at each temperature with respect to the three response categories for each type of sensor. The meaning of the +, −, and 0 has been discussed; question marks denote that the sensor response is not known or questionable. The characterizations in table I are general trends for the given type of off-the-shelf sensor; it is conceivable that an individual brand of sensor may behave differently. The evaluations do not include either massive modification of the sensor that may improve its performance under a given set of conditions or preconditioning of the gas. The reasoning behind each of the appraisals is given in the discussion.

Examination of the table illustrates in what applications a sensor may be used as well as areas in which further development work on commercially available point-contact hydrogen sensors is necessary to meet the needs of aerospace applications.

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TABLE I.—OPERATIONAL CHARACTERISTICS OF HYDROGEN SENSORS

[Each type of sensor is evaluated for detection, response time, and power requirements.]

(a) In air

Conditions	Catalytic combustion sensors (CC)			Electrochemical sensors (EC)			Semiconducting oxide sensors (SO)			Thermal conductivity detectors (TC)		
293 K/200 ppm	+	0	−	+	+	+	+	+	+	+	0	+
293 K/2% H_2	+	0	−	+	+	+	+	+	+	+	0	+
293 K/100% H_2	−	−	−	+	+	+	+	+	+	+	0	+
77 K/200 ppm	+	?	−	−	−	−	+	?	?	+	?	?
77 K/2% H_2	+	?	−	−	−	−	+	?	?	+	?	?
77 K/100% H_2	−	−	−	−	−	−	+	?	?	+	?	?

(b) In helium

293 K/200 ppm	−	−	−	+	+	+	−	−	−	−	−	−
293 K/2% H_2	−	−	−	+	+	+	−	−	−	−	−	−
293 K/100% H_2	−	−	−	+	+	+	−	−	−	−	−	−
77 K/200 ppm	−	−	−	−	−	−	−	−	−	−	−	−
77 K/2% H_2	−	−	−	−	−	−	−	−	−	−	−	−
77 K/100% H_2	−	−	−	−	−	−	−	−	−	−	−	−

(c) In nitrogen

293 K/200 ppm	−	−	−	+	+	+	−	−	−	+	0	+
293 K/2% H_2	−	−	−	+	+	+	−	−	−	+	0	+
293 K/100% H_2	−	−	−	+	+	+	−	−	−	+	0	+
77 K/200 ppm	−	−	−	−	−	−	−	−	−	+	?	?
77 K/2% H_2	−	−	−	−	−	−	−	−	−	+	?	?
77 K/100% H_2	−	−	−	−	−	−	−	−	−	+	?	?

(d) In vacuum

293 K/200 ppm	−	−	−	−	−	−	−	−	−	+	0	+
293 K/2% H_2	−	−	−	−	−	−	−	−	−	+	0	+
293 K/100% H_2	−	−	−	−	−	−	−	−	−	+	0	+
77 K/200 ppm	−	−	−	−	−	−	−	−	−	+	?	?
77 K/2% H_2	−	−	−	−	−	−	−	−	−	+	?	?
77 K/100% H_2	−	−	−	−	−	−	−	−	−	+	?	?

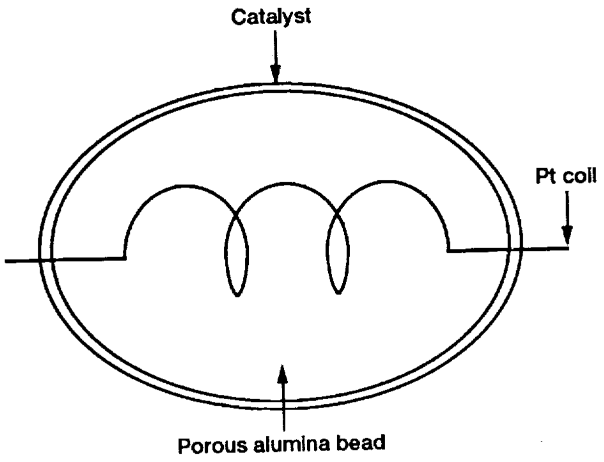


Figure 1.—Pellistor calorimeter showing catalyst on alumina bead surrounding platinum coil.

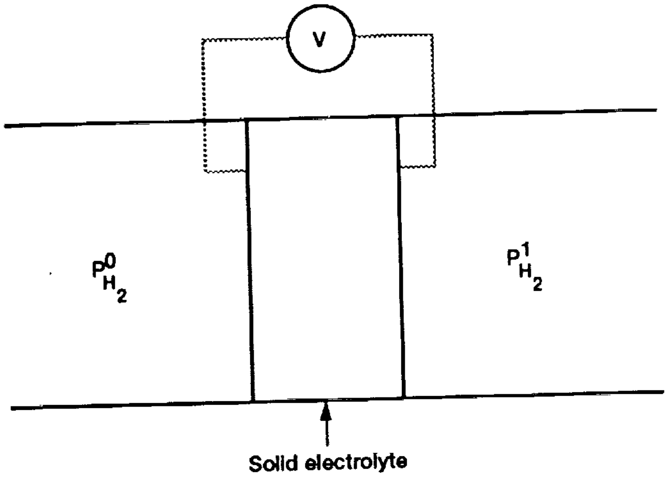


Figure 2.—Schematic representation of potentiometric hydrogen sensor.

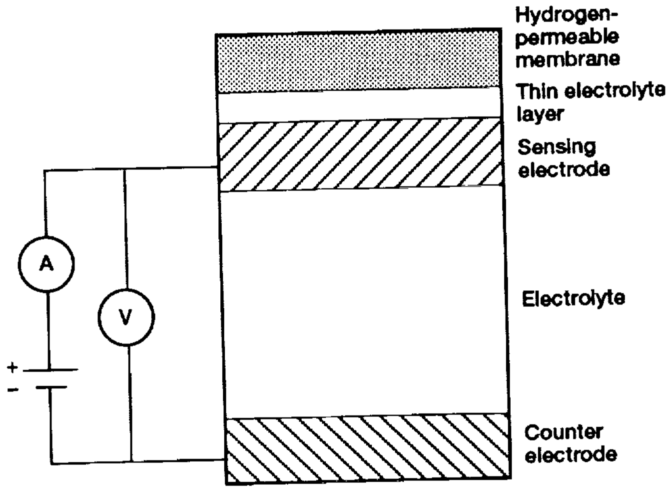
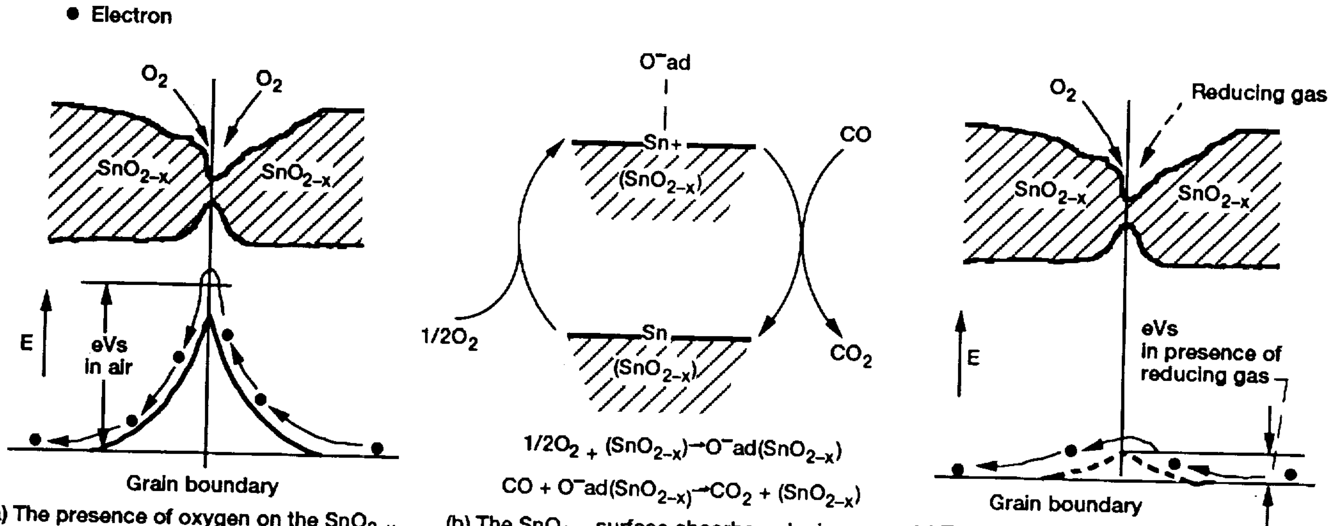


Figure 3.—Schematic construction of amperometric, current-limiting sensor.



(a) The presence of oxygen on the SnO_{2-x} creates a potential barrier at the grain boundaries, restricting the flow of electrons and causing the resistance to increase.

(b) The SnO_{2-x} surface absorbs reducing gases in the atmosphere, such as carbon monoxide, and causes oxidation, thereby removing oxygen from the grain boundary.

(c) The resulting grain boundary has a lower potential barrier, which allows electrons to flow more freely, thereby reducing the resistance.

Figure 4.—Gas detection mechanism of SnO_{2-x} for CO (ref. 38).

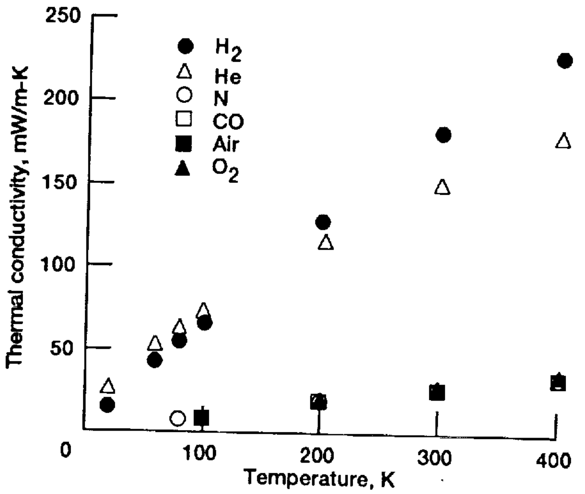


Figure 5. —Thermal conductivity of hydrogen, helium, nitrogen, carbon monoxide, and oxygen as a function of temperature (ref. 64).

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13. ABSTRACT ***(Maximum 200 words)***

The performance requirements for hydrogen detection in aerospace applications often exceed those of more traditional applications. In order to ascertain the applicability of existing hydrogen sensors to aerospace applications, a survey has been conducted of commercially available point-contact hydrogen sensors, and their operation has been analyzed. The operation of the majority of commercial hydrogen sensors falls into four main categories: catalytic combustion, electrochemical, and semiconducting oxide sensors and thermal conductivity detectors. The physical mechanism involved in hydrogen detection for each main category is discussed in detail. From an understanding of the detection mechanism, each category of sensor is evaluated for use in a variety of space and propulsion environments. In order to meet the needs of aerospace applications, the development of point-contact hydrogen sensors that are based on concepts beyond those used in commercial sensors is necessary.

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