

RESPONSE TIME MEASUREMENT OF HYDROGEN SENSORS

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ABSTRACT

The efficiency of gas sensor application for facilitating the safe use of hydrogen depends considerably on the sensor response to a change in hydrogen concentration. Therefore, the response time has been measured for five different-type commercially available hydrogen sensors. Experiments showed that all these sensors surpass the ISO 26142 standard; for the response times t_{90} values of 2 s to 16 s were estimated. Results can be fitted with an exponential or sigmoidal function. It can be demonstrated that the results on transient behaviour depend on both the operating parameters of sensors and investigation methods, as well as on the experimental conditions: gas change rate and concentration jump.

1.0 INTRODUCTION

Fast response to a change in gas composition is one of the key features for assessing the suitability of a sensor for hydrogen safety. Response time is a term commonly used to define the response speed of gas sensors that is relevant for many applications and therefore a subject of contemporary investigation. According to ISO 26142 [1] the time of response is defined as the time interval, with the sensor in a warmed-up condition, between the time when an instantaneous variation between clean air and the (hydrogen containing) test gas, is produced at the sensor inlet, and the time when the response reaches a stated percentage of the stabilised signal on the standard test gas. The time taken for a sensor to reach 90 % of the final indication (the response time or t_{90}), when exposed to a certain hydrogen concentration, shall be less than 30 s. These values for hydrogen sensor response may be considered by some customers as too long for application and actually, several hydrogen sensors have response times of only a few seconds. For example, sensor response times of less than 3 s and even less than 1 s are required in automotive applications [2,3]. It is obvious that short response times are the basis for an early alarming to avoid damages of humans or equipment in case of hydrogen leakage.

Precise measurements of fast response times require some experimental skills and efforts. The recording of a sensor dynamic behaviour can be misleading, e.g. because the measured change in signal depends not only on the intrinsic reaction of the gas sensing mechanism, but also on a delayed change in test gas concentration. The influence of different methods of determination and of specific arrangements are discussed in detail by Boon-Brett et al. [2]. From an experimental point of view, the results of investigation of sensor dynamic behaviour can be split in two parts, an extrinsic and an intrinsic time of response. The extrinsic time reflects the dynamic behaviour of test gas supply to the sensor inlet and of the data acquisition system for sensor signals, and can result in a certain delay. The intrinsic response time is determined by the physicochemical operating principle of the sensor element as a transducer of chemical composition into an electrical signal, and by the primary measurement circuit. Thus, for experimental investigation it is necessary to estimate the transient behaviour of the gas supply, whereas the electronic data collection time, which is supposed to be no more than a few microseconds, can be mostly neglected.

The aim of this paper is to present and evaluate the results of experimental measurements of hydrogen sensor response times under specified conditions. We discuss the extrinsic contributions of the facility to the transient response, as well as the intrinsic, sensor-related contributions to the sensor's response. Therefore, five different commercial sensors of different response behaviour were randomly chosen as examples for this investigation.

2.0 EXPERIMENTAL

2.1 Sensors

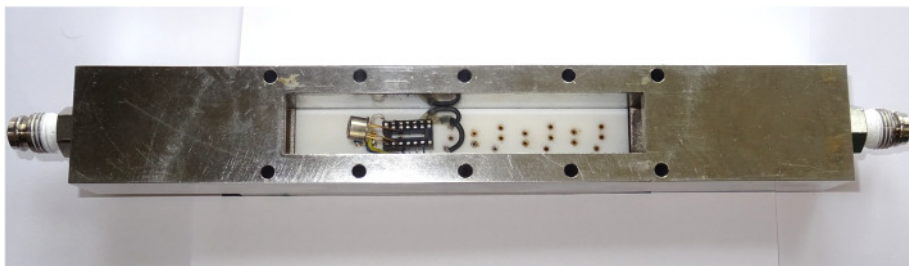
The performance of five commercial sensors was investigated. A catalytic combustion sensor (CAT) that evaluates the heat of hydrogen combustion. Also a thermal conductivity microsensor (TC, nacked die size $2.5 \times 3.33 \text{ mm}^2$) was examined. The increase in hydrogen concentration causes an increase of the thermal conductivity in a gas mixture and enlarges therefore the heat transfer from a sensing element to the surrounding atmosphere. Two sensors are based on semiconductor (MOS I and MOS II). Their sensing principle relies on the change of the surface conductance due to the absorption of hydrogen onto a metal oxide semiconductor (e.g. Pd-doped SnO_2) heated thick film on a ceramic substrate. Also, a sensor based on a metal-insulator-semiconductor (MIS-FET) unit was investigated. The sensor can exploit the change of work function caused by the hydrogen absorption on a palladium thin film.

2.2 Sensor Testing Facility

The measurements were made in a special testing facility [4]. The facility consists of a climate chamber for adjusting the surrounding gas temperature to $\pm 1 \text{ K}$ and a computer-controlled test gas generation device with mass-flow controllers (MFC). Pure hydrogen, or hydrogen-containing gas mixture, was diluted in air. A humidification of the test gas was not applied. The exhaust gases can additionally be analysed by a quadruple mass-spectrometer to check the actual gas composition of gas mixture. Stainless steel supply tubes of an inner diameter of 6 mm and Swagelok connections were used. For time-dependent test gas generation, a personal computer controls all parts of the system via an IEEE-bus net using a program based on LabVIEW. It can also be used for data acquisition. The data acquisition is specific to the sensor type and requires precise measuring instruments (multimeter or network analyser) for sensor signals, i. e. voltage, current or resistance, or measuring controller and measurement cards integrated in the PC.

Three different methods (M1, M2, M3) were applied for the response time measurements. Two sensors were placed in a stainless-steel test chamber of a volume of about 75 cm^3 (method M1) (Fig. 1). However, the insertion of sensors reduces the free volume to be filled with test gas.

a)



b)

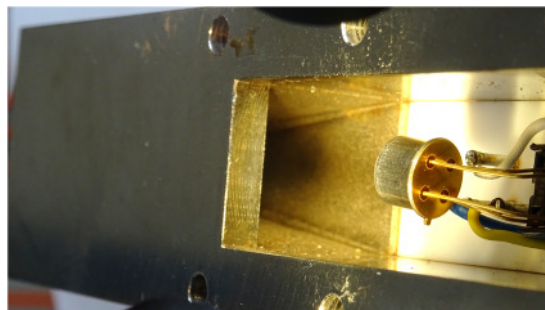


Figure 1. Dynamic test chamber for sensor (M1), a) overview of the chamber, b) the shape of chamber's inlet and outlet channel (truncated-pyramid shape ensures laminar flow of the test gas).

For testing the sensors of a very fast response time, like a MIS-FET sensor, a dynamic test chamber with pneumatic switching was used (method M2). The volume of the circular mini chamber is 3.4 cm^3 (see Fig. 2).

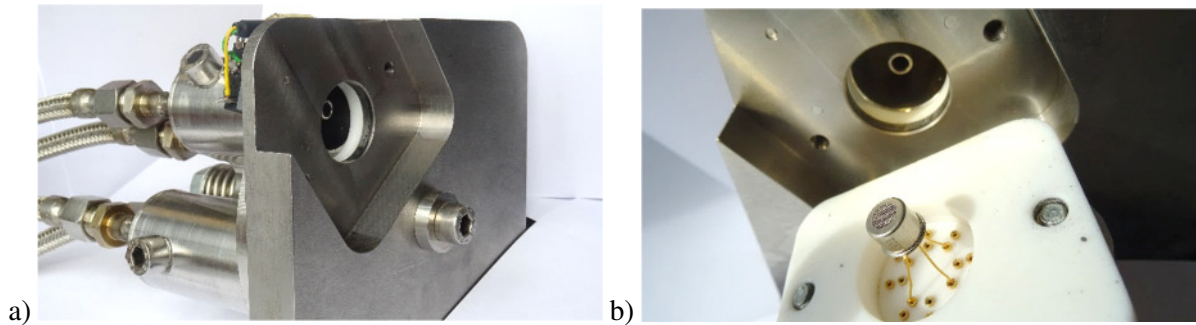


Figure 2. Pneumatically switched dynamic test chamber (M2), a) the view of the facility, b) the chamber (it consists of a shallow cylindrical recess in the Teflon plate with sensor's connection terminals and the cylindrical recess in the metallic body of the facility).

The test chamber and the gas supply pipes are made of stainless steel (electropolished inside), combined with electrically insulating PTFE for the sensor socket. For a quick exchange of gases at the sensor inlet, the device provides simultaneously two streams of gas, flushing alternatively onto the sensor. By pneumatic switching of the gas supply, the sensor is exposed alternatively to test gas concentration either of gas A or of gas B (Fig. 3). The switching takes about 0.1 s. The time interval between two subsequent measurements was 0.7 s or 1 s with an accuracy of 0.1 s. The use of a CAN-bus allows time intervals for data acquisition of 0.1 s.

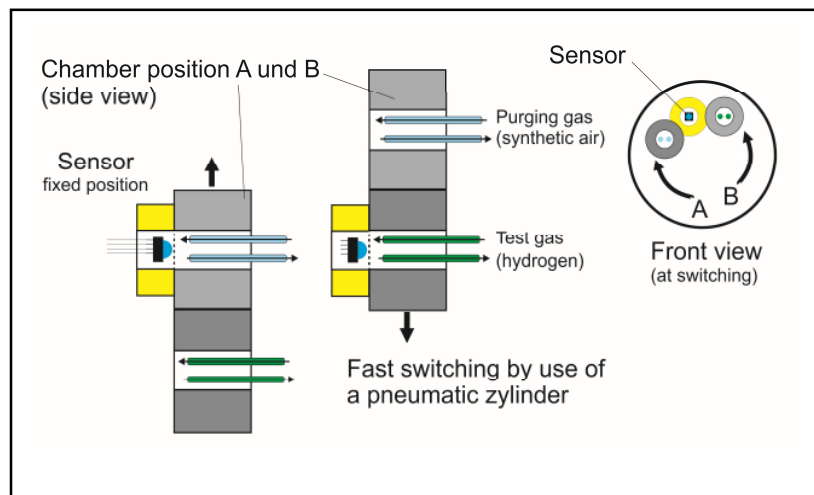


Figure 3. Schematic illustration of the switching between two gas flows flushing the sensor inside the dynamic test chamber (M2).

The third test method (M3) is based on two electronically controlled solenoid valves for test gas switching (see Fig. 4). The used valves are direct-acting, media-separated pivoted armature valves in a stainless steel (316L) housing, operating in 3/2-way. The valves have a switching time of 12 to 18 milliseconds. The electronic control of the valves is carried out by a dedicated software. At first, the sensor is exposed to zero gas, and after switching the valves to hydrogen-containing gas (see Fig. 5). A prior purging of the tandem system with test gas reduces the volume to be filled after switching to about 0.5 cm^3 . The valve system, data acquisition and visualisation are PC-controlled using a software which was developed with LabVIEW.

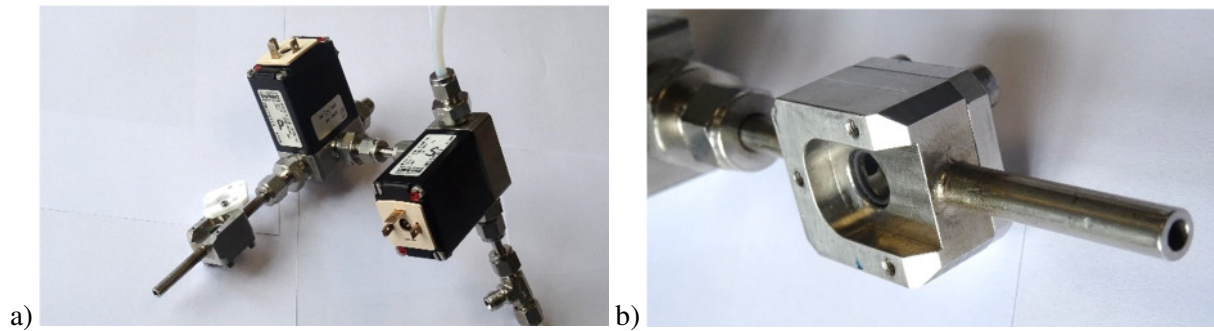


Figure 4. Dynamic test chamber for sensor with two solenoid valves(M3),
a) overview of the setup, b) the mini-chamber.

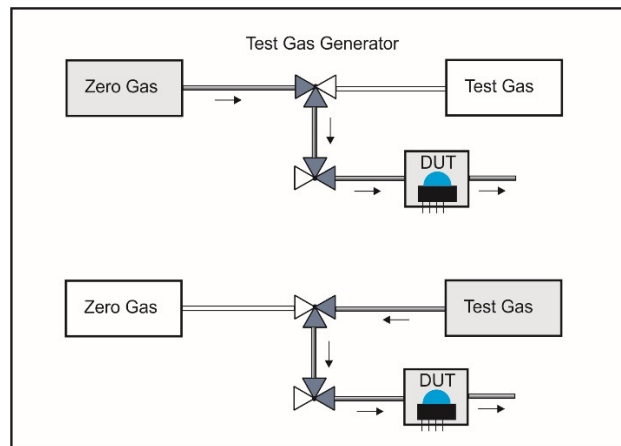


Figure 5. Schematic illustration of the flow path from the zero gas container (upper part of the figure) or the test gas container (lower part of the figure) to the dynamic test chamber for sensor (M3).

Table 1 compiles characteristic data for the three response time test methods (M1, M2, M3) for a gas volume flow of 1000 cm³/min.

Table 1. Experimental conditions for sensor testing.

Parameter	M 1 (laminar chamber)	M 2 (pneumatic switch)	M 3 (solenoid valves)
Length / volume of pipe to test chamber	2.5 m / 31 cm ³	- *	4 cm / 0.5 cm ³
Volume of test chamber	76 cm ³	3.4 cm ³	1 cm ³
Flow velocity in test chamber (assuming laminar flow: \dot{v}/A)	4 cm/s	3.4 cm/s	133 cm/s
Time constant ($\tau = \frac{V}{\dot{v}}$) for filling pipes and free volume of test chamber	4.5 s	0.06 s	0.03 s
Switching time (MFC, valves)	< 1 s	0.1 s	0.012 – 0.018 s
time to reach 99 % of test gas concentration (stirred-tank reactor)	15 s	1 s	0.15 s
Time delay for sensor (assuming plug-flow, sensor in the centre of the chamber)	4 s	0.2 s	0.03 s
*because of immediate switching of the chamber no tube length needs to be considered.			

3.0 RESULTS

Typical curves of response as a reaction to a step change of hydrogen concentration in the test gas for a hydrogen sensor are shown in Fig. 6. Even though a very fast first response can be observed, a delay of the sensor signal increase is detectable. Then, the signal changes rapidly; however, it can demand a remarkable long time span to reach the final indication. The signal curve is not smooth due to internal electronic switching processes.

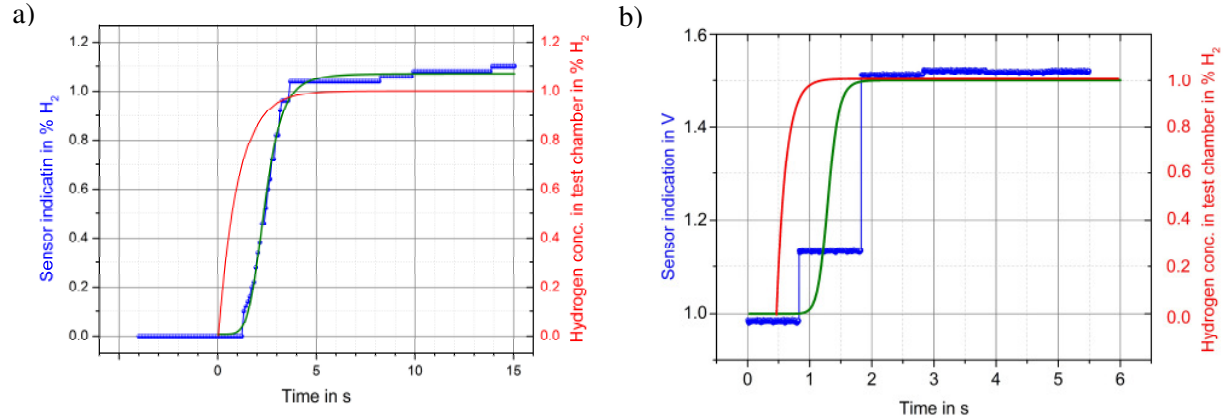


Figure 6. Response curves of a MIS-FET (a) and a TC hydrogen sensor (b).

In Fig. 6a is shown the response curve of a MIS-FET sensor obtained using method M2 (by pneumatic switching the test gas composition) with data output from CAN-bus (reading every 0.1 s), and in Fig. 6b the response curve of a TC sensor by using method M3 is depicted (solenoid valves, readout every 1 ms). The red lines indicate the hydrogen concentration in the test chamber according to the stirred-tank model.

As a result of the measurements of dynamic behaviour of all five sensors, response times were calculated taking into account the respective (extrinsic) time delay of the facility. The data are collected in Table 2. For each sensor a time interval is given because a data scattering occurs even when repeating the measurements under identical conditions, and it is caused especially by variation of the concentration step. The aging of a sensor can induce an increase in its response time.

Table 2. Measured response time of the tested hydrogen sensors.

Sensor	Response times t_{90} (s)	Method
TC	1.8 - 2.0	M3
MIS-FET	3.3 - 3.5	M1
	2.1 - 2.3	M2
MOS I	2 - 6	M2
MOS II	5 - 16	M2
CAT	20 - 50	M1

4.0 DISCUSSION

4.1 Comparison with Results from Literature

The compilation of data in Table 3 shows that the obtained results on response time of this work (see also table 1) are comparable with data from literature. This is due to the rapid change of gas concentration on sensor inlet by the used test methods. The data for MOS sensors for t_{90} in the range from 17 s to 35 s given by Mishra [5] in 1998 are remarkably longer and may illustrate the progress in sensor technology.

Table 3. Response time t_{90} of hydrogen sensors.

Sensor	This work (in s)	Results from literature (in s)	Source
TC	1.8 - 2.0	4 - 6	[2]
MIS-FET	2.1 - 2.3	< 2 2 - 4	[8] [2]
MOS	2 - 6	17 - 35 16 ≤ 15	[5] [6] [7]
CAT	20 - 50	8	[9]
Remark: The step change is in the range from "0 to 0.01 %" to "0 to 4 % H ₂ " (see sec. 4.4)			

4.2 Transient Behaviour of Test Equipment

It is of great importance for investigation of time-dependent sensor responses to know how fast a step change of gas concentration can be generated. A slow concentration change would have a large impact on the change of the sensor signal and could significantly distort the result. The time-dependent change of the gas concentration $c(t)$ in the test chamber depends above all on the volume (V) to be filled and the gas flow rate (\dot{v}). The critical parameter is the time constant: the ratio between test chamber volume and gas flow, $\tau_v = \frac{V}{\dot{v}}$ (see Table 1). The change of the gas concentration in the test chamber can be characterised by two models: the continuous stirred-tank reactor or the ideal plug-flow reactor [10]. The dependence of the gas concentration from the running coordinate (x) in the test chamber (plug-flow-reactor) and the time dependence of gas concentration (stirred-tank reactor) can be described by the following equations:

$$c(x) = c_0 \exp(-k\tau_v), \quad (1)$$

and

$$c(t) = \frac{c_0}{1 + k\tau_v}, \quad (2)$$

where c_0 is the final value of the concentration.

Both models represent the fastest and the lowest settling of the new gas concentration, although the continuously stirred-tank reactor seems more appropriate for larger test chambers (method M1), whereas the plug-flow reactor model is proper for a small volume in tubes (method M2 and M3). It was concluded that in case of low gas flow and big volume of the test chamber wherein the sensors are positioned, the time-dependent sensor response reflects the increase of gas concentration in the test chamber and not a

sensor inherent property [11]. A discussion of this statement is given according to Fig.7 as an example. It illustrates the concentration change in a test chamber of a time constant of 60 s and the time-dependent sensor signals. As a deviation from the ideal step change, according to the continuously stirred-tank reactor, for this model it would take more than 130 s to reach 90 % of the final gas concentration. A large test chamber or a time constant of nearly 1 min seems not suitable for response time measurements. On the other hand, Fig. 7 shows two delayed and different sensor responses. Even though the impact of the test equipment is obvious, the conclusion given in [11] must not be accepted at least in the case of the results presented here.

For method M1 it is required to pass the step change around 4 s at a gas flow rate of 1000 cm³/min (see Table 1). It also includes the assumption of a laminar flow and that this new gas concentration reaches the sensor inlet immediately. Otherwise, up to 15 s is needed according to the stirred-tank reactor model. The extrinsic time delay for the pneumatic switching test chamber, which has a smaller volume, is only around 0.2 s to 1 s (method M2) and for the solenoid valves 0.03 s to 0.15 s. Therefore, more reliable characteristic data of the dynamic sensor behaviour can be obtained in test arrangements with a time constants of $\tau_v \leq 1$ s such as for methods M2 and M3.

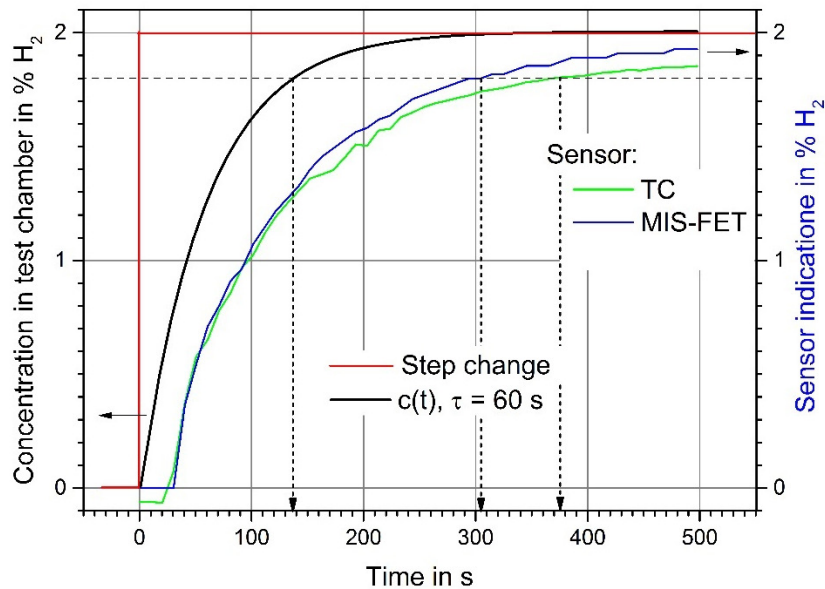


Figure 7. Step change of hydrogen concentration from 0 to 2 % H₂ and sensors' responses (example for the free test chamber of 1 L volume and the gas flow rate of 1 L/min).

4.3 Contributions to Time Delay of Sensors

A retardation of sensor indication is caused by several effects, which are here divided into two parts, as illustrated in Fig. 8. First, the extrinsic time due to the electronics time constant for valves switching and the time necessary to fill the gas pipes and the test chamber till the sensor inlet is reached. The intrinsic time response of the sensor consists of a certain dead time, and a continuous signal change until final indication. That results from the time constant of the physicochemical reaction onto or inside the sensor element and the time interval needed for the change of the electrical signal. This can be discussed e.g. by using a diffusion-based model for MOS-type sensors [12]. The time constant of the primary measuring circuit of the sensor needed for signal conversion and amplification is estimated to be below 0.01 s and is usually neglected. Also the time constant of the electronic units for measurement of the sensor output and display is expected to be less than 0.01 s. However, as shown in Fig. 6, the indication of the sensor signal can occur stepwise and exhibit a time delay up to 1 s for the TC and the MIS-FET sensors.

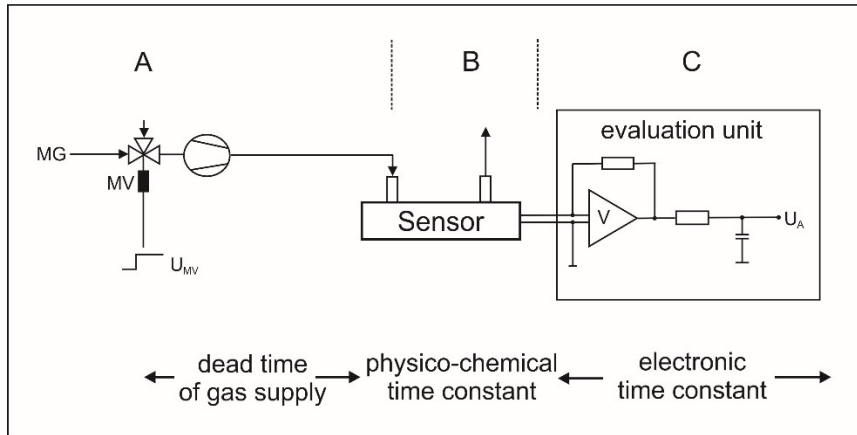


Figure 8. Three components of time delay in response measurements.

4.4 Influence of Hydrogen Concentration Change Magnitude on Time Response

The magnitude of the hydrogen concentration change may have influence on the measured response time. Larger concentration changes, e.g. from zero to 1 % H₂ (25 % of LFL) are indicated faster than smaller changes such as from 0 to 0.01 % H₂. This phenomenon has been already reported in literature [2,4] for MOS sensors (see Fig. 9).

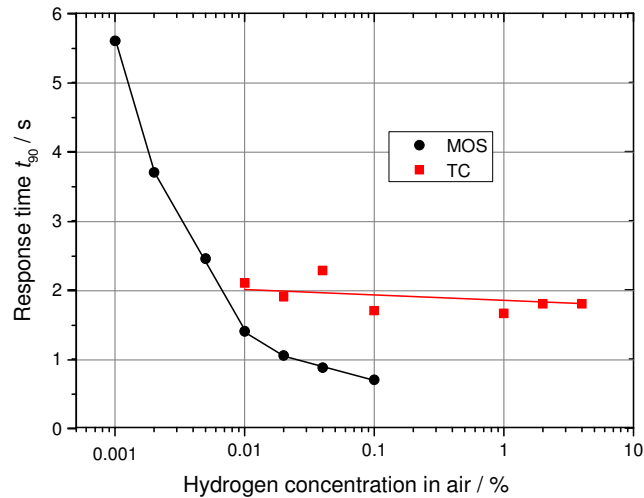


Figure 9. Response time versus hydrogen concentration step change for a MOS and a TC hydrogen sensor.

A dependence on concentration change may be due to basic effects of surface covering kinetics and diffusion. Also electronic effects may have influence, e.g. the semiconductor can be considered as an RC filter that has a time constant of $\tau = RC$. In the case of increasing hydrogen concentration, the resistance decreases and thus also the time constant. This effect was also observed for a MIS-FET sensor [2]. On the other hand, for the thermal conductivity-based sensor operation at higher hydrogen concentrations there is only a small or no impact of hydrogen concentration change magnitude in the gas on the response time.

4.5 Modelling of Response Time

The measured data were fitted to the following equation (3) and the results of approximation are collected in Table 4.

$$S(t) = S_{START} + (S_{END} - S_{START})[1 - \exp(-t/\tau)]. \quad (3)$$

The parameter τ is the time constant which characterizes the sensor's signal change for increasing hydrogen concentration. The time delay was not taken into account. Therefore, the values for response time in Table 4 are higher. A sufficient correlation coefficient was obtained, which may support the basic assumptions about the transfer function.

In view of a fast indication of a gas as a possible hazard, further characteristic time parameters can be used. These are for example t_{63} that refers to $\frac{t}{\tau} = 1$ in an exponential approach proportional to $1 - \exp(-1)$ or the inflection point of the rising signal curve, e.g. t_{50} for some sigmodial functions. With respect to the limit of quantification, an incipient response time t_{10} (10 % of the final signal value) could be a suitable parameter for early detection of hydrogen, too; however, the prediction's uncertainty may be higher.

Table 4. Results of data fitting for exponential approach.

Sensor type	Calculated response time parameters		
	τ (s)	t_{63} (s)	t_{90} (s)
TC	1.7±0.1	2.1±0.2	2.8±0.2
MIS-FET	2.5±0.1	2.1±0.3	3.4±0.3
MOS I	2.1±0.6	2.4±0.3	4.8±0.3
MOS II	9.6±0.8	10.6±0.2	23.1±0.2
CAT	27±6	26±6	57±8

The modelling of the time response of the sensor signal by a first order exponential approach does not regard the initial state of the signal and a possible transient oscillation or noise. This can be considered applying a sigmodial function resulting in a S-shaped curve (see green curves in Fig. 6) of the following approach:

$$S(t) = S_{END} + \frac{(S_{START} - S_{END})}{1 + \left(\frac{t}{t_{50}}\right)^p}, \quad (4)$$

where S_{START} and S_{END} are the initial and the end value of the normalised signal (0, 1), t_{50} is the time needed for reaching 50 % of the full change of sensor signal and p is the steepness of the curve. Small values of t_{50} and large values of p can indicate a fast response. Table 5 compiles the results of sigmodial fit according to this approach and calculated values for the response time t_{90} .

In repeated experiments, step changes of gas concentration yield in many cases different values for the response time with random scattering or trends. This may be due to the signal noise or systematic deviation. The data in Table 2 give therefore a range of values. Further contributions to the total uncertainty are from the method of parameter determination, e.g. graphical, or by means of a curve fitting program (see Tables 3 and 4). However, these contributions do not usually exceed 10 % of the magnitude.

Table 5. Results of data fitting for sigmoidal approach.

Sensor type	Calculated response time parameters				
	S_{START}	S_{END}	p	t_{50}	t_{90}
TC	-0.01 ± 0.05	0.95 ± 0.03	15.0 ± 14.6	1.3 ± 0.2	1.6 ± 0.3
MIS-FET	0.009 ± 0.006	1.07 ± 0.01	5.1 ± 0.2	2.3 ± 0.1	3.1 ± 0.5
MOS I	0.006 ± 0.002	0.996 ± 0.001	13.1 ± 0.5	2.00 ± 0.01	2.4 ± 0.1
MOS II	0.03 ± 0.01	1.04 ± 0.01	2.5 ± 0.1	7.7 ± 0.2	16.0 ± 0.7
CAT	-0.01 ± 0.03	0.98 ± 0.02	15 ± 5	37 ± 1	44 ± 3
For all approximation fits, the correlation coefficient is $r \geq 0.9$.					

4.5 Premature Alarm Indication

Fast sensor response is of specific relevance for alarm indication, usually the display of a concentration of a flammable gas which is a certain part of the lower flammability limit concentration (LFL), e.g. 25% LFL or 50 % LFL. The sensor is exposed to gas mixture containing hydrogen which is 10 % above the alarm level concentration. An alarm has to be indicated within twice of the t_{90} time (see ISO26142:2010). An earlier t_{90} and alarm indication can be estimated from the change rate of sensor signals in relation to the known final signal S_{haz} for hazard gas concentrations. However, the determination of the starting time of a signal change may be uncertain, and has to be distinguished from the noise of the signal S_0 . Assuming the exponential signal growth, and neglecting delays due to electronics, the signal change between 0.2τ and τ corresponding to 18 % and 63 % of the final signal for a hazard gas concentration can be chosen. Thus, from this time interval already at time τ an alarm can be indicated, whereas from the t_{90} values alarm occurs not until 2.3τ has passed. However, an uncertainty of alarm indication has to be taken into account for this procedure.

5.0 CONCLUSIONS

The five tested commercial hydrogen sensors have, with one exception (CAT), remarkably fast response times and fulfil the requirements of ISO 26142:2010 with large margin in this area. The investigation demonstrated the influence of the testing facility and method applied, as well as of experimental parameters such as the magnitude of concentration change on hydrogen sensor response time measurements. Defined experimental conditions have to be met for collecting precise, reliable and comparable data. The fastest response times were obtained with electronically switched solenoid valves or a pneumatic switched test chamber. It was shown that the hydrogen concentration step magnitude at which measurements were made, also influences the results. The estimated values of response times indicate a different dynamic behaviour of the hydrogen sensors, due to their construction and sensing principle. The field effect transistor-based sensor and the micromaschined thermal conductivity-based sensor yielded the fastest response time. This may be plausible, because of the decisive role of thin films for surface hydrogen absorption and heat exchange. A fitting of time response data with a single exponential (step response of a first order lag system), or a sigmoidal function, result in good approximation. The determination of the total sensor signal sequence in a step change of gas concentration permits a more precise estimation of the usual response parameters (e.g. t_{90}) as well as calculation of beneficial characteristics (e.g. t_{63}) that allow an earlier indication of hazardous conditions.

REFERENCES

1. ISO 26142:2010: Hydrogen detection apparatus - Stationary applications
2. Boon-Brett, L., Bousek, J., Black, G., Moretto, P., Castello, P., Hübert, T., Banach, U., Identifying performance gaps in hydrogen safety sensor technology for automotive and stationary applications, *International Journal of Hydrogen Energy*, **35**, 2010, pp. 373-384.
3. Venturi, M., Fischer, R., Henkel, F., Hydrogen Sensors for Automotive Fuel Cell Applications, *SAE Technical Paper*, 2013-01-0497.
4. Hübert, T., Banach, U., Response time of hydrogen sensors, Proceedings of the Fifth International Conference on Hydrogen Safety, 9-11 September 2013, Bruxelles, Paper ID 124, pp.1-8.
5. Mishra, V.N., Agarval, R.P., Sensitivity, response and recovery time of SnO₂ based thick-film sensor array for H₂, CO, CH₄ and LPG, *Microelectronics Journal*, **29**, 1998, pp. 861-874.
6. UST GmbH 2013, priv. comm.
7. Figaro, www.figaro.co.jp
8. ams, HLS-440 Datasheet, <http://ams.com/eng/Products/Environmental-Sensors/Hydrogen-Sensors/HLS-440P-A>.
9. n.e.t., NEMOTO Sensortech Division, Data sheet NP-AHS 2006.
10. Schmidt, L., The engineering of Chemical Reactions, 1998, Oxford University Press, New York.
11. Ménil, F., Modélisation des temps de réponse des capteurs chimiques, *C.R. Acad. Sci. Paris, Chimie/Chemistry*, **4**, 2001, pp. 889-905.
12. Gardner, J.W., A Non-linear Diffusion-reaction Model of Electrical Conduction in Semiconductor Gas Sensors, *Sensors & Actuators, B1*, 1990, pp. 166-170.