INTERNATIONAL JOURNAL OF HYDROGEN ENERGY XXX (2014) 1–10

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Developments in gas sensor technology for hydrogen safety

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Keywords:
Hydrogen sensor
Hydrogen safety

ABSTRACT

Gas sensors are applied for facilitating the safe use of hydrogen in, for example, fuel cell and hydrogen fuelled vehicles. New sensor developments, aimed at meeting the increasingly stringent performance requirements in emerging applications, are reviewed. The strategy of combining different detection principles, i.e. sensors based on electrochemical cells, semiconductors or field effects in combination with thermal conductivity sensing or catalytic combustion elements, in one new measuring system is reported. This extends the dynamic measuring range of the sensor while improving sensor reliability to achieve higher safety integrity through diverse redundancy. The application of new nanoscaled materials, nanowires, carbon tubes and graphene as well as the improvements in electronic components and optical elements are evaluated in view of key operating parameters such as measuring range, sensor response time and low working temperature.

Introduction

Different sensing technologies are employed to detect hydrogen. Classification of hydrogen sensors based on a range of technologies including catalytic combustion, thermal conductivity, work-function based, mechanical effects and optical effects has been established and reviewed by Hübert [1]. A market analysis shows a wide selection of highly qualified commercially available hydrogen sensors [2]. However, it has been shown that not all sensor performance requirements can be fulfilled for specific applications by any individual product. There is for example a strong need to monitor and check the environment of the fuel cells for traces of leaked hydrogen. In particular, monitoring of the exhaust duct, especially the waste air duct is necessary. Membrane leakages as well as potentially explosive H_2–O_2 gas mixtures can be detected by the measurement of hydrogen in the waste air duct. In most existing applications monitoring of the single cell voltage is used to indicate possible membrane leakages. Sensors for temperature, pressure, flow and humidity are used for control functions. In addition to system design measures e.g. redundant provision of shutoff and safety valves, hydrogen sensors can also contribute to the safety of the system. Therefore, a lot of research is on-going to develop new sensing materials and to improve and optimise various elements of established hydrogen sensor types. We give an overview on new commercially available sensors and upcoming sensors under

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http://dx.doi.org/10.1016/j.ijhydene.2014.05.042

development using new materials or novel technologies. The presented results on scientific activities are based on different literature reviews. For the time range from 2010 to 2013, for instance, more than 400 cited publications related to hydrogen sensor research were found.

Requirements on hydrogen safety sensors

Hydrogen sensors are by no means 'new' devices as they have been used for decades in various industrial environments such as the petroleum, food, chemical and aerospace industries. For these environments, the sensor operating conditions are well defined by the expected ambient conditions and exposure to potential interfering species associated with the specific application. The sensors used in these settings are typically installed and operated by skilled and trained personnel according to documented sensor maintenance and calibration procedures. As the use of hydrogen becomes increasingly commonplace in the emerging hydrogen economy, hydrogen safety sensors will become widespread in different applications under more diverse working conditions. Therefore, it is useful to identify a number of generic performance requirements for safety sensors. These various requirements can be summarised as follows, in which fuel cell applications are listed separately if appropriate [1,3]:

- indication of hydrogen concentration in the range 0.01–10%[1] (safety) or 1–100% (fuel cells)
- safe performance, i.e. explosion proof sensor design and protective housing
- reliable response with sufficient accuracy and sensitivity (uncertainty 5–10% of signal)
- stable signal with low noise
- robustness including low sensitivity to environmental parameters such as:
    - temperature, −30 to 80 °C (safety), −70 to 150 °C (fuel cells)
    - pressure, 80–110 kPa
    - relative humidity, 10–98%
- gas flow rate independence
- mechanical robustness
- fast response and recovery time (<1 s)
- low cross sensitivity (e.g. hydrocarbons, CO, H_2S)
- long life time (>5 years)
- low power consumption (<100 mW)
- low cost (<100 USD per system)
- small size
- simple operation and maintenance with long service interval
- validated and certifiable according to international standards
- simple system integration and interface

[1] The content of gases is always given as a volume fraction in percent.

Requirements on sensor performance and functional safety are also stated in international standards to ensure reliable and safe use of hydrogen [4–9].

Recent advancements in commercial hydrogen sensors

Several studies on commercial off-the-shelf hydrogen sensors have demonstrated the inability of any one hydrogen sensing technology to meet all the performance requirements expected by customers for the wide variety of possible applications [2]. For this reason hydrogen sensor developers and manufacturers are making large efforts to optimise their detection technologies and are investigating innovative ways to combine different sensing technologies in one detection device, sometimes called smart or intelligent sensor. In this section we report a number of hydrogen sensors, which were brought onto the market recently and highlight innovative aspects concerning their design and performance, based on data provided by the manufacturer.

Combination of two hydrogen sensing platforms

Semiconductor-based hydrogen sensors have a limited measuring range. The limit of detection is typically around 10 ppm and the upper concentration which can be detected is in the range of some percent of hydrogen. The sensor can show saturation effects that may reduce its sensitivity. The concentration of oxygen or humidity may have influence on the sensor response. Thermal conductivity sensors on the other hand can detect hydrogen concentrations up to 100% and, advantageously, this sensor platform does not need oxygen for its operation. Therefore, they can be applied as orthogonal (i.e. independent) sensing platforms. An example of the combination of these two different sensing platforms in a relatively small sized device is the H_2-Semicon®-Detector of UST Umweltsensortechnik GmbH (see Fig. 1). It comprises a semiconductor gas sensing element based on SnO_2 and a thermal conductivity sensing element in a diverse redundancy gas detection device. The signals of both sensors are evaluated in a conjoint unit and combined via a weighting

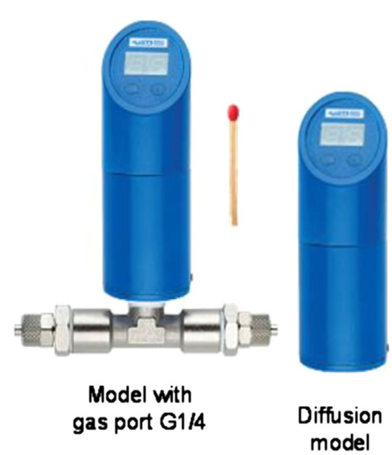

Fig. 1 – H_2-Semicon®-sensor system [10].