Hydrogen-Specific Sensing for Specialised Applications

Monitoring hydrogen in the presence of other gases is an important requirement in many process industries for both process optimisation and for safety. These measurements are often difficult or costly to perform, however, Milton Keynes based instrumentation specialist Quantitech is finding a broad spectrum of applications for a new technology from the United States that resolves these issues.

Commenting on the market for hydrogen sensing, Quantitech Sales Director Dominic Duggan says, "Hydrogen monitoring does not take place in many applications because of the problems or costs associated with the available technologies, (e.g. lack of specificity) however, the new sensors from H2scan resolve these issues offering significant advantages in process control and safety management. For example, we have recently delivered a large number of hydrogen detectors to monitor potentially explosive concentrations in battery charging rooms."

Hydrogen leak detection

The U.S. company H2scan has developed inline, solid-state palladium-nickel based sensors that are highly selective to hydrogen, do not require oxygen to operate, and can detect hydrogen in concentrations from a few ppm to 100%.

Hydrogen has the potential to be an important source of clean fuel in our energy-driven economy. The use of hydrogen (H_2) is widespread in both traditional applications, such as petroleum refineries, and growing rapidly in newer sectors such as fuel cells and power generation. Global hydrogen consumption grew from 21 million metric tons (Mmt) in 2005 to more than 32 Mmt in 2007. Global hydrogen usage is expected to surpass 50 Mmt by 2012 and is expected to exceed 79 Mmt by 2016.

Currently, over 90% of all hydrogen produced is used in the petroleum refining industry, where continuous monitoring of hydrogen is highly desired to improve both the quality and yield of hydrocarbon-based fuels. Because of hydrogen's combustible and explosive properties, accurate leak detection is also important for safe hydrogen transport, storage, and use.

Hydrogen Basics

Hydrogen is a flammable gas when combined with air in concentrations between 4% by volume (lower flammable limit) and 75% by volume (upper flammable limit). It has a larger window of flammability in comparison to natural gas, gasoline, propane, ethane, methane, and propylene. In fact, the flammability limit of hydrogen is seven times wider than that of methane. For safety applications, it is therefore critical that a hydrogen sensor has a wider measurement range (1%–99% v/v H_2) than is required for most common fuels.

Since hydrogen is the lightest of elements and the smallest molecule, it has the greatest tendency to leak. In terms of process safety, a hydrogen leak can be more dangerous and harder to detect than leaks of other gases, because of its wider flammability and fast diffusion rate.

Hydrogen Sensors, Operation, and Drawbacks

Any hydrogen sensor technology needs to satisfy the three basic requirements—sensitivity, selectivity, and specificity. It should be functional over the range of interest and be free of cross-interference from other gases present in the environment. Sensing technologies for hydrogen have been studied since the early 1900s and several traditional sensing mechanisms are still widely used in the industry: gas chromatography, mass spectrometry, catalytic bead, and thermal conductivity.

Solid-state metal oxide and catalytic bead sensors use heated catalysts to sense hydrogen. They require heating to around 300°C to enable surface reactions that promote hydrogen sensing and are not hydrogen-specific. Electrochemical sensors are based on known electrolytic reactions of hydrogen and use liquid or solid electrolytes. Sensors that use liquid electrolytes tend to have limited lifetimes because they employ a consumable (the electrolyte), their membranes have limited life-spans, and they can have leakage issues.

The hydrogen sensors based on thermal conductivity, catalytic bead, metal oxide, and electrochemical technologies require the presence of oxygen for sensor operation. Sensors that use palladium (Pd), a hydrogen-specific material, do not require oxygen for operation. Palladium-based sensors are gaining popularity in the industry because of their reliability and high specificity to hydrogen.

A Novel Hydrogen Sensor

The hydrogen-specific sensor technology developed by H2scan is based on the unique interaction between hydrogen and palladium. Molecular hydrogen dissociatively adsorbs on palladium surfaces and atomic hydrogen readily diffuses into the palladium lattice in a quantity proportional to the hydrogen partial pressure above the surface.

H2scan hydrogen-specific sensors have two components that measure hydrogen atoms which have diffused into the palladium lattice:

1. A metal insulator semiconductor (MIS) device (e.g., capacitor, FET, or Schottky diode) that detects hydrogen atoms as a charge at the interface of palladium and an underlying dielectric material

2. A thin-film resistor whose resistance increases with increasing hydrogen uptake as the hydrogen atoms distort the palladium lattice and increase the number of scattering sites for electrons.

The MIS device (a capacitor in current products) is sensitive to hydrogen concentrations from a few ppm to about 0.5% v/v , while the thin-film resistor is sensitive from concentrations of hundreds to thousands of parts per million (depending on background gases) to 100% hydrogen at several atmospheres. Because the sensor responds only to hydrogen in the palladium lattice, the sensors are fundamentally specific to hydrogen and this creates several advantages over existing technologies. For example, H2scan sensors can operate in inert environments because they do not require oxygen to operate and they do not require a premixed reference gas or precise control of analysis gas temperature as thermal conductivity analysers do. Furthermore, because only the partial pressure of atomic hydrogen is directly measured, the sensing mechanism is fundamentally specific to hydrogen.

Hydrogen monitors for occupational safety and process monitoring

In addition to the hydrogen-sensitive MIS and resistor devices, the H2scan sensor has integrated temperature control elements - a temperature measurement device and a resistive heater - created using the company's "chip on a flex" technology. This independent temperature control allows the sensor to tolerate a wide range of gas temperature and flow conditions.

The company has also developed a proprietary protective barrier. The molecular-level coating is deposited directly on the sensor surface where it allows the sensor to operate in the presence of carbon monoxide (CO) and hydrogen sulphide (H_2S) contaminants that would poison an unprotected palladium surface. The sensor system can tolerate continuous operation in gas streams containing up to 100 ppm of CO and 1000 ppm of H_2S. The hydrogen-specific analyser has both a fine wire mesh and an automotive-grade GORE-TEX membrane separating the sensor from the analysis gas. These protect the sensor from particulates and from liquid droplets in mixed-phase gas streams, respectively. The hydrogen specificity provided by this design enables hydrogen leak detection, accurate hydrogen monitoring for safe area operation, and continuous inline process monitoring.

The process-hardened device can be installed at multiple points in a process plant and directly linked to a DCS or PLC. The Model 700 HY-OPTIMA, for example, is an online process monitor that has been tested in gas streams of 1000 ppm H_2S, 100 ppm CO for refinery applications as well as in gas streams of 50% Cl2, 95% RH for corrosive applications. The ruggedness of the sensor extends its operational life in most process streams, including complex hydrocarbons, to more than 3 years, with low sensor replacement costs. Its robust, corrosion-resistant sensor probe can be installed into a gas stream with temperatures from –20°C to 100°C and pressures to 100 psig, using Swagelok compression fittings that make it transferable to the New Sampling/Sensor Initiative (NeSSI) platform. NeSSI is an industry initiative undertaken to standardise and simplify the design of systems used in chemical process analysis. Sensor system components are ATEX certified for operation in Class I/Div II Group B hazardous locations. The sensor's 4-20mA output can be readily integrated into existing data control systems.

Sensor Applications

In certain industrial applications—such as hydrogenating cooking oil and hydro-treating petroleum crude into heating oil, gasoline, and diesel and jet fuels—it is critical to quantify the absolute concentration (partial pressure) of hydrogen in process operations to ensure process safety and operational efficiency. A typical refinery application for an inline hydrogen sensor is to measure the total hydrogen content in a mixed gas matrix (a mixture of hydrocarbons, CO_2, H_2, and other gases) as a function of time. The H2scan inline process hydrogen sensor allows direct point-of-use analysis of hydrogen concentration from 50%–100% v/v.

Hydrogen producers are also interested in accurate sensing as a key part of hydrogen management. For instance, within the pharmaceutical industry, multiphase hydrogenation reactions involving solid catalysts play a critical role. Accurate hydrogen monitoring is also needed in hydrotreating and in hydrogenation processes in hydrogen production facilities.

Online Hydrogen process analyser

Hydrogen monitoring in nitrogen atmospheres can be useful for atmosphere control in semiconductor industries. A hydrogen-nitrogen protective atmosphere (rather than ammonia) in heat-treating operations provides a safer, non-toxic alternative to dissociated ammonia in metal and materials processing applications and provides improved reliability, better regulatory compliance, improved safety, lower maintenance requirements, and lower capital costs.

Currently, hydrogen measurements are not taken at all needed monitoring points because establishing monitoring techniques (e.g., mass spectrometry and gas chromatography) are cost-prohibitive for multi-point installations. The H2Scan inline hydrogen sensor can enable these applications.

During molten aluminium processing, aluminium can react with moisture to form aluminium oxide and hydrogen. Hydrogen is far more soluble in liquid aluminium than it is in solid aluminium and can cause porosity during solidification if the concentration of dissolved hydrogen is too high. A proposed use of these newest process hydrogen sensors is to quantify the hydrogen content directly from the nitrogen gas used to blanket the molten aluminium, which may allow the process control system to respond to the hot off-gas at an earlier stage during the process.

In chlorine manufacturing, energy generation, nuclear power plants, and power transformers, hydrogen monitoring is important in preventing failures and explosions. Monitoring is also important in hydrogen refueling stations, service pump areas, and in the engine compartment of hydrogen-powered fuel cell vehicles.

Hydrogen sensors can now be applied to current and future gas- or liquid-filled pipelines, offering safety improvements with a hydrogen-specific sensor that can be wrapped around pipeline joints and valves to detect the first level of leakage, or additional sensors can be employed to quantify the hydrogen content of natural gas within the pipeline.

In summary, the applications for hydrogen-specific sensors have increased markedly as a result of the new technology and because accurate hydrogen monitoring is a key component of several emerging areas of the hydrogen-driven energy economy.

AUTHOR DETAILS

Keith Golding
Managing Director
Quantitech
Unit 3
Old Wolverton Road
Milton Keynes MK12 5NP
Tel: 01908 227722
Fax: 01908 227733
Email:
sales@quantitech.co.uk