AN OVERVIEW OF
HYDROGEN SAFETY SENSORS AND REQUIREMENTS

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ABSTRACT

There exists an international commitment to increase the utilization of hydrogen as a clean and renewable alternative to carbon-based fuels. The availability of hydrogen safety sensors is critical to assure the safe deployment of hydrogen systems. Already, the use of hydrogen safety sensors is required for the indoor fueling of fuel cell powered forklifts (e.g., NFPA 52, Vehicular Fuel Systems Code [1]). Additional Codes and Standards specific to hydrogen detectors are being developed [2, 3], which when adopted will impose mandatory analytical performance metrics. There are a large number of commercially available hydrogen safety sensors. Because end-users have a broad range of sensor options for their specific applications, the final selection of an appropriate sensor technology can be complicated. Facility engineers and other end-users are expected to select the optimal sensor technology choice. However, some sensor technologies may not be a good fit for a given application. Informed decisions require an understanding of the general analytical performance specifications that can be expected by a given sensor technology. Although there are a large number of commercial sensors, most can be classified into relatively few specific sensor types (e.g., electrochemical, metal oxide, catalytic bead and others). Performance metrics of commercial sensors produced on a specific platform may vary between manufacturers, but to a significant degree a specific platform has characteristic analytical trends, advantages, and limitations. Knowledge of these trends facilitates the selection of the optimal technology for a specific application (i.e., indoor vs. outdoor environments). An understanding of the various sensor options and their general analytical performance specifications would be invaluable in guiding the selection of the most appropriate technology for the designated application.

1.0   INTRODUCTION

The US Department of Energy (DOE) is committed to the development of hydrogen as a clean and renewable alternative to carbon-based fuels. DOE and the National Renewable Energy Laboratory (NREL) have been working with standards and code development organizations (SDOs and CDOs) to develop relevant codes and standards to facilitate the implementation of the necessary hydrogen infrastructure. One critical aspect for the safe and efficient deployment of hydrogen is the ability of chemical sensors to meet the required performance specifications for the growing hydrogen infrastructure. Several crucial applications for hydrogen sensors have been recently identified by DOE, which include the Fuel Producer/Supplier Environment and the End-user Environment [4]. Already, the use of hydrogen detectors is already required by NFPA 52 [1]. It is recognized that the availability of safety sensors will be critical for the successful utilization of hydrogen. Accordingly, DOE has published a list of target specifications for hydrogen safety sensors [5], which are summarized in Table 1.

Table 1: DOE targets specifications for hydrogen safety sensor R&D (from Table 3.7.2 in [5])

Parameter	Value
Measurement Range	0.1 to 10%
Operating Temperature	-30 to 80°C
Response Time	< 1 second
Accuracy	5% of full scale
Gas Environment	Ambient air, 10 to 98% RH
Lifetime	10 years
Interference	Resistance (e.g., hydrocarbons)

1.1   Sensor Platforms for Hydrogen

A chemical sensor has been defined as "A small device that as the result of a chemical interaction or process between the analyte gas and the sensor device transforms chemical or biochemical information of a quantitative or qualitative type into an analytically useful (electronic) signal" [6]. An illustration of a general sensor platform is shown in Figure 1. Associated with any sensor is the chemical interface (**CI**), the region in which the target analyte and possibly other chemicals interact with the sensor. The chemical interaction may be a transfer of electrons (electrochemical devices), a transfer of heat (combustion gas analyzers, thermal conductivity sensor), adsorption into a matrix (coatings, such as palladium) or other chemically induced process which result in a change in properties of the **CI**, which is then manifested as an electrical signal or change in electrical signal on the transducer platform at the transduction interface (**TI**). Common electrical signals in chemical sensors include current (I), voltages (V), resistances (R), and frequency (HZ).
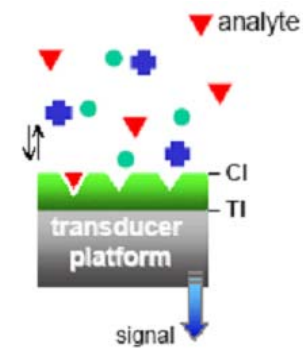

Figure 1: Sensor design

A large number of commercially available hydrogen safety sensors currently exist. Furthermore, new hydrogen sensor technologies based on unique platform systems are being developed and can be expected to be commercialized. Each sensor type has unique operating principles that will ultimately control its performance, and thus each technology has its advantages and limitations. No existing technology will be ideally suited for all applications, and none has been shown to meet all of the DOE target specifications. Some sensor platforms may be strongly affected by variations in ambient temperature but would be insensitive to relative humidity (e.g., electrochemical sensors), and the converse might be true for other technology types (e.g., metal oxide sensors). Because end-users have a broad range of sensor options, the final selection of an appropriate sensor technology can be complicated. Facility engineers and other end-users are expected to select the optimal sensor technology, which is especially true for safety systems. However, some sensor technologies may not be a good fit for a given application. Informed decisions require an understanding of the general analytical performance specifications that can be expected by specific sensor technologies. The number of commercial sensors is quite large. Fortunately, most sensors can be classified into relatively few specific sensor types. Although specific performance metrics of individual sensors may vary between manufacturer designs, to a significant degree each type have characteristic analytical trends, advantages, and limitations. Knowledge of these trends may facilitate the selection of a sensor technology for specific applications (i.e., indoor vs. outdoor environments). An understanding of the various sensor options and their general analytical performance specifications would be invaluable in guiding the selection of the most appropriate technology for a specific application. The most common commercial mature sensor platforms for hydrogen include:

- Electrochemical
- Metal Oxide (MOX sensors)
- "Pellistor"-type combustible gas sensor
- Thermal conductivity
- Optical Devices

- Evanescent wave – with film of Pd or other material
- Colorimetric and indicator dyes
- Pd-film and Pd-alloy films (on various transduction platforms)

2.0 SENSOR REQUIREMENTS AND PERFORMANCE METRICS

The use of hydrogen safety sensors in hydrogen fueling operations is specifically mandated by NFPA 52, Vehicular Fuel Systems Code [1]. NFPA 52 applies to the design, installation, operation, and maintenance of compressed hydrogen (GH2), liquefied compressed hydrogen (LH2), and blends of hydrogen up to 20 percent with the balance natural gas (NG) vehicle fueling (dispensing) systems and engine fuel systems and facilities. However, NFPA 52 does not specify detector performance or deployment parameters. Codes and Standards are being developed by national [2] and international [3] SDOs which specifically address the performance of hydrogen detectors. The sensor requirements recommended by these standards are more comprehensive than the DOE target specifications, covering a broader range of sensor analytical and deployment specifications than those presented in Table 1. Specific test protocols for sensor specifications may also be required in the standards. Although similarities exist between the various standards, performance specifications for a particular parameter or test procedure may vary between agencies and with the DOE targets. An expanded list of possible sensor performance parameters or specifications is presented in Table 2. These encompass a range of specifications ranging from analytical parameters (e.g., how well the sensor can accurately measure hydrogen) to logistic parameters (e.g., operational and deployment requirements) which include cost, installation considerations, and operational requirements. Some but not all of the listed specifications are covered by the sensor standards [2, 3]. Other parameters not covered by the standards may still be relevant to the specific application. Ultimately it is up to the end-user to identify the critical parameters for the application. This list is extensive and it is likely that additional metrics may be identified. It is noted that the values and importance for each parameter is application specific, and that the relative importance of a specific parameter will vary significantly with different applications.

Table 2: Sensor performance metrics

ANALTYICAL METRICS	
Analytical Characteristics	Selectivity, Lower Detection Limit, Analytical Resolution, Linear (and Dynamic) Range, Response Time, Recovery Time, Repeatability, Signal Drift, Environmental Effects (e.g., Pressure, Temperature, and RH/Moisture), Reversibility, Limits of Quantitation
LOGISTICAL METRICS	
Operational Parameters	Operational Lifetime, Consumables, Calibration and Maintenance Requirements (frequency and complexity), Sample size, Matrix requirements, Signal Management, Orientation Effect, Device Repeatability, Warm-Up Time
Deployment Parameters	Capital Cost, Installation Costs, Physical Size, Control Circuitry, Power Requirement, Electronic Interface, Pneumatic Connections, Shelf life, Maturity/availability, Placement, Government Regulations (codes)

2.1 The NREL Safety Sensor Laboratory

The NREL Hydrogen Sensor Test Laboratory was established to support the U.S. Department of Energy's (DOE) commitment to the development of hydrogen technology as an alternative energy source. A critical role of the Sensor Laboratory is to work with sensor manufacturers to develop sensor technology that will satisfy DOE target specifications. In this way, end-users will be assured that they have the sensing technology they need, whether dictated by code or by the technical requirements of the application. The Sensor Laboratory has the capability to independently test sensors and prototypes under controlled conditions to provide quantitative analytical performance specifications. The focus of the Sensor Laboratory has been on commercial sensors and those devices that are nearing commercialization. Currently the NREL Sensor Laboratory is using a sensor test apparatus developed through DOE funding by the International Center for Sensor Science and

Engineering (ICSSE) at the Illinois Institute of Technology (IIT) [7], shown in Figure 2 (left). With this system, chemical sensors are subjected to precisely defined and repeatable test protocols in order to quantitatively determine the analytical characteristics. Established protocols for Short Term Repeatability/Basic Performance, Dynamic/Linear Range, Pressure Test, Temperature Test, Orientation Test, and Interferant Response exist. Fixtures and protocols for Response Time, Long-Term Stability and an improved Relative Humidity Test are under development. This apparatus was used extensively in a DOE program to evaluate sensors for automotive PEM Fuel applications, including safety considerations. From this work, an assessment of existing safety sensors was presented at a DOE workshop on hydrogen safety sensors [8]. A more recent assessment of representative hydrogen safety sensors performance at the Joint Research Center (JRC), Institute for Energy in the Netherlands was recently reported by Boon-Brett and coworkers [9]. Generalized performance expectations for various hydrogen sensor platforms are discussed below.

The National Renewable Energy Laboratory is currently enhancing its sensor evaluation infrastructure. Towards this end, it has initiated the design and construction of a fully automated, upgraded facility with significantly enhanced capability, including multiple sensor testing, broader ranges on test parameters, traceable sensors for establishing test conditions, and improved controls; this system will be completed by July of 2009. At present, sensor testing is limited to hydrogen safety sensors with hydrogen concentration restricted to less than 4% in air, which corresponds to the lower flammable limit (LFL). The long-range goals include upgrades to expand on the testing capability and data quality of the Sensor Laboratory, and ultimately establish a premier sensor test laboratory for calibration and pre-certification of hydrogen safety sensors with capability to test to 100% hydrogen concentration. Ultimately, the NREL Sensor Laboratory is to be modeled after the NREL National Center for Photovoltaics (NCPV) device/module testing [10].

Figure 2: Hydrogen safety sensor test apparatus. (Left) Apparatus designed and build at the Illinois Institute of Technology currently deployed at NREL. (Right) New sensor test apparatus under construction at NREL with enhanced performance capabilities

2.2   Sensor Types and Performance

General performance parameters for the various sensor types are discussed below. The focus is on sensor technology. Thus laboratory methods or complex costly laboratory instrumentation, such as mass spectroscopy, will not be included in this discussion. From an evaluation of numerous sensor technologies, generalized performance metrics can be assessed for a specific platform. It is to be noted however, that the actual performance between commercial devices can show significance variability. In some cases, devices with very similar design parameters have dramatically different behavior. Figure 3 is an extreme example of the potential variability between devices fabricated with ostensibly

identical design parameters but manufactured by different vendors. In each case the sensor was powered up and allowed to stabilize for a period of time in accordance with manufacturer recommendations. Sensor control circuitry and operation was also in accordance to manufacture recommendations. After warm-up, the sensor was then subjected to three series of 10-minute exposures comprised of 0.0, 0.2, 1.0, and 2.0% hydrogen at a constant flow rate of 500 sccm. The device on the left exhibits excellent repeatability and had a signal that was highly correlated to concentration. A second sensor was subjected to the same protocol, and the results are shown in the right trace of Figure 3. The trace on the right tended to show less repeatability and was prone to saturation. Although this device responded with high sensitivity to the low concentration of hydrogen, it would be impossible to correlate the signal with hydrogen concentration. These results clearly show that performance can vary dramatically between commercial devices and emphasize the need for performance validation prior to selection of a technology for a particular application. Nevertheless, general performance trends can be defined by the sensor platform since these are defined primarily by the chemical interaction of the analyte and environment with the platform.
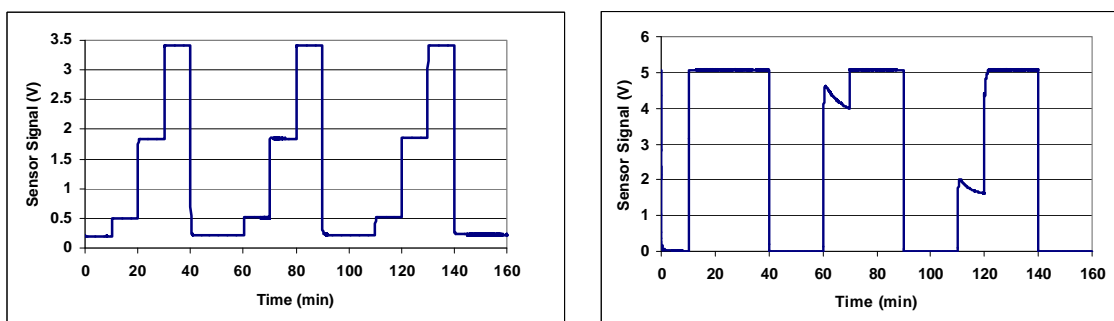

Figure 3: Sensor response to three series of 10-minute exposures comprised of 0.0, 0.2, 1.0, and 2.0% hydrogen. The response curves for two different commercial devices are shown. The basic design features between the two devices was nearly identical, although they were provided by different manufacturers.

Electrochemical Sensors (EC) – Amperometric and Potentiometric sensors are two main electrochemical sensor platforms [11].   Amperometric hydrogen sensors are more common commercially. Amperometric sensors operate by electrochemically reacting with the gas of interest and producing an electrical signal proportional to the gas concentration. In amperometry, the target molecule will undergo a change in oxidation state, which involves transfer of electrons between the molecule and the electrode. Hydrogen gas (H_2) is oxidized to hydrogen ions (H^+), a process that involves the loss of 2 electrons per hydrogen molecule to the electrode. A typical electrochemical sensor consists of a sensing electrode (or working electrode), and a counter electrode separated by a thin layer of electrolyte. Gas that comes in contact with the sensor first passes through a small capillary-type opening and then diffuses through a hydrophobic barrier, and eventually reaches the electrode surface. This approach is adopted to allow the proper amount of gas to react at the sensing electrode to produce a sufficient electrical signal for measurement while preventing the electrolyte from leaking out of the sensor. The gas that diffuses through the barrier then reacts at the surface of the sensing electrode involving either an oxidation or reduction mechanism. These reactions are catalyzed by the electrode materials specifically developed for the gas of interest. With a resistor (or more sophisticated circuit) connected across the electrodes, a current proportional to the gas concentration flows between the anode and the cathode. Amperometric gas sensors are typically controlled by an electronic circuit known as a potentiostat, which not only controls the electrochemical conditions (e.g., bias) of the sensor but also provides a ready means to measure the current. The current can be measured to determine the gas concentration. Because a current is generated in the process, the electrochemical sensor is often described as an amperometric gas sensor or a micro fuel cell.

Hydrogen can be easily detected by electrochemical sensors, especially amperometric devices, which are readily available from numerous vendors. Amperometric gas sensors are physically small, have good sensitivity and typically have a broad linear range. The sensors are stable with lifetimes of up to 2 years being routine, although this is considerably less than the DOE target. Limitations include limited selectivity (e.g., CO may affect the sensor), a restricted temperature range due to a liquid electrolyte, and a dependence on barometric pressure. Alternatively, humidity fluctuations have nearly negligible effect on the devices. To some extent, the temperature and pressure dependencies can be compensated via electronics or microprocessor controlled corrections. Many amperometric gas sensors require oxygen for long-term stability, and thus should not be used in nitrogen or other inert atmosphere without prior validation for a specific model. Prices currently range from $10 – $100, dependent to a large part on quantity and severity of application. With conventional designs, the price is expected to remain at around $10 – $100.

Metal Oxide Sensors (MOX) – Metal oxide sensors are fabricated with a wide band gap semiconductor material such as tin oxide or other metal oxide as the active element of the sensor [12]. The material is usually embedded in a porous ceramic matrix traditionally configured as a bead formed around an internal heater coil. Operation at elevated temperatures (ca. 400°C or greater) is required to obtain a stable measurable conductivity (or resistance). Gaseous analytes, such as hydrogen diffuse into the porous structure and react with the sensor to decrease the surface concentration of oxygen. This then lowers the surface potential between grains, thereby decreasing resistance. In addition to the embedded heater, a probe wire is also embedded and is used to measure device resistance (the ground point of the embedded heater often serves as the second probe point for resistance measurements). The MOX sensor is a small readily produced device. The device readily has sufficient sensitivity for hydrogen safety application. As a high temperature device, the MOX sensor is not dramatically affected by temperature variations. However, the MOX sensor is not considered a selective device and may react with other compounds which might be present, including moisture. Moisture variations may also affect the MOX calibration curve. The response of the classic MOX was not linear and tended to follow a power law relationship with concentration [12]. Another major disadvantage of the classic MOX sensor was a long response and even longer recovery time. The performance of a MOX sensor can be permanently degraded when exposed to certain silicon compounds (which can include common sealants). Generally, these devices require oxygen for stable responses and have not been widely applied to process streams or very high concentrations of hydrogen, thus these devices can not be readily deployed in a nitrogen purged environment.

However, recent advances in MOX technology have been made, particularly in the development of miniaturized thin film designs. The film geometry not only requires significantly less power for operation, improved analytical performance has been observed in linearity as well as response time. Figure 4 shows the response of a commercial MOX hydrogen sensor from 2004 compared to a more recently developed device manufactured in a thin film configuration. The robustness of these thin-film designs to environmental parameters (pressure and RH) and selectivity needs to be further investigated.
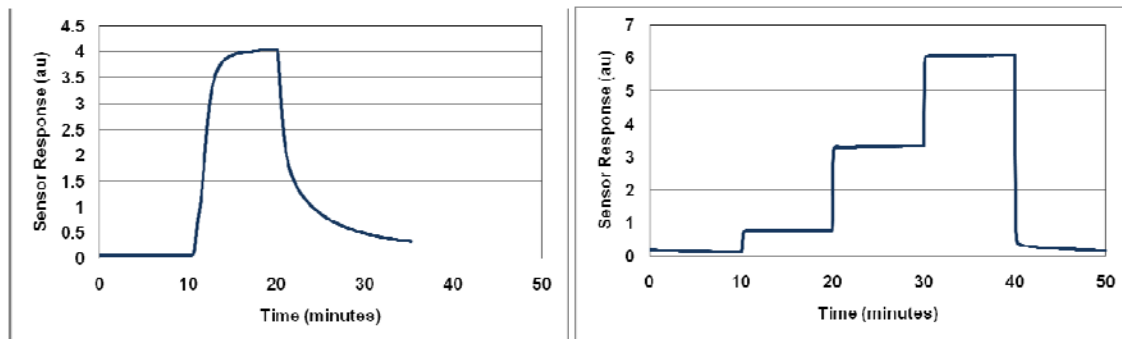

Figure 4: Response of a classic MOX sensor (bead structure, circa 2004) to 2% hydrogen (left) compared to the response of a thin-film MOX sensor to 0.2, 1, and 2% hydrogen (2009).

"Pellistor"-type combustible gas sensors (CGS) – Heated ceramics embedded with platinum or other noble metal catalysts provide a catalytic surface for hydrogen in air combustion. A thin platinum wire is encapsulated with the ceramic. The sensor is often called a Pellistor Sensor. The device is heated electrically to approximately 550°C. The coated surface catalyzes combustion when exposed to hydrogen or other combustible vapors. The catalyzed combustion is localized to the surface of the sensor and results in an increased temperature of the device. Since the resistance of any material is affected by temperature, the surface combustion changes the resistance of the internal platinum wire, which essential serves as an internal RTD device. Higher concentrations of combustible vapors result in greater heat generation and therefore larger resistance changes of the probe wire. For improved stability, the CGS is often referenced to a second nearly identical but catalytically inactive bead; both the active and inactive elements are typically integrated into a single housing. The CGS is routinely used for 0-10% hydrogen in air and these sensors have been used for more than 20 years in confined space and safety applications. The CGS is essentially the industry standard (especially in the petroleum industry) for the detection of combustible vapors. The pellistor is however, not selective and can not differentiate between different combustible gases. Of course, the nature of the specific application could be such that only one combustible gas could be present, and thus imperfect selectivity is not always a relevant issue. Conversely, some applications could have numerous possible combustibles present, for example at a mixed hydrogen-gasoline fueling station. While insensitive to temperature and RH fluctuations, a barometric pressure dependence may exist. Fundamentally, these devices will not function without oxygen since oxygen is essential for any combustion process. Furthermore, the high operating temperature of the CGS requires significant electrical power for operation. As with other solid-state sensors, improvements in power requirements and response times are possible with miniaturized thin-film structures that utilize modern MEMS technology for fabrication.

Thermal conductivity (TC) – As with CGS, TC sensors rely upon a temperature-induced change of an electrically-heated sensing element following exposure to the analyte. The signal is a change in resistance. However, the TC sensor is not heated to a temperature that induces combustion, but only to a temperature in which the resistance of the sensing element deviates from the linear limit of Ohm's law ($V = I* R$). This requires significantly lower power than that required for catalytic combustion. This is illustrated in a voltage-current plot of the TC device, as shown in Figure 5. A linear increase in induced current is observed as an increasing voltage is first applied to the sensing element. The slope of the linear region is the reciprocal resistance (1/R) of the element. As the applied electrical power (I*V) increases, the ability to dissipate heat to the surrounding environment (air matrix) is exceeded, resulting in an increase in device 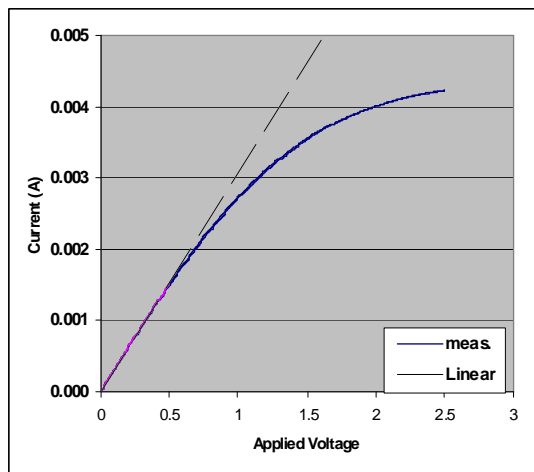temperature. The resistance no longer remains constant, and a deviation from a linear I-V plot is observed. Factors that affect the shape of the I-V curve include the thermal conductivity (λ) of the surrounding gas. The higher the thermal conductivity coefficient, the more efficient the transfer of heat, which in turns changes the shape of the I-V curve. In other words, for a given applied power, the resistance (temperature) of the sensing element will depend upon the surrounding gas. Thermal conductivity is a property of the gas (see Table 3). Hydrogen has the highest thermal conductivity of any known gas. Thermal conductivity sensors exploit this property for detection and monitoring of hydrogen. Some manufacturers claim a 0-100% range for hydrogen, and more recently devices for lower concentration ranges relevant to safety have been appearing on the market.

Figure 5: Empirical current-voltage curve for a TC sensor

TC sensors are stable devices, and since they do not chemically interact with the analyte (heat transfer is a physical process), are less prone to contamination. They tend to be non-selective, but with proprietary coatings, vendors have reported improved selectivity.   They are affected by environmental parameters including temperature, pressure and humidity. As with many technologies, the environmental affects can be compensated, but this requires independent measurement of ambient conditions.   The TC device is amenable to MEMS technology, which not only lowers the power requirements to much less than a milliwatt (useful for battery operation), but miniaturization also results in rapid response times. Response times of significantly less than 1 second have been reported [13]. Unlike almost every other sensor platform, the TC sensor does not require oxygen for operation, which makes it amenable for use in process streams or for those applications which use a nitrogen purge.

Table 3: Thermal conductivity coefficients

Gas	λ {mW/(m K)}
Hydrogen	174
Helium	142
Methane	30.0
Oxygen	24.7
Nitrogen	24.3
Argon	17.7
Carbon Dioxide	14.2

Optical Devices (Opt) – Sensors for the direct optical detection of hydrogen are not readily available because hydrogen is non-adsorbing in the ultraviolet-visible or IR. However, very sensitive sensor platforms have been developed which undergo changes in optical properties upon exposure to hydrogen.   Many devices are based on optical properties of palladium films [e.g., 14-16]. Other devices are based on chemical mediators that undergo color changes upon exposure to hydrogen. Two main classes of chemically mediated optical hydrogen sensors have been developed at NREL and licensed, which include fiber optic based devices [17] and a recently developed colorimetric indicator [18, 19]. A design for a hydrogen sensitive fiber optic sensor developed at NREL is shown in Figure 6 (Left). The tip of the sensor is coated with several layers which include a hydrogen sensitive chemical (tungsten or molybdenum oxide) that undergoes a very sensitive color change when exposed to hydrogen. The colorimetric agent is very specific to hydrogen. The tip is also coated with a hydrogen permeable protection layer to protect the sensor from environmental parameters and chemical poisons [20]. Environmental effects from T, P, and RH are still present. As with all fiber optics systems, remote deployment is achieved. This device also features a good sensitivity to hydrogen, simple operation, long-term stability, and reversibility. Oxygen is required for reversibility. Alternatively, the response time is relatively slow and while the sensor does provide quantitative data, the accuracy is less than the DOE targets. There has also been some difficulty in production which has impeded commercialization. Numerous fiber optic sensors based on palladium films have also been developed [14-16] but many of the palladium based fiber optics sensors are not readily commercially available.

Colorimetric indicators are being developed for hydrogen [18, 19]. Tungsten oxide or molybdenum oxide are typically used. The oxide is partially reduced in the presence of hydrogen in concentrations as low as 300 ppm and changes from a light off-white color to a dark color. The contrast that can be achieved is illustrated in Figure 6 (Right). Such systems do not require electronic circuitry for operation or detection, and therefore can complement electronic sensor technology. Visual detection is all that is required. However, the indicator can also be incorporated into an electronic platform however. These systems are passive and undergo a spontaneous color change when exposed to hydrogen.   Reversible and irreversible formulations have been developed. The active material can be easily incorporated into a low cost hydrogen-indicating paint or ink.

A number of possible configurations for the colorimetric indicators have been successfully demonstrated in the laboratory including hydrogen indicating paints, tape, cautionary decals, and coatings for hydrogen storage tanks. The material has been shown to be environmentally stable and the net process is not significantly affected by temperature, pressure, or RH. The transformation rate does increase at higher temperature, and conversely may be impeded at low temperatures. This system is low-cost and easily implemented. However, quantization is not readily achieved.
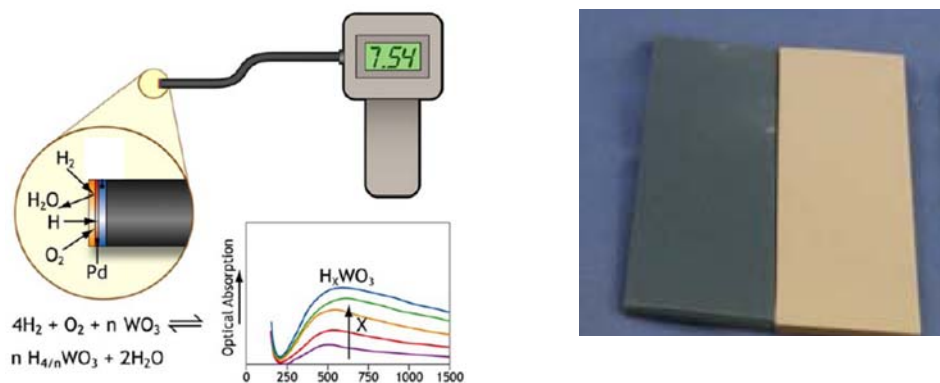
Figure 6: Left: A hydrogen fiber optic sensor. Right: H_2 colorimetric indicator. Showing exposed coatings (left) compared to an unexposed coating (right).

Pd-film and Pd-alloy films (Pd) – Because of the unique and highly selective permeability of hydrogen into palladium (Pd), Pd-film technology has been applied to several classes and types of hydrogen sensors. One basic technology that appears promising is the Pd- and Pd-alloy resistor films, whose conduction (or resistance) varies with hydrogen concentration. The film resistance changes with adsorption of hydrogen and this resistance can be monitored directly as in a chemi-resistor. Such devices have the advantage of a very simple transduction signal. Alternatively, thin Pd films have been incorporated into field effect transistor devices wherein the gate is Pd and the transistor performance is controlled by the changes in the gate resistivity (Figure 7).

Pd-films can be applied to other sensor classes (e.g., mechanical devices such as the surface acoustic wave sensor--SAW or quartz crystal microbalance sensor--QCM) to achieve hydrogen selectivity; for example as a coating on a SAW or a QCM device. When used in this manner, adsorption of hydrogen changes the mass of the Pd-film, and this mass change affects the resonant frequency of the mechanical sensor. Small changes in frequency can be accurately measured, which makes for an excellent lower detection limit and range of these devices. The change in frequency and performance of the mechanical structure can be used to measure hydrogen. Commercialization of the hydrogen SAW and QCM devices has however been limited.

In general, Pd-film devices suffer from poor performance under anaerobic conditions, partly because of a phase change and because the oxygen in the air is needed to enhance reversibility of the hydrogen in Pd effect. Pd-films are also susceptible to chemical poisoning, especially by sulfide. However, several vendors have alleviated much of the deleterious effects of sulfur and other potential poisons by the incorporation of a protective, hydrogen-permeable but sulfur impermeable coating over the Pd [20]. The long-term stability of the coating is not fully characterized in many real-world environments, but promising performance has been reported by some vendors. The devices tend to show slow response time relative to other sensors, particularly thermal conductivity devices and some of the new thin film sensor platforms. Permeation into palladium films can be significantly slowed down at low temperature.
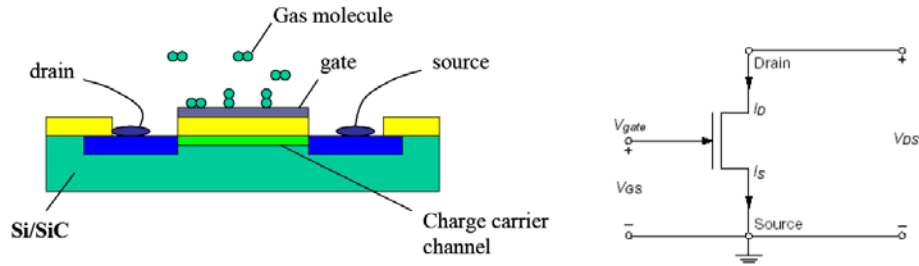
Figure 7: Schematic illustration of a ChemFET sensor that uses a palladium film at the gate. Adsorption of hydrogen changes the potential at the gate and thereby increases the conductivity between the source and drain.

3.0   SUMMARY

The number of available sensor technologies is quite large, and the number of vendors marketing commercial sensors increases every year. Although new platforms are being developed and commercialized, most mature hydrogen sensor technology can be categorized into a relatively small number of platforms. Each of the technologies discussed in this paper is a good sensor platform with significant positive performance metrics. Many are commercially successful. However, none is ideally suited for every application; indeed none would likely be *ideally* suited for any application. One must, therefore, strive to choose the most appropriate technology that will best meet the application requirements.

Although specific performance may vary between vendors, some generalized trends can be observed [8, 9]. A comparison of pertinent performance strengths and weakness is necessary to help guide the selection of an appropriate safety sensor. The relative merits of a sensor platform can be assessed through a ranking of pertinent performance metrics. There are numerous ways this can be performed. One method is a numerical ranking, such as on a 1 to 5 scale. A ranking of 5 is equivalent to IDEAL (or near ideal) behavior, while 0 would be POOR. Naturally, in a real world most ranking would be intermediate to these two extremes, and somewhat arbitrary and strongly dependent upon specific applications. Thus, the higher a numerical rank, the better the overall expected performance for a sensor. Such a ranking was done in Table 3 for a selected subset of analytic and logistical metrics. Graphical displays were performed previously [8], which allows for a visual assessment. The rankings in Table 3 were based on general performance parameters, exact value may change with individual sensor and especially with application. However, with such a ranking, the relative merits of a sensor technology can be quickly and conveniently compared to alternatives.

These evaluations were performed on sensors, the actual sensing element that responds to the analyte. Sensors are typically packaged in instrument systems which can include control electronics and user interfaces. It should be noted that an instrument design can correct or compensate for some sensor behavior. For example, temperature compensation is frequently performed in instrumented systems, either by electronics or microprocessor controls. There are still fundamental limitations, such as the freezing of the liquid electrolyte at temperatures below -10°C precludes operation of conventional electrochemical sensors under sub-freezing conditions, at least without an internal (power-consuming) heater. Other parameters such as pressure and RH effects can be compensated as well, but this adds complexity and cost to an instrument.   Some metrics impose fundamental limitations. A slow responding sensor cannot be instrumented in a system designed for fast response times. An expensive high performance sensor will not be amenable for a low-cost instrument. Thus, although instrument specifications should be considered by the end user, an understanding of the various detection platform options can guide the selection process.

Table 4: Generalized ranking of various sensor platforms to selected performance metrics (5 is Ideal, 0 is Poor)

Analytical Metrics						
Metric	**EC**	**MOX**	**CGS**	**TC**	**Opt**	**Pd**
Detection Lime/Sensitivity	4	4	4	4	4	4
Selectivity	3.5	3	3.5	3.5	4.5	5
Linear Range	5	3 (4.5)*	4 (4.5)*	4	3	4
Response Time	4	3 (4.5)*	4	4.5	3	3.5
Repeatability	3.5	4	4	4	3	4
Environmental Effect	3.5	3.5	4	3	4	4
Logistic Metrics						
Metric	**EC**	**MOX**	**CGS**	**TC**	**Opt**	**Pd**
Level of Maturity	5	5	5	4.5	3.5	4.5
Size	4	4	4	4.5	4	3.5
Power	4	3	3	4.5	5	4
Maintenance	3.5	3.5	4	4	5	4
Lifetime	3.5	4	3.5	4	4	3.8
Matrix	4	3	3	5	4	3.5

* Recently developed thin-film devices have shown dramatically improved performance, as indicted by the assessment in parenthesis.

Several critical sensor performance metrics have been identified by DOE. NREL independently tests hydrogen safety sensors under controlled conditions and provides the obtained data to sensor manufacturers, who may then use this data to develop sensors that meet the needs of end-users. The ultimate goal of the Hydrogen Sensor Testing Laboratory is to ensure that end-users get the sensing technology they need, whether dictated by code or by the technical requirements of the application. The immediate objectives of the NREL sensor program are as follows:

- Provide independent assessment of hydrogen safety sensor performance relative to DOE published targets and other national and international standards
- Support hydrogen sensor codes and standards development (national and international)
- Test/validate new sensor R&D
- Interact with manufacturers to improve sensor performance to meet DOE 2012 targets
- Foster collaboration between industry and government agencies for sensor testing validation
- Foster international development through collaborations with international SDO and government laboratories, including
  • Interactions with other government laboratories with sensor testing capabilities, including the Joint Research Center (JRC), Institute for Energy, in Petten, Netherlands [21] and Bundesanstalt für Materialforschung (BAM) in Berlin Germany.
  • ISO TC 197 "Hydrogen Technologies", member of working group 13, hydrogen safety sensors, ISO DIS 26142, hydrogen specific standard for sensor testing [3]

Strategically, the NREL Sensor Laboratory will serve as an unbiased interface between end-user needs and sensor producers. Accordingly, NREL will share with the manufacturers and vendors the sensor performance data on their technology; otherwise NREL will maintain confidentiality of data pertaining to the performance of specific technologies. In this manner, sensor manufacturers will be able to review their product performance in terms of the ability to meet required codes and target performance specifications, and respond accordingly to assure the applicability of their technology for deployment.

4.0   ACKNOWLEDGEMENTS

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