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Reliability of commercially available hydrogen sensors for detection of hydrogen at critical concentrations: Part II – selected sensor test results

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ABSTRACT

Reliable hydrogen sensors are essential to detect accidental hydrogen releases when hydrogen will be used to fuel future vehicles. To assess the performance of hydrogen safety sensors under conditions typical of automotive applications a test protocol has been defined. It has been experimentally evaluated by performing tests on commercially available hydrogen sensors. Catalytic sensors measured hydrogen concentration accurately and sensor response was largely independent of ambient parameters. However they were significantly cross sensitive to carbon monoxide and the detection limit was high. Metal-oxide semiconductive sensors had a low detection limit and showed a low cross sensitivity to carbon monoxide however almost all of these samples showed poor accuracy and a strong dependence on ambient parameters. Electrochemical sensors also had a low detection limit however ambient parameters, cross sensitivity and accuracy tests showed a high variation in results. Tests on a limited number of thermal conductivity sensors highlighted their high detection limit and strong dependence on temperature.

1. Introduction

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 4 vol% [1]. 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. Hydrogen safety sensors have been developed, used and relied upon for decades in industrial [2–4] and space applications [5] and have an established track record for reliable and accurate hydrogen detection under controlled industrial conditions. However as hydrogen energy technologies enter the commercial market hydrogen will be brought closer than ever to the public and in a less controlled and predictable consumer environment. In this case, in addition to low-cost, hydrogen sensors need to be robust, reliable, accurate and resistant to changes in ambient conditions which are typical of the sensors service environment. Independent assessment and demonstration of the

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proper performance of such devices can increase consumer confidence in the safety of hydrogen thereby increasing its acceptance and ultimately contributing to facilitating a transition to a hydrogen-inclusive economy.

Hydrogen sensors are devices which transform the concentration of hydrogen into an electrical signal. Detection occurs by interaction of hydrogen with the sensor's receptor (or sensing element) changing some of its inherent properties. 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 semiconductive metal-oxide sensors. A brief description of each of these sensing technologies is given in Section 2. Samples of all these types were procured and tested and their performance assessed based on the results from the following selected tests:

- Accuracy test
- Measuring range test
- Detection limit test
- Cross sensitivity to carbon monoxide test
- Ambient temperature test
- Ambient relative humidity test
- Ambient pressure test

While these tests were proposed as being of interest by the car manufacturers further tests, including response and recovery time tests, were also identified as being important and are planned as part of a future testing campaign.

Tests 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. The test protocol and the facility used to perform these tests have been described in Part I of this series. The performances of different 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. While preliminary performance assessment tests on commercially available hydrogen sensors have been reported [6], to the author's knowledge, this is the only study of its kind in which several sensors of different types have been directly compared for such a wide range of performance tests.

2. Sensor types tested

2.1. *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. One pellistor is coated in a catalyst material which selectively catalyses 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

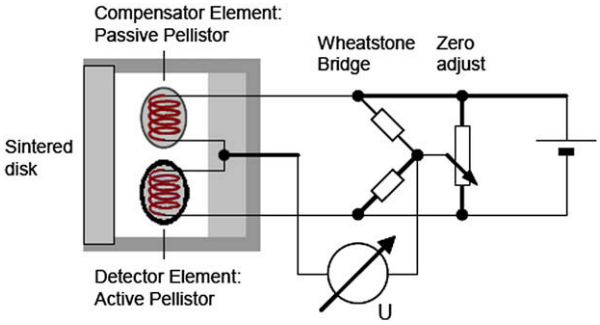

Fig. 1 – Schematic of a typical catalytic type combustible gas sensor [7].

through the circuit to promote the oxidation reaction. Hydrogen is oxidised 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.

2.2. *Electrochemical hydrogen sensors*

These sensors generally consist of three electrodes, an electrolyte and a semi-permeable membrane which is selective to hydrogen diffusion, as depicted in Fig. 2. Hydrogen is oxidised at the surface of the sensing electrode which consists of a catalyst, such as platinum:

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

An oxidation reaction occurs at the counter electrode:

$$O_2 + 4H^+ + 4e^- \rightarrow 2H_2O$$

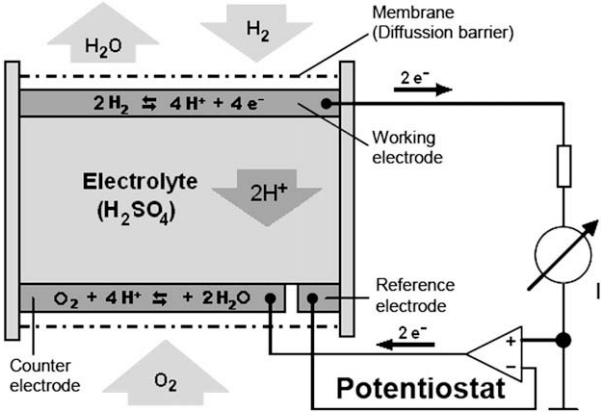

Fig. 2 – Schematic of an electrolytic type hydrogen sensor [7].

These reactions cause a potential difference between the electrodes and H_2 concentration is correlated with this potential difference by a non-linear relationship. A third, reference electrode is added to the cell to improve repeatability and stability of measurements. The principle of operation is demonstrated in Fig. 2. 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. The influence of polarisation phenomena on the counter electrode is thus suppressed.

Electrochemical hydrogen sensors are widely available commercially and current research relates to electrode development [8], electrolyte development [9], improved sensitivity and faster response times [10]. 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. MOx hydrogen sensors

The abbreviation MOS is routinely used for two types of sensors with completely different detection principles, namely metal-oxide semiconductor sensors and metal-oxide semiconductor sensors. To avoid confusion and misunderstanding these sensors are differentiated here.

Metal-oxide semiconductor sensors have a structure consisting of three layers; a metal layer (M), an insulator layer (I) and a semiconductor layer (S). In most cases the insulating layer is formed by an oxide (O) leading to the abbreviation MOS. This class of sensor works on the principle of charge building and changing of the work function of the sensing layer material which is usually some noble metal or noble metal alloy e.g. palladium based alloys. This MOS structure may work as a capacitive sensor, a MOS-FET transistor or a Schottky diode.

On the other hand in metal-oxide semiconductor sensors the active element of the sensor is an oxide layer, usually tin oxide, which has semiconductive properties. The accepted detection mechanism [11] 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. In this work only metal-oxide type sensors were tested and the abbreviation MOx is used to refer to this type of sensor.

All MOx sensors tested have a heated metal-oxide layer with semiconductive properties onto which hydrogen adsorbs (as illustrated in Fig. 3). Adsorption of hydrogen depends on the specific area, particle size and porosity of the metal-oxide material as well as the thickness of the sensing film [12]. An important parameter in governing the sensitivity of metal-oxide sensor is the surface to volume ratio. Reduction of the metal-oxide grain size increases their sensitivity [13]. MOx sensors are small, easily mass produced and low-cost, nonetheless solid state metal-oxide sensors are reported to have numerous disadvantages including low selectivity and long response times [14].

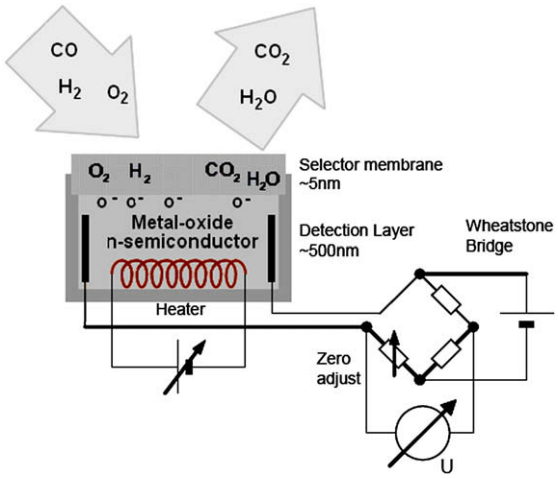

Fig. 3 – Schematic of a MOx type chemical sensor [7].

2.4. Thermal conductivity hydrogen sensors

Hydrogen gas has the highest thermal conductivity of all known gases (186.9 mW m^{-1} K^{-1} compared to 26.2 mW m^{-1} K^{-1} for air, both at 298 K and 101.325 kPa [15]). Thermal conductivity sensors exploit this property for detection and monitoring of hydrogen. In principle thermal conductivity sensors consist of two identical cells connected into a Wheatstone bridge circuit as shown in Fig. 4. A reference gas flows through the reference cell and the test gas containing hydrogen flows through the measuring cell. An increase in the hydrogen concentration in the test gas causes a change in the sensor temperature which changes the resistance of the element and causes a measurable imbalance in the Wheatstone bridge.

However most thermal conductivity sensors have a simpler design, avoiding the use of a reference cell as illustrated. Measurement is then based solely on the heat lost to the test gas with a reference point being set under defined ambient conditions in the absence of hydrogen. In this case the electrical connection is similar to that shown for the MOx sensor in Fig. 3. Thermal conductivity hydrogen sensors are commercially available and while they are unable to detect low concentrations of hydrogen they offer a dynamic measuring range up to 100 vol% hydrogen (i.e. they do not require the presence of air/oxygen to operate [16]). They are reported to suffer less from long term drifts and are not prone to contamination like catalytic and MOx sensors. For these

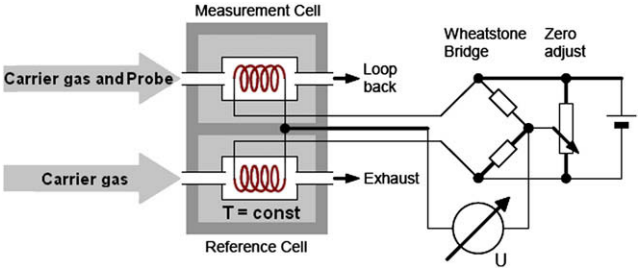

Fig. 4 – Schematic of a thermal conductivity type sensor [7].

reasons they have also been proposed as suitable hydrogen sensors in safety applications such as hydrogen detection in vehicles [17,18].

3. Results

A test protocol has been developed for testing hydrogen safety sensors aimed for use in future hydrogen fuelled vehicles using a facility specially designed for this purpose [15]. The test protocol was verified by testing and evaluating the performance of commercially available sensors. Tests were performed under various ambient conditions typical of those expected during the service life of such sensors. Hydrogen sensors were procured based on the results of market surveys performed in 2006 and 2007 with the purpose to investigate the performance and types of hydrogen sensors which are commonly available. 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.

The available hydrogen sensors were all tested according to the same test protocol and under similar ambient conditions. This allows a direct comparison to be made not only between the performances of individual sensors but also between sensors of different functional type. Sensors were tested strictly within the operating conditions given by the manufacturer. Seven different performance assessment tests were carried out on 39 hydrogen sensors.

During tests the sensor outputs were converted from electrical current and voltage signals to vol% H_2 in air using the sensor sensitivity relationship provided by the manufacturer. The performances of sensors were assessed by comparing the converted sensor output directly with the hydrogen concentration as measured by calibrated gas chromatography (GC). For safety reasons the maximum hydrogen concentration used in tests was limited to 2.0 vol% in air.

3.1. Catalytic sensors

17 catalytic sensors were procured of which 11 sensors were successfully tested. The remaining sensors either failed to give a signal or failed to respond to hydrogen and were deemed broken.

3.1.1. 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. Fig. 5 summarises 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.

3.1.2. Measuring range

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

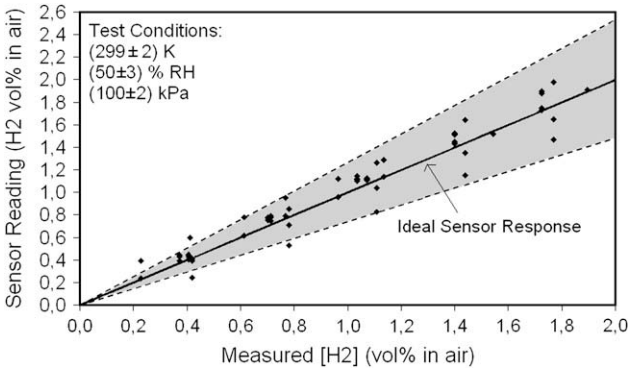

Fig. 5 – Catalytic sensors: accuracy of hydrogen concentration measurements. The readings from sensors at different hydrogen concentrations are shown and compared with the hydrogen concentration measured by gas chromatograph (represented on the graph as the Ideal Sensor Response).

3.1.3. Detection limit

Seven of the catalytic sensors yielded a well defined step in sensor output in the presence of 0.03 vol% H_2. The remaining sensors only yielded such a well defined step in their output at higher hydrogen concentrations reported in Table 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%.

3.1.4. Cross sensitivity to CO

Some catalytic sensors tested showed a significant cross sensitivity to carbon monoxide. As shown in Table 1 sensors

Table 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).

Sensor	Detection 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

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.

3.1.5. *Ambient parameters*

The influence on sensor output resulting from changes in temperature, pressure and relative humidity are summarised in Fig. 6. It was found that pressure and relative humidity had no influence on sensor reading when compared with the hydrogen concentration measured by the GC. Changes in temperature had only a modest effect on catalytic sensor response.

3.2. *MOx sensors*

Nine MOx sensors were procured and of these only four sensors showed a response to the presence of hydrogen and could be successfully tested. The remaining sensors showed either no response to the presence of hydrogen or no response to changes in hydrogen concentration.

3.2.1. *Accuracy of response*

As can be seen from Fig. 7, metal-oxide semiconductive type sensors were less accurate in their measurement of hydrogen concentration compared with catalytic type sensors. MOx sensors consistently overestimated the actual hydrogen concentration typically between 50 and 200%. Hysteresis and memory effects in MOx sensor response were also observed (see Fig. 8), 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.

3.2.2. *Measuring range*

MOx 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. 7).

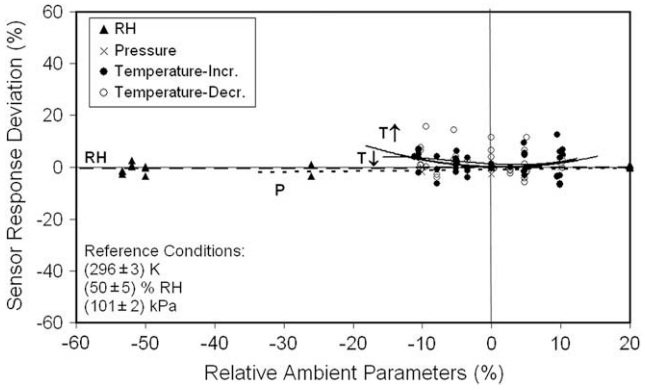

Fig. 6 – Catalytic sensors: deviation of response to hydrogen from the response at the reference conditions as a function of changes in ambient temperature, pressure and relative humidity.

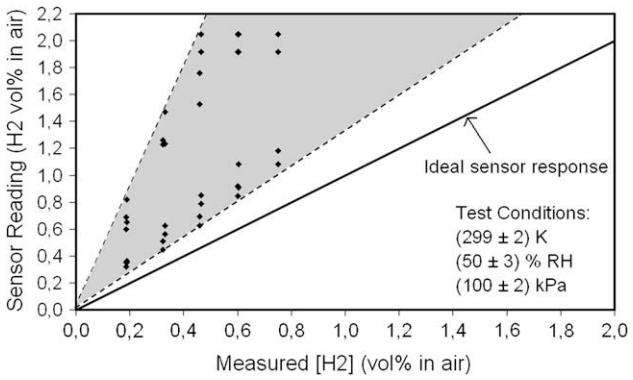

Fig. 7 – MOx sensors: accuracy of hydrogen concentration measurements. The readings from sensors at different hydrogen concentrations are shown and compared with the hydrogen concentration measured by gas chromatograph (Ideal Sensor Response). Note the consistent overestimation of the actual hydrogen concentration by all the MOx sensors tested.

3.2.3. *Detection limit*

Detection limit and cross sensitivity data for MOx sensors are given in Table 2. All MOx 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%.

3.2.4. *Cross sensitivity to CO*

As seen from Table 2 all the MOx sensors tested showed no reaction to CO up to concentrations of 0.3 vol%.

3.2.5. *Ambient parameters*

Ambient parameter tests performed on MOx 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 MOx sensors tested. Their dependence on ambient parameters is shown in Fig. 9. However, in many cases the sensor response had reached its maximum value thereby

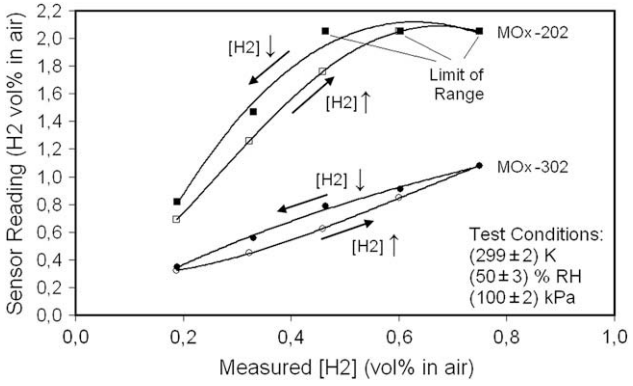

Fig. 8 – Hysteresis behaviour shown by two different MOx sensors during accuracy of response test.

Table 2 – MOx 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.

Sensor	Detection 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

hiding further increases in sensor reading due to increased humidity or decreased temperature. For example sensor readings from MOx-201 and MOx-202 had already reached their maximum value (2.05 vol%) for a gas mixture containing only 0.35 vol% H_2 with relative humidity of 30% and 50% respectively (see Fig. 9 in Ref. [16]).

3.3. *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.

3.3.1. *Accuracy of response*

The accuracy of electrochemical sensors was lower than other sensor types tested and is highlighted in Fig. 10 which shows the large variation in the response from the electrochemical sensors at each hydrogen concentration.

3.3.2. *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. 11 which shows the response of four identical electrochemical sensors tested under identical

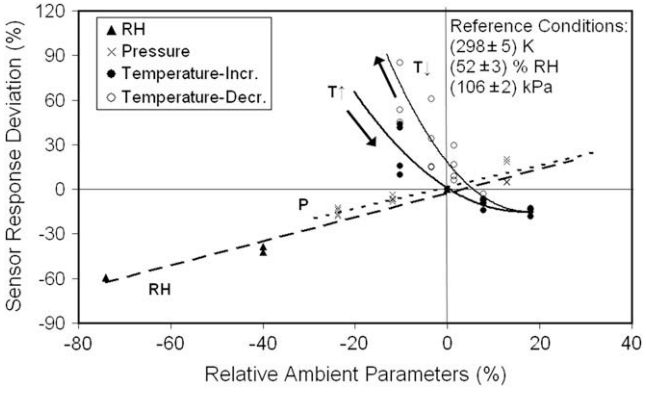

Fig. 9 – MOx sensors: deviation of response to hydrogen from the response at the reference conditions as a function of changes in ambient temperature, pressure and relative humidity. Note the larger scale on the sensor response deviation axis compared with Figs. 6, 12 and 14.

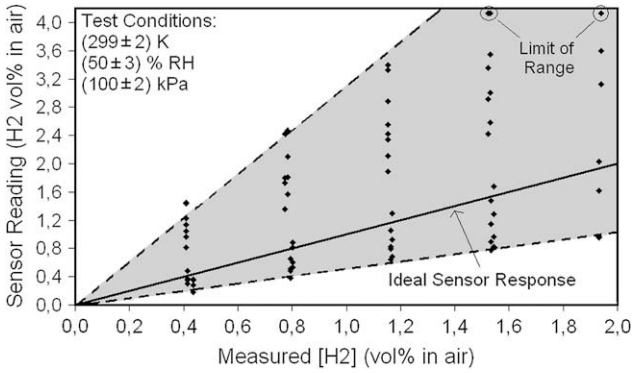

Fig. 10 – Electrochemical sensors: accuracy of hydrogen concentration measurements. The readings from sensors at different hydrogen concentrations are shown and compared with the hydrogen concentration measured by gas chromatograph (Ideal Sensor Response).

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.

3.3.3. *Detection limit*

Table 3 summarises 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% H_2 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%.

3.3.4. *Cross sensitivity to CO*

The observed cross-sensitivity of some sensors to CO was high, as can be seen from Table 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.

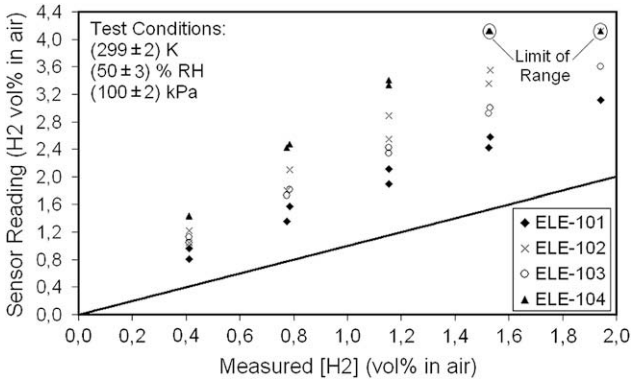

Fig. 11 – Response from four identical electrochemical sensors at different hydrogen concentrations. Saturation of sensor response occurred at a reading of 4.125 vol%.

Table 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).

Sensor	Detection 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

3.3.5. *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 summarised in Fig. 12. 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).

3.4. *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.

3.4.1. *Accuracy*

The results from accuracy of response tests performed on the thermal conductivity sensors are plotted in Fig. 13. 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.

3.4.2. *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 behaviour was apparent.

3.4.3. *Detection limit*

Table 4 summarises 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%).

3.4.4. *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

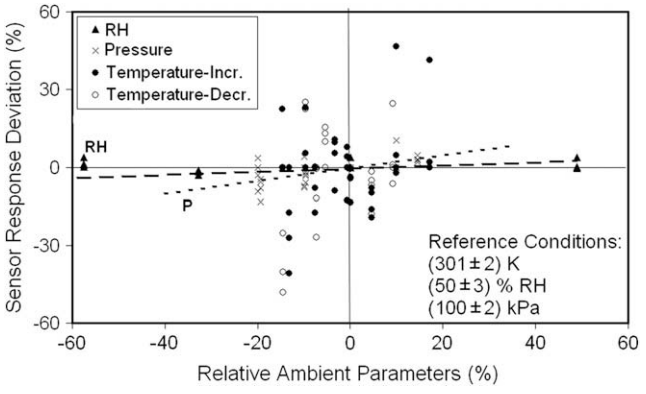

Fig. 12 – Electrochemical sensors: deviation of response to hydrogen from the response at the reference conditions as a function of changes in ambient temperature, pressure and relative humidity.

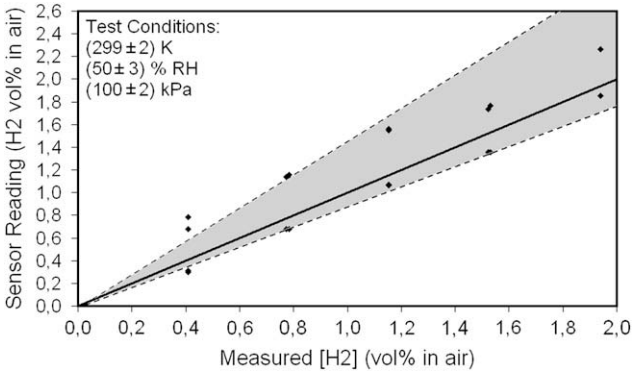

Fig. 13 – Thermal conductivity sensors: accuracy of hydrogen concentration measurements. The readings from sensors at different hydrogen concentrations are shown and compared with the hydrogen concentration measured by gas chromatograph (Ideal Sensor Response).

Table 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).

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

sensor TCD-201 to carbon monoxide was not possible because of damage to the sensor before this test.

3.4.5. *Ambient parameters*

The results from ambient parameter tests performed on thermal conductivity sensors are summarised in Fig. 14. 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. 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.

4. Discussion

4.1. *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.

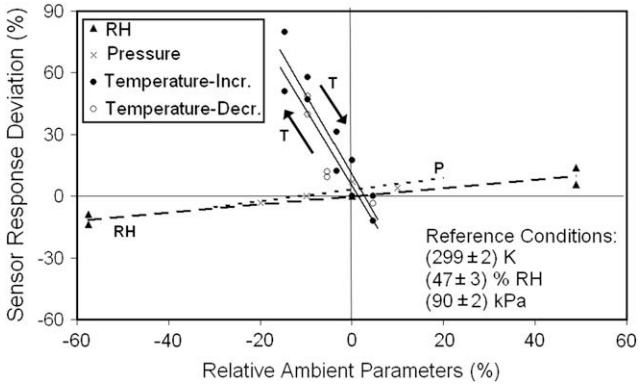

Fig. 14 – Thermal conductivity sensors: deviation of response to hydrogen from the response at the reference conditions as a function of changes in ambient temperature, pressure and relative humidity.

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.

4.2. *MOx sensors*

The detection limit of MOx sensors is low and all MOx sensors tested were capable of detecting a hydrogen concentration of 0.03 vol%. 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 MOx 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 MOx 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 MOx 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.

4.3. *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. 10 of Ref. [16]. 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. 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

Table 5 – The advantages and disadvantages noted for the various hydrogen sensor types tested based on observations during tests.

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

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.

4.4. *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 (0–100 vol% H_2). The detection limit was high in fact that one sensor failed to detect hydrogen at the 10% LFL level (0.4 vol%). 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.

5. Conclusions

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 summarised in Table 5.

While catalytic sensors showed the best performance during the tests their suitability for use as safety sensors in hydrogen fuelled 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 [19] and MEMS technology [20]). 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.

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