University of Piraeus

National Technical University of Athens

POSTGRADUATE STUDIES IN
ADMINISTRATION AND MANAGEMENT OF INDUSTRIAL SYSTEMS
SPECIALISATION: SYSTEMS OF ENERGY AND ENVIRONMENTAL MANAGEMENT

Master Thesis

Design of Hydrogen Leak Detection System – Safety & Reliability Issues

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Piraeus 2015

Abstract

Hydrogen is being widely promoted as the future primary energy carrier to replace current hydrocarbon fuels. Governments and industries are investing in research and development programs to develop hydrogen production, transport and storage technologies. In addition, hydrogen gas is currently used in chemical processing and aerospace applications. Hydrogen gas is combustible with a wide flammability range of about 4 to 75 percent, a low ignition energy, and a low gas density. With the expanding application of hydrogen gas coupled with its highly combustible nature, focus must be placed on safety. Detection and monitoring technologies are needed which can provide low limits of detection, high sensitivity, a wide detection range, fast response times and ease of implementation to ensure public safety. Hydrogen sensors are of increasing importance in connection with the development and expanded use of hydrogen gas as an energy carrier and as a chemical reactant. Also they are essential to facilitate the detection of accidental hydrogen releases wherever hydrogen will be produced, distributed, stored, and used.

This thesis highlights the importance of hydrogen sensing regarding the safety and reliability. The first chapter describes and classifies the different types of hydrogen sensors and the technology behind them. Characteristic performance parameters of these sensor types, such as measuring range, sensitivity, selectivity and response time are reviewed.

In the second chapter the methods of the tests performed on the commercially available hydrogen sensors are described. Parameters such us detection limits and response times are measured and the advantages and disadvantages of those sensors are written down.

In the third chapter new hydrogen detecting technologies will be mentioned either available in the market or under development and afterwards we will refer to the improvements of knowledge on hydrogen safety, according to the standards and guidelines of the International Energy Agency's Hydrogen Implementing Agreement. Regulations will be also mentioned.

The fourth chapter describes the framework of the Hydrogen Safety Engineering (H2SE) profession which is defined as an application of scientific and engineering principles to the protection of life, property and environment from adverse effects of incidents/accidents involving hydrogen. Finally a reliable and comprehensive safety risk analysis model has been developed.

In the fifth chapter of this thesis there is a summary with the conclusions deducted of this work.

Keywords: Hydrogen sensor, detection technology, reliability, safety, accuracy, hazards, safety engineering, risk analysis

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Introduction

The global need for energy is rising and an ever-increasing need for an energy carries can be felt. Hydrogen is one of the most promising substances with many advantages that can be utilized in this sector. Hydrogen is an environment-friendly fuel, the only matter that is produced when hydrogen is burned in an internal-combustion engine is harmless water vapor. Hydrogen can be easily stored in different ways including high pressure cylinder, in the form of a cryogenic liquid fuel, hydrides, or on carbon fibers. Hydrogen is fuel not only for aerospace, but also possibly for common use in transportation, where only emissions are water. The public is, however, concerned about the safety of hydrogen, which is essential due to the nature of hydrogen. Despite all the advantages, producing, storing, transporting, and using hydrogen as a secondary fuel always bring various risks to the surrounding environment. The hazards of hydrogen arise from its wide range of flammability and the substantial amount of energy released if it burns or explodes. Furthermore, hydrogen-related accidents are not rare and history has witnessed several accidents associated with hydrogen.

Hydrogen has a number of unusual properties in comparison to other combustible gases and vapors, such as methane, propane or gasoline vapor. These include a very low density (0.0899 kg/m^3) and boiling point (20.29 K) combined with a high diffusion coefficient (0.61 cm^2/s in air) and buoyancy. In terms of its combustion characteristics, it has a low minimum ignition energy (0.017 mJ), high heat of combustion (142kJ/g H_2) and wide flammable range (4-75%), as well as a high burning velocity, detonation sensitivity and an ignition temperature of 560 °C [1]. Hydrogen also acts as a strong reducing agent for many elements and has a high permeability through many materials, which demands special precautions in certain applications. It is lighter than air and mixes with air to create a flammable and explosive mixture. Lower flammable limit (LFL, also lower explosion limit - LEL) of hydrogen is 4% of volume, while Upper flammable limit (UFL) is 75% of volume.

As a colorless, odorless and tasteless flammable gas hydrogen cannot be detected by human senses, and other means are therefore required to detect its presence and quantify the concentration. Rapid and accurate hydrogen gas concentration measurement is essential to alert to the formation of potentially explosive mixtures with air and to help prevent the risk of an explosion.

The detection and concentration measurement of hydrogen has a history of over 100 years beginning with hydrogen measurements at filling stations for airships. However, there is a continued need for faster, more accurate and more selective detection of hydrogen gas in various areas of industry for monitoring and controlling hydrogen concentration. For example hydrogen gas concentration monitoring is important in the synthesis of ammonia and methanol, the hydration of hydrocarbons, the desulphurization of petroleum products and the production of rocket fuels [1]. In coal mines hydrogen can be produced in the ppm range by methane or coal-dust explosions or by the spontaneous heating and low-temperature oxidation of coal. In the lighting industry also, hydrogen is a contaminant that must be quantified during the production of krypton, xenon and neon. Hydrogen leak detection is performed at gas supply tubes and in process plants, where its presence can indicate corrosion or where hydrogen is used as a coolant for turbine generators. Liquid hydrogen is used as a fuel in space applications and hydrogen sensors are therefore used for leak detection during shuttle launches and other aerospace operations. Hydrogen sensing can also play a role in biomedical applications as an indicator for certain diseases and for the detection of environmental pollution.

Hydrogen is an energy carrier and can contribute to overcoming the problems of dwindling fossil fuel reserves, energy supply security and global warming. Ongoing research, development and as yet small-scale deployment of hydrogen technologies seek to realize this potential. In this emerging hydrogen economy, the detection of hydrogen leaks and the measurement of hydrogen concentration are necessary during production, storage, transportation and use in both stationary and mobile applications. Sensors will therefore be used for safety monitoring of hydrogen production plants, pipelines, storage tanks, refueling stations and automotive vehicles.

Hydrogen sensors are transducer devices that detect hydrogen gas molecules and produce an electrical signal with a magnitude proportional to the hydrogen gas concentration [1]. Hydrogen sensors have several advantages over the conventional hydrogen detection methods, including their lower cost, smaller size and faster response. These advantages make them more suitable for portable and in situ hydrogen detection in a range of applications. Such sensors are well-established for use in industry where they can be calibrated regularly and operated by trained personnel. However, the emergence of a hydrogen economy provides the impetus to produce low cost, low maintenance, easy to install, easy to use, accurate hydrogen sensors appropriate for use by untrained individuals in a variety of applications.

There are many different types of hydrogen sensors commercially available or in development. Most hydrogen sensing principles have been known for decades and hydrogen sensors have been commercially available for many years. In order to meet the demands of a future hydrogen economy however, a lot of research is ongoing to continuously improve sensitivity, selectivity, response time and reliability in addition to reducing sensor size, cost and power consumption.

To use hydrogen in large scale and mainly in hydrogen-powered cars new facilities must be implemented to replace today’s gasoline-based infrastructure with that of hydrogen. This will bring serious safety problems because hydrogen gas is not only highly explosive with flammability limit in air about 4% but also invisible and non-odorant. In comparison with other fuels, methane gasoline for example, hydrogen has also much lower ignition energy. For safety of hydrogen-power facilities a sensitive leak detection system is therefore crucial.

Abbreviations

MEMS	Microelectro-Mechanical System
LFL	Lower Flammable Limit
LEL	Lower Explosion Limit
UFL	Upper Flammability Limit
MOx	Metal-Oxide
FBGs	Fibre Bragg Gratings
LPGs	Long Period Gratings
OTDR	Optical Time Domain Reflectometry
BAW	Bulk Acoustic Waves
QCM	Quartz Crystal Microbalance
PSRC	Piezoelectric Sound- Resonance Cavity
SAW	Surface Acoustic Waves
IDT	Interdigital Transducers
IEC	International Electrotechnical Commission
ADC	Analogue-to-Digital Converter
FDC	Frequency-to-Digital Converter
SIL	Safety Integrity Level
CNT	Carbon Nanotubes
RFID	Radio Frequency Identification
CFD	Computational Fluid Dynamics
H2SE	Hydrogen Safety Engineering
EDST	Elementary Design Safety Tool
DD	Draft for Development
QDR	Qualitative Design Review
DDT	Deflagration-to-Detonation Transition
QRA	Quantitative Risk Assessment
PID	Piping and Instrumentation Diagram
HAZOP	Hazard and Operability
PRA	Preliminary Risk Analysis
QRA	Quantitative Risk Assessment
ETA	Event Tree Analysis

CHAPTER 1

HYDROGEN SENSORS

Hydrogen detection technologies

Sensors can be used simply to identify the presence of hydrogen or to measure its concentration. Quantification of hydrogen concentration is important at the ppm level for the analysis of impurities, at the Lower Flammable Limit (LFL) level of 4% hydrogen in air for safety applications or at higher concentrations for monitoring and controlling processes [1]. Interaction of hydrogen with the sensing element of a hydrogen detection device can cause changes in temperature, refractive index, electrical properties and mass as well as mechanical changes. A transducer is needed to transform these changes into an electrical signal.

Most of the known sensing principles for the detection of combustible or reducing gases are applied to hydrogen also. However this implies a possible cross sensitivity to other combustible or reducing gases. Selective hydrogen sensors are based on the specific interactions (catalytic reactivity and solubility) of hydrogen with some noble elements such as palladium and platinum. Either the reaction itself (reaction heat, exchanged charge carriers) or the resulting changes in properties of the sensing material (resistance, volume expansion etc.) can be used to detect and quantify the hydrogen gas concentration.

Although palladium and platinum are widely used in hydrogen detection, these metals are susceptible to mechanical damage on exposure to hydrogen. Aside from their surface catalytic activity, they can also absorb hydrogen into the bulk material, which causes it to expand. Palladium has a much greater capacity to absorb hydrogen than platinum, and undergoes a phase transition as the hydrogen content increases. The two non-stoichiometric hydride phases, a ($\sim PdH_{<0.03}$) and β ($\sim PdH_{<0.83}$) can be distinguished below 300 °C because of a phase separation [1]. Although platinum takes up hydrogen to a lesser extent, this absorption nonetheless results in a volume increase. These volume changes associated with repeated hydrogen absorption and desorption induce a weakening of the metal structure, and can cause cracking, blistering and delamination of metal films. This so-called embrittlement effect has negative consequences for the stability of hydrogen sensors based on these noble metals.

In this chapter seven types of hydrogen detection technology are classified as listed below.

1. Catalytic hydrogen sensors
2. Thermal conductivity hydrogen sensors
3. Electrochemical hydrogen sensors
4. Resistance based hydrogen sensors
5. Mechanical hydrogen sensors
6. Optical hydrogen sensors
7. Acoustic hydrogen sensors

1. Catalytic hydrogen sensors

A catalytic sensor detects hydrogen based on the temperature change which accompanies the exothermic oxidation reaction on a heated catalytic surface. It consists of two thin platinum wires each embedded in a ceramic bead (pellistor) and connected to each other in a Wheatstone bridge circuit as illustrated in Fig. 1.1. One pellistor is coated in a catalyst material which selectively catalyzes the oxidation reaction of hydrogen, the surface of the other pellistor is inertised. The pellistors are heated to 500-550 °C by passing a current through the circuit to promote the oxidation reaction. Hydrogen is oxidized on the bead surface and the heat of reaction causes an increase in temperature which changes the resistance of the platinum filament. This causes the Wheatstone bridge to be imbalanced and the measured imbalance of the bridge is linearly related to the hydrogen concentration.

Catalytic sensors employ a well-developed technology however they are not specific to hydrogen and will respond to any combustible gas. Other chemical species, such as Sulphur containing compounds (e.g. H_2S), halogenated compounds and silicon containing compounds may cause a temporary or permanent loss of sensitivity to hydrogen [2].

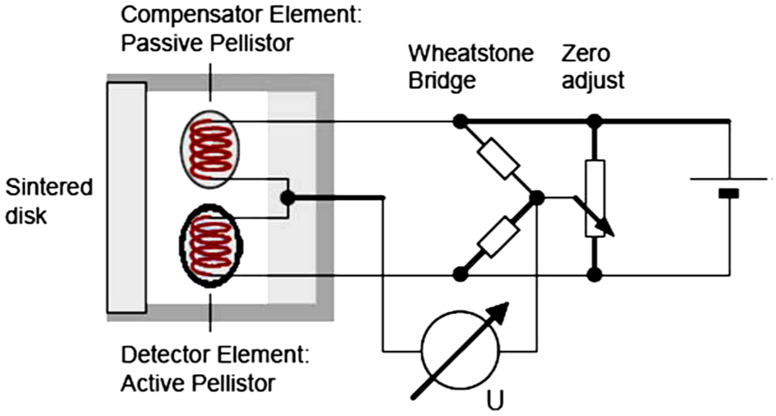

Fig.1.1 – Schematic of a typical catalytic type combustible gas sensor [2]

1.1. Pellistor

Pellistor element hydrogen gas sensors consist of two platinum coils each embedded in a ‘pellet’ or ceramic bead (e.g. porous γ- alumina). The platinum coils serve two functions, they act as a heater as well as being a resistance thermometer. The surface of one of the beads is activated with a suitable catalyst which is usually a noble metal such as platinum or palladium [1].The other, inactive bead has no catalyst on its surface and acts as a compensating element. Changes in environmental parameters such as relative humidity, temperature or thermal conductivity of the ambient gas being monitored influence both beads similarly and so this influence is compensated and has no significant effect on the sensor output. The beads are mounted in a Wheatstone bridge circuit to facilitate the comparison of the coil resistances as illustrated in Fig. 1.2. During operation electrical current is passed through the platinum coils causing them to heat up to temperatures typically above 300 °C [1]. At these high temperatures hydrogen molecules chemisorbed on the catalyst (e.g. platinum) surface are oxidized with adsorbed oxygen to form water. The exothermic reaction raises the temperature of the activated bead which results in a change in the electrical resistance of the activated coil. This creates an imbalance in the Wheatstone bridge circuit which constitutes the sensor signal.

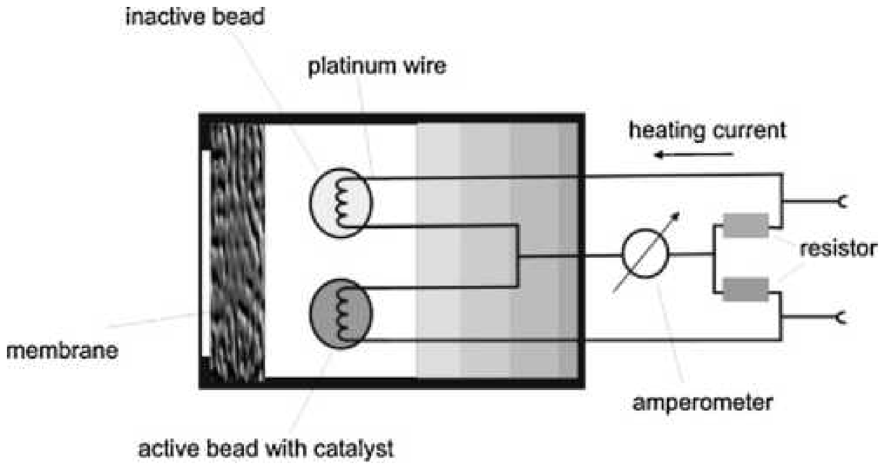

Fig. 1.2. Wheatstone bridge circuit connecting the active and inactive beads in a pellistor [1]

The first catalytic combustion type sensor was first used in mines for methane detection. Pellistor-type catalytic hydrogen sensors are a well-developed technology and a recent market survey of commercially available hydrogen sensors has shown that this type of hydrogen sensor is widely available and typically used for hydrogen concentrations up to 4.0% [1].

Despite being a well-developed and commercialized technology pellistor-type hydrogen sensors have a number of disadvantages. Firstly they are not selective for hydrogen and will respond to other combustible gases such as hydrocarbons and carbon monoxide. Selectivity can be improved by using a filter or molecular sieve coating. Secondly the performance of hydrogen pellistor sensors is affected following exposure to *inhibitors*, which have a reversible effect, or *poisons*, which have an irreversible effect. These species adsorb onto the catalyst more strongly than hydrogen reducing the number of sites available to catalyze the oxidation of hydrogen. Typical poisons include organic silicon and phosphorous containing compounds, and these cause a permanent drop in sensor response even at low concentrations. Halogen-containing hydrocarbons are inhibitors and generally the pellistor response recovers when the inhibitor is removed [1]. Sulphur containing compounds e.g. H_2S can either inhibit or poison sensors depending on the concentration, period of exposure and sensor operating temperature. A pellistor can be made more resistant to these interferants by increasing the number of catalytic sites for oxidation. This can be done by i) simply increasing the active bead size however this approach is not suitable for sensors with low power consumption requirements or by ii) making the active bead porous and distributing the catalyst material over the surface and in the pores. In this way the small size and low power consumption requirements can be met while poison resistance is improved. A further disadvantage of pellistor sensors is their high power consumption, ranging between 0.5 and 3.0 W, due to heating the pellistor to its operating temperature. In addition they require a minimum of between 5% and 10% oxygen in the gas mixture for the oxidation reaction. [1].

1.2. Thermoelectric

As another type of catalytic sensor, thermoelectric sensors also generate an electrical signal based on the catalyzed exothermic oxidation reaction of hydrogen, but use the thermoelectric effect to generate the electrical signal. The thermoelectric effect, or more specifically the Seebeck effect, arises when there is a temperature difference between two points of a conductor or semiconductor material which results in a voltage difference between these points. In a hydrogen thermoelectric sensor the temperature increase at the active sensor part is due to oxidation of hydrogen and the induced thermoelectric voltage correlates to the hydrogen concentration. The sensor signal, *U*, depends on the amount of oxidized hydrogen according to the following expression [1]:

$$U = \alpha \cdot \Delta T \approx \alpha \cdot \left\{ \text{const.} \cdot \exp\left(\frac{-E_a}{RT}\right) \right\} \cdot \Delta H$$

Where *a* is the Seebeck coefficient, ΔT is the temperature difference between the combustion heated part of the sensor and the cold reference, {const.-exp($-E_a/RT$)} describes the reaction rate of combustion (E_a is the activation energy of the combustion reaction, *R* is the universal gas constant) and ΔH is the heat of hydrogen combustion. The first application of the thermoelectric effect for sensing combustible gases was reported in 1985. More recently reported thermoelectric hydrogen sensors are fabricated as a thick or thin film of a thermoelectric material deposited on an insulating substrate material. Half of the thermoelectric film is coated with a catalyst which heats upon exposure to hydrogen as a result of the exothermic oxidation reaction. The resulting temperature gradient is converted to a voltage signal measured via an electrical circuit. Glass, alumina and magnesium oxide are often used and have been compared as the substrate material. One reported advantage of thermoelectric sensors compared with pellistors is their ability to operate at lower temperatures i.e. room or slightly elevated temperature (<100 ° C). Platinum is used extensively as the catalyst because of its high catalytic activity at relatively low operating temperatures. Since only hydrogen can be oxidized effectively by Pt catalyst near room temperature, thermoelectric sensors have, in principle, a low cross sensitivity to other combustible species.

2. Thermal conductivity hydrogen sensors

Thermal conductivity measurements for gas analysis have been used for many decades and were first applied for hydrogen measurements during the filling of airships in 1913 [1]. The relatively high thermal conductivity of hydrogen makes this technology suitable for measuring hydrogen concentration in air.

Hydrogen gas has the highest thermal conductivity of all known gases (186.9 $\text{mWm}^{-1}\,\text{K}^{-1}$ compared to 26.2 $\text{mWm}^{-1}\,\text{K}^{-1}$ for air, both at 298 K and 101.325 kPa) [2]. The relatively high thermal conductivity of hydrogen makes this technology suitable for measuring hydrogen concentration in air.

The principle of operation is based on the measured heat loss from a hot body to the surrounding gas. There are two variants of this technology. The first, or pellistor-like sensor, consists of two inert resistor beads each with an embedded thermoresistor, similar in fact to the compensator bead in a catalytic pellistor. The detecting resistor is exposed to the gas being measured while the reference resistor is sealed in a chamber containing a reference gas (usually air). Typically the two beads are connected in a Wheatstone bridge circuit as shown in Fig. 1.3. When both resistors are exposed to the same gas they lose heat at the same rate which results in a zero reading. When the detecting resistor is exposed to the target gas mixture it loses more or less heat depending on the thermal conductivity of the target gas relative to the reference gas. This then leads to either an increase or decrease in the temperature of the bead and consequently a change in its resistance which is measured as an imbalance in the Wheatstone bridge [1].

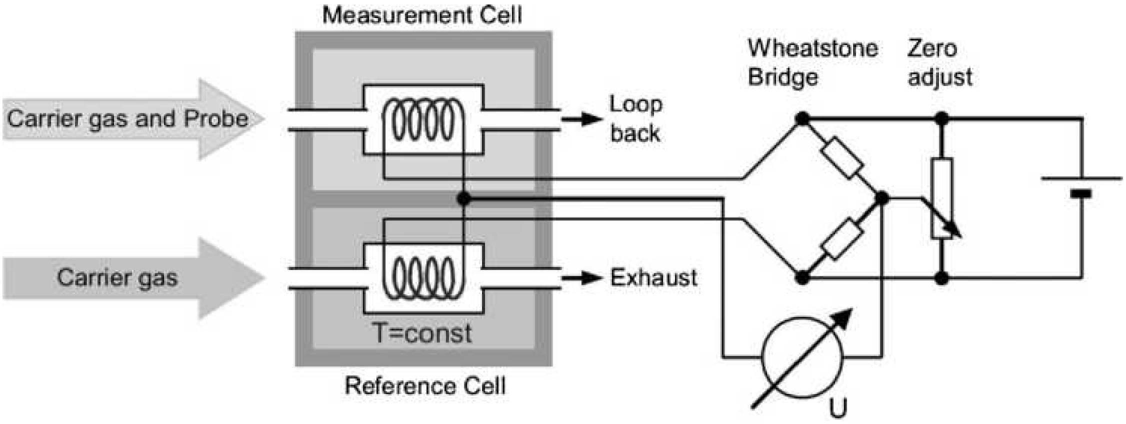

Fig. 1.3. Measurement and reference cell of a thermal conductivity sensor connected in a Wheatstone bridge circuit [1]

The second, more modern variant of this type of sensor does not require the use of a reference cell [1]. It has a ‘hot’ and a ‘cold’ element with a known temperature difference between them which is kept constant. Heat is transferred from the hot to the cold element by thermal conduction through the investigated gas. The power required to maintain the ‘hot’ element at a constant temperature is a direct measure of the thermal conductivity of the investigated gas, which can then be related to the concentration of the target gas.

An important advantage of hydrogen thermal conductivity sensors is their wide detection range which often covers <1-100% H_2 (i.e. they can operate in the absence of oxygen) [1]. On the other hand it is difficult to detect very low concentrations of hydrogen. For this reason thermal conductivity sensors are often used together with another, more sensitive technology, in a combined sensor unit. Such combined sensor units are not uncommon on the commercial market and boast a wide measuring range together with a low detection limit. Thermal conductivity sensors are also resistant to poisoning as they do not contain any catalytic metals and commercial products claim long operating lifetimes (>5 years) with low signal drift.

3. Electrochemical

Electrochemical sensors detect changes in charge transport or electrical properties due to electrochemical reactions occurring at a sensing electrode. There are two types of electrochemical sensors as seen below.

3.1. Amperometric

Amperometric sensors work at a constant applied voltage and the sensor signal is a diffusion limited current. There are three major constituents of an amperometric sensor, as illustrated in Fig. 1.4. The first of these are the electrodes, at which electron transfer occurs. The basic set up requires two electrodes - the working or sensing electrode and the counter electrode. However, most sensors also include a reference electrode and a potentiostat. The potentiostat provides a feedback control and assures that the voltage of the reference electrode is always close to zero regardless of the actual sensor current [2]. The electrodes are usually composed of a noble metal, often platinum, which also acts as a catalyst for the hydrogen oxidation reaction [1].

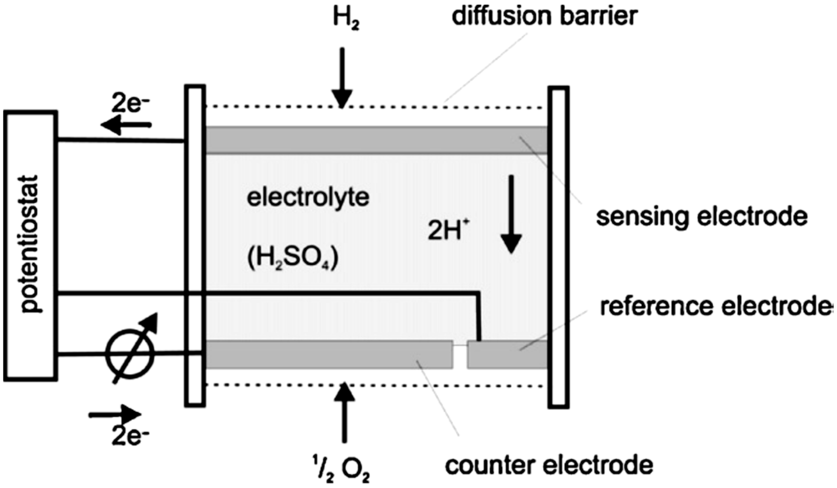

Fig. 1.4. Schematic of a 3-electrode amperometric sensor [1]

Secondly, an electrochemical cell contains a solid or liquid electrolyte to allow for the transport of ions between the electrodes. In hydrogen sensing, the electrolyte is usually a proton conducting material. The most commonly used liquid electrolyte is sulphuric acid [1]. However the use of a solid electrolyte removes the problems of leakage, corrosion and volatilization that may occur in the case of liquid electrolytes. Proton conducting solid polymer electrolytes, such as Nafion are often used, while ceramic materials are employed for high temperature applications.

Finally, a gas permeable layer covers the inlet to the sensing electrode and helps to limit diffusion such that it becomes the rate-determining step. This layer also serves to prevent leakage or drying out of the electrolyte and, if the appropriate material is used, to allow selective passage of the analyte only thereby preventing interference from other gases. In many cases, this layer consists of a perfluorinated polymer, such as Teflon PTFE [1].

Hydrogen gas diffuses through this layer and is oxidized at the sensing electrode according to the following equation [1]:

$H_2 \rightarrow 2H^+ + 2e^-$

This results in a change of the sensing electrode potential. At the counter electrode the reduction of oxygen takes place as follows [1]:

$\frac{1}{2} O_2 + 2H^+ + 2e^- \rightarrow H_2O$

The flow of electrons from the anode to the cathode constitutes an electric current, which is proportional to the hydrogen gas concentration.

Electrochemical hydrogen sensors are widely available commercially and current research relates to electrode development, electrolyte development, improved sensitivity and faster response times. Electrochemical sensors consume very little power during operation which is particularly convenient in automotive applications. Electrochemical sensors employing a liquid electrolyte cannot be operated or stored at low pressures or at sub-zero temperatures [2].

3.2. Potentionmetric

Potentiometric sensors differ from amperometric sensors in that they ideally operate at zero current and the measured quantity is the potential difference or electromotive force between the sensing electrode and the reference electrode. The electrode potential is related to the hydrogen gas concentration and can be written according to the Nernst equation as [1]:

$$E = E^0 + \left[\frac{RT}{zF}\right] \ln\left(\frac{a}{a_0}\right)$$

where E = electrode potential, E^0 = standard electrode potential, R = universal gas constant, T = absolute temperature, F = Faraday constant, z = number of electrons taking part in the reaction, a = chemical activity of the analytes (proportional to hydrogen concentration), a_o =the activity of the reference. The processes of diffusion and chemical reaction must be at equilibrium before an accurate signal can be obtained from these sensors.

The structure of a basic potentiometric sensor is similar to that of an amperometric one, consisting of two electrodes in contact with an electrolyte. The electrodes are usually made from noble elements such as palladium, platinum, gold or silver. Solid proton conducting electrolytes are commonly used, including a-alumina, phosphoro-silica glass, hydronium Nasicon, In-doped $CaZrO_3$, $(NH_4)_4Ta_{10}WO_{30}$ and $SrYb_{005}Ce_{095}O_{3-x}$ [1].

Unlike amperometric sensors, the measured signal from a potentiometric sensor is nearly independent of sensor size and geometry, which is an advantage from the point of view of sensor miniaturisation. However, their response shows a logarithmic dependence on hydrogen concentration, which can result in lower accuracy at high concentrations compared with the linear response of amperometric sensors. The latter are also more sensitive and are more widely available commercially.

Electrochemical sensors offer the advantages of low power consumption and room temperature operation and are well-established commercially. Ongoing research efforts are primarily aimed at increasing the detection range, decreasing signal drift due to material degradation, improving selectivity through the use of new or modified membrane materials and developing hybrid proton conducting materials for improved electrolytes [1].

4. Resistance based

4.1. Semiconducting metal-oxide sensor

It has been known since the 1950s that the electrical properties of metal oxides change when they are exposed to reducing gases. In 1962 was firstly applied this phenomenon to the detection of gases using a ZnO thin film. In the same year it has been patented and subsequently marketed a SnO_2 based semiconductor device capable of detecting low concentrations of combustible and reducing gases using a simple electrical circuit [1].

The MOx sensor is a polycrystalline solid-state device with a wide band-gap material as the sensing element. MOx semiconductors use tin oxide (SnO_2) or other metal oxides as the sensing material. The MOx sensor is typically an insulator at room temperature but becomes conductive at elevated temperatures. The adsorption of a gas changes the electron density within the band structure of the MOx polycrystalline material, which leads to a conductivity change. The amount of that change depends on the nature and concentration of the gas and on the type of MOx material. In the presence of hydrogen, the resistance of the MOx decreases [3].

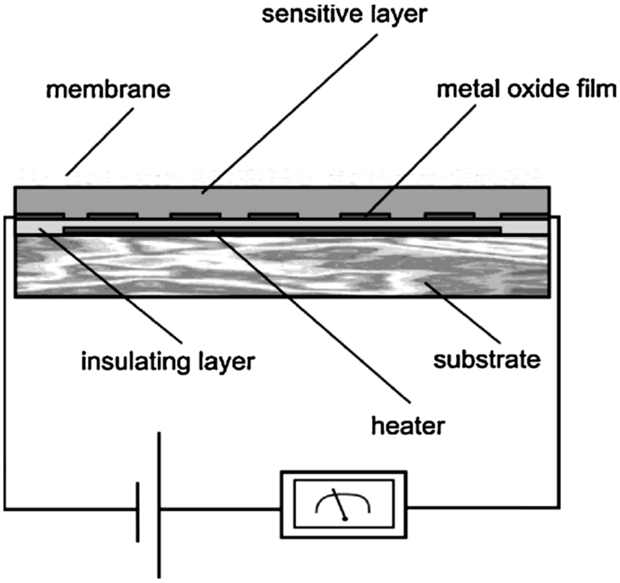

Fig. 1.5. Schematic of a metal–oxide sensor [1]

Typically a metal-oxide film is applied on to an insulating substrate material in between two electrodes as shown in fig. 1.5. Al_2O_3 is often the substrate of choice due to its high electrical resistance, thermal stability and the ability of many metal oxides to adhere effectively to it. The oxide can be deposited on the substrate as a thick film via a screen printing process followed by a heat treatment for sintering, or as a thin film by gas phase deposition processes. During operation the film is heated to high temperature to promote the reaction with the reducing gas and to remove water formed during this reaction. The operating temperature depends on the metal-oxide used and is generally between 180 and 450 °C, however for Ga_2O_3 based sensors it can be higher than 650 °C. The measured resistance, R, of the sensor element changes depending on the concentration of the reducing gas and a good approximation of this dependence is given by [1]:

$R(c) = a \cdot cb$

Where *a* and *b* are sensor specific constants and *c* is the gas concentration.

As a reducing gas hydrogen can be detected and quantified by metal-oxide type sensors. Semiconducting oxides, including SnO_2, ZnO, TiO_2, FeO, Fe_2O_3, NiO, Ga_2O_3, In_2O_3, Sb_2O_5, MoO3 and WO3, show a large change in their electrical resistance following adsorption of hydrogen gas [1].

The sensing mechanism of metal-oxide sensors is complex and is the subject of discussion in several works. Basically the change in the metal-oxide resistance results from a gain of surface electrons following reaction of hydrogen with adsorbed oxygen. The surface reactions involve two steps [1]. Firstly, oxygen chemisorbs on the metal-oxide surface, $O_2 + 2e^- \rightarrow 2O^-_{ads}$, which decreases the surface conductivity. Subsequently, hydrogen adsorbs and reacts with the adsorbed oxygen in a reaction expressed simply by $H_2 + O^-_{ads} \rightarrow H_2O + e^-$. For n-type semiconducting oxides (e.g. SnO_2) the electrons are donated into the conduction band. As a result the resistance of this type of oxide decreases in the presence of hydrogen and the magnitude of the resistance change can be related to the hydrogen concentration.

Typically semiconductor hydrogen sensors measure resistance changes under a fixed applied voltage. However the potential advantages of varistor-type ZnO and SnO_2 sensors have also been investigated. The beneficial effects of doping ZnO varistors with Bi_2O_3 have been reported [1], where the optimal grain structure and maximal sensitivity to hydrogen were found to occur at a doping level of 1 mol% Bi_2O_3. Thin sol-gel derived silica coatings on SnO_2 increase the potential barrier height between the grains, which results in a higher hydrogen sensitivity.

One significant shortcoming of semiconductor gas sensors is their low selectivity. These sensors are cross-sensitive to other reducing and hydrogen containing compounds such as carbon monoxide, methane, alcohols, humidity etc. Improvements in sensor selectivity and sensitivity to hydrogen have been achieved by doping the metal oxides with catalytic metals such as Pt, Pd, Au, Ag and Cu [1].There are many metal-oxide hydrogen sensors available on the market and most if not all use tin oxide which has semi-conductive properties. The accepted detection mechanism of this class of sensor is that, in the presence of reducing gases such as H_2 and CO, the gas particles diffuse into the sensing layer through pores and react with adsorbed oxygen on the semiconductor metal-oxide surface. This results in a decrease in the electrical resistance of the sensing layer [2].

4.2. Metallic resistor

The electrical resistivity of some metals and alloys changes markedly on the absorption of hydrogen. Hydrogen has a high solubility in palladium in particular and this interaction is also selective making palladium the metal of choice in this type of sensor. Detection is based on an increase in electrical resistivity following absorption of hydrogen from the ambient due to the higher electrical resistance of palladium hydride compared to palladium. Typically metallic resistor sensors are fabricated by deposition of a film of metal on a substrate (e.g. silicon) between two electrical contacts. Film deposition techniques include vacuum evaporation, electrodeposition, sputtering and pulsed laser deposition [1].

A low cost, thick film palladium resistive sensor measures hydrogen concentration. This sensor has four palladium resistors arranged in a Wheatstone bridge structure. The surface of two of the resistors is covered by a passivation layer, so that they serve as reference resistors compensating for changes in the resistance of the palladium due to ambient temperature variations. Detection is selective to hydrogen, but the sensor can be poisoned by gases like CO, SO2 and H_2S [1].

5. Mechanical

Hydrogen, when absorbed by a metal, occupies interstitial sites in the metal lattice causing this lattice to expand and thereby changing the physical properties of the metal. Micro-fabricated palladium coated cantilevers utilize the expansion of palladium following hydrogen absorption as the detection principle. These sensors consist of a palladium film coated on one side of a cantilever. However volume expansion on absorption of hydrogen is prohibited by the substrate on which the film is coated and the induced stresses are transduced into the mechanical bending or curvature of the cantilever [1]. There is a limited amount of research published on cantilever hydrogen sensors and one problem associated with this type of sensor arises from interfacial sliding, delamination and even detachment of the palladium film as a result of expansion/contraction induced weakening of the palladium/substrate adhesion. The initial adhesion strength between the palladium film and the underlying substrate depends on the method used to deposit the palladium film. It has been shown that palladium films fabricated by sputtering bombardment have superior adhesion characteristics and ultimately exhibit superior hydrogen detection characteristics as a result of efficient mechanical transduction. Further enhancement of the Pd adhesion by the fabrication of trenches in the surface of the cantilever beams led to improve hydrogen sensing down to 50 ppm and faster response.

Another novel mechanical hydrogen sensor is described and comprises a micro-machined cantilever fabricated out of the cleaved edge of an optical fibre. A 10 nm Cr adhesion layer and a 150 nm palladium layer were deposited on the cantilever and vertical displacement of the cantilever following hydrogen absorption was measured by optical techniques [1]. The absence of any electrical components at the sensing element makes it a potentially interesting sensor design for use in hostile environments. The sensor can detect hydrogen concentrations between 0.1% and 100% with a linear response range between 10% and 90%. The measured response time, t_{90}, of the unheated cantilever to 1% hydrogen in air is rather slow being 90s at 25 $^{\circ}$C and 0% relative humidity [1]. Humidity negatively influenced both the hydrogen sensitivity and the response time of this sensor however, as would be expected, heating the cantilever reduced these effects. Another robust mechanical-type hydrogen sensor uses the lattice expansion of $LaAl_{0.3}Ni_{4.7}$ films in a differential capacitive configuration to detect hydrogen. The $LaAl_{0.3}Ni_{4.7}$ film forms one electrode of a simple parallel plate capacitor and an Ag film forms the opposite electrode. Expansion of the metal hydride film upon exposure to hydrogen results in an increase in the measured capacitance. The device shows a stable response to 400 ppm hydrogen and can measure up to 100% hydrogen. The sensor is not poisoned by CO and is mechanically robust following repeated exposure to hydrogen. The measured response time, $t90$, is greater than 10 s [1].

A micromachined hydrogen sensor based on an array of nanoswitches in palladium has recently been suggested to detect 1.5-4% hydrogen in nitrogen [1]. This novel sensor consists of a trimorph poly-Si/Ti/Pd electrode suspended on a vertical spacer and separated from a second Ti/Pd electrode by a 10 nm wide nanogap. In the presence of hydrogen, Pd expands and deflects the trimorph which then makes electrical contact with the Ti/Pd electrode allowing current to flow. The process is reversible and the sensor operates at room temperature and has an ultra-low power consumption of a few picowatts. The measured response time, $t90$, is however rather slow being 30 s at a hydrogen concentration of 4% and increasing at lower concentrations.

6. Optical

The optical properties of certain materials change when they interact with hydrogen and this can be exploited as a means of hydrogen detection. The first optical hydrogen sensors were described in 1984 [1]. There has been reported a sensor consisting of an optical fibre coated along a small portion of its length with palladium and using a thin underlayer of titanium to improve adhesion of the metal to the quartz fibre. Expansion of the palladium layer on exposure to hydrogen stretches the fibre in both axial and radial directions, thereby causing a change in its effective optical path length. This is detected by means of interferometry.

Most optical hydrogen sensors are still based either on thin films of palladium and/or chemochromic oxides coated onto the tip or along the length of an optical fibre. Such fibre optic sensors are known as optrodes or optodes.

6.1 Measurement techniques

Various techniques are employed in the optical detection of hydrogen. The most widely used of these are [1]:

6.1.1. Reflectivity measurements on micromirrors

Micromirrors consist of a thin layer of the sensing material, usually palladium, coated onto the cleaved end of an optical fibre, Fig. 1.6. The change in reflectivity of the palladium layer on exposure to hydrogen is detected and correlated to the hydrogen concentration.

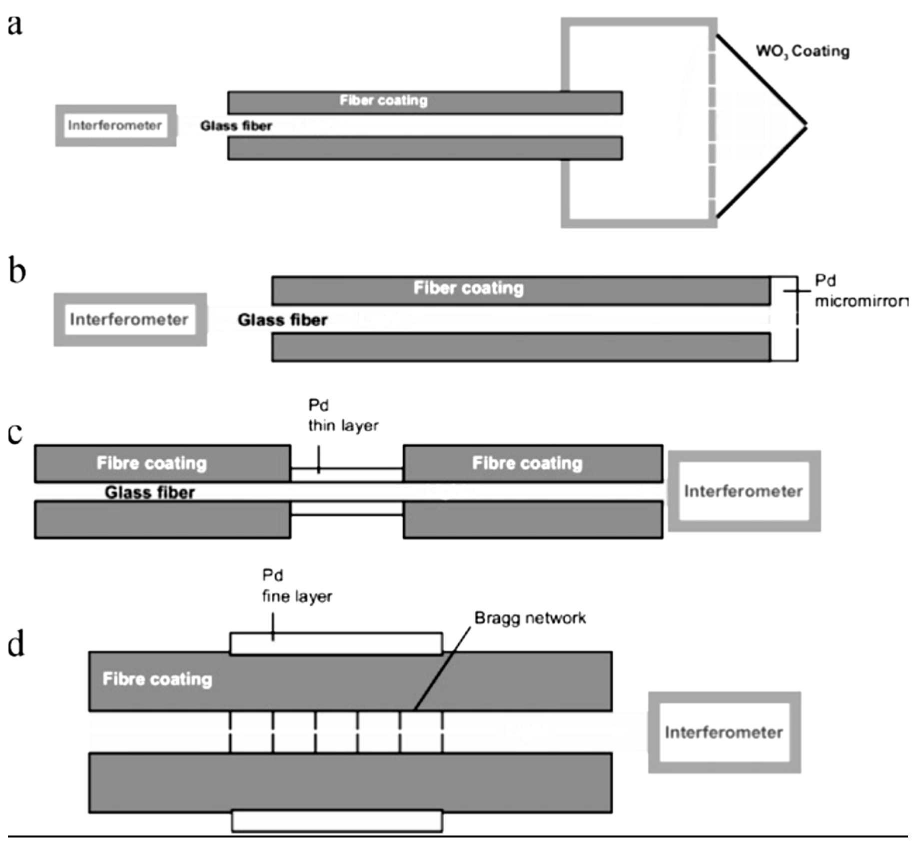

Fig. 1.6. Optical sensor configurations - (a) a hydrogen sensor based on tungsten oxide, (b) a fibre optic sensor with palladium micromirror, (c) a fibre optic sensor covered with a palladium layer, (d) a Bragg network fibre optic [1].

6.1.2 Interferometric measurements

A change in the dimensions or the refractive index of the sensing material produces a phase change in the fibre light beam, which can be detected by means of interferometry.

6.1.3 Surface plasmon resonance (SPR)

Surface plasmons are surface electromagnetic waves that propagate parallel to a metal/dielectric interface and that are therefore sensitive to changes in the structure of the metal surface. A number of different methods exist for the excitation of surface plasmons, including the use of prism couplers, grating couplers or optical waveguides such as optical fibres. Only certain materials are capable of supporting SPR. The most commonly used are gold and silver, but Pd is also an SPR active metal and due to its selective interaction with hydrogen, is often used in hydrogen detection using this method. Changes in the refractive index of the SPR support due to the presence of hydrogen may be detected as a change in the resonant wavelength or resonant angle of the incident light wave or in the intensity of the reflected light [1].

6.1.4. Measurement of evanescent field interaction

An evanescent field is an electromagnetic field that is formed at the boundary between certain types of medium, such as at the core of an optical fibre. This field decays exponentially with distance from the core. In evanescent field based sensors, the cladding of the fibre is removed and the core coated with a sensing layer, (see Fig. 1.6). Interaction of hydrogen with this layer causes a change in its refractive index, which in turn causes an attenuation change in the evanescent field. This can be detected as a change in transmittance.

6.1.5. Fibre Bragg Gratings (FBGs)

These are gratings that are etched into the core of an optical fibre in order to periodically modulate the index of refraction (see Fig. 1.6d) [1].They are then coated with palladium so as to render them sensitive to hydrogen. The grating reflects light of a specific wavelength and expansion of the palladium in the presence of hydrogen produces a change in this Bragg wavelength. The wavelength is also influenced by temperature and this must be compensated for when interpreting the sensor signal, by the use of a reference grating for example.

Similarly, Long Period Gratings (LPGs) exhibit a shift in their resonance wavelength on interaction of the sensitive palladium coating with hydrogen. However, while the period of an FBG is of the same order as the optical wavelength, that of an LPG is significantly longer - typically 0.1-1 mm. Improved sensor performance has been reported using LPGs. The LPG sensor shows much greater sensitivity to hydrogen and, as a consequence the relative influence of temperature has been reduced.

6.1.6. Optical time domain reflectometry (OTDR)

Using this method, the reflectance is measured along the length of a fibre optic cable rather than at a single point, therefore allowing for distributed sensing over a wide area using only one device. Given the time resolution of the reflectance measurement and the speed of light in the fibre optic, the signal can be spatially resolved.

6.2. Sensing Materials

6.2.1. Palladium in optical hydrogen sensing.

Structural changes due to the interaction of H_2 with palladium induce a change in its optical as well as its electrical properties.

On exposure to H_2 a reversible increase in the optical transmittance of palladium in the visible region takes place (the opposite effect has also been observed in the case of extremely thin films of Pd) [1]. Palladium may therefore be used directly in the optical detection of hydrogen, such as in the case of micromirror sensors. Palladium may also serve the purpose of supporting surface Plasmon resonance in SPR sensors.

Optical measurement of changes in the thermal properties of a palladium film due to hydride formation has also been investigated as a means of detecting hydrogen. Palladium is also employed in optical hydrogen sensing simply as a dissociation catalyst for generating free H atoms, which then interact with the sensing material itself.

Despite the widespread use of palladium in both optical and other methods of hydrogen sensing, it is susceptible to cracking, blistering and delamination on repeated exposure to hydrogen. Two principal approaches have been adopted to address this susceptibility to mechanical damage. Firstly, alloying of palladium with nickel shifts the damaging phase transition to higher hydrogen concentrations. Alloys of palladium with gold and with silver have also been reported to result in greater stability as well as a faster response to hydrogen in some cases. Secondly, the use of a supporting sub-layer may improve the stability of the Pd sensing layer. Different materials have proved effective for this purpose including nickel VO_x , V_2O_5, CaF_2 and PVDF polymer [1].

6.2.2. Chemochromic materials

The colour of some metal oxides changes with their oxidation state and this property can be exploited for optical hydrogen detection. Tungsten oxide is commonly used as it reacts with hydrogen to produce tungsten bronze according to the equation [1]:

$$2xH_{ad} + WO_3 \leftrightarrow WO_{3-x} \cdot xH_2O$$

This results in an increase of absorption in the visible range. A coating of WO_3 at the end of an optical fibre therefore acts as an optrode that senses the presence of hydrogen in air.

Thin films of MoO3 coated with a catalytic layer of Pd have also been demonstrated in hydrogen sensing. Composite films of gold and cobalt oxide (Au-Co_3O_4) that exhibit absorbance changes in response to hydrogen in air have also been prepared.

Non-oxide materials that show an optical response to hydrogen have been investigated, including metal hydrides such as yttrium and lanthanum hydride, while magnesium containing alloys have also shown promise.

There are few optical hydrogen sensors available on the commercial market - a survey carried out in 2009 identified only one manufacturer producing such devices. According to the technical specifications, these are capable of measuring in the range 0.1-100% H_2 at temperatures from -15 to 50 °C, with a measured response time of 60 s and a lifetime of >5 years in air [1]. A number of problems remain to be overcome before these sensors can be expected to become established commercially. The almost ubiquitous use of palladium in such sensors means that long term stability is an issue due to mechanical stresses induced in the material on repeated exposure to hydrogen. This mechanical damage due to the phase transition of palladium hydride may also limit the measuring range of the sensor. A number of approaches to this problem have been proposed. In addition to this, palladium is susceptible to poisoning by sulphur compounds in particular, resulting in permanent damage to the sensor. The development of suitable alloys or protective barriers to prevent poisoning is the subject of continuing research. Optical sensors may be sensitive to interference from ambient light and to changes in temperature and, as with most sensor types, further miniaturization is desirable.

Despite the existence of more well-established hydrogen sensing technologies however, much research is going into overcoming these drawbacks. This can be attributed to a number of advantages that optical detection holds over other methods. Firstly, it eliminates the danger of the sensor itself providing a source of ignition at the location of the leak. This is because the raw signal is optical rather than electrical and because the use of optical fibres allows for the controlling electronics to be located remote from the sensor itself. Optical sensors therefore have the potential for inherently safe detection in explosive atmospheres. Secondly, this type of sensor offers the possibility of distributed as opposed to spot detection. The use of an optical fibre with sensing material coated at different points along the length allows for wide area monitoring using only one device. A further advantage of optical sensors is that they are less sensitive to electromagnetic noise than other detection technologies.

7. Acoustic

Acoustic gas sensors usually detect changes in the properties of acoustic waves due to an adsorbate on the surface or adsorbate in the bulk of a piezoelectric material. The first acoustic gas sensor was suggested in 1964 based on the measurement of bulk acoustic waves (BAW) in a piezoelectric quartz crystal.

7.1. Quartz crystal microbalance

The piezoelectric quartz crystal microbalance (QCM) is the oldest and simplest acoustic wave device. A QCM typically consists of a thin disk of quartz with electrodes on either side, which are used to produce deformation of the crystal and thereby cause it to resonate. The resonance frequency is sensitive to the accumulation of mass on the surface of the crystal and can therefore be measured as an indication of the concentration of analyze in the ambient. Due to their high mass sensitivity however, sensors based on piezoelectric resonance are very vulnerable to interference from coexisting gases, including humidity. The resonance frequency is also strongly influenced by temperature. This may be compensated by the use of a reference element.

A hydrogen sensor based on a piezoelectric-sound- resonance-cavity (PSRC) has also been developed [1]. The detection mechanism exploits the differences in the acoustic properties of hydrogen and air. Changes in hydrogen concentration result in a shift of the sound-resonance state of the PSRC. The sensor has a sensitivity limit of 8 ppm, detection capabilities over a broad concentration range and a fast response time.

7.2. Surface acoustic wave sensor

In hydrogen sensing, surface acoustic waves (SAW) are generated by means of a piezoelectric substrate with two sets of interdigital transducers (IDT) deposited onto it [1]. One of these transducers converts an applied electrical input signal into the acoustic wave, while the second converts this wave back into an electrical output signal. There are different types of surface acoustic wave, but Rayleigh waves are employed in gas-sensing applications because of the ease with which they can be generated using IDTs, Fig. 1.7. These are acoustic waves that propagate along the surface of a solid and that are localized within 1 or 2 acoustic wavelengths of the surface. As a result, they are highly sensitive to any perturbation of the surface, such as mass loading or a change in its electrical properties.

The piezoelectric substrate material most often used is LiNbO3 but $LiTaO_3$ has also been employed [1]. A hydrogen selective layer is then coated onto the piezoelectric substrate between the two sets of IDTs. When the palladium layer absorbs hydrogen both its mass density and electrical conductivity change and this produces a detectable change in the frequency of the SAW.

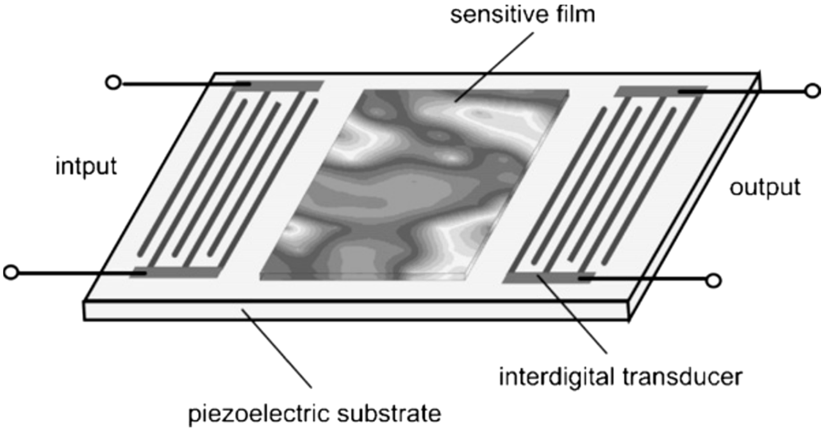

Fig. 1.7. Structure of a SAW sensor [1]

SAW sensors require that the sensitive coating be deposited in a reproducible way in order to give reproducible electrical resonances. In practice however, such precise deposition is difficult to realize in production.

7.3. Sound velocity measurements

Hydrogen has a high sound velocity of 1314 m/s compared with that of air of 346 m/s at 298 K [1]. This difference can be exploited for hydrogen concentration measurement in gas mixtures. A relevant work reports a hydrogen sensor based on sound velocity measurements in which they generate acoustic waves in the gas medium by laser irradiation of a chemically inert sensitizer and measure the propagation time of these waves as a function of hydrogen concentration [1].

The velocity of sound in palladium has also been measured as a means of detecting hydrogen [1]. The acoustic wave velocity in a solid waveguide depends on the material density and on the amount of stress and strain to which it is subjected. When palladium absorbs hydrogen its density and mechanical properties change and this can therefore be detected as a difference in the velocity of sound waves travelling through it. Variations in temperature also affect the acoustic velocity in the palladium wire however and must be compensated for.

Acoustic sensors have the potential to detect hydrogen over a wide concentration range extending from the ppm level to 100%, with rapid response time and relatively low power consumption. However, improvements are required in terms of their long term stability and their sensitivity to temperature and interference from other gases. A 2009 survey of the hydrogen sensor market found no acoustic sensors available commercially [1].

CHAPTER 2

TESTING HYDROGEN SENSORS

The risk of a hazardous event involving hydrogen can be mitigated through the use of hydrogen safety sensors. These sensors facilitate the early detection of hydrogen before its concentration rises above the lower flammability limit (LFL) in air. The LFL for hydrogen, defined as the minimum concentration of hydrogen in air below which flame propagation does not occur, is 4vol% [2]. The LFL is a critical concentration since ignition sources should be assumed to be present when leaking hydrogen reaches its lower combustible proportions in air. Hydrogen sensors should be able to alert to the presence of hydrogen at concentrations significantly below this lower limit. This will allow timely corrective actions to be taken in the event of a leak to avoid or mitigate risks.

Sensitive and reliable hydrogen sensors are therefore essential to enable the detection of leaks when hydrogen is used as a fuel in internal combustion engine or fuel cell vehicles. As a key enabling technology for safety monitoring of hydrogen systems in automotive applications, hydrogen sensors should be accurate, sensitive, respond rapidly, be insensitive to other gaseous species, resistant to long term drift and environmental conditions and capable of reliably alerting to the occurrence of accidental hydrogen releases or leaks before explosive conditions are reached.

The conditions for testing flammable gas sensors were issued in 1998 by the International Electrotechnical Commission (IEC) under the title: International Standard IEC 61779-1, electrical apparatus for the detection and measurement of flammable gases - General requirements and test methods [4]. Further standards related to flammable gas detection also exist however no standard is specific to hydrogen. Considering the unique properties of hydrogen, concerns exist as to whether existing standards sufficiently cover hydrogen applications. To address this issue an EU funded research project, StorHy [4], assumed as one of its subtasks an investigation of the need for a specific test protocol for hydrogen safety sensors to be used in automotive vehicles.

Standard IEC 61779 describes a number of tests to assess the performance of flammable gas sensors. This standard was used as the basis to develop a draft protocol to specifically test hydrogen sensors under conditions representative of their service life in automotive applications. Car manufacturing partners in the StorHy consortium were consulted regarding how far they considered the IEC 61779 as meeting their performance requirements and testing needs for hydrogen sensors envisioned for use in their vehicles. Based on the feedback obtained the test protocol was adjusted and used to test a large number of commercially available sensors. Commercially available hydrogen sensors employ different detection principles and market surveys performed in 2006 and 2007 showed that the most common sensors types are catalytic, electrochemical, thermal conductivity and semi-conductive metal-oxide (MOx) sensors. A description of each of these sensing technologies has been given in Chapter 1 of this thesis. In this work only semiconducting metal-oxide sensors (see chapter 1 section 4.1) types out of the resistance based hydrogen sensors were tested and the abbreviation MOx is used to refer to this kind of sensors. All sensors were tested following the protocol developed to experimentally assess their performance and to evaluate the suitability of the procedures used. Observations on sensor behavior made during the tests allowed further refinement of the test protocol.

1. Test methodology

A hydrogen safety sensor performance test protocol has been formulated based on the International Standard IEC 61779-1. The test protocol is specifically designed for testing hydrogen sensors which may be used for detecting unwanted hydrogen leaks and releases in future hydrogen fueled vehicles. The tests described in IEC 61779 were modified following consultation with car manufacturers to take into consideration their expectations with respect to the sensor performance requirements. The working environment of the sensors was also taken into careful consideration.
A protocol was drawn up for the following performance tests [4]:

1. Accuracy of response test
2. Measuring range test
3. Detection limit test
4. Cross sensitivity to carbon monoxide test
5. Ambient temperature test
6. Ambient relative humidity test
7. Ambient pressure test

These tests were identified as being of immediate interest by the car manufacturers. They will be supplemented in the future with further tests. Up to six sensors were mounted in the chamber at a time. Sensor performance was assessed based on the results from these tests and the performances of sensors were mutually compared. No attempt was made to perform tests under multi-variable conditions (e.g. to investigate the combined influence of temperature and humidity changes on sensor response). Instead only single variable performance tests were requested and performed within the scope of this project. The following sections describe the methods followed for each test.

1.1. Accuracy of response test method

The aim of this experiment is to determine the accuracy of sensor response to changes in hydrogen concentration. An accuracy of ±5% was considered by the car manufacturers as acceptable. Sensors were mounted in the chamber and were exposed to a gas mixture whose hydrogen concentration was changed stepwise between 0.0vol% H_2 and 2.0vol% H_2 (maximum) by online mixing of 2.0 vol% H_2 in air with synthetic air. The test was performed in a stepwise fashion instead of a continuous fashion [4]. Hydrogen concentration was changed stepwise by increasing and then decreasing the relative 2.0vol% H_2 in air flow rate in synthetic air. Following each step both sensor signals and GC measurements were allowed to stabilize before proceeding with the subsequent step. Sensor outputs and the corresponding hydrogen concentration (measured by the GC) were recorded and compared to assess the accuracy of the sensor response.

The accuracy of response test was performed immediately prior to the measuring range test described below. During the combined tests the hydrogen concentration was increased and then decreased for three cycles - the first cycle in a stepwise fashion (accuracy test) and the remaining two cycles in a continuous fashion (measuring range test) under identical test conditions. Fig. 2.1 shows how the synthetic air and 2.0vol% H_2 in air flow rates were controlled to achieve the stepwise and continuous changes in hydrogen concentration.

The standard testing conditions for the accuracy and measuring range tests were:

Temperature: 298 K ± 2 K (25 °C ± 2 °C)
Pressure: 100 kPa ± 2 kPa
Relative humidity: 50% RH (dew point 13.8 °C ± 1.8 °C)
Gas flow rate: 1000 nml/min ± 20 nml/min

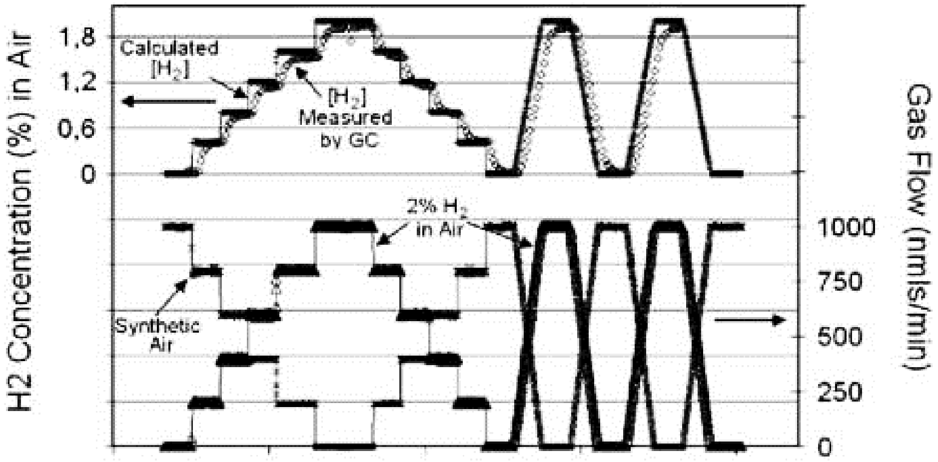

Fig. 2.1 - Example of control and measurement of hydrogen concentration during accuracy and measuring range tests. The theoretical hydrogen concentration was calculated from the relative mass flows of synthetic air and 2 vol% H_2 in air [4]

1.2. Measuring range test method

The aim of this experiment is to monitor the response of sensors to changing H_2 concentrations. Sensors were exposed to hydrogen plus synthetic air at different volume ratios in the range 0.0-2.0vol% hydrogen, starting with the lowest and finishing with the highest of the selected volume ratios [4]. This operation was carried out immediately after the accuracy of response test (see fig 2.1) and was performed two times consecutively. Repeating the procedure reveals any memory effects or hysteresis behavior of the sensors.

1.3. Detection limit test method

The aim of this test is to determine the lowest concentration of hydrogen which can be detected by a sensor. Some automobile manufacturers specified a detection limit of <0.1vol%, others accepted a detection limit of <0.2 vol%. The test was performed by online mixing of 2.0 vol% hydrogen in air and synthetic air at different volume ratios in the range from 0.0vol% to approximately 0.4vol% hydrogen, starting with the lowest and finishing with the highest of the selected volume ratios. Sensors were initially exposed to synthetic air and a baseline was recorded. The 2.0 vol% hydrogen in air flow rate was then gradually increased in a stepwise manner (as shown in Fig. 2.2) until a well-defined step in sensor output was observed in response to the change in hydrogen concentration. Stepwise increase/decrease of the hydrogen volume fraction was preferably performed in a sequence of values multiple of a base step (for example in the sequence 1x, 2x, 3x, 5x, 10x...) [4]. The stable signal indication was recorded as was the hydrogen concentration.

The hydrogen concentration was brought gradually back to zero and the procedure was repeated a further two times.

This test was carried out under conditions of temperature, pressure, gas flow and humidity within the range indicated by the sensor manufacturer, similar to those during the accuracy of response and measuring range tests.

An example of control of hydrogen concentration during detection limit tests is shown in Fig. 2.2. During this test hydrogen concentrations were varied stepwise for three cycles comprising six different hydrogen concentrations between 0.0 vol% and 0.3 vol%.

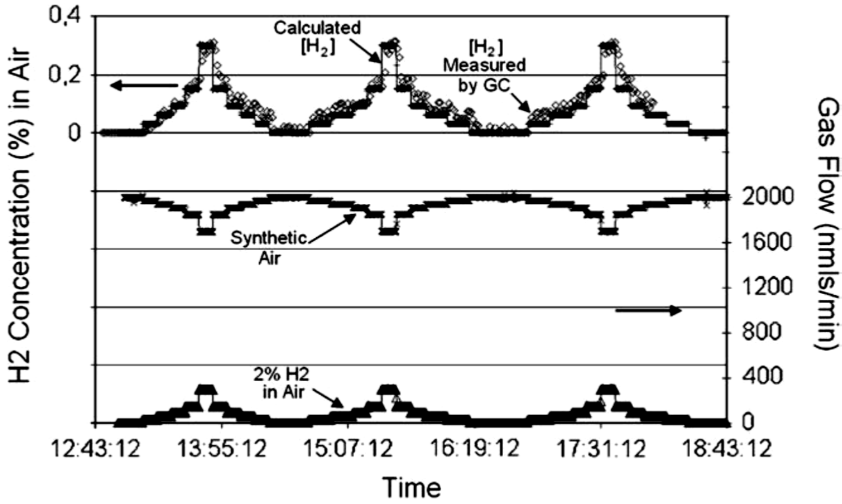

Fig. 2.2 – Example of control and measurement of hydrogen concentration during detection limit tests [4]

<u>1.4 Cross sensitivity to carbon monoxide test method</u>

Cross sensitivity of any chemical sensor should be low to prevent inference in sensor response from other contaminant species. Automotive manufacturers expressed the most interest in the cross sensitivity of hydrogen sensors to carbon monoxide. During the test the flow rate of 2.0vol% H_2 in air was kept constant (thereby maintaining a constant hydrogen concentration) and the relative flows of synthetic air and 0.5073vol% CO in nitrogen were varied stepwise to vary the concentration of CO in the gas mixture. Stepwise increase/decrease of the carbon monoxide volume fraction was preferably performed in a sequence of values multiple of a base step (similar to the sequence described in the detection limit test) however the exact sequence varied between tests signal deviation equivalent to 0.4vol% H_2 (10% LFL). The sensor cross sensitivity to carbon monoxide is expressed as the concentration of CO required to give this signal deviation. The maximum achievable CO concentration was 0.4 vol%. For sensors which exhibited a low cross sensitivity to CO (i.e. their signal deviation to the maximum achievable CO concentration was less than 0.4vol% H_2) the concentration of CO necessary to give the required signal deviation was estimated by extrapolation of the cross sensitivity results observed [4]. It was observed that the cross sensitivity of some sensors to CO may differ depending on whether the test is performed in the absence of hydrogen or at different hydrogen concentrations.

Due to the low accuracy of the GC with respect to CO measurements at concentrations below 0.4 vol% the CO concentration was calculated from the gas flow rates and not taken from the GC measurements. Fig.2.3 shows an example of the stepwise change in CO concentration during a typical cross sensitivity test and the response of a catalytic sensor to this change in CO concentration. During the test the hydrogen concentration was held constant at 0.91 vol% and the sensor response to this concentration ('reference level') was 1.14 vol%. Increasing the CO concentration caused a non-linear increase in sensor response and at 0.254 vol% CO the deviation in the sensor response was equivalent to +0.634 vol% H_2. The cross sensitivity of this sensor to CO was interpolated to be 0.21 vol% CO (i.e. 0.21 vol% CO gave a sensor signal deviation of 0.4 vol %)[4].

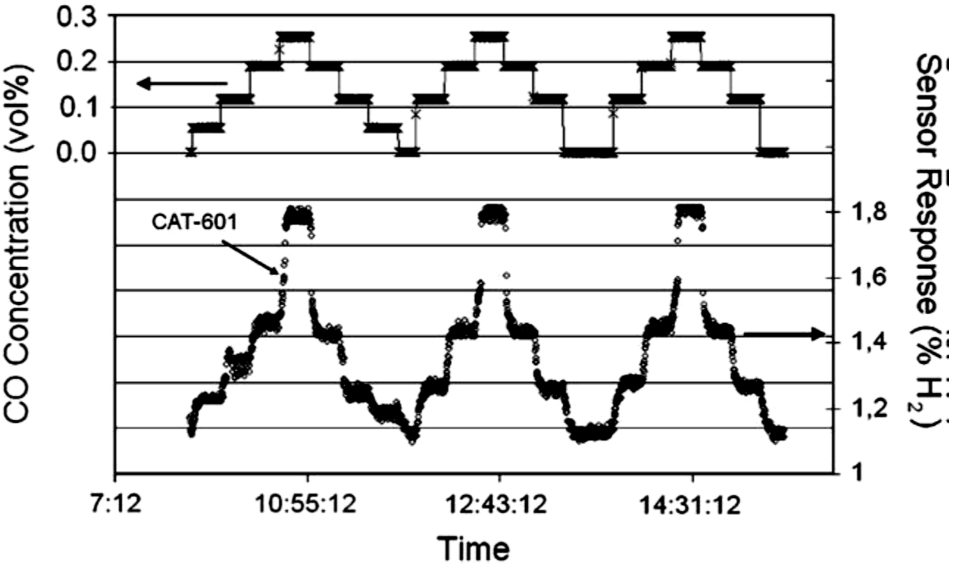

Fig. 2.3. – Cross sensitivity to carbon monoxide demonstrated by the catalytic sensor CAT-601. Hydrogen concentration was held constant at 0.91 vol% and the sensor response at this concentration, and in the absence of CO, was 1.14 vol%. Note the non-linear dependence of sensor response to CO [4].

1.5. Ambient temperature test method

The aim of this test was to assess the influence of temperature on the sensor output signal in the absence of H_2 and in the presence of H_2 in concentrations up to 2.0vol% H_2 in air. Temperature was increased in five steps within the temperature range specified by the manufacturer and at each step the temperature in the chamber was maintained within ±2 °C. At each temperature the sensors were exposed to synthetic air and then subsequently to the hydrogen in air mixture. To prevent condensation in the chamber it was imperative to keep the gas dew point below that of the lowest test temperature effectively meaning that temperature tests were performed close to dry gas conditions. When the temperature in the chamber had stabilized at the set value a zero sensor reading was taken in a gas flow comprising synthetic air only. Following this the flow of 2.0 vol% H_2 in air was started to give the desired H2 concentration. When the sensor signal had stabilized the sensor response was recorded before proceeding to the next temperature. An operating temperature range of -40 to +85 °C was deemed desirable by automobile manufacturers [4]. However during temperature tests the operating range of the sensors being tested, as specified by the manufacturer, was always respected so that no sensor was tested outside its temperature range.

Fig. 2.4 shows a typical temperature profile during a temperature test on two metal-oxide semiconductive (MOx) sensors. Sensors were heated or cooled to five different temperatures chosen within the operating temperature range specified by the manufacturer. Fig. 2.4 also shows how hydrogen concentration was varied between 0.0vol% and 0.2vol% at each temperature step [4]. It is clear from this test that temperature has little to no effect on the MOx sensor zero reading however it has a profound effect on the sensor reading in 0.2vol% hydrogen with evidence of hysteresis.

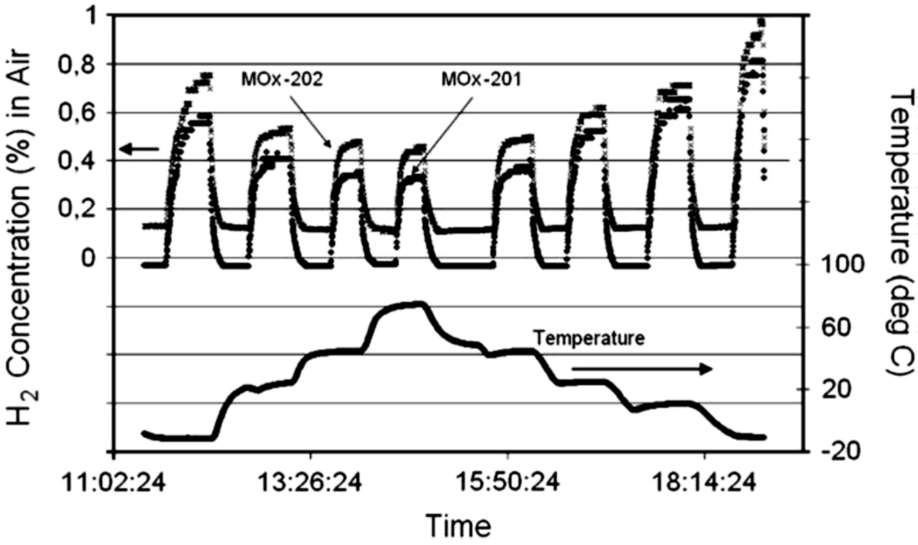

Fig. 2.4. - The variation in response of MOx sensors to hydrogen as a function of temperature. At each temperature, the hydrogen volume concentration was changed between 0.0 vol% and 0.2 vol% [4]

1.6. Ambient humidity

The aim of this experiment is to determine the influence humidity has on the sensor signal in synthetic air and in the presence of hydrogen in concentrations up to 2.0 vol% H_2 in air. Automobile manufacturers indicated a desired operational humidity range of 0-95%. According to the IEC 61779-1 test protocol test gas with at least three different humidities evenly distributed over the range specified by the sensor manufacturer was supplied to the sensor in the test chamber which was maintained at a constant temperature and pressure. The humidity deviation was maintained within ±3% RH of the desired humidity. The sensors were exposed first to synthetic air and then to a test gas comprising up to 2.0 vol% H2 in air at the same humidity levels. The results of a typical humidity test performed on four electrochemical sensors in 0.0 vol% and 1.5 vol% H_2 are shown in Fig. 2.5 [4]. From this figure it is obvious that the response of these electrochemical sensors did not vary significantly with humidity in the range investigated. Note that when the sensors were initially exposed to 1.9vol% H_2 in air, two sensors showed a hydrogen concentration higher than 4.0 vol% equivalent to their measuring range upper limit. For this reason it was decided to limit the maximum H_2 concentration to which these sensors were exposed to 1.5 vol% H2 in air.

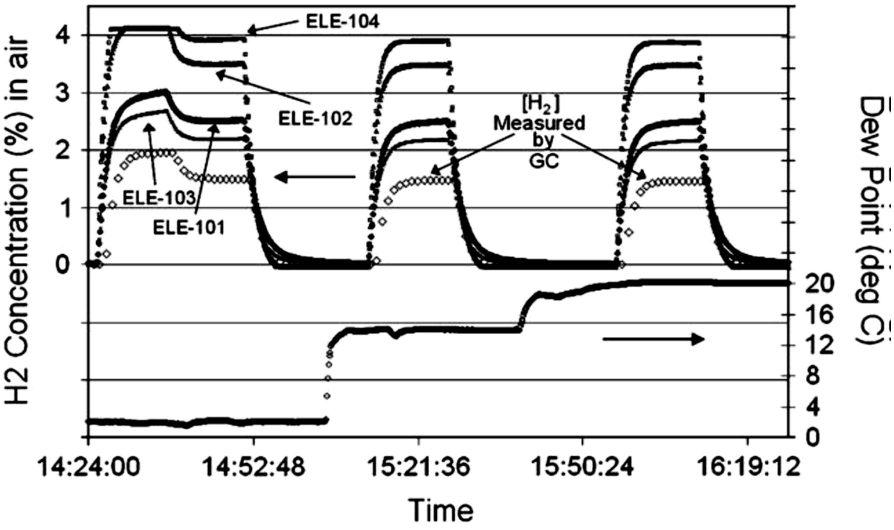

Fig. 2.5. - The influence of humidity on electrochemical sensor response. At each humidity hydrogen concentration was changed between 0.0 vol% and 1.5 vol% H_2 in air. The equivalent relative humidities to the measured dew points of 1.5 °C, 14.5 °C and 20 °C are 20%, 50% and 70% (at chamber temperature 26 °C) respectively. When the sensors were initially exposed to 1.9 vol% H_2 in air, two sensors were saturated showing their limit of the range and for this reason it was decided to limit the maximum H2 concentration to which these sensors were exposed to 1.5 vol% H_2 in air [4]

1.7. Ambient pressure test method

The aim of this test is to determine the influence of pressure on the sensor output in the absence of H_2 and in the presence of hydrogen at concentrations up to 2.0vol% H_2 in air. In automotive applications a reasonable altitude range is from -400 m to 4000 m. These altitudes correspond to approximate atmospheric pressures equal to 107 kPa and 62kPa [4]. During this test the pressure in the test chamber was set to at least three different pressures within the pressure range specified by the sensor manufacturer and the sensors exposed to air and then up to 2.0 vol% H_2 in air. The pressure deviation was maintained within ±2 kPa for at least 5 min to allow conditions to stabilize before a sensor reading was taken. At each pressure the sensor was exposed first to synthetic air and a zero reading was taken before being exposed to hydrogen at a concentration up to 2.0 vol%. The results from a pressure test performed on two identical MOx sensors are shown in Fig. 2.6. During this pressure test the hydrogen concentration as measured by GC analysis is corrected for changes in the total pressure and the corrected measured hydrogen concentration is shown together with the sensor readings. At all pressures these sensors show a significant overestimation of the hydrogen concentration and as expected the sensor output increases with increasing pressure.

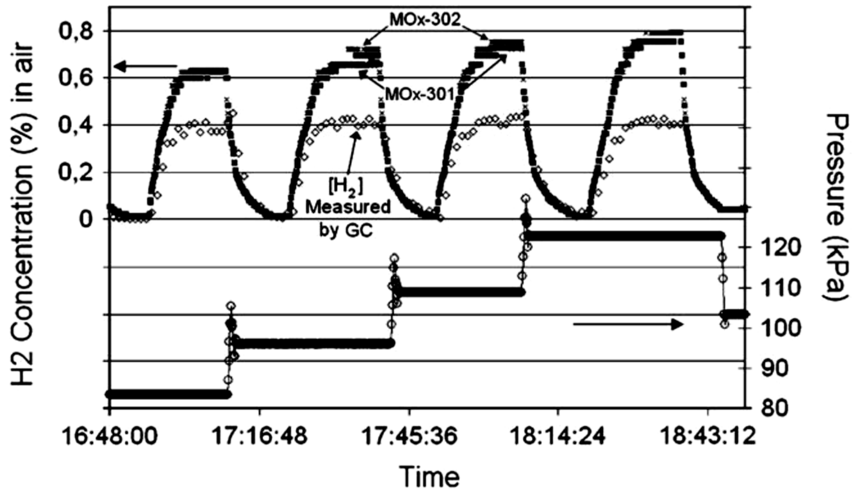

Fig. 2.6. – The response of two MOx sensors to 0.0 vol% and 0.4 vol% H2 in air at four different pressures [4]

2. Selected sensors test results

The tests described in previous section were performed following a protocol designed specifically for testing automotive hydrogen safety sensors paying considerable attention to the working environment of such sensors and the requirements of the end user. Four suitable hydrogen sensors types were found to be commercially available. Representative samples of catalytic, electrochemical, thermal conductivity and semiconductive metal-oxide (MOx) sensors were procured for testing [2]. The performances of these types of hydrogen sensors are assessed and comparisons are made between the different sensing technologies in an attempt to identify suitable detection technologies for automotive applications.

2.1 Catalytic sensors

2.1.1. Accuracy of response

The accuracy of response and measuring range tests were carried out at (299 ± 2) K, (50 ± 3) % RH, (100 ± 2) kPa and in a gas flow rate of 1 nl/min [2]. Fig. 2.7 summarizes the results from accuracy tests performed on all catalytic sensors. The shaded region indicates the range of sensor response which could be expected at the respective hydrogen concentration. Of all the sensor types tested catalytic sensors measured the hydrogen concentration most accurately however many sensors slightly overestimated the actual concentration. The accuracy of these sensors increased with increasing hydrogen concentration.

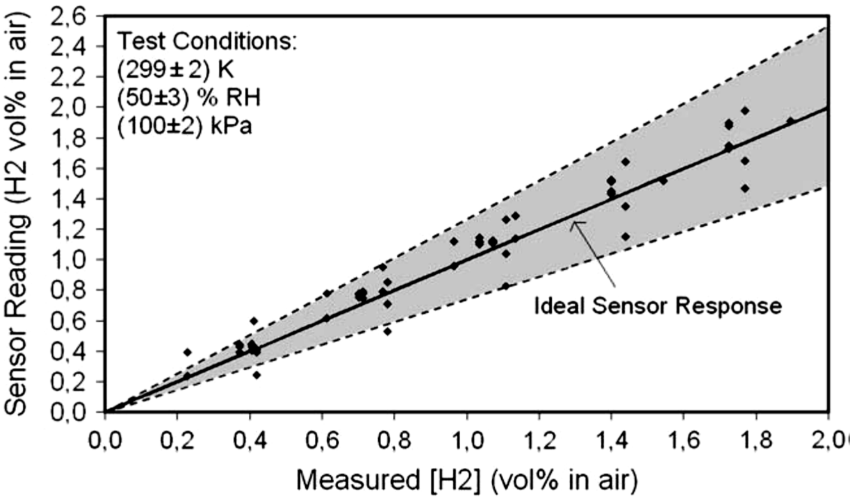

Fig. 2.7. - Catalytic sensors: accuracy of hydrogen concentration measurements. The readings from sensors at different hydrogen concentrations are shown and compared with the hydrogen concentration measured by gas chromatograph (represented on the graph as the Ideal Sensor Response) [2]

2.1.2. Measuring range

All catalytic sensors showed a linear response to changes in hydrogen concentration within the range measured (0.0-2.0vol% hydrogen in air). Only one catalytic sensor showed limiting of signal within its proclaimed measuring range [2].

2.1.3. Detection limit

Seven of the catalytic sensors yielded a well-defined step in sensor output in the presence of 0.03 vol% H2. The remaining sensors only yielded such a well-defined step in their output at higher hydrogen concentrations reported in Table 2.1. The accuracy with which these sensors measured low hydrogen concentrations was poor. In this case the deviation of some catalytic sensor readings from the actual hydrogen concentration was +125%.

2.1.4. Cross sensitivity to CO

Some catalytic sensors tested showed a significant cross sensitivity to carbon monoxide. As shown in Table 2.1 sensors CAT-601 and CAT-602 gave a signal deviation equivalent to 0.4 vol% H_2 at a CO concentration below 0.4 vol% indicating that these sensors are more sensitive to CO than to hydrogen.

Sensor	Detections limit (vol% H_2)	Cross sensitivity (vol% CO)
CAT-101	≤0.11	1.00
CAT-102	≤0.11	5.70
CAT-104	≤0.11	2.00
CAT-202	≤0.06	1.03
CAT-401	≤0.03	0.99
CAT-402	≤0.03	1.33
CAT-502	≤0.03	0.70
CAT-601	≤0.03	0.21
CAT-602	≤0.03	0.22

CAT-701	≤0.03	0.72
CAT-702	≤0.03	0.57

Table 2.1 - Catalytic sensors: summary of the results from detection limit and cross sensitivity to CO tests. The detection limit values indicate the concentration of hydrogen at which a well-defined step in sensor output was observed. Cross sensitivity values indicate the concentration of CO required to give a sensor signal deviation equivalent to 0.4 vol% H_2 (10% LFL) [2]

2.1.5. Ambient parameters

The influence on sensor output resulting from changes in temperature, pressure and relative humidity are summarized in Fig. 2.8. It was found that pressure and relative humidity had no influence on sensor reading when compared with the hydrogen concentration measured by the GC [2]. Changes in temperature had only a modest effect on catalytic sensor response.

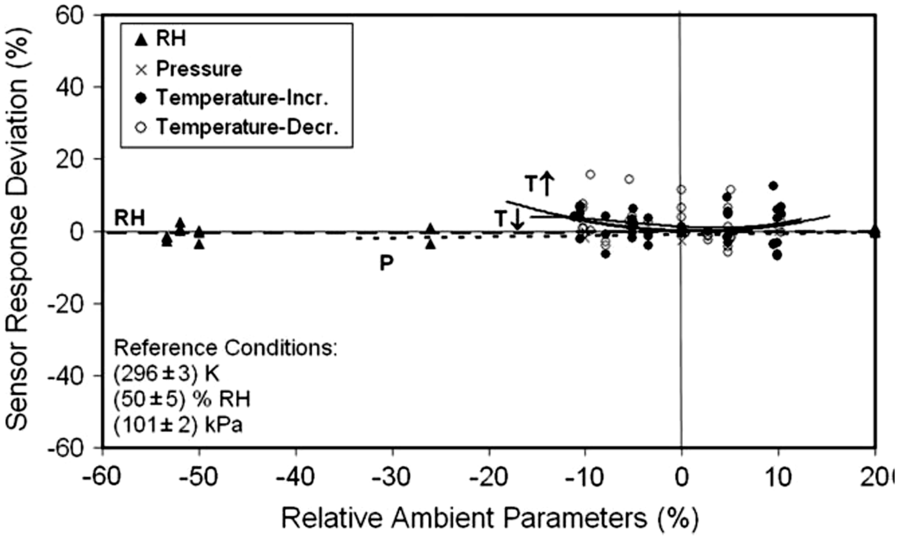

Fig. 2.8 – Catalytic sensors: deviation of response to hydrogen from the response at the reference conditions as a function of changes in ambient temperature, pressure and relative humidity [2]

2.2. MOx Sensors

2.2.1. Accuracy of response

As can be seen from Fig. 2.9, metal-oxide semiconductive type sensors were less accurate in their measurement of hydrogen concentration compared with catalytic type sensors. MO*x* sensors consistently overestimated the actual hydrogen concentration typically between 50 and 200%. Hysteresis and memory effects in MO*x* sensor response were also observed (see Fig. 2.10), with all sensors consistently showing a significantly higher signal during the stepwise decrease in hydrogen concentration when compared with the signal obtained during the initial stepwise increase in hydrogen concentration.

2.2.2. Measuring range

MO*x* sensors showed a linear response to changes in hydrogen concentration within the range measured however in all cases the sensors overestimated the hydrogen concentration and often sensor saturation was observed well before the upper hydrogen concentration limit indicated by the manufacturer was reached (see Fig. 2.9).

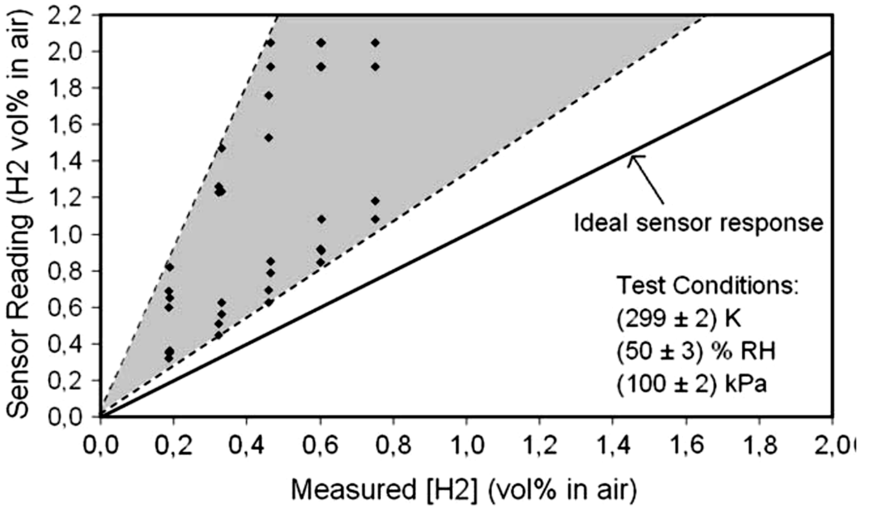

Fig. 2.9 - MOx sensors: accuracy of hydrogen concentration measurements. The readings from sensors at different hydrogen concentrations are shown and compared with the hydrogen concentration measured by gas chromatograph (Ideal Sensor Response). Note the consistent overestimation of the actual hydrogen concentration by all the MOx sensors tested [2]

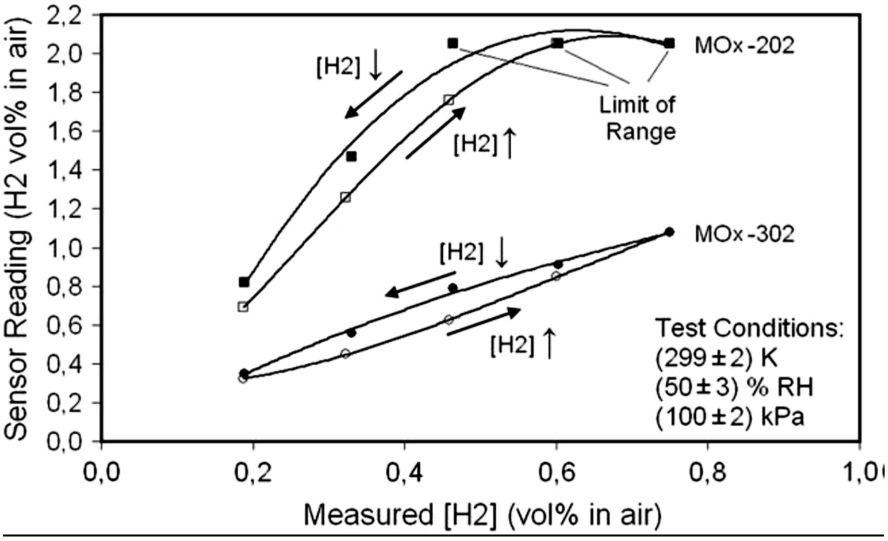

Fig. 2.10 – Hysteresis behavior shown by two different MOx sensors during accuracy of response test [2]

2.2.3. Detection limit

Detection limit and cross sensitivity data for MO*x* sensors are given in Table 2.2. All MO*x* sensors tested were capable of detecting low hydrogen concentrations (0.03 vol %) however they tended to overestimate the actual concentration, the most accurate reading at 0.03 vol% was 0.136 vol%.

2.2.4. Cross sensitivity to CO

As seen from Table 2.2 all the MO*x* sensors tested showed no reaction to CO up to concentrations of 0.3 vol%.

Sensor	Detections limit (vol% H_2)	Cross sensitivity (vol% CO)
MOx-201	≤0.03	None
MOx-202	≤0.03	None
MOx-301	≤0.03	None
MOx-302	≤0.03	None

Table 2.2. MOx sensors: summary of the results from detection limit and cross sensitivity to CO tests. The detection limit values indicate the concetration of hydrogen at which a well-defined step in sensor output was observed [2]

2.2.5. Ambient parameters

Ambient parameter tests performed on MO*x* sensors in the absence of hydrogen showed that there was no significant change or shift in their baseline signal. On the contrary in the presence of hydrogen, changes in ambient conditions, particularly temperature and relative humidity, were found to have a strong influence on the sensor response for almost all of the MO*x* sensors tested. Their dependence on ambient parameters is shown in Fig. 2.11. However, in many cases the sensor response had reached its maximum value thereby

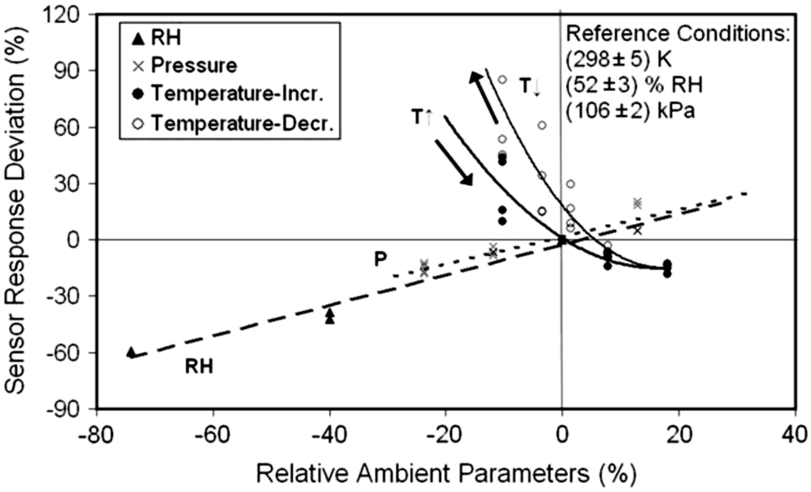

Fig. 2.11 – MOx sensors: deviation of response to hydrogen from the response at the reference conditions as a function of changes in ambient temperature, pressure and relative humidity. Note the larger scale on the sensor response deviation axis compared with Figs. 2.8, 2.14 and 2.16 [2]

2.3. Electrochemical sensors

Ten electrochemical sensors were procured and the performance of eight of these sensors was successfully tested. The two remaining sensors (same model and type) failed to show any response to hydrogen and were judged to be damaged [2].

2.3.1. Accuracy of response

The accuracy of electrochemical sensors was lower than other sensor types tested and is highlighted in Fig. 2.12 which shows the large variation in the response from the electrochemical sensors at each hydrogen concentration.

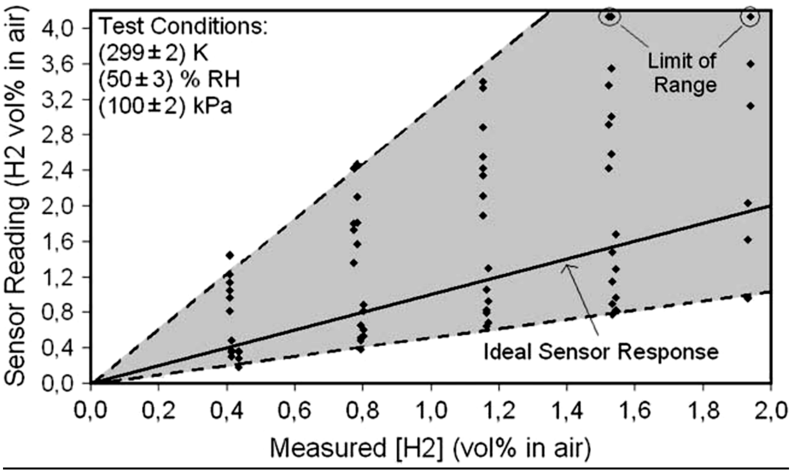

Fig. 2.12 - Electrochemical sensors: accuracy of hydrogen concentration measurements. The readings from sensors at different hydrogen concentrations are shown and compared with the hydrogen concentration measured by gas chromatograph (Ideal Sensor Response) [2]

2.3.2. Measuring range

Of all sensor types tested electrochemical sensors showed the largest variation in results not only between different models but also between individual sensor samples of the same manufacturer and model. This wide variation in performance is illustrated in Fig. 2.13 which shows the response of four identical electrochemical sensors tested under identical conditions to changes in hydrogen concentration. Response of the electrochemical sensors was linear in the hydrogen concentration range tested. Two sensors showed signal limitation when the hydrogen concentration was less than half of the manufacturers declared measuring range.

2.3.3. Detection limit

Table 2.3 summarizes the results from detection limit and cross sensitivity tests performed on electrochemical sensors. They had a low detection limit with all sensors responding to 0.03 vol% H2 in air. The variation in the ability of these sensors to accurately measure such low concentrations was large with some sensors underestimating the actual hydrogen concentration by up to -50% while other samples overestimated the actual hydrogen concentration by over 600%.

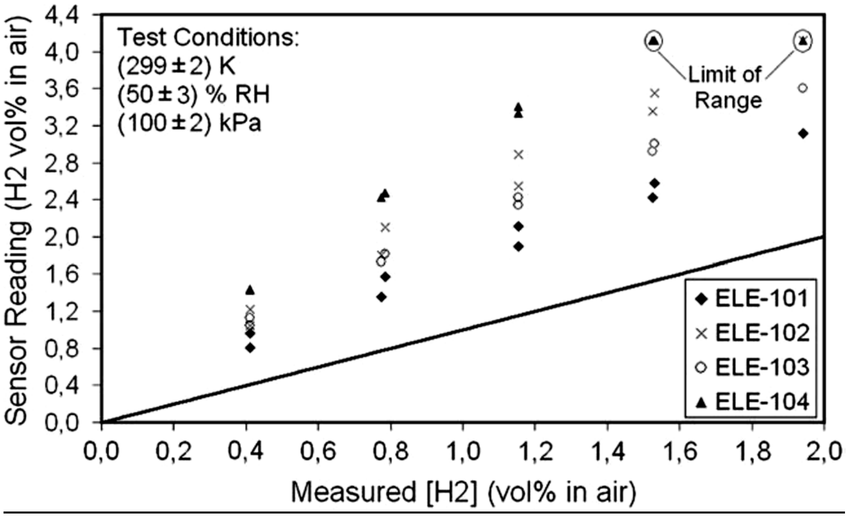

Fig. 2.13 - Response from four identical electrochemical sensors at different hydrogen concentrations. Saturation of sensor response occurred at a reading of 4.125 vol% [2]

2.3.4. Cross sensitivity to CO

The observed cross-sensitivity of some sensors to CO was high, as can be seen from Table 2.3. However in many cases the degree of influence of CO concentration on sensor response was, while obvious, difficult to quantify due to variation in test results and shift of the sensor baseline.

Sensor	Detections limit (vol% H_2)	Cross sensitivity (vol% CO)
ELE-101	≤0.03	No signal
ELE-102	≤0.03	0.31
ELE-103	≤0.03	0.33
ELE-104	≤0.03	0.46
ELE-201	≤0.03	Inconclusive
ELE-202	≤0.03	Inconclusive
ELE-401	≤0.03	Inconclusive
ELE-402	≤0.03	Inconclusive

Table 2.3 - Electrochemical sensors: summary of the results from detection limit and cross sensitivity to CO tests. The detection limit values indicate the concentration of hydrogen at which a well-defined step in sensor output was observed. Cross sensitivity values indicate the concentration of CO required to give a sensor signal deviation equivalent to 0.4 vol% H_2 (10% LFL) [2]

2.3.5. Ambient parameters

Electrochemical sensors showed only a small change in reading at different ambient pressures. There was also a low response to changes in relative humidity. Temperature on the other hand had a significant influence on sensor responses but this influence was not consistent between sensors of different manufacturers or indeed between identical sensors. The results from ambient parameter tests performed on all electrochemical sensors tested is summarized in Fig. 2.14. This figure highlights the wide dispersion of results which were observed specifically during temperature tests where temperature was varied between 255 K (-18 °C) and 355 K (82 °C).

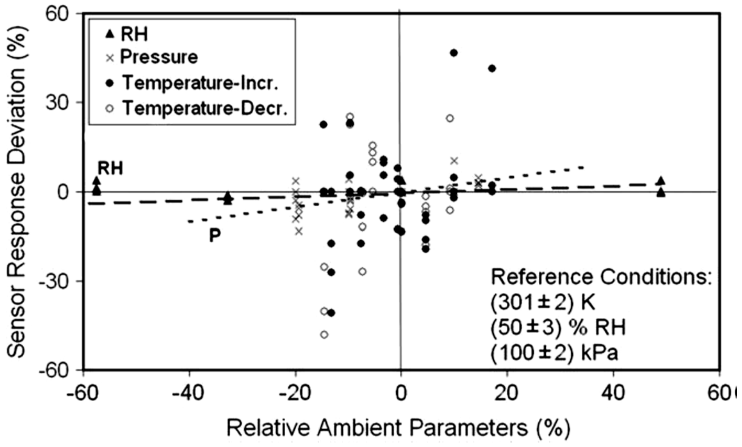

Fig. 2.14 - Electrochemical sensors: deviation of response to hydrogen from the response at the reference conditions as a function of changes in ambient temperature, pressure and relative humidity [2]

2.4. Thermal conductivity sensors

The search for commercially available and suitable thermal conductivity sensors revealed that there are a limited number of models on the market having the required specifications. Three sensors of this type were procured one of which failed to show any response to hydrogen and was deemed as not working. With such a limited number of samples reliable assessment of performance is difficult. Nonetheless the results of tests performed are consistent and are reported here [2].

2.4.1. Accuracy of response

The results from accuracy of response tests performed on the thermal conductivity sensors are plotted in Fig. 2.15. Because of the large measuring range of thermal conductivity sensors the shift of the sensor baseline is of great importance. Both sensors demonstrated a baseline shift; the shift for one sensor was equivalent to -0.1 vol% while the other was approximately +0.3 vol%. This shift was observed over the hydrogen concentration range measured and is consistent with the sensors large measuring range. One sensor responded more accurately to hydrogen slightly underestimating the actual concentration while the other sensor overestimated it. If this baseline shift is taken into account the readings from each sensor do not differ much from the actual measured hydrogen concentration.

2.4.2. Measuring range

Both sensors showed a close to linear response up to 2.0 vol% H_2 and no limitation of sensor response was observed. No evidence of hysteresis behavior was apparent.

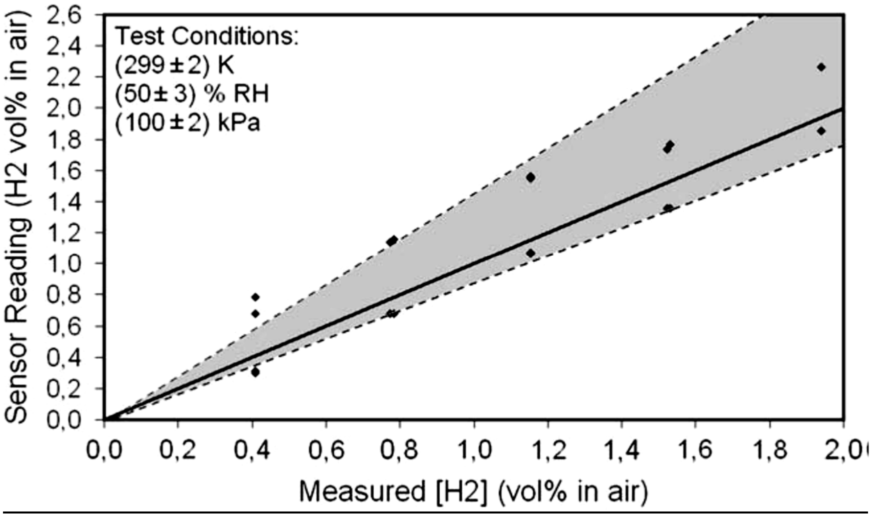

Fig. 2.15 - Thermal conductivity sensors: accuracy of hydrogen concentration measurements. The readings from sensors at different hydrogen concentrations are shown and compared with the hydrogen concentration measured by gas chromatograph (Ideal Sensor Response) [2]

2.4.3. Detection limit

Table 2.4 summarizes the results from detection limit and cross sensitivity to CO tests on the thermal conductivity sensors. The detection limit of these sensors was high, consistent with their very large measuring range. The measured hydrogen concentration for which a noise free signal was observed was 0.6 vol% for sensor TCD-201 and 0.15 vol% for sensor TCD-202. This implies that the sensor TCD-201 is not able to detect hydrogen at the critical 10% LEL level (0.4 vol%).

Sensor	Detections limit (vol% H_2)	Cross sensitivity (vol% CO)
TCD-201	≤0.60	-
TCD-202	≤0.15	0.36

Table 2.4 - Thermal conductivity sensors: summary of the results from detection limit and cross sensitivity to CO tests. The detection limit values indicate the concentration of hydrogen at which a well-defined step in sensor output was observed. Cross sensitivity values indicate the concentration of CO required to give a sensor signal deviation equivalent to 0.4 vol% H_2 (10% LFL) [2]

2.4.4. Cross sensitivity

The concentration of carbon monoxide needed to cause a signal deviation equivalent to 0.4 vol% H_2 for sensor TCD-202 was 0.36 vol% which is a relatively low concentration. This indicates a high CO cross sensitivity when compared with other sensors tested. Assessment of the cross sensitivity of sensor TCD-201 to carbon monoxide was not possible because of damage to the sensor before this test [2].

2.4.5. Ambient parameters

The results from ambient parameter tests performed on thermal conductivity sensors are summarized in Fig. 2.16. Temperature dependence was investigated in range from 255 K (-18 °C) to 313 K (40 °C) in a test gas containing 0.95 vol% H_2 [2]. There was a strong response to temperature with a sensor response deviation of nearly +80% observed at the lowest temperature relative to the response observed at 299 K. Both sensors show a slight increase in signal response with increasing ambient humidity. In the investigated range of ambient humidity (from 20% R.H. up to 70% R.H.) the change in reading was approximately 26% for TCD-201 and approximately 15% for TCD-202. In the investigated pressure range (800-1100 mbar) the pressure dependence was not pronounced.

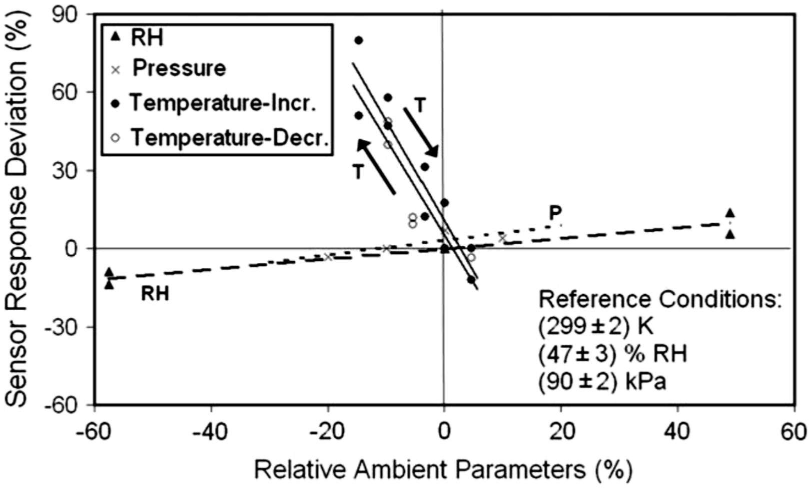

Fig. 2.16 – Thermal conductivity sensors: deviation of response to hydrogen from the response at the reference conditions as a function of changes in ambient temperature, pressure and relative humidity [2]

3. Results and discussion

3.1. Catalytic sensors

Catalytic sensors were the most accurate sensor type to measure hydrogen concentration. However the detection limit of these sensors was high as only seven of the 11 tested sensors were able to detect 0.03 vol% H_2 and in most cases the measurement of this low concentration was not accurate. Some of these sensors showed a significant cross sensitivity to carbon monoxide. All the sensors showed little to no dependence of sensor output on temperature, pressure and humidity.

The maturity of catalytic technology and the good performance of these sensors during tests, suggest that catalytic sensors may be well suited for use as hydrogen safety sensors in automotive applications, particularly if their detection limit can be lowered. However the relatively high power consumption of catalytic sensors together with their low specificity may prove problematic in this specific application.

3.2. MOx sensors

The detection limit of MOx sensors is low and all MOx sensors tested were capable of detecting a hydrogen concentration of 0.03vol%. However most MOx sensors significantly overestimated the actual hydrogen concentration in addition to displaying hysteresis during measuring range and temperature tests. The MOx sensors also showed a very strong dependence on temperature, pressure and particularly humidity while cross sensitivity to CO was low.

Results from performance tests on MO*x* sensors suggest that they may be suitable for use as safety sensors where, in their normal working environment, no hydrogen is present but on release of hydrogen they are required to give a 'once off' alarm to the presence of low concentrations of hydrogen. The behaviour of MO*x* sensors observed during tests indicate that they may be unsuitable for applications where hydrogen can be expected to be present regularly and where the 'memory effects' of MOx sensors may influence the accuracy of hydrogen concentration measurements. When considering the application of hydrogen safety sensors in automobiles, the ambient working conditions may vary immensely. Pressure variations due to changes in altitude, temperature variations due to seasonal and geographical influences and humidity variations due to meteorological influences can all be reasonably expected. For this reason the importance of a thorough investigation of the reaction of sensors strongly influenced by changes in temperature, pressure and relative humidity (e.g. MOx sensors) is emphasized. In the ambient parameter tests performed there was no significant change or shift in the baseline signal of MO*x* sensors. This is an important characteristic of these sensors as it indicates that they will not give a false positive signal in the absence of hydrogen when ambient conditions change.

3.3. Electrochemical sensors

Trends in electrochemical sensor performance were not as obvious as for other sensor types. In fact large differences in sensor response from identical sensors (same model and manufacturer) were observed in some tests as shown in Fig. 2.12. In general the accuracy observed for this type of sensor is lower than for the other sensor types. In addition many electrochemical sensors displayed unusual and unexpected results [2]. The ELE-10x series of sensors grossly overestimated the hydrogen concentration. The remaining electrochemical sensors underestimated the hydrogen concentration, some considerably, with a low accuracy. Cross sensitivity to CO was high but in many cases the degree of influence of CO concentration on sensor response was impossible to quantify due to large variation in test results and changes in the sensor baseline. Electrochemical sensors showed a low response to humidity and pressure dependence was not very pronounced. Changes in temperature had a strong influence particularly at sub-zero temperatures. Due to the variation in performance of electrochemical sensors, which was observed during tests, the reliability of this type of sensor for use as hydrogen safety sensors in automotive applications is questioned. Also the strong influence of (modest) sub-zero temperatures on the sensor performance is a cause for concern in this application.

3.4. Thermal conductivity sensors

It is difficult to draw reliable conclusions about the performance of thermal conductivity sensors because of the limited number of results which were available. However tests indicated the high detection limit of this type of sensors which is consistent with their very large measuring range (0-100vol% H_2). The detection limit was high in fact that one sensor failed to detect hydrogen at the 10% LFL level (0.4vol %). This result has serious implications for the possibility of using this type of sensor as a safety sensor in automotive applications where early detection of hydrogen leaks is essential. Furthermore thermal conductivity sensors showed a significant cross sensitivity to carbon monoxide and sensor response was strongly influenced by ambient temperature.

However, as a well-developed and robust technology, thermal conductivity sensors may be suitable for use as safety sensors if their detection limit can be lowered and if their temperature dependence can be compensated.

4. Sensors comparison

The advantages and disadvantages observed during the assessment of the four sensor types tested are summarized in Table 2.5.

Sensor type	**Catalytic**	**MOx**	**Electrochemical**	**Thermal conductivity**
Advantages	Robust	Low detection limit	Low detection limit	Accuracy
	Accurate	Small size	Low dependence on RH	Wide measuring range
	Low dependence on RH	Low Cost	Low Cost	O_2 not required for operation
	Low dependence on temperature	Stable baseline	Low power consumption	
	Low dependence on pressure	Suitable mass production		
		Wide temperature range		
Disadvantages	High detection limit	Low accuracy	Poor performance at sub-zero temperature	High detection limit
	Poisoning and cross sensitivity	Dependence on temperature	Wide variation in results	Dependence on temperature
	High power consumption	Dependence on humidity	Poisoning	Expensive
	Expensive	Sensitive to overexposure	Cross sensitivity	
	Large size	Memory effects	Operation at low Pressure difficult	

Table 2.5 - The advantages and disadvantages noted for the various hydrogen sensor types tested based on observations during tests

While catalytic sensors showed the best performance during the tests their suitability for use as safety sensors in hydrogen fueled vehicles is compromised due to their large power consumption, as safety sensors will need to operate even when the vehicle is not in use. MOx sensors performed poorly in ambient parameter tests in the presence of hydrogen however their use as safety sensors, in the absence of hydrogen under normal operating conditions, is feasible if their accuracy can be improved (for example by using nanomaterials and MEMS technology) [2]. Their small size, low cost and relatively low power consumption are advantageous properties for automotive applications. Electrochemical sensors showed a large variation in their performance during the tests performed. Their poor performance at modest low temperatures is a cause for concern if used in vehicles where such low temperatures are possible. Finally thermal conductivity sensors despite their relatively high cost do have the potential to be used as safety sensors if their detection limit can be lowered and their dependence on temperature can be compensated.

CHAPTER 3

HYDROGEN SAFETY: TECHNOLOGY AND SAFETY STANDARDS DEVELOPMENT – KNOWLEDGE ADVANCEMENT

1. 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 summarized as follows, in which fuel cell applications are listed separately if appropriate [5] [6].

- indication of hydrogen in concentration range 0.01-10% (safety) or 1-100% (fuel cells)
- safe performance i.e. explosion proof sensor design and protective housing
- reliable results of sufficient accuracy and sensitivity (uncertainty <5-10% of signal)
- stable signal with low noise
- robustness including low sensitivity to environmental parameters such as:
  - temperature (-30-80°C (safety), 70-150 °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 € per system)
- small size
- simple operation and maintenance with long service interval
- validated and certifiable according to international standards
- simple system integration and interface

2. 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 [5]. For this reason hydrogen sensor developers and manufacturers are making large efforts to optimize 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.

2.1 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. 3.1). 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 function. Thus, the H_2-Semicon sensor system offers highly selective measurement of hydrogen concentrations in a continuous range from 0 to 100%, the sensor response in the range from 0 to 4% is demonstrated in Figs. 3.2 and 3.3. The detector operates in a temperature range of -20 to +80 °C and is humidity resistant from dry air up to condensation. The response time (t_{60}) is less than 1 s for a jump from zero to 0.5% H_2. Typical sensor applications are leakage monitoring, such as in fuel cell systems or by mobile and stationary devices, as well as monitoring of chemical processes and equipment in the industrial or facility sectors.

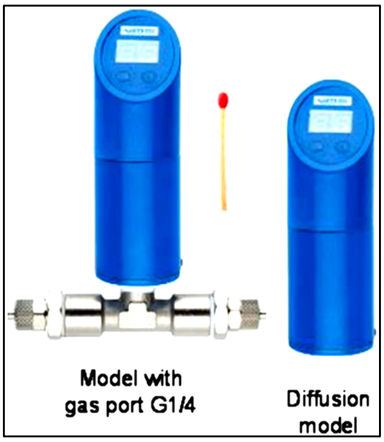

Fig 3.1 H_2 Semicon sensor system [5]

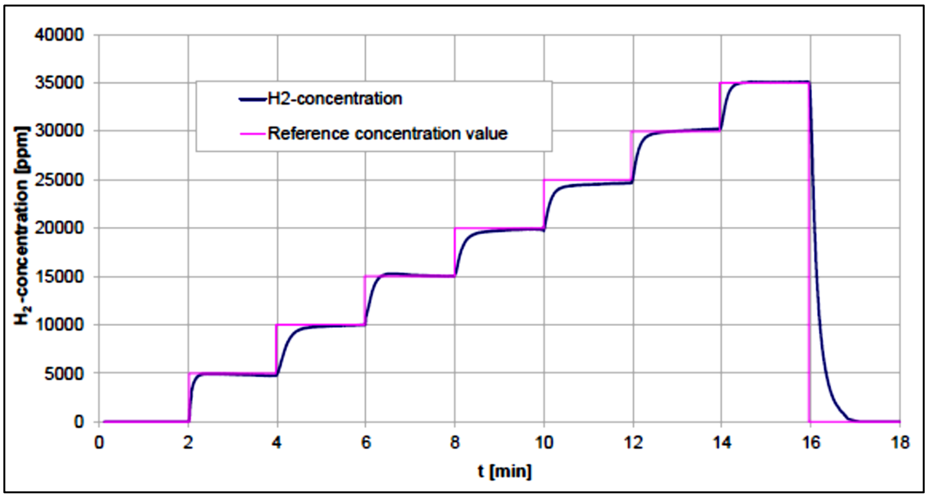

Fig. 3.2 The Indication of H_2-Semicon-sensor system and gradual increasing reference concentration [5]

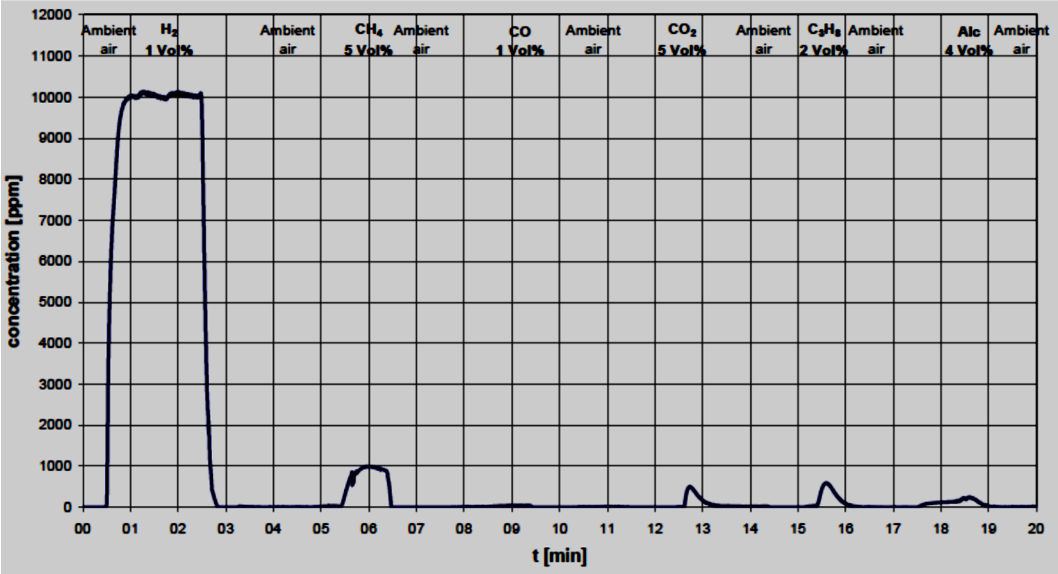

Fig. 3.3 The indication of H_2-Semicon-sensor system exposed to different gases [5]

Further commercial products combining two different sensor platforms are known. The Cyber Genius of Sensitron S.r.L. for example is a commercial sensor module that combines an electrochemical cell and a pellistor sensing platform based on catalytic combustion in a single device. Electrochemical sensors can be designed for different concentration ranges of hydrogen, typically in the range of 0.001% to 0.2%, however ranges of up to 4% are common. Sensors based on catalytic combustion of hydrogen are operating in the range of 0.05% up to 4% or even up to 100%. However, it has to be considered that the sensor needs sufficient oxygen for complete combustion of hydrogen. Theoretically for the detection of hydrogen up to the lower flammability level (4%) at least 2% of oxygen is required. The Cyber Genius exploits the advantages of both technologies in terms of measuring range, uncertainty of measurement and response time. In addition it includes a detection backup for advanced security and reliability (see Fig. 3.4).

Fig. 3.4 The Dual sensor module cyber genius [5]

An example of the use of two sensing mechanisms in one platform is realized in devices of Applied Sensor GmbH [5]. The HLS-440 sensor is based on a field effect sensing element which simultaneously uses the impact of the large heat conductivity of hydrogen for the measurement. This enables an increased measuring range of 0-10% and improved selectivity. The sensor can be used in harsh environments, which are beyond the conditions specified in the common standards for sensor safety such as fuel cell exhausts ducts to measure hydrogen. The use of a thermal conductivity sensing element in combination with a temperature sensor and a heater improves sensor performance and enlarges the hydrogen measuring range up to 100% (HPS-100). The sensors operate in the temperature range of -50 to 95 °C and in relative humidities up to 100% including condensation. The silicon technology offers a low cost sensor component. The response time (t90) and the recovery time (t10) are below 5s and 10s.

2.2. Combination of hydrogen sensing platforms with temperature and humidity sensing elements

In many cases, the sensor output signal is influenced both by the operating temperature of the sensor and the temperature of the gas in which hydrogen is to be detected. Therefore many contemporary sensors are equipped with a temperature sensor to compensate for the temperature impacts on the sensor response. Also humidity of the gas under investigation can have an impact on the hydrogen detection. Therefore sensors are commonly protected with a nearly impermeable filter cup to prevent condensation on the surface of the sensing element. Another approach is to integrate a humidity sensing element in the hydrogen detection device as is done in the XEN-5310 device from Xensor Integration BV [5]. In this device the thermal conductivity type sensor can be used for the detection and measurement of hydrogen gas in concentration ranges from 0 to 4% or 0 to 100%. Temperature is measured independently allowing compensation of any influences changes in the ambient temperature may have on the sensor response. The relative humidity sensing element compensates humidity changes which could otherwise have a significant influence on the measurement particularly at higher temperatures and high humidities. The sensor can be operated in a temperature range from -20 to +55 °C, in a relative humidity range of 1-100% and in a pressure range of 0.8-1.2 bar. The micro-machined thermal conductivity device has a power consumption of 100 mW and a response (t90) and recovery time (t_{10}) of around 1 s. The sensor has a low drift and is suitable for leak detection in emerging hydrogen applications.

2.3 Signal processing for intelligent hydrogen gas sensors

Intelligent hydrogen sensors use a micro-controller unit in order to process the signals from different sensing elements. A continuous temperature measurement and corresponding sensor adjustment ensures almost no temperature dependency of the measurement signal. Also, the integrated micro-controller allows humidity compensation with the result that a reference measurement, which is typical for many thermal conductivity sensors, is not required. Fig. 3.5 shows a schematic of the sensor components. Safety-related functions like the recognition and signaling of failure states and error handling procedures, i.e. self-testing features, even during the measurement are integrated in the intelligent sensor. The sensor output signal can be indicated by a display or provided via an analogue interface as a unit voltage (0-10 V) or current signal (4-20 mA). In order to supply further types of output signals, the sensor system contains an analogue-to-digital converter (ADC) or a frequency-to-digital converter (FDC). The results of hydrogen measuring can be transferred via different communication protocols or busses, such as Modbus, RS485, CAN and HART [5].

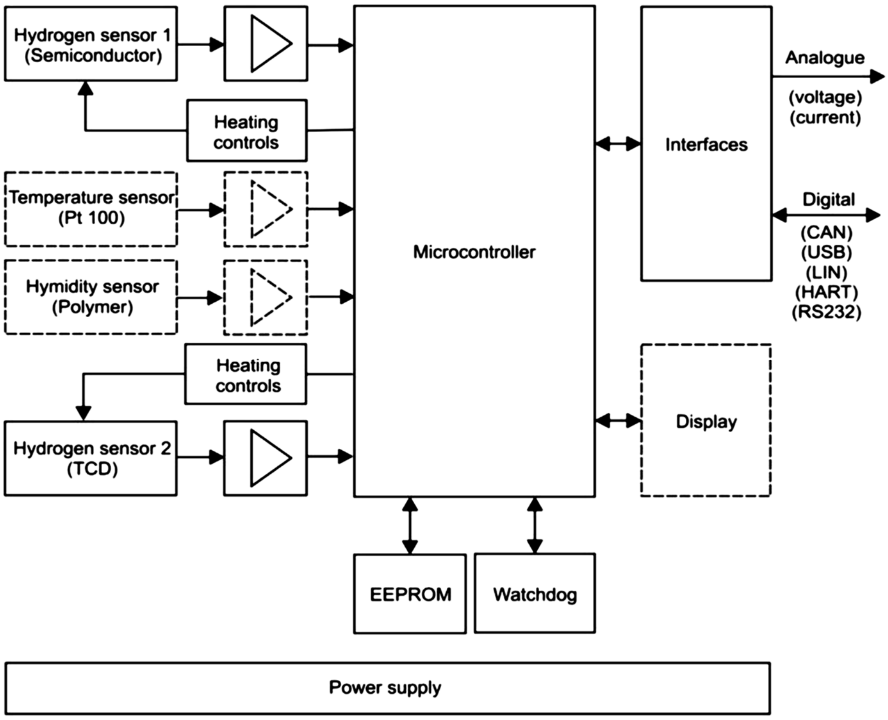

Fig. 3.5 The Schematic of a hydrogen sensor system with temperature and relative humidity compensation [5]

2.4. Accordance with regulations, codes and standards

The technical application of hydrogen sensors as detectors and measuring devices for flammable gases in potentially explosive atmospheres demands the compliance with appropriate regulations, codes and standards for the safety and human health protection. In Europe directive 94/9/EG (ATEX100a) defines the basic requirements on health protection and safety for applications of electrical equipment in such areas [5]. Three basic aspects have to be considered for the application of hydrogen sensors in potentially hazardous atmospheres for which the requirements and the appropriate tests are fixed in specific standards.

Firstly, the sensor itself shall be explosion protected, i.e. the sensor itself is not allowed to ignite an explosive atmosphere. The equipment protection and the intrinsic safety are defined in the series of standards IEC 60079.

Secondly, the hydrogen sensor shall fulfil performance requirements to detect hydrogen as a flammable gas. This is described in standard EN 60079-29-1 for gas detectors. Similarly, ISO 26142 specifically addresses the performance of hydrogen detectors in stationary applications such as hydrogen vehicle refueling stations. Globally accepted standards for other hydrogen sensor applications e.g. for fuel cell monitoring are still pending.

A third aspect for a reliable use of hydrogen sensors is its functional safety. This aims at evaluating possible malfunctions and their consequences, especially from the electronic part of systems or equipment, to avoid an unacceptable risk of physical injury or of damage to the health of people. Functional safety is described in general in the standard series of IEC 61508 for electrical/electronic/programmable electronic safety-related systems. For gas detection apparatus the requirements are specified in EN 50402 and EN 50271 [5].

Hydrogen sensors shall fulfil the requirements of these general standards for application in hazardous atmospheres. This can be certified by dedicated testing institutions, so called third parties (see section 3.1), giving confidence in precision, reliability and robustness of the tested hydrogen sensing systems to the end-user. The functional safety of hydrogen sensors can meet a safety integrity level (SIL) of 2 for hardware and of 3 for software which predicts a remarkably low probability of failure on demand equivalent to less than one hazardous failure in 10^2 or 10^3 years, respectively [5].

3. Sensor testing

Although the relationship between the basic sensor signal and the ambient hydrogen gas concentration may be known from physical laws or empirical functions, for practical applications a *calibration* is indispensable. This is usually performed first by the sensor manufacturer. After a certain time of operation however, a periodic recalibration will be required due to aging and poisoning effects. In addition, because sensors will be used under specific environmental conditions of gas composition, temperature and pressure, a *verification* procedure must be performed. The conformity of a sensor with the required specifications fixed in standards or guidelines can be attested to by *certification*. To ensure independent assessment of sensor performance and to therefore ensure greater confidence on the part of the customer, this procedure is performed by competent bodies maintaining a quality management system and being themselves accredited to carry out these activities [1]. Certification is important for commercial purposes, but should also be considered in the early stages of sensor research and development, because it indicates the required quality level and the state of development of the technology.

3.1 Certification

The term certification describes a complex procedure by which a third party gives written assurance that a product, process or service conforms to specified requirements.

This third party must be a competent, qualified and commonly accepted notified body, such as Underwriters Laboratories (UL) and the Canadian Standards Association (CSA) in North America, Notified Bodies for ATEX in the EU and ANZEx in Australia. Certification consists of the following steps:

i. test of technical and quality documents, audit at the manufacturer, experimental test of the quality of the method in an independent laboratory
ii. assessment of the results and
iii. awarding of a formal document of certification

The certification of hydrogen sensors is important in connection with their safe use in potentially explosive atmospheres, where the gas concentration can exceed the lower flammable limit (LFL) and where the presence of ignition sources must therefore be avoided. Sensors may be capable of providing an ignition source and causing an explosion due to the generation of static electricity and electrical sparks or due to the high operating temperatures of some sensor types. Various aspects of explosion protection must therefore be considered. In Europe a hydrogen sensor needs a designation according to equipment directive 94/9/EC (ATEX 95) indicating where it can be used. This designation includes the group (mining or non-mining), the category or protection level (very high, high or normal) and the type of explosive atmosphere (gas or dust) in which they may operate. Gases and vapors are classified according to their ignition properties into three explosion groups (IIA, IIB, IIC) [1] and this information is also contained in the ATEX marking. Hydrogen belongs to the IIC explosion group. In addition, the gas is assigned to a temperature class (T1-T6) according to its auto ignition temperature. Hydrogen belongs to temperature class T1 with an auto ignition temperature >450 °C. The intrinsic safety and the detection performance of a device can be certified, specifically for the purposes indicated by the ATEX marking, by accredited laboratories according to the safety standards series IEC 60079 in Europe or Japan and UL 913 or CSA 22.2 in North America [1] If the equipment passes the necessary tests it is certified for conformity for the given application. Certified catalytic combustion hydrogen sensors with an explosion proof housing obtain a special designation such as ATEX IIG EEx dia IIC T1 in Europe or Class I, Div. 1, Group B T1 in North America.

Thus certification contributes to technical harmonization, ensuring product quality especially with regard to security and human and environmental safety. It also helps to overcome technical trade barriers in a global market and supports the acceptance of new analytical methods.

4. Focus areas in hydrogen sensor research and development

Hydrogen sensor research is evolving and expanding rapidly. Development is progressing along four main lines, namely:

- preparation and evaluation of new hydrogen sensitive materials
- development of different types of hydrogen sensing technologies
- sensor designed for operation at room temperature without internal heating
- application of new techniques for mass fabrication of micro hydrogen sensors

The most common and noteworthy research and findings are briefly reviewed below.

4.1 New hydrogen sensitive materials

4.1.1 Sensor elements using nanomaterials

Nanomaterials are of interest for sensor development because of their high surface area, possible increased reactivity due to the small particle size and compatibility with miniaturization of sensor elements and sensor electronics.

Nanoscaled carbon materials including single and multiwall carbon nanotubes (CNT), as well as two-dimensional graphene or graphene oxide sheets - have outstanding properties due to their high aspect ratio, large surface area with respect to volume, superior chemical and thermal stability, high electrical conductivity, good heat conductance and excellent mechanical strength. It is expected that gas sensors based on CNT graphene networked films can provide high sensitivity, fast response, good reversibility, higher resolution, selectivity by functionalization, simplified and stand-alone operation, low power consumption and low running costs. Graphitic layers, carbon nanotubes and two dimensional graphene sheets were tested alone or in combination with other substances including palladium, for hydrogen sensing mostly in resistive mode [5].

Other new nanomaterials are used in resistive or work- function based sensing elements. Palladium interaction with hydrogen is the basis for hydrogen detection in platforms using palladium nanowires whose properties may overcome limitations experienced with palladium thin films [5]. Tin oxide nanorods are grown by gas phase methods (CVD, thermal evaporation) or liquid phase processes (sol-gel, hydrothermal). In a recently reported tin oxide nanorod sensor a change of resistance was detected at room temperature at a hydrogen concentration of just 100 ppm; however, a better sensitivity is obtained at 250 °C [5]. Zinc oxide nanorods and wires are also reported and were fabricated using anodized aluminium oxide nanotemplate or were deposited by molecular beam epitaxy (MBE). ZnO nanorod arrays exhibit a high sensitivity for hydrogen in a wide concentration range from 5 to 500 ppm, as do Pd- or Pt-coated GaN and InN nanowires [5]. Titania nanotubes are also used for hydrogen sensing and have been produced by anodic oxidation of titanium in hydrofluoric acid with subsequent annealing at about 500 °C resulting in pores with a diameter of 70 nm. This material can sense hydrogen in the range of 10 ppm to 1% at temperatures between 150 °C and 300 °. Doped silicon wires or Ag-doped molybdenum oxide nanowires can be used for hydrogen detection [5].

Whereas most palladium-based resistive hydrogen sensors reduce conductivity when hydrogen is absorbed due to electron scattering, nanogap sensors and reversible on-off switches show an opposite behavior. In these systems hydrogen absorption, causing palladium volume expansion, close nanogaps in the material resulting in an increase of conductivity [5].

4.1.2 Sensor elements using porous materials

Porous silicon is a promising material for gas sensing mainly due to the high surface to volume ratio and strong adsorption for gases. It is easy to fabricate by electrochemical anodization using a mixture of HF and ethanol in different ratios as the electrolyte solutions. Through the variation of the formation parameters, the surface morphology can be advantageously controlled. Porous silicon layers have large internal surface areas of up to 200-500 m^2/cm^3, and high activities in surface reactions. Porous silicon is compatible with silicon technology and modification with catalytic palladium makes it suitable for hydrogen detection. However the distribution of Pd over the porous silicon can have a strong influence on the hydrogen sensing parameters [5]. In addition to silicon porous GaN and SiC can be prepared by an electrochemical etching process and used for hydrogen detection, as well as porous Pd-coated WO_3 [5].

4.2 Hydrogen sensing technologies development

4.2.1 Optical sensors

Up to 20% of all publications on hydrogen sensors describe optical sensors which detect hydrogen through a change in the optical properties of the hydrogen active material. In contrast to electrical sensors, optical fibre sensors are electrically isolated which makes them interesting candidates for operating in explosive atmosphere. There will be no risk of gas ignition since the optical detector has no electrical contacts and so cannot generate sparks. Types of optical sensors include Fibre Bragg grating, interferometric, micro mirror, evanescent optical fibre, surface plasmon resonance and colorimetric technology [5].

Sensors using Bragg-gratings were prepared using different material combinations based on palladium, like Pd-Ni, Pd-Ag, Pd-Y or Pt-WO_3 [5]. The alloying of palladium results in better long term stability of the thin coatings.

Numerous optical fibre hydrogen sensors have been developed, but most of them do not meet many of the performance specifications recommended by industries or governmental agencies. In particular, their response times are often too slow and they need to be calibrated to compensate for drift and aging effects. Nevertheless research is continuing to improve these performance aspects of optical hydrogen sensors [5].

4.3 Sensors working near room temperatures

The requirement for low power consumption can be met, to a certain degree, by sensors operating at room temperature. That means the sensing element where the change of hydrogen gas concentration is transduced into an electrical signal acts at temperatures not much higher than 30 °C without additional heating. Room temperature operation can be realized in different ways depending on the type of sensor and sensing material [5]. Some sensor types working at room temperature have been known for a long time; new accomplishments have been achieved, for instance, in the area of resistive and field effect-based sensors. Examples of sensor types operating at room temperature are compiled in the following list:

i. Amperometric hydrogen sensors possessing a liquid or solid electrolyte (e.g. KOH, H_2SO_4, NAFION) and a polymer membrane (Teflon, PTFE) operate at room temperature [5]. However electrochemical sensors have a limited life time and consume a certain power for temperature stabilization and signal display.

ii. In most cases optical sensors operate at room temperatures. They can operate without oxygen and in explosive atmosphere and are hardly influenced by electromagnetic fields. The sensor element can be separated from the electrical readout (see Chapter 1, section 6: Optical Sensors) [5].

iii. Surface acoustic wave (SAW) sensors operate mostly with interdigitated structures on a piezo electric substrate near room temperature. The sensor system needs a high effort for signal generation and output. Also temperature and cross sensitivity effects have to be depressed.

iv. An absolute hydrogen concentration can be determined at room temperature by measuring the speed of sound in a test gas, the speed of sound in hydrogen being much faster than in all other atmospheric gases.

v. Resistance-based sensors based on new materials such as nanocrystalline palladium, nanowires or polymers like polyaniline, for example, can operate at room temperature (see Chapter 3 Section 3.1: Sensor Elements Using Nanomaterials)

vi. Work function based sensors work at room temperature, however, the sensors often need periodic heat pulses to refresh their sensitivity.

Sensors exploring the high thermal conductivity of hydrogen are operating at ambient temperatures. However the operation principle is based on the measured heat loss from a hot body to the surrounding gas. It is obvious that a certain electric power is consumed.

If it is possible to overcome disadvantages of slow response and recovery times or saturation effects in room temperature operating sensors, then this concept has a promising perspective. However, not only the sensor element contributes to a low energy consumption, energy is also needed by the sensor electronics which performs the transmission, processing and output of data. Low power data transmission has been demonstrated for example in a multipoint hydrogen leakage detection system applying radio frequency identification (RFID) technology [5].

4.4 Advanced manufacturing techniques

Micro hydrogen sensors are typically fabricated from silicon and have dimensions on the micrometer scale. The ability to fabricate hydrogen sensors at this scale offer advantages in terms of performance and cost. Silicon micro-fabrication offers the potential for mass production of these devices which can drive down their manufacturing costs. Performance parameters such as response time, lower detection limit and low power consumption are significantly improved when compared with conventional hydrogen sensors [5].

Micro-hydrogen sensors have been reported for various detection technologies. Many traditional technologies are conducive to miniaturization including thermal conductivity sensors, metal-oxide sensors and catalytic pellistors. A new micro-machined thermoelectric catalytic sensor, whose working principle is based on the Seebeck effect reports promising results particularly in terms of lower detection limit [5]. This sensor is capable of detecting hydrogen down to a concentration of just 50 ppm with a measuring range up to a few percent. Other micro-machined hydrogen sensor types include those based on a thin metal film whose resistance changes in the presence of hydrogen. These resistive-type sensors employ a micro-hotplate or heater to heat the metal film at low power ratings to increase hydrogen sensitivity and lower the response time to hydrogen. Micro-electromechanical systems (MEMS) hydrogen sensors have also been proposed. MEMS sensors are devices which, in addition to being fabricated on a micrometer scale, involve some mechanical motion or vibration in their detection mechanism. Micro-machined MEMS cantilevers are an example of such devices [5].

5. Development of safety standards for mobile fueling facilities

5.1 Overview of the new standard for mobile hydrogen refueling facilities

The intention of the new standard is to improve the safety of mobile hydrogen refueling facilities in engineering practice. The essential contents of the draft comprise three aspects that consist of technical safety requirements, operation management, transportation and maintenance. Other contents such as scopes, terminologies and references are supplementary parts, though there are a few highlights in them. A list of important referenced regulations, codes and standards is given below [7]. These documents lay a foundation to the new safety standard for mobile hydrogen refueling facilities.

- GB 50057 Design code for protection of structures against lightning
- GB 50058 Electrical Installations Design Code for Explosive Atmosphere and Fire Hazard
- GB 50177 Design code for hydrogen station
- GB 50516 Technical Code for Hydrogen Fueling Station
- GB/T 19773 Specification of hydrogen purification system on pressure swing adsorption
- GB/T 19774 Specification of water electrolyte system for producing hydrogen
- JT 230 Rubber Belt of Electrostatic Conductivity for Motor Vehicle
- JT 617 The regulation of automobile transportation of dangerous goods
- JT 618 Rules of transportation, loading and unloading of dangerous goods by automobile
- QC/T 816 Specification of Mobile Hydrogen Refueling Vehicles

Besides, the development of the standard for mobile hydrogen refueling facilities is based on both safety experience learned from engineering practice and safety studies on mobile hydrogen refueling facilities

5.2 Fire and explosion hazard protection technical requirements

Hydrogen detectors with alarms should be applied both in the mobile hydrogen refueling facilities and in the work area. This indicates that there will be at least two safety barriers for detecting hydrogen release and trigger emergency mechanism. The result will be significant reduction of the risk of continuous releases. Two levels of alarm call should be set at hydrogen concentration of 0.4% and 1%, corresponding to acoustic alarming and activation of ventilation fans, respectively. These requirements are necessary safety measures to avoid the formation of flammable cloud in case of accidental releases of hydrogen.

Flame detectors should be installed in the work area and integrated into the emergency shutdown system and fire extinguishing system. To prevent the so called "domino effect” in a fire accidents, the space between two individual hydrogen storages (e.g. hydrogen tube trailers) should not less than six meters. The value is not just derived from estimation from engineering practice but on the basis of previous safety studies on hydrogen facilities and separation distance values in other codes such as in NFPA 52 Vehicular Gaseous Fuel Systems Code (2010 Edition) below [7].

There are also safety provisions for frequent hydrogen release events such as release in vent pipe. The vent exit should exceed two meters above the mobile hydrogen facilities and five meters above the ground, which is also based on previous safety studies on vertical releases for hydrogen facilities below [7].

For static safety, uniform static grounding systems should be established and the electrical resistance between the end fittings of the hose assembly shall not exceed 10 ohms. These antistatic safety requirements are expected to eliminate the ignition risks from static electricity.

There are two other technical requirements need to be mentioned. One is the zones of rating for explosion hazard, the other is safety specifications for hydrogen production. For explosion hazard zone, space inside the mobile hydrogen refueling facility is defined as grade one and a radius of 4.5 m from the outer surface of the facility is classified as grade two. Different hazard zones should follow different safety requirements as specified in GB 50058 Electrical Installations Design Code for Explosive Atmosphere and Fire Hazard [7]. For hydrogen production, the safety codes have not been renewed specifically for production-integrated mobile hydrogen refueling facilities and all provisions are directly taken from GB50177 Design Code for Hydrogen Station, GB/T 19773 Specification of Hydrogen Purification System on Pressure Swing Adsorption and GB/T 19774 Specification of Water Electrolyte System for Producing Hydrogen [7].

5.3 Future work perspectives

Future work associated with mobile hydrogen refueling facilities can be proposed as below [7].

1. The current standard is drafted for gaseous hydrogen refueling facilities and other types of hydrogen storage such as liquid hydrogen and cryo-compressed hydrogen are not included. In the future, new types of hydrogen storage options may be applied in mobile hydrogen refueling facilities and the standard needs to be renewed in that aspect.
2. Provisions associated with real-time monitoring, positioning and management are not suggested to avoid being less cost-effective, but safety level may be compromised to some extent, especially when numbers of mobile facilities are in operation as a hydrogen supply network. New real-time control provisions need to be added in the future for hydrogen supply network that contains a considerable number of mobile hydrogen refueling facilities.
3. The integrated hydrogen production system is not included in the safety standard currently. However, new integrated portable hydrogen refueling systems are in developmental stage. If the hydrogen production sectors are successfully integrated in the portable hydrogen refueling facilities, then the standard has to be revised to fit the new type.

6. Hydrogen safety knowledge base advancements

The International Energy Agency's Hydrogen Implementing Agreement (IEA HIA) was established in 1977 to pursue collaborative hydrogen research and development and information exchange among its member countries. The IEA HIA mission serves to “accelerate hydrogen implementation and widespread utilization to optimize environmental protection, improve energy security and promote economic development internationally while establishing the IEA HIA as a premier global resource for expertise in hydrogen” [8].

The work in hydrogen safety serves as a good example of how collaboration is working within the IEA HIA. Ten member countries and the European Commission participated in Task 31 (2010-2013). Its predecessor, Task 19 (2004-2010), formed the basis for illustrating how such cost-effective, task-shared activities can combine the efforts of the best hydrogen safety experts. A coordinated approach in collaborative research and development and information exchange can positively influence national programs by minimizing duplication of effort toward achieving mutually beneficial objectives.

Technical reports, presentations and publications often result from the collaborative efforts focused by a task work plan [9]. Examples abound to illustrate that even in cases for which a specific task report is not published, these collaborations can positively influence the objectives of national programs. A white paper published by Task 19 highlights how hydrogen safety knowledge tools in the form of publicly available databases, websites and specialized software were enhanced by the work of member countries.

The work conducted within Task 31 focused in four subtask areas [8]:

- Subtask A - Physical Effects and Knowledge Gaps
- Subtask B - Storage Systems and Materials Compatibility
- Subtask C - Early Markets: Risk Characterization and Hazard Analysis
- Subtask D - Knowledge Analysis, Dissemination and Use

The interactions within Task 31 illustrate how technology information and knowledge exchange among participating hydrogen safety experts, while often underreported, is serving IEA HIA objectives.

6.1 Expanding safety knowledge tools and resources

Web-based resources are playing a key role in reaching, educating and informing stakeholders whose contributions will help enable the deployment of new hydrogen and fuel cell technologies [8]. Safety event information can serve as a rich and valuable resource if systematically collected, analyzed and used to enhance hydrogen safety knowledge.

Pacific Northwest National Laboratory (PNNL) work on *Hydrogen* Lessons *Learned from* Incidents and Near-Misses [10] has been an agenda topic since the Task 19 meeting in Vancouver in 2006. Safety event information sharing and the subsequent discussion have been invaluable in enhancing the value of the database since that time.

Building on collaborations initiated in Task 19, the project leads from PNNL and the European Commission's Joint Research Centre (JRC) shared the podium during a topical session on safety event databases [8] and also provided online demonstrations of their respective tools at the September 2011 International Conference on Hydrogen Safety (ICHS) in San Francisco. The JRC and the International Association for Hydrogen Safety are responsible for the Hydrogen Incident and Accident Database [8]. Safety event records are being shared between the two databases to enhance the value of each, and other collaborations between the two projects are being considered. The engaged interactions of Task 31 members help to ensure that safety knowledge tools such as the two discussed here are kept current, relevant to the community being served and valuable to the user.

6.2 Hydrogen sensor technologies — benefitting from collaboration

Many see hydrogen sensors as key devices for facilitating the safe production, storage, distribution and use of hydrogen. Their use is critical to detecting unwanted hydrogen leaks and to activating mitigative actions to reduce the potential hazards associated with these leaks. Specifically, sensors have been used to sound audible alarms, activate ventilation systems and initiate shutdown of hydrogen systems to a safe stand-by state.

Despite the extensive research being channeled into developing smaller, faster, cheaper hydrogen sensors with improved performance characteristics, there is a lack of knowledge among sensor end-users regarding these developments and the correct choice or proper use of hydrogen sensing technology from the ever-increasing pool of commercial products. Furthermore, sensor manufacturers/developers lack an understanding of the performance requirements and expectations of sensor end-users. As a result, there is much to be gained from information exchange and knowledge dissemination in the development, selection and correct deployment of hydrogen safety sensors.

Task 31 meetings have provided excellent opportunities to collaborate and discuss sensor-related work. The collaboration between the U.S. Department of Energy National Renewable Energy Laboratory (NREL) and the JRC is a good example. Both NREL and the JRC Institute for Energy and Transport have established histories in performance testing of commercial-off-the-shelf hydrogen sensors under conditions representative of typical hydrogen applications. Through interactions facilitated by Task 31 meetings, the sensor collaboration was expanded to include the experts from the Natural Sciences and Engineering Research Council of Canada's Hydrogen Canada Strategic Research Network with expertise in microfabrication and microelectromechanical systems (MEMs), including the development of hydrogen sensors for MEMs. An assessment of miniaturized sensor technologies was presented recently at the World Hydrogen Energy Conference to highlight designs with improved performance [8]. The scope of this work has grown to include the performance evaluation of additional micro-machined commercial hydrogen sensors and a subsequent comparison with the performance of comparable conventional sensors.

6.3 Developing knowledge to improve guidelines on the indoor use of hydrogen

Hydrogen energy applications often require that systems be used indoors (e.g., industrial trucks for materials handling in a warehouse facility, fuel cells located in a room, and hydrogen stored and distributed from a gas cabinet). It may also be necessary or desirable to locate some hydrogen system components/equipment in indoor or outdoor enclosures for security or safety reasons to isolate them from the end-user and the public.

Use of hydrogen in confined environments requires detailed assessments of hazards and associated risks, including potential risk prevention and mitigation features. The release of hydrogen can potentially lead to the accumulation of hydrogen and the formation of a flammable hydrogen—air mixture.

Safety design guidelines and engineering tools need to be developed for use with specific safety strategies for these applications of hydrogen systems. Closing knowledge gaps is critical to this effort in several areas: hydrogen release conditions and accumulation, vented explosion and flame regimes (e.g., extinguishment or oscillating flames and steady burns). For each phenomena, the release position/conditions, the number, size and location of the openings in the room/ enclosure of some given size, and the type of ventilation can significantly influence the prevention/mitigation strategy.

Task 19 and 31 meetings have played a significant role in building an overall comprehension of hydrogen phenomena and related knowledge gaps. Since 2009, the French Alternative Energies and Atomic Energy Commission has presented experimental work on the accumulation of helium in a garage, highlighting different accumulation regimes [8]. The National Institute of Standards and Technology presented similar work with a comparison with the Fire Dynamic Simulator [8], and Air Liquide presented existing engineering models for openings and vent sizing, highlighting the lack of experimental data on wind influence and on hydrogen vented explosions [8]. In 2011, SNL presented experiments of hydrogen release and ignition on a scaled warehouse. Modeling of the experimental results showed excellent reproductions using SNL's in-house RANS (Reynolds-averaged Navier-Stokes) based computational fluid dynamics (CFD) solver, FUEGO, to model the transient blowdown and dispersion into the enclosure and FLACS to model the cloud combustion at a specific ignition delay computational fluid dynamics (CFD). The University of Ulster presented the first work on the pressure peaking effect in case of a sudden large release of hydrogen in an enclosure, which could be caused by the activation of a thermally activated pressure relief device [8].

The European Fuel Cell and Hydrogen Joint Undertaking project, HyIndoor, was launched in 2012 to address knowledge gaps and deliver guidelines and engineering tools on the safe design of natural ventilation and vent sizing for the indoor use of hydrogen. [8]. Collaboration to coordinate and discuss the research efforts and results through Task 31 would help ensure efficient use of the resources devoted to these aspects of hydrogen safety no matter where the work is performed.

CHAPTER 4

HYDROGEN SAFETY ENGINEERING AND SAFETY RISK MODELLING

The viability and public acceptance of Hydrogen systems and infrastructure depends on their robust safety engineering design and on education and training of the workforce, regulators and other stakeholders in the state-of-the-art in the field. This can be provided only through building up and maturity of the Hydrogen Safety Engineering (H2SE) profession. H2SE is defined as an application of scientific and engineering principles to the protection of life, property and environment from adverse effects of incidents/accidents involving hydrogen. Safe application of hydrogen, especially in a large scale, will require adopting adequate risk control, which requires investment on reliable risk analysis methodology. This chapter describes a design framework and overviews a structure and contents of elementary design safety tool for carrying out H2SE. Moreover a reliable and comprehensive safety risk analysis methodology was developed for hydrogen safety which can be used either for hydrogen usage or its production.

1. The genesis of hydrogen safety engineering (H2SE)

1.1 The hydrogen economy and public safety

H2FC technologies, systems, and infrastructure are currently at the stage of demonstration projects and early markets, before their commercialization after 2015. The hydrogen economy requires overcoming the lack of infrastructure [11]. New technologies improve units of hydrogen production as well as transportation and delivery networks at the end of which there will be the public. Sometimes, implementation of new technologies and design of infrastructure involve the use of hydrogen under circumstances that are not yet addressed by research [11]. Technical staff at maintenance workshops, refueling stations, and emergency services should be educated and trained to deal with hydrogen systems at pressures up to 100 MPa and temperatures down to -253 °C (liquefied hydrogen) in the open and confined space like tunnels, car parks, etc. Regulators and approvers should be provided with the state-of-the-art knowledge and guidance to assist in the safe implementation of H2FC technologies within the built environment. The number of professional hydrogen safety engineers required to underpin the emerging industry is expected to grow. Safety engineers and technicians, including those who have handled hydrogen in different industries for several decades, need to undergo retraining through continuous professional development courses to acquire the latest knowledge and engineering skills for use of hydrogen in a public domain. Indeed, emerging H2FC systems and infrastructure "*will create in a close future entirely new environment of hydrogen usage, which is not covered by industrial experience or through existing codes and recommended practice*" [11].

Hydrogen is not safer or more dangerous compared to other fuels, but it must be handled safely taking into account its properties and hazards. For instance, hydrogen is a colorless, odorless, tasteless gas flammable over a wide range of concentration (4%-75% by volume in air). The high diffusivity, the small molecular weight and the low viscosity of hydrogen make hydrogen easily leaking through small cracks and joints, and its use with incompatible materials lead to hydrogen embrittlement and hydrogen permeation.

'Hydrogen has a low minimum ignition energy of 0.017 mJ and this combined with the wide limits of flammability can result in it being easily ignited. The low density of hydrogen (0.0873 kg/m^3 at NTP) makes it buoyant in air and represents its main safety asset as any leak would quickly rise and disperse in the open. Nevertheless, in enclosed spaces, care should be taken to prevent any accumulation of flammable hydrogen-air mixture near the ceiling. If ignited, such mixture can produce a very powerful deflagration generating pressure of up to 8 bars when considering complete adiabatic combustion [11]. Hydrogen is also produced, transported and distributed in liquid phase. The hazards associated with low temperatures must be safely addressed as cryogenic burns can result from contact between unprotected parts of the body and cold fluids or cold surfaces. Damages to eyes and lungs, and hypothermia, can result from exposition to cold gaseous or liquid hydrogen [11].

It becomes crucial to ensure public perception of hydrogen as a safe constituent of future energy systems is essential *"if a hydrogen economy is to replace the existing fossil fuel-based economy"* [11]. It is important that the perception of hazards and risks for hydrogen applications should not exceed that of current fuels. However, unfortunately *“very little has been done to educate people about the properties and safety of hydrogen, even though public acceptance or lack thereof, will in the end make or break the hydrogen future"* [11]. Therefore, as it would be impractical to train general customers to professional level, educational programs in hydrogen safety should be developed and primarily target experts already involved in hydrogen economy. Teaching of hydrogen safety engineering and its implementation into day-by-day engineering practice requires clear understanding of what H2SE processes and their constituent parts are.

1.2 The emerging profession of hydrogen safety engineering

The Workgroup on Cross Cutting Issues of the European H2FC Technology Platform [11] indicated that educational and training efforts are key instrument in lifting barriers imposed by the safety of hydrogen. This Workgroup has estimated that during the FP7 period (2007-2013), the educated staff needed may amount to 500 new graduates from postgraduate studies on an annual basis in all of Europe. In a study of the European e-Academy of Hydrogen Safety performed within the NoE HySafe, it was estimated that the subset of these necessary graduates specializing in hydrogen safety would amount to 100 on an annual basis [11].

The higher education of researchers and engineers is a key to surmount challenges of hydrogen safety. The development of an International Curriculum on Hydrogen Safety Engineering [12] was the first step in the establishment of the profession undertaken by the European e-Academy of Hydrogen Safety in collaboration with partners around the globe. About 70 renowned international experts contributed to the draft for development of the Curriculum.

The main contributor to the establishment of the profession through a closing of knowledge gaps and educational/ training programs is the international hydrogen safety community coordinated by IA HySafe.

The H2SE discipline is developing on the experience and lessons learnt by fire safety engineering, which is today a well- established profession focused mainly on building fires. An important step in the establishment of fire safety engineering as a profession was a model curriculum for under and postgraduate courses published in 1995 [11].

Unfortunately, graduates of fire safety engineering courses are not currently able to tackle specific problems of hydrogen safety such as high pressure leaks and dispersion, spontaneous ignition and thermal effects of under-expanded jet fires, pressure loads of hydrogen- air deflagrations/detonations and blast waves, etc. However, there are common problems, knowledge and experience which H2SE can utilize to some extent, such as fire resistance of structures and life safety, emergency services intervention, etc.

Fire safety was originally regulated by prescriptive codes, aiming to protect societies from adverse effects of fires in traditional buildings with low hazard occupancies [11]. But for more complex buildings, the prescriptive approach didn't meet the needs of designers or approval bodies. Those prescriptive codes didn't offer flexibility for innovation, they didn't necessarily provide optimum solution for a particular project, they provided requirements without statement of objectives, they might lag many years behind modern design practice and their use unable to anticipate all eventualities [11]. In the late 1980s, a project led by the Warren Centre in Australia made a significant contribution by proposing fundamental improvements to fire safety. The purpose was to define a basis for a new generation of RCS. Among the numerous recommendations of the Warren Centre Report [11], some are directly applied to hydrogen safety systems: design for fire safety should be treated as "*an engineering responsibility rather than as a matter for detailed regulatory control*". Designers should develop a greater understanding of fire phenomena and human behavior and adopt appropriate engineering techniques in their design of fire safety systems, fire engineering design courses and training strategies should be developed and implemented, up to and including postgraduate level, etc. This report led to a worldwide attention towards fire safety engineering. The methodology highlighted by this approach was dedicated to measure a design's performance using different tools, e.g. simple engineering calculations and contemporary computer-based models. There was an intention to implement non-complex documents in performance-based fire safety regulations to provide greater flexibility when designing and evaluating a project, and to promote innovation in building design, materials, products, and fire protection systems. This approach nevertheless requires education of professionals and the validation of tools and methods used for quantification [11]. The developments in hydrogen safety engineering are greatly inspired by and based on the developments of fire safety engineering, including performance-based RCS, educational programs and freely available contemporary CFD (Computational Fluid Dynamics) tools like Fire Dynamics Simulator [13]. The statements of the framework for fire safety can be directly transferred to define the H2SE framework [11]:

- Provide a systematic approach. The process used to undertake H2SE and evaluate the performance of a design, should be clearly defined and explained. The framework will set the basis of the methodology that should be applicable for a H2SE study.
- Define acceptance criteria. The performance of a design is evaluated by comparison with deterministic, comparative or probabilistic criteria.
- Simplify the problem. The H2SE process is separated into analysis of Elementary Design Safety Tool (EDST) that can be used individually to address specific issues or together to address all of the safety aspects of a hydrogen system.

- Illustrate interactions. The complexity of phenomena and interactions between elements of hydrogen system, people and the built environment in a case of incident requires a simplified approach by underlining interactions between different EDST.
- Ensure adequate consideration of all those factors relevant to any aspect of the design. In order to identify all significant variables in a quantification process, it is essential to list relevant scenarios. Doing this, it is possible for each scenario to inventory critical factors from hydrogen system/infrastructure such as parameters of accident scenario including occupancy, etc.
- Insist on clear presentation and comment on calculation methods and data sources. As the application of H2SE might be subject to review and approval, it is essential that findings, calculations and assumptions, are presented in a report that can be clearly and readily understood.

1.3 The subject and scope of hydrogen safety engineering

H2SE is defined as the application of scientific and engineering principles to the protection of life, property and environment from adverse effects of incidents/accidents involving hydrogen.

The H2SE can be applied to existing and new hydrogen systems, including but not limited to stationary, e.g. combined heat and power systems, or portable, e.g. mobile phone and computers, applications for indoor and outdoor use, hydrogen transportation and refueling infrastructure, power generation, hydrogen production and distribution units, storage, infrastructures such as garages, parking, tunnels, pipelines networks, etc. A hydrogen system could be defined as an equipment dealing with hydrogen e.g. storage, production, delivery, distribution, consumption, etc. Hydrogen should remain contained within hydrogen system from its production/delivery to its final use.

2. The design framework, EDST and procedures

H2SE comprises a design framework and elementary design safety tool both explaining how to apply scientific and engineering principles to safety design of a H2FC system and/or infrastructure.

2.1 The design framework outline

The H2SE design framework described in this section is inspired by British Standard BS 7974 and relevant Published Documents, which 55 organizations contributed to [11]. The Draft for Development (DD) of the future standard with a tentative title “Application of hydrogen safety engineering principles to the design of hydrogen systems” is outlined below. The DD will include a number of documents to describe the design framework and H2SE procedures, details of EDST, and a document to describe procedures for the quantitative risk assessment. A series of documents describing each EDST will contain the state-of- the-art information and guidance on how to undertake a quantitative safety analysis by selected validated engineering tools. The design framework document will:

- Describe the philosophy of H2SE
- Provide means of establishing acceptable levels of hydrogen safety economically and without imposing unnecessary constraints
- Provide guidance on the design and assessment of hydrogen safety measures
- Give a structured approach to measure the performance compared to defined design objectives
- Be used to create and evaluate trial design without compromising safety
- Recognize that alternative and complementary hydrogen safety strategies can be used to achieve defined objectives
- Identify requirements for further research

The three main steps or procedures of H2SE are (see Fig. 4.1):

- Qualitative design review (QDR)
- Quantitative analysis
- Assessment against criteria

These steps are the same as in fire safety engineering [11]. The H2SE design has to demonstrate the compliance with regulatory requirements and be completed by a fully documented Report on Hydrogen Safety Engineering that can be readily assessed by the approvals bodies. Representatives of the approvals bodies should be involved in the process at the QDR stage to facilitate the final permitting.

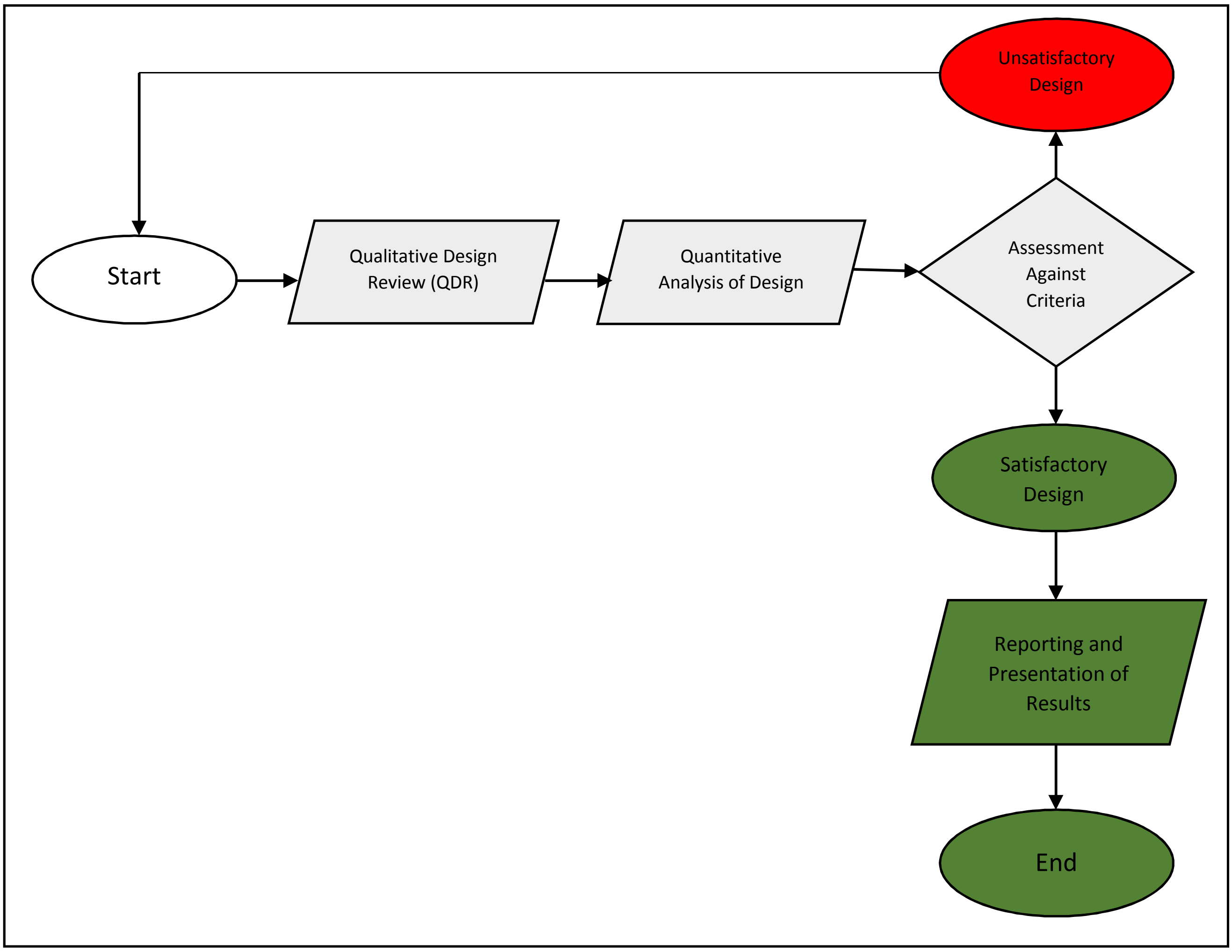

Fig. 4.1 The Hydrogen safety engineering procedures

2.2 Elementary design safety tool: definition and content

H2SE is a system (a set of interacting or interdependent components forming an integrated whole or a set of elements as a whole), composed of interacting engineering and technical tools. To simplify the evaluation of a design during an H2SE study, the quantification process is broken down into Elementary design safety tools (EDST). The following requirements should be accounted for when developing individual EDST:

- EDST should together, as reasonably as possible, cover all possible aspects of hydrogen safety
- EDST should be balanced between their uniqueness or capacity to be used individually, and their complementarities and synergies with other EDST (i.e. capacity to generate output and necessity to receive inputs)
- EDST should be a selection of the state-of-the-art in the particular field of hydrogen safety science and engineering, validated engineering tools, including empirical and semi-empirical correlations and contemporary tools such as CFD models and codes
- EDST should be flexible to allow update of existing or use of new appropriate and validated methods, reflecting recent progress in hydrogen safety

The suggested EDST titles and the outline of their technical contents are as follows:

2.2.1 EDST1: initiation of release and dispersion

It will include information on potential sources and scenarios of hydrogen leaks, the effect of hydrogen on different materials, e.g. embrittlement or permeation, methods to calculate flow parameters at the real nozzle exit, including parameters of highly under-expanded jets, e.g. mass flow rate, density, temperature, etc., for different storage pressures and leak diameters, including a correction due to friction and minor losses [11]. The original under-expanded jet theory and the similarity law, validated recently for both expanded and under-expanded jets, will be used to calculate concentration decay in a single round and plane jet using only hydrogen density at a real nozzle exit and a real leak diameter. Specific engineering tools and methods should also be used to characterize the parameters, behavior and dispersion of liquid hydrogen leaks. Methods to calculate hydrogen dispersion including permeation, in an enclosure and requirements to passive ventilation will be included in EDST1 to tackle dispersion of permeated hydrogen and larger leaks [11]. The correlation to account for an effect of buoyancy on safety distance in case of downward and horizontal jets will be presented. The methodology to calculate dynamics of blowdown from a storage vessel through orifice of known size will be given. Best practices, e.g. recommendation to reduce mass flow rate in piping to technological limit or use of a restrictor to limit mass flow rate during accidental release, etc.

2.2.2 EDST2: ignitions

It will provide information on different ignition mechanisms, including “diffusion” mechanism of spontaneous ignition of hydrogen during sudden release, flammability limits for upward, downward and lateral flame propagation and their dependence on pressure, temperature, and diluents concentration, minimum ignition energy for initiation of deflagrative flame propagation and direct initiation of detonation of hydrogen-air and hydrogen-oxygen mixtures, the auto ignition temperature and its dependence on hydrogen concentration, pressure and temperature, the size of maximum experimental safe gap, etc. [11].

2.2.3 EDST3: deflagrations and detonations

It will provide information on how to assess hydrogen explosion hazards, calculate pressure effects of hydrogen explosions, i.e. overpressure and impulse of unconfined deflagrations and detonations using Sach's variables [11], calculate shock propagation velocity and pressure in reflected shock. It will present information on how to assess the overpressure generated by the physical rupture of hydrogen tank under fire conditions or caused by the uncontrolled boil-off of liquid hydrogen. Pressure peaking phenomenon for non-reacting release in vented enclosure, characteristic for hydrogen only, will be explained and a nomogram to calculate overpressure in an enclosure with known volume, vent area and mass flow rate of hydrogen release, will be presented. It will describe how to assess the potential of hydrogen-air mixture to undergo deflagration-to-detonation transition (DDT), discuss the overpressure generated by delayed ignition of high pressure releases [11], etc.

2.2.4 EDST4: fires

It will provide guidance on how to estimate severity of different types of fires from micro-flames to high mass flow rate jet fires (correlation for jet flame length e.g. Refs, radiative heat fluxes and air temperature in downstream currents , etc.) will be provided [11]. The data on how to evaluate the potential for lift-off, blow-out and blow-off of hydrogen jet fires will be given. The simple engineering nomogram for flame length and flame width determination will be included, etc. This nomogram is validated against experimental data and accounts for pressure limit of flame existence at small size orifices using experimental results presented by different research groups [11]. Fire resistance of hydrogen system elements will be characterized where it is possible, including onboard storage, etc.

2.2.5 EDST5: impact on people, structures, and environment

It will outline issues relevant to life safety and evacuation strategy and will propose guidance on how to estimate consequences of a hydrogen incident on life, property and the built and natural environment depending on the severity of an accident and potential targets (customers, member of public, first responders, buildings, windows, walls, adjacent structures, etc.). Consequences will be estimated with regard to [11]:

- Radiant fluxes
- Hot air currents from jet fires
- Direct (blast load) and indirect effects (body translation, missiles) of explosions
- Oxygen depletion in relation to asphyxiation
- Release of cold liquid or gaseous hydrogen
- The potential flying debris and missile effect, etc.

2.2.6 EDST6: mitigation techniques

It will provide guidance on the use of different detection and mitigation techniques and strategies, and how to evaluate and take into account their impact on prevention of hydrogen incident/accident and/or mitigation of its adverse effects. The impact of barriers on the development of reacting and non-reacting hydrogen jets, and on the reduction of overpressure generated by jet explosion, can be evaluated by comparison with experimental data and numerical simulations. Available and validated tools for hydrogen engineering, like the vent sizing technique for mitigation of deflagration in confined spaces, will be gathered and introduced. Requirements for passive and forced ventilation to tackle indoor hydrogen releases will be described. The role of pressure relief devices will be discussed in this EDST [11].

2.2.7 EDST7: emergency services intervention

It will provide information, relevant for emergency services information on hydrogen behaviour during releases and combustion and guidance on control strategies and tactics during the initial response phase of the incident, the evaluation of the rate of buildup of resources of the emergency services, no harm distances, etc. [11].

2.2.8 Quantitative risk assessment (QRA)

In addition to outlined EDST documents, a supplementary document on Quantitative Risk Assessment for hydrogen systems should be prepared by a group of international experts similar to the approach of BS 7974-7 [11]. It will set out the general principles and techniques of risk analysis that can be used in hydrogen safety engineering. It will outline the circumstances where this approach is appropriate and gives examples illustrating their use.

This document will give information on various techniques to conduct a quantitative risk assessment from simple statistical analysis, logic trees (fault trees and event trees) to complex analysis (reliability analysis, partial safety factors, etc.). Ideally, this risk-informed document should also include information on risk acceptance criteria and provide statistical data on frequencies of leak of various sizes for different components, probability of failure of mitigation and detection systems, probability of ignition, etc.

The document on Quantitative Risk Assessment is not an EDST as it cannot be used individually to conduct a H2SE study, but must be used as part of the analysis of any or all of the elementary design safety tools. Indeed, risk is a combination of consequences (output of the EDST) and probability of occurrence (output of the Quantitative Risk Assessment).

QRA is considering safety on a higher level and the associated document should tackle a serious problem not solved yet in general adequately, namely, how to deal with uncertainty and with human factor in design, engineering, construction, use and decommissioning of systems.

3. Qualitative design review (QDR)

QDR is a qualitative process based on the experience and knowledge of a team. It allows its members to think of the possible ways a hydrogen incident/accident might be initiated and establish a range of strategies to maintain acceptable level of safety and risk. Ideally, QDR has to be carried out early in the design process and in a systematic way, so that any substantial findings and relevant items can be incorporated into the design of H2FC application or infrastructure before the working drawings are developed. In practice however, the QDR process is likely to involve some iteration as the design process moves from a broad concept to greater detail.

3.1 Personnel involved in QDR

The formation of the QDR team depends on the nature and size of the project and on the extent of the analysis to be conducted. It should always include qualified hydrogen safety engineer(s) who will carry out the quantified analysis. The participation of architect, structural engineer, fluid mechanics engineer and a member of operational management ensures that all aspects of the design can be investigated in the context of the hydrogen safety objectives and that the impact of proposed solutions on other aspects of the design, are fully appreciated. A non-exhaustive list of other personnel that has to be involved in QDR includes: owner, representative of approval bodies, representative of insurers, emergency services, and owners of any occupancy in the vicinity of the hydrogen system and/or infrastructure.

3.2 Review of technical characteristics, site layout and management

3.2.1 Hydrogen system characteristics

The hydrogen system should be usually described by using Piping and Instrumentation Diagram (PID) representing the piping systems (diameter, length, materials, and pressure), the position and type of valves, the location of hydrogen vents, detection and mitigation systems, instrumentation connections, etc. The technical characteristics of components such as compressors, storages, fuel cells, dispenser, etc. should also be described.

To ensure the commercial and technical viability of the hydrogen system, the operational management should provide their requirements, e.g. operational pressure, hydrogen production and/or consumption/delivery rate. It is also important to estimate the required hydrogen storage inventory, as this parameter will be used to classify the hydrogen system under land use planning legislation. For instance in the UK, the NIHHS [11] requires the operators to provide a pre-construction safety report to Health and Safety Executive before a new construction can begin for storage above 2 tones. Above 5 tons of hydrogen stored, the COMAH Regulations applies and impose conditions to the operators; storages above 50 tones require further restrictions.

3.2.2 Site layout, building and structures characteristics

The site and surroundings should be described by reference to schematic drawings or models. On the site itself, buildings and structures are likely to be built around or near the hydrogen system, e.g. protection against adverse weather, systems to prevent of intrusion, commercial building, etc. Information would be then required on the presence of dwellings, shops, barriers, canopy, type of materials used for walls and pavement, presence of electric cables, firefighting equipment, bollard to prevent collisions, lightening protection equipment, etc. [11]. All the relevant available information about the use of these buildings and structure, their anticipated contents, the possible environmental influences, occupant's characterization, should be reviewed.

In addition, information should be provided on the location of the facility, the accessibility by road or by other means, the type of buildings, structures and occupancy (industry, leisure, habitation, etc.) at the boundaries of the property, any known information on land use planning that might affect in the future the characteristics of buildings and structures beyond lot lines, any unusual factor that might influence the H2SE project.

3.2.3 Management

The following factors should also be taken into account when assessing the likely nature and extent of management in an infrastructure: knowledge of ownership; staffing and level of hydrogen safety training; security; control over work, e.g. repairs to structure; the frequency of maintenance and testing of detection and mitigation technologies, liaison with the emergency services, contingency planning, degraded system planning, management of risk, and the continuity in the compliance with RCS [11]. There is a greater confidence in management procedures when answers to these questions are positive.

3.3 Establishment of safety objectives

Safety objectives should be defined during the QDR. They should be appropriate to the particular aspect(s) of the design under consideration, as H2SE may be used either to develop a complete hydrogen safety strategy or to consider one aspect of the design. The main hydrogen safety objectives are life safety, loss control and environmental protection [11].

3.3.1 Life safety

A hydrogen system can represent a hazard for occupants, first responders and members of the public. The main life safety objectives may include provisions to ensure that [11]:

I. The occupants are able to leave the facility in reasonable safety or consequences to occupants are acceptably low.
II. First responders are able to operate in reasonable safety.
III. Collapse or falling debris does not endanger people, including fire-fighters, who are likely to be near the facility.

The H2SE process should address all likely exposures to life threatening conditions like oxygen depletion, radiant heat flux, air temperature, overpressure, cryogenic temperatures, etc.

3.3.2 Loss prevention

As the effects of a hydrogen accident on the continuing viability of a business can be substantial, consideration should be given to reduce the damage to designated structures and valuable contents. This should guarantee the business capability, the preservation of the corporate image and reduce the potential for large financial losses.

3.3.3 Environmental protection

When estimating potential hazards to other facilities, constructions, flora and fauna in the vicinity of a hydrogen system and infrastructure, consideration should be given to the limitation of [11]:

I. The severity of accident on adjacent facilities, especially in urban area or when hydrogen is handled in large industrial complex with a potential of "domino effect”.
II. The release of hydrogen into the built environment/nature to limit adverse effects of asphyxiation and cold burns on fauna and flora.

3.4 Identification of hazards and associated phenomena

A systematic review of the hydrogen system and its close environment should be conducted to establish the sources of potential hazards, taking account of the following factors [11]: circumstances of production, transport and use of hydrogen, conditions of storage (volume, pressure, temperature, tank's material, location, etc.), potential for ignition (e.g. electric, electrostatic, hot surface, potential for spontaneous ignition of sudden release, risk of mixing with oxidizer, etc.), architectural characteristics (dimensions, location, structure, confinement, degree of congestion, potential for accumulation, materials of construction, etc.), presence of other combustible contents, nature of other activities within and beyond the infrastructure/facility, possible sources and frequency of leak, any unusual factors, etc.

Several methodologies can be used to identify hazards (simple checklist, HAZID, FMEA, etc.) [11] depending on the level of detail required. The potentially hazardous phenomena, e.g. formation of flammable cloud, jet fire, deflagration, etc., arising from an incident/accident should be reviewed qualitatively by the QDR team. In order to control hazards and consequences the QDR team should suggest possible trial safety designs providing safety at acceptable level in their opinion, which should be checked at the quantitative stage by hydrogen safety engineer.

To identify potential system failures or foreseeable faulty events that might have a significant influence on the outcome of the H2SE study, it is necessary to conduct an assessment of "what-if events" [11]. Examples of "what-if events" could include: full bore rupture of pressurized hydrogen pipe, unscheduled mixing of hydrogen with oxidizer within the system, e.g. electrolyser, failure of detection and/or mitigation system, failure of emergency shutdown valves to go in safe position, blockage of emergency exits during the accident, management fails to implement hydrogen safety system training and maintenance procedures, etc. In a probabilistic study the likelihood and consequences of such event will generally be quantified. In addition, for deterministic studies the QDR team should judge the significance of "what-if events" by considering whether:

I. Consequences are tolerable or not worse than in a code compliant design, or
II. Additional protection measures are essential to provide a degree of redundancy.

3.5 Trial safety designs

To achieve an acceptable level of safety, the initial design could be amended or additional protection measures could be provided. To do so, the QDR team should establish one or more trial safety designs taking into consideration selected accident scenario(s). The different designs could satisfy the same safety objectives and should be compared with each other in terms of cost-effectiveness and practicability. At first glance, it is essential that trial designs should limit hazards by implementing prevention measures and ensuring the reduction of severity and frequency of consequences. Although H2SE provides a degree of freedom, it is also necessary to fully respect relevant regulations when defining trial designs. A first step would be to base an initial trial design on the recommendations of established codes, including prescriptive, if possible. Then other designs could follow the principles below [11]:

- Inherently safer design: the aim is to minimize the source of harm from identified hazards and limit the impact of consequences
- Procedural safeguards: this is in relation with the respect of safety codes and standards and quality assurance together with the training and behaviour control of staff. In the H2SE approach this will mainly concern the safety management of the premises
- Safe fail: the system should fail safely (for example, valves of any hydrogen system should automatically go to the safe position in the event of a power failure)
- Safety reserves: they are used to ensure the strength of construction.

The application of these principles to the development of trial designs of hydrogen systems could be done in the following order [11]:

- Eliminate occurrence of severe accident by inherently safer design or by appropriate safety management
- Limit hydrogen inventory
- Limit the number of hydrogen sources
- Promote hydrogen dilution
- Suppress ignition sources
- Avoid conditions for flame acceleration (no high hydrogen concentration, no confinement, no congestion)
- Avoid conditions for detonation (no high hydrogen concentration; limit cloud size)
- Limit consequences of explosion by strong construction

3.6 Acceptance criteria and methods of analysis

The QDR team has to establish the criteria against which the performance of a design can be judged. Three main methods can be used: deterministic, comparative, and probabilistic [11]. The QDR team can, depending of trial designs, define acceptance criteria following all three methods.

3.6.1 Deterministic studies

The objective of a deterministic study is to analyze the performance of trial safety design(s) selected by QDR team for chosen scenarios with models based on physical, chemical, thermodynamic and human behavioural relationships, derived from scientific theories and empirical correlations [11]. Among advantages of the deterministic approach are: provides a simple yes/no result, widely used for life safety evaluation, use of well validated calculation procedures available, considerable data available. Disadvantages of deterministic studies include: dependence on initial assumptions, provides no direct measure of costs and benefits, limited benefit for loss control purposes compared with a probabilistic approach.

3.6.1.1 Life safety criteria

The deterministic life safety criteria are based on physiological response to severity of impact and can be defined for life threatening, injury and incapacitation from evacuating. The criteria can be specifically chosen for the population under consideration, as it can be members of staff, occupants evacuating the facility, member of the public or first responders with personal protective equipment. They can be used in the process assessment against criteria by comparison with an output of the quantitative analysis.

Firstly, it is important to note that regarding the health hazard properties of hydrogen molecule itself, it appears to be non-toxic and not classified as a carcinogen [11]. Nevertheless, attention should be paid to the level of hydrogen concentration in relation to asphyxiation. Hydrogen level in air will impair evacuation from concentration in air between 9 and 28% by volume, and is live threatening for concentration above 42% by volume in air.

Hydrogen fires are a source of hazard due to heating of entrained surrounding air that can lead rapidly from hard breathing to unbearable pain. The maximum air temperature to escape can be chosen as 115 °C [97] while unbearable pain and irreversible injuries can occur for exposures to temperature above 150 °C [11]. Also, the radiant heat flux generated is absorbed by a person's skin causing pain, non-lethal and fatal burns. The gravity would depend on several factors, such as the source strength, the distance from the source, the view angle between hydrogen fire and radiated object, the level of clothing, the exposure time and atmospheric conditions (especially amount of water vapor). For calculation purposes it is possible to use the scale of threshold of pain for clothed persons, or simple equation or Probit function [11]. For instance a tolerable value of radiant heat flux for member of the public is often chosen as 1.5 kW/m^2 by standardization bodies to define separation distances to lot line.

Deflagrations and detonations generate direct and indirect physiological impact on human. A Probit function can be used to calculate the probability of fatality by using overpressure. Probit functions can also provide an estimate of the indirect impact of explosions like missiles effect and the whole body translation [11].

Liquefied hydrogen has extremely low temperatures and cryogenic burns can result from contact between unprotected parts of the body and cold fluids or surfaces. A sudden release of liquid hydrogen can result in hypothermia in case of prolonged exposure while prolonged inhalation of cold vapor or gas may damage lungs [11].

3.6.1.2 Loss prevention and environmental protection criteria

Considering hydrogen systems, we can distinguish between the system/infrastructure itself, its content and the environment. The level of accident severity can impact the built environment objects and nature to different degree. If damaged, their value should not only be considered "*as a direct financial replacement cost, but also as a loss of an asset and productive time"* [11]. Also, the time necessary to replace damaged components can result in business disruption or deviation of customers towards competitors. Consideration should be given to reducing the escalating effects of objects, events and layouts on damages. Attention should also be paid to the value and importance of the property in and around a facility.

Acceptance criteria may include the definition of value for: number of specific valuable objects that are acceptable to damage, maximum zone of direct damage due to hydrogen release, fire and/or explosion, maximum zone of extinguishing water damage, maximum time periods for recovery from an accident. Damages caused by hydrogen accident can be evaluated by taking into account critical values that causes irreversible damages (overpressure, impulse, radiative heat flux, etc.) [11]. These acceptance criteria should be adequately chosen by the QDR team and hydrogen safety engineer, depending on particularities of a case.

For instance, the distance to axial hydrogen concentration decay of 4% by volume is used in relevant standards, as the safety distance between H2FC technologies and air intakes of building.

3.6.2 Comparative studies

In some projects, recommendations of prescriptive codes and standards when they are available might provide the near optimum solution for a safer design. If the hydrogen system is regulations and codes compliant, a full H2SE study may not be necessary. For comparative type of study, the acceptance criteria may simply be defined in terms of compliance with existing code requirements.

Current applicable prescriptive solutions can be found in various standards. However, standards are not mandatory except if they are referred to in Regulations and unlike H2SE, standards don't include state-of-the-art of knowledge in hydrogen safety. Some standards are appropriate to the design of hydrogen refueling station equipped with an electrolyser [11].

However, a design under consideration can sometimes be innovative and recommendations of prescriptive code might not be directly applicable. In that case, it is possible that the design presents limited departures from prescriptive code and a comparative study can be conducted. The objective of such study is to demonstrate that the hydrogen system, as designed, presents at least the same level of safety performance and is as effective and reliable as a similar type of system designed in accordance with prescriptive codes and standards. This type of approach can be often made without calculation and requires less extensive analysis than deterministic or probabilistic studies that use absolute criteria.

Nevertheless, particular intentions and objectives of these prescriptive solutions should be known, and assumptions and methods of calculations used to define these design criteria must be clearly understood by hydrogen safety engineers [11]. Prescriptive solutions can overestimate or underestimate separation distances from H2FC technologies. Then alternative designs may be developed to address the specific underlying objectives identified.

Another comparative study approach could consist in transposing existing prescriptive recommendations for alternative fuel such as CNG/LPG to hydrogen systems when reasonable with taking into account difference in physical and chemical properties [11].

The advantages of the comparative method of analysis are that it is relatively quick, consistent with established prescriptive codes, not usually dependent on initial assumptions, may be used where definitive design data are not available, explicit safety factors are not required, allows the use of quantitative risk assessment without the need for absolute acceptance criteria. The disadvantages are: generally only suitable for one or two significant departures or several minor deviations from prescriptive codes, might incorporate the weaknesses of the prescriptive codes [11].

3.6.3 Probabilistic studies

The objective of a probabilistic study is usually to show that the risk of a given event occurring is acceptable or tolerably small. The modern definition of risk is provided by ISO/IEC Guide 73:2002 stating that it is the "*combination of the probability of an event and its consequence*" while safety is defined as the "*freedom from unacceptable risk*" [11]. This means that safety is a societal category and cannot be numerically defined while risk is a technical measure that can be calculated. Society, in consequence, establishes acceptable levels of risk or risk acceptance criteria. The use of risk acceptance criteria is a key element required to develop risk-informed codes and standards. Their primary concern is the potential for people's injury or death. Such criteria must be established for all the category of people exposed to the consequences of facility- related accidents (mainly occupants, staff, public, first responders). But a major difficulty comes from the current absence of mandatory risk acceptance criteria specific to hydrogen systems that could severely hinder the reliability of results of the quantitative risk assessment.

Nevertheless some risk-informed separation distances have been implemented in recent hydrogen standards (NFPA 2 and 55) and were based on a guideline of 2E-5 fatalities/year as chosen by NFPA 2 Working Group [11].

The advantages of the probabilistic approach [11] are: provides comparison between dissimilar safety systems, provides a numerical value of risk, can quantify the probability of unlikely events with severe consequences, can quantify the risk associated with failure of one or more elements of safety system, and provides data for cost-benefit analysis. The disadvantages are [11]: limited or absent statistical data; time consuming and thus expensive analysis.

3.7 Establishment of scenarios for analysis

3.7.1 Choice of scenarios

It is the role of QDR team, based upon their experience and knowledge, to establish the scenarios that require analysis and the ones that don't need to be considered. Indeed, to evaluate the performance of a trial hydrogen safety design, an infinite number of possible scenarios can be applied. And, as it is not possible to quantify them all due to the limited availability of data and resources, scenarios should be restricted to the most significant or worst-credible ones. Furthermore, scenarios with a very low probability of occurrence should not be analyzed unless their outcome is potentially catastrophic and a simple remedy is available. Finally, it is usual to identify a number of worst-case scenarios for supplementary evaluation.

3.7.2 Description of scenarios

The description of scenario(s) should be appropriate for the quantification process and based upon assumption and experience of the QDR team members. This could include the following [11]: hydrogen inventory (pressure, volume, etc.), leak parameters (nozzle size, location, orientation, shape, phase, duration, etc.) potential for dispersion and accumulation (confinement, obstacles, passive and forced ventilation, etc.) ignition (location, strength, time of ignition, etc.) performance/failure of detection/mitigation or fire suppression systems considered in the “what-if” approach, severity of external source of hazard (intensity, duration, etc.), etc.

The scenarios should also be chosen in order to meet the safety objectives and primarily life safety objectives. So, considering exposition to instantaneous or cumulative untenable conditions, it is important to review the occupancy in relation to occupant's initial position compared to the possible immediate hazardous area, the factors most likely to influence human behavior and movement during evacuation. Additional considerations on occupancy should also be taken with regards to: occupant's number and their familiarity with the premises, their alertness and mobility. Furthermore, attention should be paid to means of escape, design parameters such as travel distance, escape routes, number and position of exits and exit widths.

3.8 Document outputs of QDR

The QDR team should provide a set of qualitative outputs to be used in the quantitative analysis [11]: results of the architectural review, hydrogen safety objectives, significant hazards and associated phenomena, specifications of the scenarios for analysis, one or more trial designs, acceptance criteria and suggested methods of analysis.

Following QDR the team should decide which trial design(s) is likely to be optimum. The team should then decide whether quantitative analysis is necessary to demonstrate that the design meets the hydrogen safety objective(s).

4. Quantitative analysis

Following QDR a quantitative analysis may be carried out using EDST where various aspects of the analysis can be quantified by a deterministic study or a probabilistic study. The quantification process is preceded by the QDR for two main reasons [11]: to ensure that the problem is fully understood and that the analysis addresses the relevant aspects of the hydrogen safety system and to simplify the problem and minimize the calculation effort required.

The reduction of calculation effort is made by the QDR team when establishing which potential threats are significant and require quantification. In addition, the QDR team should identify appropriate methods of analysis among [11]: simple engineering calculations, CFD simulations, simple probabilistic study, and full probabilistic study.

A deterministic study using comparative criteria will generally require fewer data and resources than a probabilistic approach and is likely to be the simplest method of achieving an acceptable design. A full probabilistic study is only likely to be justified when a substantially new approach to hydrogen system design or hydrogen safety practice is being adopted. The analysis may be a combination of some deterministic and some probabilistic elements.

4.1 Use of elementary design safety tool

To perform a full H2SE analysis it is necessary to use several EDST. However, various types of H2SE studies with specific hazards, accident scenarios and trial safety designs may require different calculation approaches. For each project it is then necessary to [11]: establish required numerical outputs, consequently identify the EDST that will be used in the quantitative process, address the list of useful interactions between these EDST, set up relevant calculation procedures.

Calculations to be performed within each EDST will use inputs pre-determined in the QDR and inputs from other EDST. Yet care should be taken when assigning values to these inputs. Indeed, a conservative approach would require using worst-credible conditions and probably safety factors for defining these variables. However, considering a series of unlikely events in the development of a scenario would lead to an over-conservative design and increase of the H2SE study cost. On the other hand, the use of average values does not provide a design with an acceptable level of safety [11]. To perform a successful quantitative analysis it is necessary to rationalize the problem qualitatively during the QDR stage. Attention may then be focused on the quantitative interpretation of the design and, in particular, the uncertainties that the quantification may involve.

4.2 Deterministic procedures

Deterministic procedures quantify the development of an incident/accident involving hydrogen, its severity and associated consequences [11]. Deterministic techniques will be described in detail in EDSTs. Inputs and outputs to/from EDST may be used to carry out a time-based analysis of the hydrogen safety system performance.

In many cases, the use of nomograms, hand calculations or simple computer models will provide adequate accuracy. The empirical, semi-empirical and theoretical correlations and relationships validated against experimental data will be implemented in different EDST. Caution should be taken to use tools within limits of their applicability. In adopting any engineering tool or modelling technique the user should ensure that: it has adequate predictive capability; it is appropriate to the scenario under consideration, simple engineering tools have been adequately assessed and contemporary CFD tools were thoroughly verified/validated and the governing equations and validations are published in peer reviewed journals.

Provided the modelling techniques and/or tools are appropriately chosen, deterministic studies have to account for uncertainties in initial and boundary conditions. For example, this can be done by assuming the worst-credible initial conditions. However, if this approach is not satisfactory, sources of uncertainties might be addressed in a sensitivity analysis to check the robustness of the results and to investigate the criticality of each input parameters. In particular, the following uncertainties might be considered [11]:

Uncertainties of input parameters

The most significant uncertainties are probably in the initial assumptions. A sensitivity analysis can help to determine the level of accuracy required of these input data. Such analysis may be conducted by investigating the response of the output parameters to changes in the individual input parameters. When modelling for life safety, the initial inputs that are most likely to impact on the outcome are: storage pressure, capacity and leak diameter (QDR, EDST1).

Uncertainties due to QDR simplifications

QDR aims at defining simplifications and assumptions to facilitate a full H2SE analysis. Yet a single element of hydrogen safety system or assumption might be critical to the outcome of the study. The QDR team should then test the criticality of “what-if events”. For example, the QDR team might have assumed that leaks would quickly activate the emergency shut down while an alternative scenario would assume a failure and the release of the total hydrogen inventory. The comparison of outcomes from the quantitative process would enlighten the criticality of the failure under consideration. Further consideration could be given to provide a degree of redundancy in the design (addition of valves, detectors, etc.) or to carry out a specific probabilistic study to investigate the reliability of such particular mitigation system.

Uncertainties due to modelling or use of engineering tools

When there is a doubt about the reliability of calculation technique employed, the outcome can be compared against another tool, e.g. one based on different modelling approach. Any significant discrepancies may be accounted for by choosing the most conservative of the results or by introducing an appropriate safety factor.

4.3 Probabilistic procedures

The probabilistic approach is different from the use of EDST and should be treated as a particular methodology to be presented in the separated dedicated document. Probabilistic risk assessment study aims at estimating the likelihood of a particular unwanted event occurring. This can be achieved by the use of statistical data on the frequency of leaks and reliability of mitigations technologies, combined with a deterministic evaluation of the consequences of possible hydrogen incident/accident [11].

By assigning probabilities of failure to hydrogen safety system elements and frequency to unwanted events, it is possible to assess the likelihood of a particular set of consequences. This can be used as a basis to: estimate the frequency of high-consequence events (e.g. multiple fatalities), evaluate the potential of failure of complex safety systems, compare the effectiveness of safety systems, establish the most cost-effective design.

Full probabilistic study can be very time consuming and expensive method of analysis in H2SE. In addition, a risk analysis for hydrogen systems "*can be severely limited by data availability*" as "*a key input into a quantitative risk analysis, which is the data required to quantify the frequency of potential accident scenarios*" [11], is hardly available. Indeed, practically in all accident scenarios, an initiation event is unwanted release of hydrogen. Despite the existence of databases gathering such events little data are available on hydrogen- specific component leakages. Furthermore, the number of operating hours represented in these databases makes the analysis of data "*difficult if not impossible*" [11].

Yet methods to calculate risk-informed separation distances for H2FC systems have been proposed. The Hierarchical Bayesian approach used in the NFPA 55 is based on generic leakage frequency as a function of leak size (i.e., small leaks, large leaks, and ruptures) covering different industries. Leak size of 3% of pipe cross-section area was chosen in NFPA 55 (Edition 2010) for calculation of separation distances. But only limited hydrogen-specific data were used in this analysis, and consequently "*more hydrogen data is needed to provide more robust leakage frequencies*" [11].

It has to be underlined that the use of probabilistic approach also requires a quantitative analysis using deterministic calculations in order to quantify the consequences of hydrogen incident/accident.

5. Assessment against criteria

Following the quantitative analysis, the results should be compared with the acceptance criteria identified during the QDR exercise. Three basic types of approach can be considered: deterministic one shows that on the basis of the initial assumptions a defined set of conditions will not occur, comparative approach shows that the design provides a level of safety equivalent to that in similar systems and/or conforms to prescriptive codes (as an alternative to performance- based H2SE), probabilistic approach shows that the risk of a given event occurring is acceptably low.

If none of the trial designs developed by the QDR team satisfies the specified acceptance criteria, QDR and quantification process should be repeated until a hydrogen safety strategy satisfies acceptance criteria and other design requirements. Several options can be considered when re-conducting QDR [11]: development of additional trial designs, adoption of more discriminating design approach, e.g. using deterministic techniques instead of a comparative study or probabilistic instead of deterministic procedures, re-evaluation of design objectives, e.g. if the cost of hydrogen safety measures for property loss prevention outweighs the potential benefits. When a satisfactory solution has been identified, the resulting H2SE strategy should be fully documented.

6. Reporting and presentation

The H2FC system and/or infrastructure designed by H2SE might be a subject to review and approval. As H2SE provides a flexible approach using performance-related objectives, it is not possible for approval bodies to simply compare the proposed design against a set of well-defined recommendations. It is hence important that all stakeholders understand assumptions made and findings achieved during carrying out H2SE.

6.1 Report on hydrogen safety engineering

The implementation of H2SE procedures and results in a fully documented “Report on Hydrogen Safety Engineering” guarantees the hydrogen safety design to be readily assessed by a third party. The Report should set out clearly the basis of the design, the calculation procedures used, any assumptions made during the study, and conclusions achieved. For the understanding by all the stakeholders of the purpose of proposed safety measures, there should be a clear distinction between the protection of life, property and environment.

Depending on particularities and scope of the H2SE study, the reporting of the results and findings could contain the following information [11]:

a) Objectives of the study
b) Full description of the H2FC system/infrastructure
c) Results of the QDR
d) Quantitative analysis:
    1) Assumptions
    2) Engineering judgements
    3) Calculation procedures
    4) Validation of methodologies
    5) Sensitivity analysis
e) Assessment of analysis results against criteria
f) Conclusions:
    1) Hydrogen safety strategy
    2) Management requirements
    3) Any limitations on use
g) References (e.g. drawings, design documentation, technical literature, etc.).

6.2 Briefing for owner/occupier

Management of hydrogen safety is both critical and integral to the success of a hydrogen system/infrastructure safety design. Provisions of all H2SE strategy elements have to be implemented effectively and properly maintained. Indeed, available statistics shows that human errors and management insufficiencies are factors in more than 50% of incidents/ accidents involving hydrogen [11]. Hence, any specific aspect of the hydrogen safety strategy depending upon a high standard of hydrogen safety management, should be documented in a "Hydrogen Safety Manual” that should be available in each H2FC facility for the benefit of internal and external controls. The "Report on Hydrogen Safety Engineering” should be incorporated into this Manual. The general management and operational procedures in the "Hydrogen Safety Manual” should be written with references to the Report. The Manual should contain the technical specifications for all aspects of the facility or infrastructure and should particularly include the hydrogen safety policy statement (e.g. prevention of accidents, creation of separation distances, contingency planning, etc. [11]), the safety management structure, continuing control, audit and maintenance procedures, staff education and training, record.

6.3 Audit

In order to maintain the effectiveness of the hydrogen safety strategy, it is essential that regular and effective testing and maintenance procedures are conducted. In a large H2FC facility with the public access an independent audit should be carried out periodically. The frequency of such audits should be determined according to the nature and complexity of the system/infrastructure concerned and in relation with the relevant regulations. Audits should ensure that policies adopted by the management of hydrogen safety system are appropriate and being implemented effectively, and that testing of equipment and systems is being carried out.

7. Safety risk model and analysis

In this section, a comprehensive safety risk analysis was developed. The framework is comprised of two qualitative methods (HAZOP and PRA), a hybrid method (ETA) and a quantitative method (QRA along with a process risk and consequence simulator). In order to introduce the framework, this section provides a brief overview of its parts, as shown in fig. 4.2.

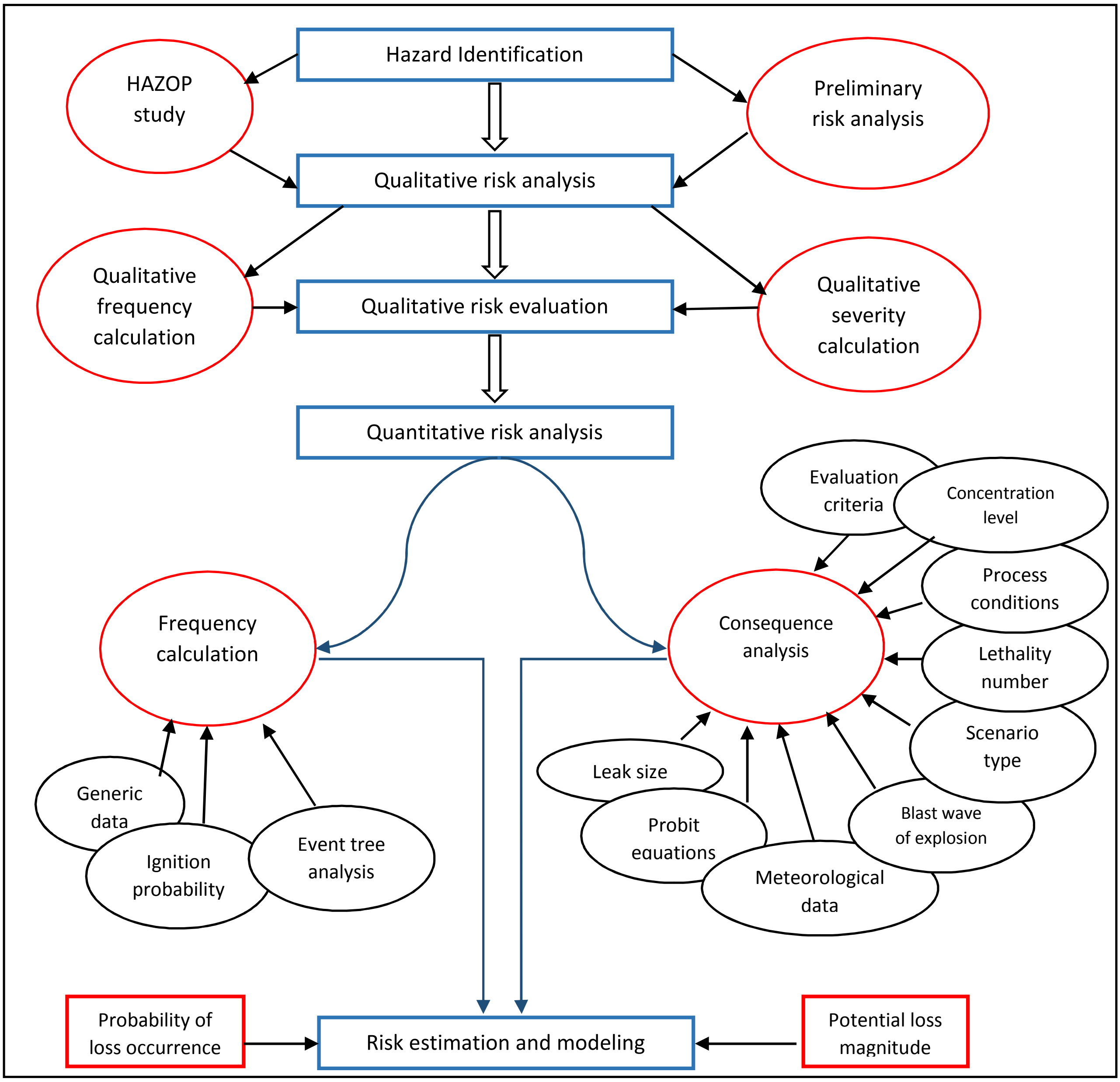

Fig. 4.2 Overview of the risk analysis framework

7.1 Hazard identification

Different methods can be utilized at different stages of a project to identify hazards. Two of the more systematic methods of hazard identification used in chemical industry are Hazard and Operability (HAZOP) study and Preliminary Risk Analysis (PRA) [14]. A HAZOP study along with the PRA technique was used for determining main hazardous sources and carrying out a qualitative risk analysis. All subsystems from the viewpoints of safety risks are analyzed by HAZOP and PRA. At the end, all potential safety risks and process deviations from normal operation were found. Also all functions, deviations, causes, consequences, safeguards and related factors from all subsystems have been completely investigated and analyzed.

7.2 Qualitative risk analysis

After identifying the potential hazards, their severity and frequency were assigned and their risk were determined based on the American Military Standard (MTL-STD-882) [14]. At the end of this step, a qualitative assortment of safety risks are provided.

7.3 Quantitative risk analysis

In this step, subsystems that had unacceptable risk at the end of the previous step were studied in more details. Consequences of all selected scenarios are modeled by means of a process safety risk simulator and their frequency and accident outcomes are calculated.

Consequence analysis

The consequence analysis (modeling) has the following purposes: calculating incidents consequences, calculating concentration levels, assessing radiation level and blast wave of the fire and explosion, and the lethality number. The consequence models used in every study can be provided by software such as the PHAST simulator (Process Hazard Analysis Software Tool) [14]. PHAST is a professional simulator used for consequence modeling in chemical process risk assessments. This simulator is specially validated for the release of hydrogen and it is one of the most accurate and precise tool for QRA and consequence modeling. It is capable to simulate the progress of a potential incident from its initial leakage to the final possible consequences.

Frequency calculation

The frequency of the initial event (scenario) is calculated using the generic data from risk assessment data directory of each organization according to the case that we want to investigate, and the incident outcomes can be calculated using event tree analysis (ETA). ETA is a pictorial representation of logic models. Its theoretical foundation is based on logic theory [14]. The probability of all succeeding conditional events leading to that incident outcomes were estimated using loss prevention in the process industries.

7.4 Risk estimation

The risk is estimated by the determination of qualitative and quantitative values of risk. It requires calculation of two risk components: the potential loss magnitude and the probability that the loss will occur. The qualitative risk analysis is based on an analytical estimation process, through holding various meetings between the managers and specialized engineers. Whereas, in the quantitative approach, risk is estimated and expressed by mathematical relations and using consequence modeling and risk simulator.

CHAPTER 5

SUMMARY AND CONCLUSIONS

There are a number of technologies that have been developed and demonstrated for the detection of hydrogen gas. Some of these are well-established commercially and devices based on these principles have been available for years, produced by various manufacturers and with a range of performance capabilities and costs. Other technologies are less well-developed, but ongoing research indicates that they show promise for emerging hydrogen detection applications that impose new performance requirements such as faster response, lower power consumption or multipoint detection, among others.

Hydrogen sensors can play an important role in ensuring the safety of people and property wherever hydrogen is produced, stored, transported or used. The emerging hydrogen economy is leading to the development of new hydrogen sensors in greater quantities and also with greater variety because different sensor technologies are more suitable for different applications. Further work is required in terms of basic research into new materials and sensor principles as well as applied research and development to fully meet the demands of current and emerging technical applications. Testing and validation procedures combined with relevant standards can support the ongoing development of hydrogen sensing technologies.

The second chapter's work has been the development of an experimental protocol to test the performance of hydrogen sensors under representative service life conditions for use in automotive applications. Hydrogen sensors have been identified as an enabling technology directly linked to the safe demonstration of hydrogen vehicles. Careful consideration was given to the expected environment of the sensors during their service life. The protocol was verified by using it to test and evaluate samples of commercially available sensors which were procured following an extensive market survey. During initial tests, performed as part of the development of the test protocol, it was apparent that many sensors displayed unexpected behavior, deviating not only from the manufacturer's specifications but also showing a wide variation in response between identical sensors. Moreover several sensors available for testing either failed to give a signal or failed to respond to the presence of hydrogen. The relatively large proportion of 'failed' samples may have been due to damage caused during transportation, handling or electrical connection of these sensors however these reasons are speculative. A larger sample number for testing is required before any relationship between the number of 'failed' samples and sensor reliability can be made.

The developed test protocol may be used as a guideline to test hydrogen sensors suitable for detecting unwanted hydrogen leaks in future hydrogen fueled vehicles under representative service life conditions. In addition to being used for sensor performance assessment a harmonized test procedure can also be used for inter-laboratory comparisons or round-robin testing of hydrogen sensors. It has been experienced that, considering the sometimes unexpected behavior of sensors, independent testing of safety sensors will play an important role in identifying R&D needs and offering feedback to sensor manufacturers and end-users. When used as devices for ensuring public safety it is essential that hydrogen sensors can reliably detect critical concentrations of hydrogen defined in this work as 10% LFL (0.4 vol%). Independent assessment and demonstration of the proper performance of such devices can help facilitate a transition to a hydrogeninclusive economy by increasing consumer confidence in and improving the public's perception of hydrogen safety and ultimately increasing its acceptance.

The test results from performance tests of hydrogen sensors have been presented. A total of seven different performance assessment tests were carried out on 39 commercially available sensors employing either catalytic, electrochemical, metal-oxide semiconductor or thermal conductivity detection principles. The results from these tests were used to compare the performance of the different sensor types and to assess their suitability for use as hydrogen safety sensors in automobile applications. The advantages and disadvantages observed during the assessment of the four sensor types tested are summarized in Table 2.5. While catalytic sensors showed the best performance during the tests their suitability for use as safety sensors in hydrogen fueled vehicles is compromised due to their large power consumption, as safety sensors will need to operate even when the vehicle is not in use. MOx sensors performed poorly in ambient parameter tests in the presence of hydrogen however their use as safety sensors, in the absence of hydrogen under normal operating conditions, is feasible if their accuracy can be improved (for example by using nanomaterials and MEMS technology). Their small size, low cost and relatively low power consumption are advantageous properties for automotive applications. Electrochemical sensors showed a large variation in their performance during the tests performed. Their poor performance at modest low temperatures is a cause for concern if used in vehicles where such low temperatures are possible. Finally thermal conductivity sensors despite their relatively high cost do have the potential to be used as safety sensors if their detection limit can be lowered and their dependence on temperature can be compensated.

New commercial off-the-shelf hydrogen sensors with superior performance metrics have been presented in chapter 3. They promise to fulfil many of the performance requirements demanded by end-users in existing and emerging hydrogen applications. The proven product certification by most of the sensor manufacturers indicates the improved reliability and accuracy of these products. Use in the field will confirm their true performance under the ambient conditions of an application. Research on new hydrogen sensing materials, the development of novel sensing technologies and the miniaturization of sensor platforms, which yield devices with improved performance at a lower cost, have also been presented. Many sensing platforms use palladium or platinum for hydrogen detection and while these platforms are prone to aging effects and signal drift alloying can mitigate these effects. Reducing the use of noble metals in sensors through miniaturization can remarkably reduce the costs of sensor elements. A new standard, Safety Technical Regulations for Mobile Hydrogen Refueling Facility, has been developed and its highlights are also addressed in the 3rd chapter. Safety experience learned from engineering practice is integrated into the safety specifications. Safety studies on mobile hydrogen refueling facilities are also applied to the development of the safety standard. Highlights of the specifications and the progress of the draft are summarized in terms of technical safety requirements, operation management and other special provisions. Also future perspectives on the development of standards for mobile refueling facilities are proposed. Finally we saw that collaboration, information exchange and knowledge building can occur in many different ways. This section has provided examples of how the IEA HIA addressed hydrogen safety-related barriers to facilitate the implementation and utilization of hydrogen and hydrogen related systems. We should be encouraged to build on these successes by continuing to address high priority safety knowledge barriers via mechanisms that support collaborations of many types.

Hydrogen safety engineering (H2SE) is a key to the success of the hydrogen economy and its public acceptance. It is the powerful tool for provision of hydrogen safety by qualified engineers in the growing market of H2FC systems and infrastructures. The fourth chapter outlines the draft for development of a future standard with a tentative title "Application of hydrogen safety engineering for design of hydrogen and fuel cell systems and infrastructure". H2SE provides the methodology and makes it possible to develop inherently safer H2FC systems/infrastructure, innovative safety strategies, and breakthrough engineering solutions. The H2SE procedure includes three main steps. Firstly, the qualitative design review (QDR) is performed by a qualified team composed of relevant stakeholders, whose experience and knowledge is used to analyze a H2FC system/infrastructure, suggest scenarios and trial safety designs, formulate acceptance criteria. Secondly, the quantitative analysis is carried out using the state-of-the-art knowledge in hydrogen safety science and engineering, and validated contemporary models and tools. Thirdly, the assessment of the trial safety design performance against pre-defined acceptance criteria is undertaken. The next development is a completion of the state-of-the-art Elementary design safety tool description comprising validated engineering models and tools. The essential part of the EDSTs development strategy is its ability to adopt new scientific findings and engineering solutions from ongoing and future studies. The development, dissemination and teaching of the H2SE discipline at Universities will help to recognized H2SE as a new profession and an important cornerstone supporting the safe introduction and underpinning of hydrogen and fuel cell technologies, systems, and infrastructure to the global market.

Finally we presented a comprehensive safety risk analysis model (fig 4.2). The proposed framework in this work is better for use in the preliminary phases of life cycle of a system to prevent additional operating and maintenance costs in future, but, it is also more valuable that the framework be applied for improving the existing installation. Very important step is to identify the potential hazards. After that, the hazards' severity and frequency were assigned and their risk were determined. Then, consequences of all selected scenarios were modeled by a safety risk simulator and their frequency and accident outcomes are calculated. The risk is estimated by the determination of qualitative and quantitative values of risk. It requires calculation of two risk components: the potential loss magnitude and the probability that the loss will occur.

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