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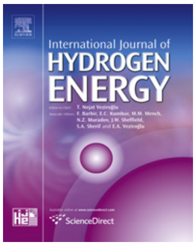

Identifying performance gaps in hydrogen safety sensor technology for automotive and stationary applications

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ABSTRACT

A market survey has been performed of commercially available hydrogen safety sensors, resulting in a total sample size of 53 sensors from 21 manufacturers. The technical specifications, as provided by the manufacturer, have been collated and are displayed herein as a function of sensor working principle. These specifications comprise measuring range, response and recovery times, ambient temperature, pressure and relative humidity, power consumption and lifetime. These are then compared against known performance targets for both automotive and stationary applications in order to establish in how far current technology satisfies current requirements of sensor end users. Gaps in the performance of hydrogen sensing technologies are thus identified and areas recommended for future research and development.

1. Introduction

An effective transition to a carbon-lean, hydrogen-inclusive energy economy requires technology improvements and breakthroughs in several disciplines including safety of applications. As a colourless, odourless and tasteless gas, the importance of using hydrogen detection devices is gaining recognition in alerting to the approach of hazardous hydrogen concentrations and dispelling public fear and concern associated with a change in energy technology. Public acceptance of hydrogen has a direct implication for the success of a transition to a hydrogen economy.

The risk of a hazardous event involving hydrogen can be mitigated through the use of reliable, robust and accurate hydrogen safety sensors which will facilitate the early detection of hydrogen before concentrations rise to hazardous levels. Development of hydrogen detection technologies and improvement of the performance of detection devices are essential to reducing the risks associated with hydrogen use and thus increasing safety. Independent, impartial and expert performance assessment of such devices can increase consumer confidence in the safety of hydrogen, thereby increasing its acceptance and ultimately facilitating the transition to a hydrogen-inclusive economy.

Hydrogen differs from other combustible gases in that it is the lightest of all gases and as such, diffuses rapidly from the source of a leak. It also has relatively wide flammability limits (4–75 vol% in air) and, at certain concentrations, an extremely

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low ignition energy. These considerations must be taken into account in the development of hydrogen safety sensors. Such sensors have been used and trusted for decades in industrial applications for the reliable and accurate detection of hydrogen under controlled industrial conditions [1–3]. However, if as expected, new hydrogen energy technologies enter the commercial market then hydrogen will inevitably be brought closer to the public in an environment which is less controlled and predictable. Close attention will need to be paid, not only to the detection capabilities of sensors but also to the performance requirements which will be imposed on these devices. Currently these performance targets, when available, are broadly described to cover a very wide spectrum of potential applications. Care should be taken to prudently set performance requirements of hydrogen sensors based on the specific purpose, location and ambient conditions of the sensor.

The purpose of this work is to investigate the number, range and types of hydrogen sensors which are available for purchase on the market and to inventorise the performance of these sensors based on the technical specifications provided by the sensor manufacturers. Where available, the technical requirements and performance targets which are specified by sensor users for both automotive and stationary applications are also provided. A comparison is made between the claimed performance specifications of sensors and the desired performance targets for a number of parameters (e.g. measuring range, response time, operating temperature range, power consumption, etc.). An analysis is carried out to identify areas where the claimed performance falls significantly short of the demands and suggestions are made to focus on particular areas which would benefit from additional R&D in order to close the existing performance gaps.

2. Hydrogen sensing principles

An extensive market survey has been performed to identify commercially available hydrogen sensors. A greater number and wider variety of hydrogen sensors were found when compared with similar market surveys previously performed [4]. Sensors considered were those capable of detecting and measuring the hydrogen concentration. Sensors used as in-line hydrogen-specific process monitors have been excluded from this study, as the focus here is on safety sensors. A total of 53 different models from 21 different manufacturers were included. The different working principles and the number of models of each type considered are summarised in Table 1. Of the 21 manufacturers, 9 were based in the US, 3 in Japan and the remainder were European manufacturers (primarily from the UK and Germany). It was found that most manufacturers tend to specialise in just one functional type however some offer detectors using different working principles. A brief description of the seven different working principles of the sensors surveyed is given here, although more detailed descriptions are available in the literature.

Table 1 – The number of each type of commercial hydrogen sensor surveyed and of manufacturers providing each type. Note that some manufacturers produce more than one functional type, so that the total shown here is not the sum of the last column.

Working principle	Abbreviation	No. of models	No. of manufacturers
Electrochemical	EC	19	9
Semiconductive metal-oxide	MOx	11	6
Catalytic	CAT	9	6
Combined technologies	COMB	7	4
Thermal conductivity	TCD	4	3
Metal-oxide semiconductor	MOS	1	1
Optical	OPT	2	1
Total		53	21

2.1. *Electrochemical sensors*

In electrochemical (EC) sensors [5] hydrogen is oxidized at the surface of a sensing electrode coated with a catalyst, such as platinum. This reaction gives rise to a potential difference with a reference electrode which can be correlated by a non-linear relationship with the hydrogen concentration. The counter reaction taking place at the cathode usually involves the reduction of oxygen, which must therefore be present for correct operation of this sensor type. Electrochemical sensors have a high sensitivity to hydrogen and consume very little power during operation which is particularly useful in some applications, e.g. automobiles. The sensitivity of electrochemical sensors decreases with time, mainly due to deterioration of the electrode catalyst.

2.2. *Semiconductive metal-oxide sensors*

Semiconductive metal-oxide (MOx) sensors [6] consist of a metal-oxide layer with semiconductive properties, usually doped tin oxide, deposited on a heater. The heater raises the temperature of the layer to the operating temperature (~500 °C). Hydrogen gas particles diffuse into the sensing layer and react with oxygen which is adsorbed on the semiconductive metal-oxide surface, thereby changing the layer's electrical resistance. The presence of oxygen is therefore also required for this sensor type. MOx sensors are small, low-cost and easily mass produced.

2.3. *Catalytic sensors*

Catalytic (CAT) sensors [7] consist of two thin platinum wires each embedded in a ceramic bead (pellistor) and connected to each other in a Wheatstone bridge. One pellistor is coated with a catalyst material which selectively catalyses the oxidation of hydrogen while the surface of the other pellistor is inertised. The pellistors are heated to around 500–550 °C and hydrogen is oxidized on the active bead surface causing an increase in temperature and an increase in the resistance of the platinum filament. The resulting imbalance of the Wheatstone bridge is linearly related to the hydrogen concentration. Catalytic sensors employ a well developed technology, but are not specific to hydrogen and will respond to any combustible gas. The presence of oxygen is essential to their operation.

2.4. *Thermal conductivity sensors*

Hydrogen gas possesses the highest thermal conductivity of all known gases. A thermal conductivity (TCD) sensor [8] consists of two identical cells connected via two arms of a Wheatstone bridge. Each cell consists of a heated metal element over which the test gas is streamed (measuring cell) and a reference gas is streamed (reference cell). A change in the hydrogen content of the test gas causes a change in the sensor temperature which varies the resistance of the element and causes a measurable imbalance in the Wheatstone bridge. Modern thermal conductivity sensors have a simpler design, avoiding the use of a reference cell. The measurement is 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. Thermal conductivity hydrogen sensors are less sensitive, but offer a measuring range up to 100 vol% hydrogen (and therefore in the absence of oxygen) and are not prone to poisoning like other hydrogen sensor types.

2.5. *Metal-oxide semiconductor sensors*

Metal-oxide semiconductor (MOS) sensors [9,10] 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 active layer, which is usually a noble metal or noble metal alloy, e.g. palladium based alloys. This MOS structure may work as a capacitive sensor, a MOSFET transistor or a Schottky diode. The MOS sensor included in this study is a MOSFET transistor. This type of technology can operate in the absence of atmospheric oxygen.

The acronym MOS is often used in the literature and by sensor manufacturers to describe both the triple layer metal-oxide semiconductor sensor just described and also metal-oxide sensors described above [11]. This conflicting use of the acronym often results in confusion and so for the purposes of this paper the acronym MOS is used exclusively for metal-oxide semiconductor sensors and the acronym MOx is used for metal-oxide sensors.

2.6. *Optical sensors*

Optical sensor (OPT) technology [12–17] has been of interest in the development of hydrogen sensors for some time. The principle of operation is based on the change in the properties of a sensitive layer following hydrogen absorption. For example, micro-mirror sensors detect changes in reflected light due to the absorption of hydrogen, while optical fibre hydrogen sensors may operate in two ways. They may either detect a change in light transmittance across an optical fiber due to a change in the absorption coefficient and refractive index, or exploit a special feature known as Surface Plasmon Resonance. Surface plasmons are surface electromagnetic waves that propagate in a parallel fashion along a metal/dielectric interface. Typical metals that support surface plasmons are silver and gold, but also other precious metals, including palladium and platinum. On absorption of hydrogen, the resulting change in the resonance energy of the surface plasmons may be detected. Optical sensors may operate in the absence of oxygen.

2.7. *Combined technology sensors*

Combined sensors (COMB) utilise a combination of different detection technologies, e.g. catalytic and thermal conductivity and for this reason they may have the added advantage of being able to measure hydrogen concentrations over a very broad range. The oxygen requirement of such sensors will correspond to that of the constituent sensor types.

3. Requirements on hydrogen sensors

3.1. *Application areas*

Hydrogen sensors have previously been developed for use in industrial applications, such as the production of ammonia or methanol for example, or for safety monitoring in nuclear power plants, where hydrogen is produced via the thermo-chemical splitting of water. However, the drive towards a hydrogen-inclusive economy has given increased impetus to the development of technologies for the detection and measurement of hydrogen concentration wherever hydrogen will be produced, stored, transported or used. Future contact of the public with hydrogen will be closest at the point of use, i.e. hydrogen powered vehicles or private stationary power systems. The employment of hydrogen sensors in such applications, which are outside the current window of experience associated with industrial hydrogen sensor use, is considered essential for the safety of persons and property. As an example, all major car manufacturers contacted by Liu et al. confirmed their use of or intention to use hydrogen sensors in their vehicles [18]. Furthermore BMW have reported the use of five hydrogen sensors [19] located in various enclosed spaces [20] in their Hydrogen 7 Series.

3.2. *Performance targets*

In sections 3.2.1–3.2.3 sensor performance targets known to the authors are detailed. These targets will then be compared with the specifications of a wide number of commercially available hydrogen sensors. In the graphs to follow in section 4, the most stringent of the three targets is shown in each case.

3.2.1. *ISO/DIS 26142*

Gas sensors should fulfil requirements described in general in EN IEC 60079-29-1: Gas detectors – Performance requirements of detectors for flammable gases [21], but for new fields of application hydrogen-specific performance requirements must be defined. Few targets have been published or indeed exist, but a specific new standard (ISO/DIS 26142 [22]) is under development for hydrogen sensors in stationary applications such as hydrogen vehicle refuelling stations. According to this draft standard, hydrogen sensors are to be tested in the condition ranges given in Table 2 and the observed deviation of the indication shall not exceed 20–50%.

3.2.2. *US DoE hydrogen sensor workshop*

A Hydrogen Sensor Workshop was held in 2007 as part of the United States Department of Energy (US DoE) Hydrogen, Fuel Cells & Infrastructure Technologies Program. Approximately 50 experts from industry, government, national laboratories, and universities contributed to the workshop. The purpose was to draft technical requirements and targets for hydrogen safety sensors for specific environments/applications. Tables 3 and 4 summarise the technical requirements and performance targets proposed at this workshop for automotive and stationary power systems respectively.

3.2.3. *Automotive end-users group requirements*

Direct input regarding the performance requirements for hydrogen sensors envisioned for use in vehicles was obtained from automotive manufacturers as part of the EU's Sixth Framework Programme Integrated Project – StorHy [11]. A survey was sent out to end users asking for details on their hydrogen safety sensor performance requirements. Four out of five car manufacturers replied to the survey and the performance indications received from the different end users were in good agreement with each other and are considered representative of the general needs of the automotive industry. The principal results of the survey are shown in Table 5.

3.3. *Further considerations*

For a specific application, it may not be necessary for a sensor to meet all of these targets, some of which may be considered too demanding for automotive applications. For example, the requirement that a sensor should operate at 0% relative humidity does not appear warranted under real conditions. It is also worth noting that the safe commercial use of sensors will not be assured without reliable, comprehensive and independent testing to validate the technical specifications of the manufacturers.

Further requirements exist for hydrogen sensors in automotive applications. These relate for example to air velocity and to integration of the sensor into a given system in terms of the power requirements in particular.

Table 2 – Technical performance requirements for hydrogen sensors for use in stationary systems according to ISO/DIS 26142 [22].

Parameter	Performance requirement
Measuring range	Up to 4 vol% H_2 in air min; survivability at 100%
Detection limit	<100 ppm
Response time (t_{90})	<30 s
Recovery time (t_{10})	<60 s
Ambient temperature	−20 to +50 °C
Ambient pressure	80–110 kPa
Ambient humidity	20–80% relative humidity
Accuracy	±25 or 50% depending on hydrogen concentration

Table 3 – Technical performance requirements for hydrogen sensors intended for use in automotive systems [23].

Parameter	Performance requirement
Measuring range	0–4 vol% H_2 in air; survivability at 100%
Response time (t_{90})	<3 s
Recovery time (t_{10})	<3 s
Ambient temperature	−40 to +125 °C
Ambient humidity	0–100% relative humidity

Another parameter which is extremely important is the cross-sensitivity. The response of all sensors is influenced more or less by interfering gases in the atmosphere and the extent of this interference depends on the sensor type and construction. Electrochemical sensors show cross-sensitivity to hydrocarbons, such as ethene, ethane and methanol, but also to trace gases such as CO, Cl_2, SO_2, H_2S and NOx. The signal of MOx sensors can be influenced by all reducible and oxidisable gaseous components, while catalytic sensors may show cross-sensitivity to other combustible gases, e.g. CH_4, CO or gasoline vapour. Sensors using combined technologies exhibit the cross-sensitivity of the constituent sensor types. MOSFET sensors do not show high cross-sensitivity to other gases, whereas thermal conductivity sensors show a signal due to the presence of other gases with a significantly different thermal conductivity to air (assuming this to be the reference gas), such as He, Ar, CH_4 or CO_2. Optical sensors may be influenced by gases that can adsorb on the surface of the sensor element, thereby reducing the sensitivity to hydrogen.

The influence of interfering gases can be reduced by technical measures (filter) and operation methods (sensing temperature) as well as through adjustment of the output signal if both the interfering gas and its influence on sensor response are known. In some cases, correction factors or procedures may be supplied by the manufacturers.

In addition, the presence of poisoning substances, which are those that permanently affect the sensitivity of a hydrogen sensor, must be avoided. These include very reactive gases such as HCl, O_3 or SO_2 and semi-volatile organic components like silanes, as well as polymerising compounds, sulphur, heavy metals and halogenated hydrocarbons.

Neither these additional requirements nor the accuracy have been included in this study because they are not reported in the majority of manufacturers' technical specifications with the consistency required to produce a comparative overview.

Table 4 – Technical performance requirements for hydrogen sensors intended for use in stationary power systems [23].

Parameter	Performance requirement
Measuring range	Up to 1 vol% H_2 in air (alarm limit)
Lower detection limit	<0.1 vol%
Response time (t_{90})	<30 s
Recovery time (t_{10})	<30 s
Durability/lifetime	3–5 years; calibration > lifetime
Accuracy	10%

Table 5 – Technical performance requirements desired by automobile manufacturers for hydrogen safety sensors.

Parameter	Performance requirement	Additional comments
Measuring range	Up to 4 vol% H_2 min; survivability at 100%	One car manufacturer expressed the need for a wider (unspecified) detection range
Detection limit	<0.1 vol%	Some car manufacturers accepted a detection limit of <0.2 vol%
Response time $t(90)$	<1 s	Some car manufacturers found <3 s sufficient
Recovery time $t(10)$	<1 s	One car manufacturer found <3 s sufficient while another found <30 s sufficient
Ambient temperature	−40 to +85 °C	Some manufacturers required an operating temperature range of −40 °C to +120 °C for sensors directly exposed to the operating temperature of an internal combustion engine
Ambient pressure	62–107 kPa	Pressure corresponding to a required altitude range of −400 to 4000 m
Ambient humidity	0–95% relative humidity	One manufacturer specified 0–100%
Power consumption	<1 W	Some manufacturers required <650 mW
Lifetime	6000 h	Discontinuous operation was deemed sufficient by all car manufacturers. One set a goal of 15 years
Overall accuracy	±5% of reading	This target was too restrictive for some car manufacturers and they proposed to replace it with a value of 5–10% of the lower flammability limit (LFL)

4. Declared performance of hydrogen sensors

The performance specifications for each sensor model considered were taken from the relevant on-line technical datasheets or obtained from the manufacturers' sales departments. The claimed performance specifications for selected parameters are classified by the sensor functional type and presented in graphical form. In this way it is possible to compare sensing technologies and analyse in how far each one is able to meet the performance requirements for various applications.

4.1. *Measuring range*

4.1.1. *Upper measuring limit*

A sensor upper measuring limit of 4.0 vol% H_2 (100% LFL in air) for automotive purposes and of 1.0 vol% H_2 (25% LFL) for stationary power system sensors were suggested at the US DoE workshop. Surveyed car manufacturers also required an upper limit of 4 vol%. While an upper limit for the sensor measuring range was given for all the hydrogen sensors surveyed, only a limited number of them specified the lower detection limit (LDL). Fig. 1 shows the upper measuring limit of all sensors and, when provided, the lower detection limit. A double ended arrow indicates when both upper and lower limits were given for a sensor model.

In general, the upper measuring limit of metal-oxide sensors tends to be the lowest, with all but one model having an upper limit below the target of 4.0 vol% H_2. The widest measuring range is exhibited by sensors employing combined technologies, with three of the models surveyed extending significantly beyond both the lower and upper limits of the target range. Indeed, one of the advantages of combining sensing technologies is that this may result in an extended measuring range. As with these combined technology models,

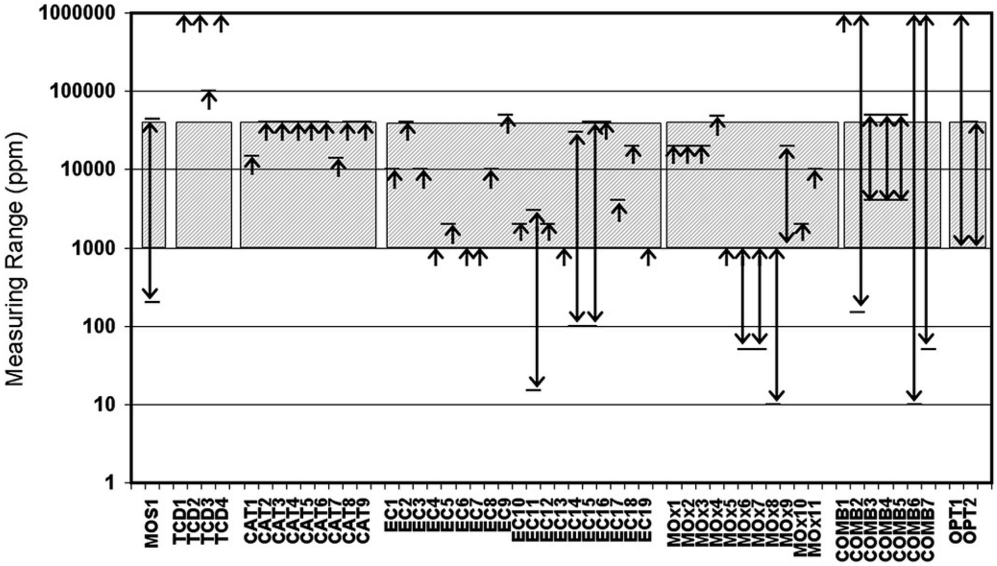

Fig. 1 – Sensor measuring ranges specified by manufacturers and grouped according to working principle. The shaded area indicates the target measuring range (0.1–4.0 vol% H_2) as proposed by car manufacturers for hydrogen sensors used in automotive applications. When a downward arrow is not shown, the lower detection limit was not specified by the manufacturer.

thermal conductivity sensors are also capable of measuring up to 100 vol% H_2 (and hence in the absence of oxygen), but though the lower limits of their measuring ranges are unspecified, their sensitivity to low concentrations of hydrogen (<0.4 vol%) has previously been shown to be poor [24]. The two optical sensors considered cover the target measuring range, with one model also capable of detecting up to 100 vol% H_2.

4.1.2. *Lower detection limit*

The sensitivity of hydrogen sensors is a very important parameter and specification of the minimum hydrogen concentration detectible, or the lower detection limit, is a convenient indication of a sensor's ability to detect low concentrations. Although the draft ISO standard proposes testing procedures for lower concentrations (<100 ppm), a detection limit of <0.1 vol% H_2 is given both by car manufacturers and the US DoE (for stationary applications). Despite the importance of this parameter the detection limit was only specified for 16 of the 53 sensor models surveyed (see Fig. 1). Of these, the LDL of three combined technology sensors failed to meet the target of <0.1 vol%.

4.2. *Response and recovery times*

The time taken for a sensor to respond to the presence of hydrogen is another critical property. It is imperative that sensors respond and alert quickly to the presence of hydrogen in air. Response time (t_{90}) is generally expressed as the time interval between the instantaneous variation from clean air to a hydrogen gas mixture and the time when the sensor response reaches 90% of the final (maximum) indication. Likewise the recovery time (t_{10}) is generally expressed as the time interval between the instantaneous variation from hydrogen gas mixture to clean air and the time when the sensor response reaches 10% of the initial (maximum) indication.

Fig. 2 shows response times of available hydrogen sensors as specified by the manufacturer and grouped according to working principle. Response times are provided for nearly all sensors surveyed. Recovery times are only provided for 7 models and these are also shown in Fig. 2. The MOSFET sensor comes closest to meeting the 1 s target and a further 7 sensor models (electrochemical and semiconductive metal-oxide) have a response time of 5 s or less. However, electrochemical sensors generally have longer response times (>30 s) with over half of the models considered taking >60 s to respond. All MOx sensors respond in 20 s or less, due perhaps to their small size and to the fact that this type of sensor is heated to a typical operating temperature of 500 °C.

4.3. *Temperature range*

The desired operating temperature range of a hydrogen sensor should be defined by the expected environmental conditions of the specific application. The upper temperature limit requirement stipulated by the car manufacturers surveyed therefore varied somewhat depending on the exact location of the hydrogen sensor in the vehicle. An upper operating temperature of +85 °C was considered sufficient for sensors located in the passenger compartment while those sensors located in the vicinity of the combustion engine require an upper operating temperature of +120 °C. It is worth noting here that a higher upper operating temperature may also be required for sensors located in the vicinity of fuel cells, although the operating temperature of a fuel cell varies depending on the nature of the electrolyte. The US DoE workshop agreed a slightly higher operating temperature of +125 °C with no distinction of different requirements for sensors used in different locations. The draft ISO standard proposes a markedly lower value of 50 °C as the maximum temperature for testing hydrogen sensors for use in stationary applications.

Fig. 3 shows the operating temperature ranges of available hydrogen sensors as specified by the manufacturer and

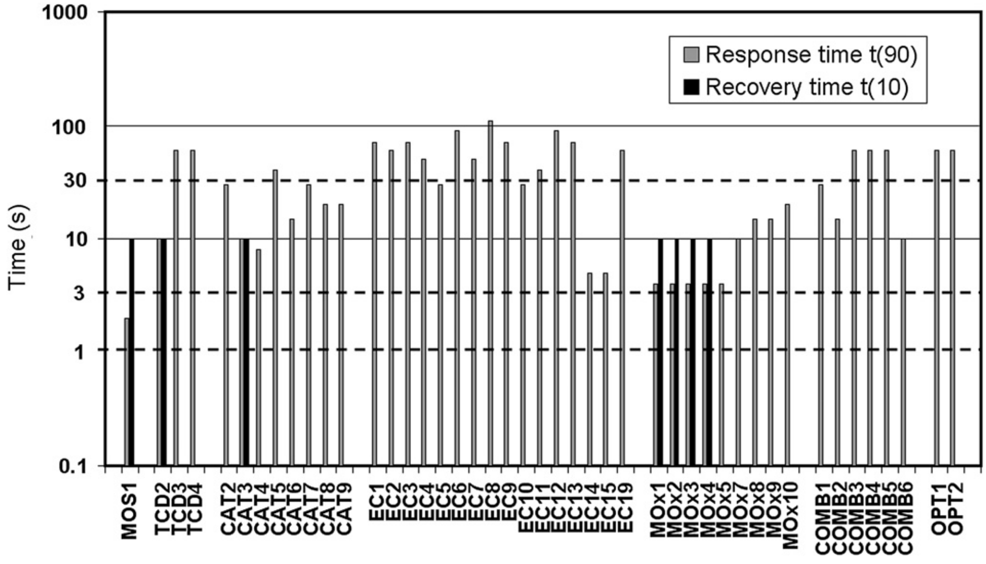

Fig. 2 – Sensor response times and recovery times (when provided) specified by manufacturers and grouped according to working principle. Target response and recovery times are 30 s for stationary applications, and both vary from 1 to 3 s for automotive applications. These target times are indicated in the graphic by the dashed lines.

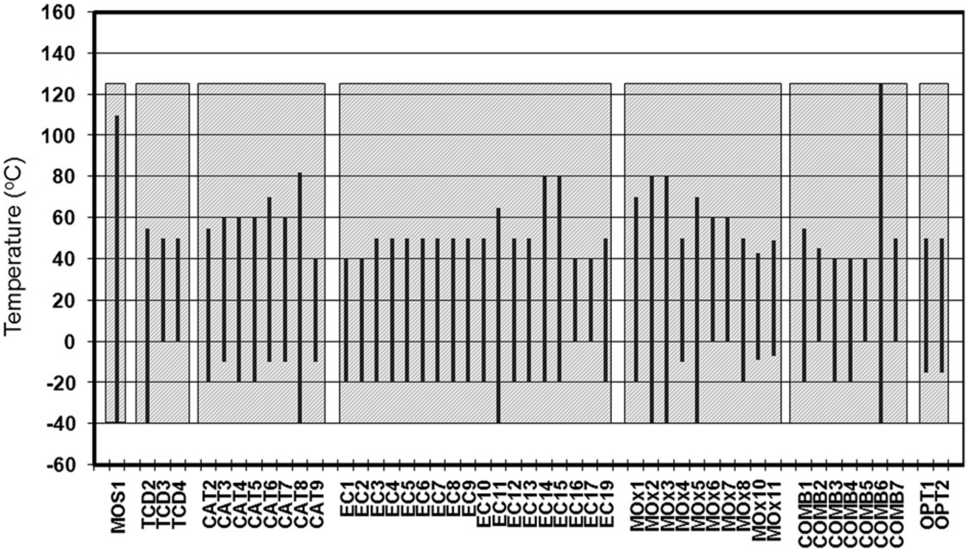

Fig. 3 – Sensor operating temperature ranges specified by manufacturers, grouped according to working principle. Also indicated in the graphic (shaded area) is the widest target operating temperature range as agreed at the US DoE Hydrogen Sensor Workshop for hydrogen sensors intended for use in automotive applications.

grouped according to working principle. The shaded areas in the figure indicate the widest target temperature range proposed at the US DoE workshop, i.e. −40 °C to +125 °C. From Fig. 3 it is clear that only one combined technology sensor meets this requirement. With an operating temperature range of −40 °C to +110 °C, the MOSFET sensor also comes close to fulfilling this requirement. Perhaps unsurprisingly given their method of operation, thermal conductivity sensors have a narrow temperature range however one was capable of operating at −40 °C. Some catalytic, electrochemical and semiconductive metal-oxide sensors were capable of working up to +80 °C, just below the operating target suggested for vehicle compartment sensors. Only one electrochemical sensor is capable of operating down to the lower temperature limit of −40 °C.

While the variation in the environmental temperature operating ranges of different commercial sensors is quite large, in only a few cases was additional information given by sensor manufacturers concerning the influence of temperature on sensor response.

4.4. *Pressure range*

Arguably the most demanding application for hydrogen sensors with respect to the operating pressure range will be in vehicles. Fig. 4 shows the operating pressure ranges, when provided, of available hydrogen sensors as specified by the manufacturer and grouped according to working principle. The figure also shows the target operating pressure range desired by automobile manufacturers, 62–107 kPa, which compares with that proposed in the draft ISO standard of 80–110 kPa for stationary applications.

As in the case of temperature, additional information was rarely supplied by manufacturers concerning the influence of pressure on sensor response. However, changes in pressure, and therefore in the amount of hydrogen per unit volume, can alter the output of the sensor even though the relative hydrogen concentration (the concentration expressed relative to the other components in the mixture, e.g. 2 vol% H_2 in air) remains the same. This problem may be overcome by incorporating a pressure sensor in the device and compensating for changes in pressure.

According to the specifications given, no sensor model meets the very demanding low pressure target, while all models but one are capable of operating to at least 110 kPa. For sensors used in automotive applications where driving at high altitudes in mountainous regions can be expected, it is particularly important that they be capable of operating reliably at low pressure.

Noteworthy from Fig. 4 is the very limited operating pressure range of electrochemical sensors when compared with other sensor types. This may be explained by the possible leakage of liquid electrolyte from the sensor following exposure to low pressure, resulting in permanent damage.

4.5. *Ambient humidity range*

Automobiles are also a demanding application for hydrogen sensors with respect to the humidity range. All but one of the car manufacturers surveyed demanded an operating relative humidity (RH) range of 0–95%. This range may be considered lenient as a relative humidity greater than 95% is feasible under specific meteorological conditions even inside a vehicle, and condensation cannot always be excluded. This view is reflected in the 0–100% operating range target proposed for automotive applications by the US DoE. As with the other ambient parameters – temperature and pressure – the influence of humidity on sensor response was rarely specified by the manufacturers.

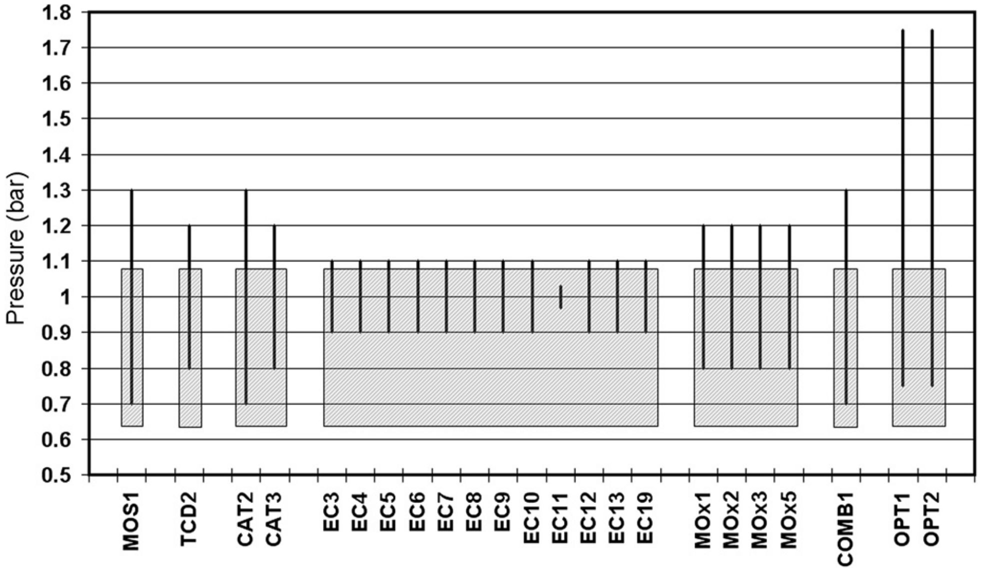

Fig. 4 – Sensor operating pressure ranges specified by manufacturers and grouped according to working principle. The shaded area in the graph indicates the widest target operating pressure range (62–107 kPa) demanded by automobile manufacturers.

Fig. 5 shows the operating relative humidity ranges (when provided) of available hydrogen sensors as specified by the manufacturer and grouped according to working principle. The figure also shows the widest target operating relative humidity range as 0–100% RH. Only three sensors (one catalytic and two semiconductive metal-oxide) were able to work up to 100% RH, but non-condensing conditions were specified by the manufacturers.

Some sensor types, notably electrochemical and semiconductive metal-oxide sensors, are restricted in their operation under very dry and very humid conditions. For electrochemical sensors operation at very low or very high humidity can result in a change in the water content of the electrolyte affecting the operation of the cell. At high humidity this can result in an increase in the volume of the electrolyte, causing the cell to leak. An increase in moisture content can also cause the electrolyte to freeze more quickly. At low humidity the acid content of the electrolyte can rise, causing crystallisation and or corrosion of seals. Operation at 100% RH can be difficult due to condensation of water on the sensor's active surface hindering interaction with hydrogen gas.

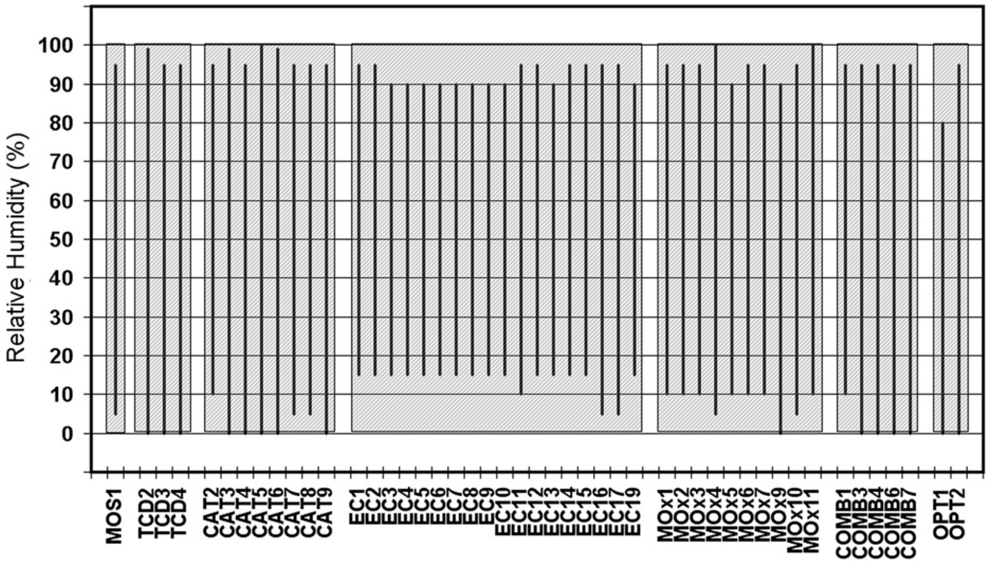

Fig. 5 – Sensor operating relative humidity ranges specified by manufacturers and grouped according to working principle. The shaded area in the graph indicates the widest target operating relative humidity range (0–100%) as proposed for hydrogen sensors used in automotive applications at the US DoE Hydrogen Sensor Workshop.

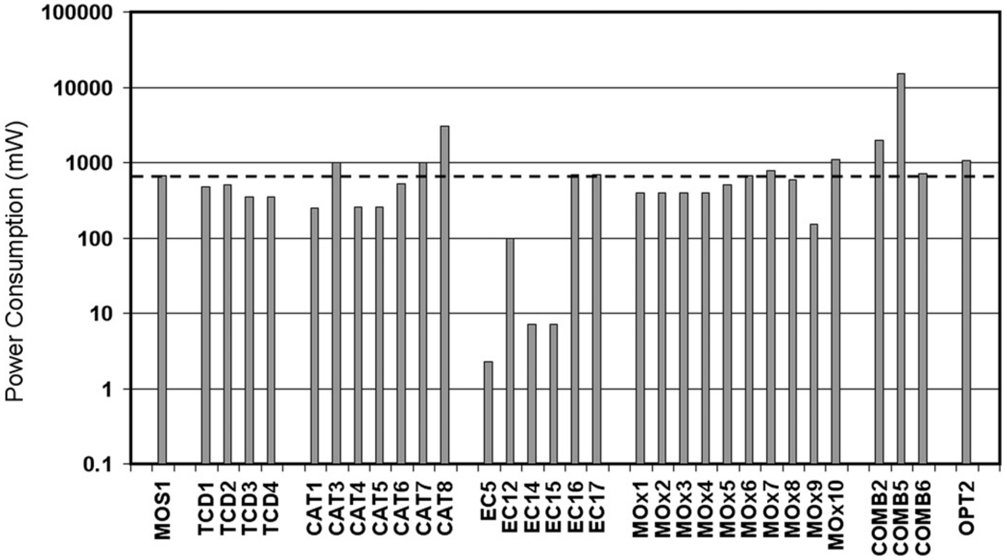

Fig. 6 – Sensor power consumption specified by manufacturers and grouped according to working principle. The dashed line indicates the most stringent power consumption target given by car manufacturers of 650 mW.

4.6. *Power consumption*

The power consumption of a sensor during operation must be considered if sensors are to be operated continuously. This is particularly relevant in applications where power is supplied to the sensor by a battery as is the case in vehicles. Low power consumption is essential to prevent rapid draining of the vehicle's battery. Fig. 6 shows the power consumption of a number of hydrogen sensors when this information is provided by the manufacturer. The lowest desired power consumption target (650 mW) is also indicated by the dashed line in the figure. The power consumption of electrochemical sensors was not provided in most cases. When it was, however, the power consumed by this type of sensor is, for the most part, substantially lower than for other sensor types. However, there are a number of models of the remaining sensor types (with the exception of the combined technology, MOSFET and optical sensors) which meet the power consumption target indicated by car manufacturers.

4.7. *Lifetime*

The lifetime provided by manufacturers for their particular sensors may have different definitions. It may be measured during continuous use and defined as the time after which the sensor response has reduced by a certain value (e.g. 10%) under the specified operating conditions. Another possibility is that the storage or shelf life of the sensor is provided. In most cases the lifetimes provided by the manufacturers for the hydrogen sensors considered in this survey were specified as operating lifetimes. Fig. 7 shows the operating lifetime of a number of hydrogen sensors, as specified by the manufacturer and grouped according to working principle. The highest target lifetime (43,800 h equivalent to 5 years continuous operation) for stationary applications is also indicated by the dashed line in the figure. Immediately obvious from Fig. 7 is the relatively short lifetime of electrochemical sensors compared with other sensor types. At least one model of the remaining sensor types is capable of meeting and in some cases exceeding this lifetime target. The 15 year (equivalent to >130,000 h) lifetime target desired by one car manufacturer is not achieved by any sensor considered in this survey.

5. Discussion

The performance specifications for each type of technology over all the models surveyed are summarised in Table 6. Considering available performance targets and the above-outlined capabilities of commercially available hydrogen sensors, shortcomings of current detection techniques are then highlighted in Table 7.

Only the combined technology sensor covers the widest target operating temperature range. While all the remaining sensor types fall short of the upper temperature limit, only the optical type fails to meet the lower limit.

No sample type meets the lower operating pressure target, but all types of technology allow for detection of hydrogen at the upper end of the target range.

Both MOSFET and electrochemical sensors fail to conform to the humidity requirements, while the thermal conductivity, combined technology and optical sensors surveyed cannot operate at the 100% humidity target, according to the specifications supplied.

Where the lower detection limit is given, the measuring range requirements are satisfied by all sensor types. For thermal conductivity and catalytic sensors however, the detection limit is not specified – surprising given the importance of this parameter – although they do meet the upper measuring limit target.

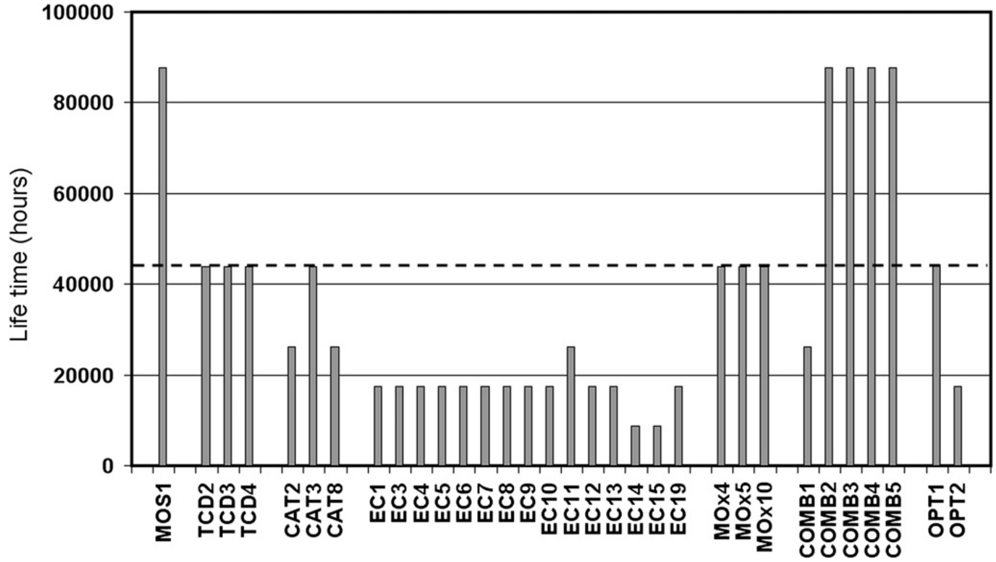

Fig. 7 – Sensor expected operating lifetime as specified by manufacturers and grouped according to working principle. The dashed line indicates the highest lifetime target for stationary application sensors (43,800 h), set at the US DoE hydrogen sensor workshop.

Only one sensor type – MOSFET – meets the stringent 3 s response time target, while no sensor conforms to the same recovery time target (though this data was not supplied for three of the sensor types). It is worth observing here that reported response and recovery times may be dependent on the measurement method used and that a truly informative comparison between the values specified by the manufacturers requires that the same experimental procedure be followed in each case.

The power consumption requirement of 650 mW was not met by MOSFET, combined technology or optical sensors, while only the electrochemical sensors did not satisfy the lifetime target.

While these findings are based on the declared performance, experimental assessment of commercially available hydrogen sensors [11] has shown significant discrepancies between the technical specifications of the manufacturer and the actual performance. In some cases the performance was even found to vary greatly between identical sensors.

It has also been demonstrated experimentally that, depending on the sensor detection principle, ambient parameters – temperature, pressure and relative humidity – can have a large influence on sensor output [24]. However, this observed influence is rarely considered in the manufacturers' technical specifications, which usually stipulate only the operating range and not the variation in sensor response over that range.

These experimental findings emphasise the need for independent performance assessment of hydrogen safety sensors in order to verify the technical specifications of the manufacturers and to highlight insufficiencies in their testing procedures. Such impartial performance testing of hydrogen sensors is essential to their safe use and to the creation of public confidence in the safety of hydrogen.

Table 6 – Summary of performance data for each type of commercially available sensor considered in the market survey.[a]

Criteria	MOS		TCD		CAT		EC		MOx		COMB		OPT	
	Min	Max	Min	Max	Min	Max	Min	Max	Min	Max	Min	Max	Min	Max
Temperature range (°C)	−40	110	−40	55	−40	82	−40	80	−40	80	−40	125	−15	50
Pressure range (kPa)	70	130	80	120	70	130	90	110	80	120	70	130	75	175
Humidity range (% RH)	5	95	0	99	0	100	10	95	0	100	0	95	0	95
Measuring range (ppm)	200	44,000	–	100%	–	40,000	15	50,000	10	48,000	10	100%	1000	100%
Response time (t_{90} s)	2		10		8		5		4		10		60	
Recovery time (t_{10} s)	10		10		10		–		10		–		–	
Power consumption (mW)	675		350		256		2.25		150		720		1080	
Lifetime (h)	87,600		43,800		43,800		26,280		43,800		87,600		44,000	

a Where omitted, data were not available from the manufacturer's specifications.

Table 7 – Indications where commercially available sensors meet or fail to meet current performance targets.

Criteria	Target		MOS		TCD		CAT		EC		MOx		COMB		OPT	
	Min	Max	Min	Max	Min	Max	Min	Max	Min	Max	Min	Max	Min	Max	Min	Max
Temperature range (°C)	−40	125	✓	×	✓	×	✓	×	✓	×	✓	×	✓	✓	×	×
Pressure range (kPa)	65	107	×	✓	×	✓	×	✓	×	✓	×	✓	×	✓	×	✓
Humidity range (% RH)	0	100	×	×	✓	×	✓	✓	×	×	✓	✓	✓	×	✓	×
Measuring range (%)	0.1	4.0	✓	✓	–	✓	–	✓	✓	✓	✓	✓	✓	✓	✓	✓
Response time (t_{90} s)	3		✓		×		×		×		×		×		×	
Recovery time (t_{10} s)	3		×		×		×		–		×		–		–	
Power consumption (mW)	650		×		✓		✓		✓		✓		×		×	
Lifetime (h)	43,800		✓		✓		✓		×		✓		✓		✓	

6. Conclusions

The purpose of this work has been to summarise the current state of the market with respect to hydrogen sensing technologies and to identify disparities between existing performance targets for hydrogen safety sensors and the actual performance specifications given for commercially available sensors, with the intention that this should then help to direct future research and development in the area.

The principal hydrogen sensing technologies recognised in this survey are listed in Table 1 and the targets against which their performance is compared are detailed in Tables 2–5. A summary of the ability of each type of technology to meet these performance targets is given in Table 7. On this basis, it may be concluded that further research and development is required in a number of areas:

1. The upper limit of the operating temperature range of all samples surveyed, but one, falls short of the target and the extension of this range to higher temperatures is thus desirable for all types of technology. It is worth bearing in mind however that the required operating temperature range is dependent on the location of the sensor and the relatively high upper limit of 125 °C is in practice relevant only to sensors that are to be used in the vicinity of the engine, whereas sensors located elsewhere need not conform to such a stringent target.
2. The operating pressure range must be extended to lower pressures, as none of the technology types surveyed was capable of operating at the 62 kPa pressure limit desired by automobile manufacturers. As this pressure corresponds to an altitude of approximately 4000 m, it is not an unreasonable requirement for automotive applications.
3. For many of the sensor types, the maximum of the operating relative humidity range was 95%, as compared to the target set at the DoE hydrogen sensor workshop of 100%, which is also a realistic requirement for automotive applications. Indeed, under certain conditions it may be necessary for a sensor to operate in the presence of condensation, which none of the samples surveyed is capable of doing.
4. Both the response and recovery time capabilities of currently available sensor technologies fall short of the targets set by car manufacturers and at the DoE workshop. Both need to be reduced for all sensor types surveyed and a standardised test procedure is also essential in order to allow for a level comparison – examples of such a procedure are proposed in the draft ISO standard [22].
5. Though the 5 year lifetime target was met by all except one sensor type surveyed, the 15 year requirement of one car manufacturer is far beyond current capabilities. However, as the cost of hydrogen sensors decreases, as is likely to happen over time, a shorter lifetime may be tolerated.

As regards the remaining parameters surveyed, the power consumption is generally satisfactory for most sensor types, although reducing this is always desirable. The measuring range specifications satisfy requirements, although the lower detection limit is not always given. There are also a number of parameters, which were not addressed in this work due to the lack of available and consistent technical data, but which may be considered relevant to developments in sensor technology. These include accuracy, air velocity, cross-sensitivity to interfering and poisoning agents, as well as system integration of the sensor.

It is important to note that each sensor type has its own limitations, with no one technology meeting all of the requirements specified. In this context, the idea of combined technology sensors is particularly useful in that it allows for each method of operation to compensate for the other.

Finally, while these findings are based on the technical data provided by manufacturers, independent verification of such specifications is essential to the safe commercial use of hydrogen sensors. A hydrogen sensor performance assessment study [24] has revealed that changes in ambient conditions can have a huge influence on sensor output, which is rarely taken into account in technical datasheets. Accurate knowledge of the influence of these parameters is essential so that they may be considered with respect to each specific application.

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