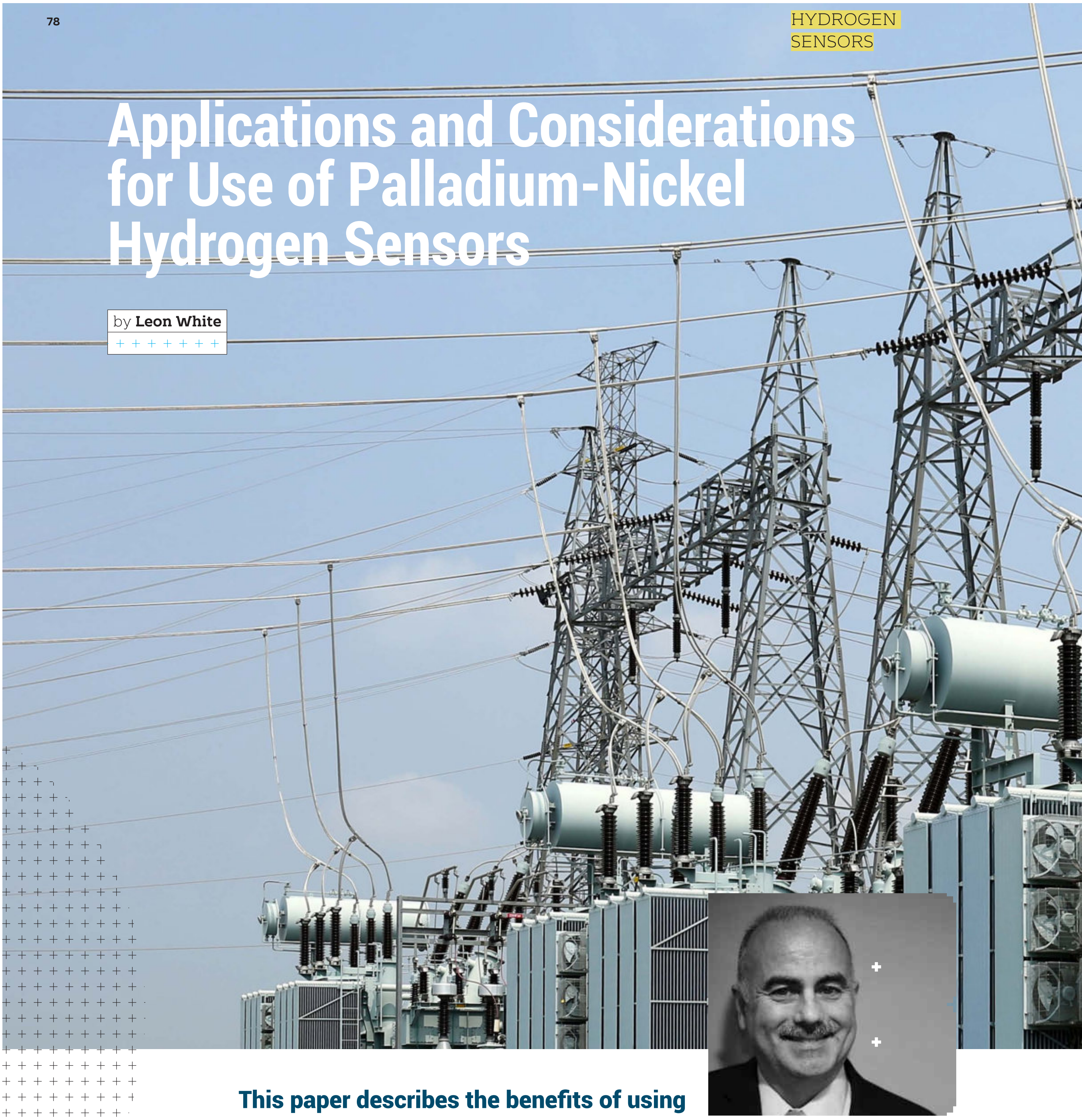

Applications and Considerations for Use of Palladium-Nickel Hydrogen Sensors

by **Leon White**

This paper describes the benefits of using Palladium Nickel Alloy Hydrogen sensors for various applications where Hydrogen specific sensors are required. Typical applications for liquid filled transformers, safety monitors, fuel cells, electrolyzers, and Hydrogen in natural gas pipelines are explored as well.

Keywords: Hydrogen sensor, Palladium, Nickel, Palladium Alloys, Solid-state Sensors, Thin Films

With over 30 years of electric utility and online monitoring experience, **Leon White**, P.E. has a strong background in the application of online sensors for a variety of applications. While at Ameren, the electric utility in St. Louis, Missouri, he held various positions including substation design, transmission regulatory and real time power trading. He has worked for GE and Qualitrol where he developed strong working knowledge of online sensors, substation communications and project management. He is a Professional Engineer and a member of the IEEE Power and Energy Society. He received his Electrical Engineering and MBA degrees from Southern Illinois University at Edwardsville.

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Most sensors used for dissolved gas analysis in transformers require gas to be extracted from the liquid to enable measurement of the Hydrogen content. Palladium Nickel sensors can accurately measure the Hydrogen content directly in the insulating liquid, which ensures the best accuracy since there is no error introduced in the gas extraction process.

Introduction

Although many technologies exist to measure Hydrogen, users need the best technology to fit their application. Sensors must be designed and manufactured to work in a variety of environments where other gases or compounds may affect the Hydrogen measurement. Additional considerations besides the measurement environment are: the required accuracy, the measurement range, the possibility of sensor drift over time, and how the data will be obtained. In addition, users must also evaluate the lifetime cost of using one technology versus another.

The typical Palladium Nickel sensor die is attached to a flexible circuit as shown below. A thin film of Palladium Nickel is deposited onto a substrate to form a resistor. Included on the sensor die is the Palladium Nickel alloy Hydrogen sensing element, a heating element and a temperature sensing element. The material properties of palladium alloys, as well as proprietary coatings, allow the sensor to provide Hydrogen specific measurement without sensitivity to other gases.

I. ENVIRONMENT

When users determine the need to measure Hydrogen, they must evaluate the environment where the sensor will be installed. Can Hydrogen be measured in the native environment, or will a sample be required? What temperatures will the sensor be subjected to? What other gases or substances could affect the Hydrogen measurement? Will the pressure of the environment affect the measurement? Will the life of the sensor be negatively affected by the environment where the sensor is installed? Let us investigate each of these questions in more detail and look at typical applications for Hydrogen measurement.

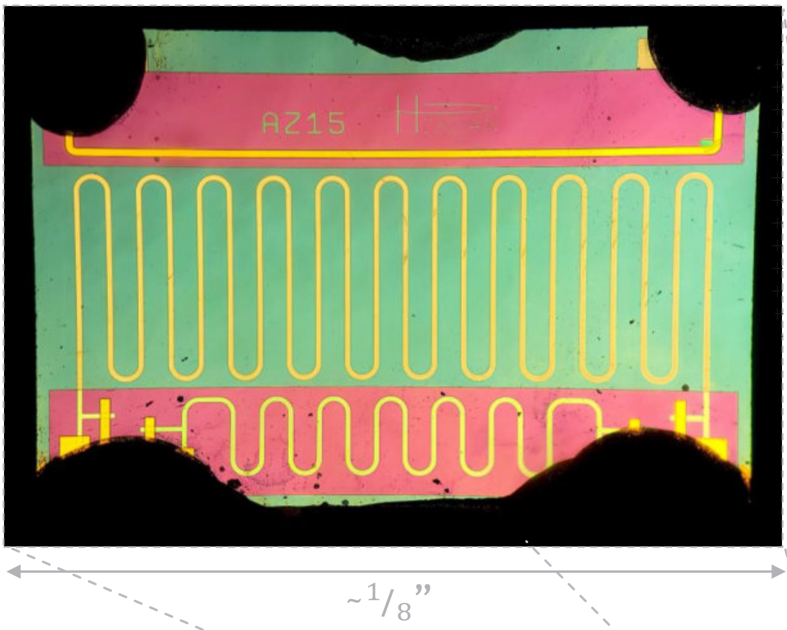
A. Native Environment or Sample?

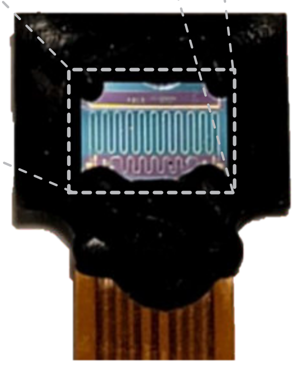
If Hydrogen cannot be measured in the native environment, a representative sample must be obtained from the native environment in a suitable manner and injected into a monitor or analyzer for measurement. Sample extraction can be manual or automatic. Since the procurement of manual samples can introduce errors due to imperfect sampling techniques, automated sampling or measurement in the native environment are preferred. Measurement devices that analyze samples typically control the temperature and pressure of the measurement environment which increases accuracy. Whether samples are taken manually or automatically, some amount of time delay will exist between the time the sample is procured and when the results of the measurement are provided. Many applications require continuous real-time measurement. In those cases, the sensors must be able to survive in the primary environment where the Hydrogen measurement is required. Some advanced systems use a sample conditioning system that removes a sample from a process stream and automatically measures Hydrogen real-time.

B. Temperature

If the sensor is to be mounted in the primary environment, the sensor must be able to withstand the temperatures of that environment. In many cases, sensors must be rated for -40 to 105°C. Palladium

Figure 1. Example of a Palladium Nickel sensor die





When determining the right sensor for the application, users must understand which technology best fits the application and whether a low cost/short life sensor is appropriate or if the application requires a more expensive, long-life solution.

Nickel sensors can withstand most environments that require very high or low temperature ranges. These sensors monitor the temperature of the environment and can use that information to provide more accurate measurement.

C. Cross Sensitivity

Cross sensitivity is a key issue that users must consider. General purpose sensors like thermal conductivity detectors (TCDs) are sensitive to many gases and are typically only applied in gaseous environments. Devices that use a TCD to measure Hydrogen must separate the Hydrogen from other gases in the sample using an extraction technique. While this typically provides accurate Hydrogen measurement, the equipment necessary to extract and/or separate the Hydrogen is costly. There is also a typical time delay of 15 to 60 minutes between the time the sample is obtained and when the result is available. Palladium Nickel sensors can normally be mounted in the primary environment and are designed to be Hydrogen specific, negating the need to separate the Hydrogen from the primary environment. These sensors can also be conditioned to survive in harsh background environments like carbon monoxide and hydrogen sulfide. The use of proprietary coatings and conditioning techniques allow Palladium Nickel sensors to survive in harsh environments for the life of the sensor.

D. Pressure

Since most measurement devices require samples to be obtained from the primary environment for testing, the measurement device can provide a controlled environment for testing, typically at normal atmospheric pressure. When the sensor is installed in the primary environment, the gas pressure is likely to affect the Hydrogen measurement. Palladium Nickel sensors are partial pressure devices. These sensors are typically calibrated at 1 atmosphere, so they are very accurate at that pressure. If the pressure changes, the hydrogen measurement directly correlates with the increase or decrease in pressure. For instance, if the pressure is increased from one atmosphere to two atmospheres, the sensor will read twice the measurement it would read at one atmosphere. For that reason, operating a Palladium Nickel sensor in a high-pressure environment requires the pressure to be measured to compensate the Hydrogen measurement to a normalized value.

II. OTHER SENSOR CONSIDERATIONS

A. Sensor Life

For most applications, users desire a Hydrogen sensor or monitor that lasts as long as possible without the need for calibration or replacement. Typical sensor life of most Hydrogen sensors is one to five years because the sensor element is either consumed or otherwise reaches end of life. The sensor can become 'worn out' due to chemical changes in the sensor when exposed to Hydrogen or due to other environmental factors like exposure to destructive gases, heat, or moisture. Palladium Nickel sensors are not consumed in the presence of Hydrogen. Proprietary protective coatings enable Hydrogen to enter the Palladium Nickel lattice where the presence of Hydrogen changes the resistance of the sensor. The change in resistance is measured in nano-ohms (10-9 ohms). Hydrogen moves freely in and out of the Palladium Nickel lattice without being consumed or changing the chemical makeup of the sensor. For this reason, the Palladium Nickel element is not the limiting factor to the life of the sensor. The limiting factor is determined by the electronics design that measures the resistance of the sensor, controls the temperature at the sensor (if required), and otherwise manages administration of the sensor, data processing, communications, and power supply. Robust designs allow for Palladium Nickel sensors to last 10 to 15 years or longer.

The largest application for Hydrogen sensors to date has been to measure Hydrogen generated in the insulating liquids of electrical transformers. Hydrogen is also monitored in battery rooms, and more recent applications include Hydrogen electric generation facilities, electric fuel cells, electrolyzers and natural gas pipelines that are now utilizing a mixture of Hydrogen with natural gas.

B. Lifetime Cost

Hydrogen sensors are available for a variety of applications which provide varying accuracies, measurement ranges and which survive in a variety of environments. When determining the right sensor for the application, users must understand which technology best fits the application and whether a low cost/short life sensor is appropriate or if the application requires a more expensive, long-life solution. For instance, manned facilities where qualified 'analyzer staff' is readily available may choose a low-cost sensor that requires periodic calibration and/or can be replaced regularly. If a user is designing a system to monitor for Hydrogen leaks at a remote, unmanned Hydrogen filling station, the designer would most likely choose a more expensive sensor that has a long life and does not require periodic calibration.

Recent advancements in Palladium Nickel sensor technology allow for continuous measurement with no calibration required for the life of the sensor.

C. Data Access

Once the Hydrogen is measured, the data needs to be provided to another system or the end user. While some applications simply require alarm relay contacts, others might require analog outputs (typically 4-20mA) or a communication protocol like Modbus RTU. It is important to recognize the data requirements to ensure the sensor communications are correct for the application.

III. POPULAR HYDROGEN SENSOR APPLICATIONS

Historic applications for Hydrogen sensors include processes and equipment that generate Hydrogen, Hydrogen storage facilities, and facilities where Hydrogen is used. Interestingly, perhaps the largest application for Hydrogen sensors to date has been to measure Hydrogen generated in the insulating liquids of electrical transformers. Hydrogen is also monitored in battery rooms where lead-acid batteries generate Hydrogen during charging cycles. More recent applications include Hydrogen electric generation facilities, electric fuel cells, electrolyzers and natural gas pipelines that are now utilizing a mixture of Hydrogen with natural gas.

A. Liquid Filled Transformers

Hydrogen monitors have been used for more than 40 years to detect Hydrogen that is generated due to the breakdown of transformer insulating liquid (typically mineral oil). Tens of thousands of Hydrogen and multi-gas monitors are installed globally because Hydrogen generation indicates problems inside the transformer. Most sensors used for dissolved gas analysis (DGA) in transformers require gas to be extracted from the liquid to enable measurement of the Hydrogen content. Palladium Nickel sensors can accurately measure the Hydrogen content directly in the insulating liquid. This ensures the best accuracy since there is no error introduced in

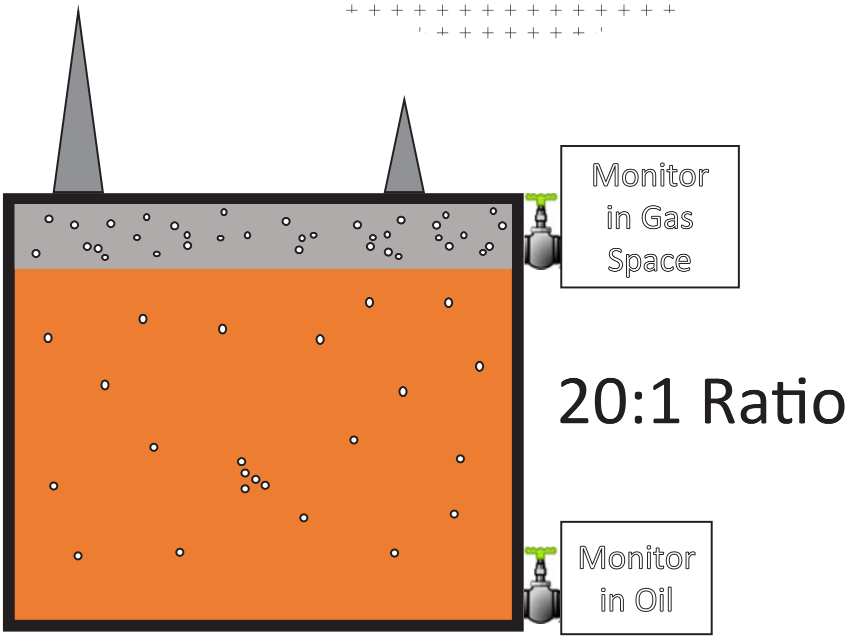


Figure 2. Sensors may be mounted in the insulating liquid or in the gas space to measure Hydrogen inside liquid filled transformers.

the gas extraction process. Common insulating liquids today include mineral oil, natural esters (vegetable oil), synthetic esters, and silicone oil. Not all sensors are rated for use with these liquids, so users need to ensure the sensor used is rated for the liquid in their transformers. Since Hydrogen dissolves at different rates in each liquid, a factor called the Ostwald Coefficient defines the dissolution rate in each liquid. By understanding the properties of each liquid and factoring in the use of the Ostwald Coefficient, Palladium Nickel sensors can accurately measure Hydrogen in each of these liquids. Measurement accuracy is maintained by adjusting the calculation algorithm with the appropriate Ostwald coefficient for the desired liquid.

Many liquid filled transformers have an inert gas space above the liquid. In these transformers, Hydrogen can be measured in either the liquid or in the gas space. Hydrogen that is generated in the liquid also fills the gas space. At equilibrium, the Hydrogen concentration in the gas space is approximately 20 times the amount dissolved in the liquid. Therefore, it is important that users choose sensors with the appropriate measurement range for each environment. Typical Palladium Nickel sensors measure up to 5000 PPM in the insulating liquid and up to 100,000 PPM (10% Hydrogen) in the gas space. In rare cases, transformers in operation can reach up to 30,000 to 40,000 PPM of Hydrogen in liquid or 60-80% Hydrogen in the gas space. Recent advances in Palladium Nickel sensors now allow measurement of very high levels (up to 100%) in these transformers with sensors that require no periodic calibration. See "Fig. 2" for typical sensor mounting locations for liquid filled transformers.

B. Safety Monitors/Battery Rooms

When users are interested in monitoring for Hydrogen leaks, they install sensors in areas where the leaks can be detected. In this case, the sensor must be able to measure low levels of Hydrogen and remain stable when Hydrogen is not present for long periods of time. It is important to note that Hydrogen becomes combustible at a level of 4%. Therefore, typical safety application solutions designed for battery rooms activate a vent fan at 1%, then have an alarm setpoint of 2% to ensure employees are notified if dangerous levels of Hydrogen are present. Many safety solutions refer to the Hydrogen level in terms of the Lower Explosive Limit (LEL). For instance, in this case the fan is turned on at 25% LEL (1% in air) and the alarm is triggered at 50% LEL (2% in air).

Many systems include audible alarms and flashing lights to ensure employees working in the area are made aware of the possible danger. Most sensors used for this application require periodic calibration and replacement every one to five years. Palladium Nickel sensors are available for this application with a 10-to-15-year life requiring no field calibration for the life of the sensor. See "Fig. 3" for a typical battery room safety solution.

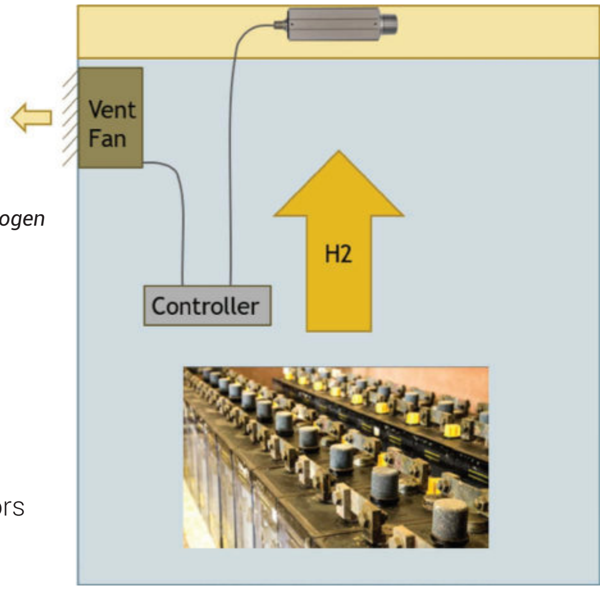


Figure 3. Example of a Hydrogen monitoring safety solution for a battery room that uses vented lead acid batteries

C. Fuel Cells

In addition to monitoring for leaks in the primary Hydrogen system, fuel cell manufacturers also need to know if Hydrogen migrated through the fuel cell and reached the exhaust without being consumed. In addition, manufacturers need to measure excess Hydrogen that was fed to the fuel cell but exceeded the amount required for fuel cell operation. See "Fig. 4" for sensor locations in a fuel cell.

D. Electrolyzers

Electrolyzers separate Hydrogen and Oxygen from water. Due to recent interest in green fuels, electrolyzer system installations are increasing rapidly. Since the electrolyzer is designed to produce pure Hydrogen, the Hydrogen output of the electrolyzer is monitored to ensure other gases or compounds are not contaminating the desired pure Hydrogen output. A Hydrogen sensor is also installed on the Oxygen side to ensure Hydrogen is not mixed with the Oxygen. See "Fig. 5" for sensor locations in an electrolyzer.

E. Hydrogen in Natural Gas
Natural gas companies are investigating how they can inject Hydrogen into natural gas pipelines. This concept presents many challenges since Hydrogen molecules are significantly smaller than Methane molecules. Methane is the primary component of natural gas. Gas companies are working on ways to ensure Hydrogen does not leak out of the pipeline prior to reaching the desired destination. There are many locations where gas companies will need to install Hydrogen sensors. Those include the Hydrogen production facility, the blending/injection stations, the compressor stations, the storage locations, along the pipeline, and at local commercial, residential and fueling locations.

The global growth of Hydrogen use in everything from fuels cells to natural gas pipelines has given rise to the demand for high quality Hydrogen sensors. Palladium Nickel sensors are available for most environments, have a long life, and remain Hydrogen specific in the presence of other gases, providing designers with an excellent option that ensures end users see the value of using these maintenance free sensors.

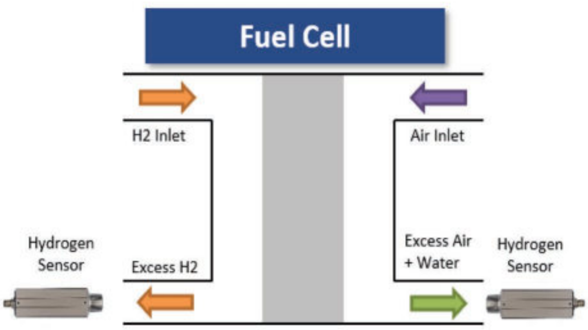


Figure 4. Example of sensor locations in a Hydrogen fuel cell

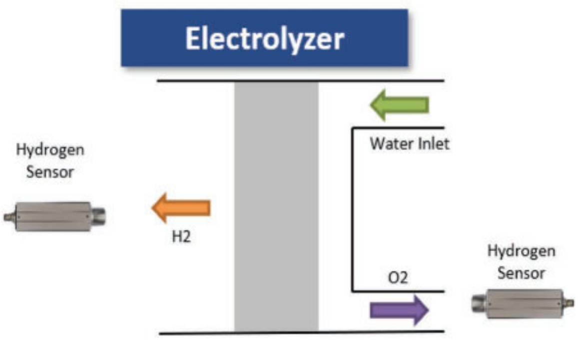


Figure 5. Example of sensor locations in an electrolyzer

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IV. CONCLUSION

With the global growth of Hydrogen use in everything from fuels cells to natural gas pipelines, the demand for high quality Hydrogen sensors is on the rise. Designers will need Hydrogen sensors with the right features and functionality for their applications. Since Palladium Nickel sensors are available for most environments, have a long life, and remain Hydrogen specific in the presence of other gases, designers have an excellent option that ensures end users see the value of using these maintenance free sensors. Since the sensors auto-calibrate during operation, users will also have confidence in the accuracy of the sensors and enjoy no down time for sensor calibration or replacement.