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Detlef Stolten, Thomas Grube (Eds.):
18th World Hydrogen Energy Conference 2010 - WHEC 2010
Parallel Sessions Book 5: Strategic Analyses / Safety Issues / Existing and Emerging Markets
Proceedings of the WHEC, May 16.-21. 2010, Essen
Schriften des Forschungszentrums Jülich / Energy & Environment, Vol. 78-5
Institute of Energy Research - Fuel Cells (IEF-3)
Forschungszentrum Jülich GmbH, Zentralbibliothek, Verlag, 2010
ISBN: 978-3-89336-655-2

# Methods for Response and Recovery Time Measurement of Hydrogen Sensors

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## 1 Introduction

Hydrogen sensors will play an important role in ensuring the safety of a future hydrogen economy and the performance requirements imposed on these devices must be carefully set based on their conditions of use. In determining whether actual sensor performance meets these requirements, the particularities of the test methods used may influence the findings. It is therefore important to optimize and standardize these methods as a means of ensuring the greatest accuracy and consistency possible.

The draft standard for stationary hydrogen detection apparatus, ISO/FDIS 26142 [1], is currently being finalized. It specifies performance requirements and details of methods for the measurement of various performance characteristics, including response and recovery times. The response time, t(x), of a sensor is defined as the interval between the time when an instantaneous variation from clean air to the standard test gas is produced at the sensor and the time when the response reaches a stated percentage (x) of the final indication. This is often reported as t(90), which is the convention adopted in this work. Conversely, the recovery time t(x) is the interval between the time at which an instantaneous variation from the standard test gas to clean air is produced at the sensor and the time when the response reaches a stated percentage (x) of the maximum indication. Recovery times are usually reported as t(10), which is the case here. Sensor response times are particularly important from a safety perspective because they partly determine the speed of safety response, such as evacuation of personnel or activation of shut-off valves. For the purposes of this paper, response and recovery times shall be referred to collectively as “reaction times”.

A number of methods exist for the measurement of reaction times [2,3]. These can be broadly classed as those which make use of flow for gas transport to the sensor and those which rely on diffusion for the exchange of gases. ISO/FDIS 26142 describes two test methods for the measurement of hydrogen sensor reaction times – one flow-based and one diffusion-based. These provided the starting point for the methods tested in this work. The diffusion-based method was modified significantly to produce two variant methods, which were also tested. Thus, the results of tests on four methods for the measurement of sensor reaction times are reported here.

## 2 Experimental

The sensor testing facility at the JRC-IE has been described in detail in the literature [4,5] and has been used extensively for testing of hydrogen sensors [6]. In this work, the facility was developed to allow for reaction time testing as described below. Sensor samples were tested individually and at room temperature (292 K ± 2 K) under dry gas conditions. A calibrated compact gas chromatograph (GC) was used during diffusion-based tests to confirm the hydrogen concentration.

**Flow-through method**: The Flow-through method measures the reaction time under dynamic conditions and relies on the transport of gas to the sensor's sensing element. The set up and method described here are the product of a series of tests during which improvements and optimisations were made to the flow-through method described in Annex B of ISO FDIS 26142 [1].

The sensor being tested was mounted on a flange above a hole drilled in the side of a copper pipe. Synthetic air or test gas was selectively flowed through the pipe by means of a 3-way valve. Variations on the ISO method involved changing the diameter of the hole and the diameter and geometry of the pipe. Optimum results were obtained using a circular pipe with an internal diameter of 4 mm and gas flow rates between 50–120 sccm. A short section of the circular pipe was replaced by a rectangular part with internal dimensions 12×3 mm and the sensor support flange was attached to this section. Use of this rectangular pipe section with a larger cross sectional area significantly reduced gas flow disturbances and pressure fluctuations in the system and also resulted in a cleaner sensor output signal.

**Membrane method:** The Membrane method measures the response time of sensors under static conditions and relies on the diffusion of test gas to the sensor's sensing element. The set up used for these tests is based on that described in Annex A of ISO FDIS 26142 [1] and on the work of Sawaguchi et al. [2]. An aluminium box with an internal volume of 30L was used, inside of which a small aluminium holder housed the sensor under test. The sensor was mounted inside the sensor holder which was sealed with a natural latex membrane, tautly stretched over a 'ridge' on the holder rim and sealed in place with tape. The sensor holder was positioned in the diffusion chamber on a movable metal stand. The desired quantity of hydrogen was then injected into the diffusion chamber and mixing was promoted by 2 fans located at the base of the chamber and one at the level of the hydrogen inlet. Following homogenisation of the test gas mixture, as confirmed by GC, the membrane was ruptured by means of a scalpel fixed to the end of a lever, which was manoeuvred from outside the diffusion chamber. The corresponding start time of the experiment was signalled by manually pressing a switch at the point when the membrane ruptured.

**Lid method:** To overcome some of the difficulties experienced when measuring sensor response time using the Membrane method, a number of modifications to the experimental set up and procedure were made, resulting in the development of the Lid method. The latex membrane was replaced by a latched aluminium lid, which was held firmly in place on the sensor holder by a taut elastic band on one side and by a removable clip on the other side. The clip was removed by manipulation of the lever from outside the chamber. This caused the lid to snap off, releasing a micro switch, which generated an electronic signal accurately defining the start time of the experiment. Otherwise all other aspects of the method remained identical to the Membrane method.

**Gate valve method:** The Gate valve method was developed as an alternative to the Membrane and Lid methods with the advantage of being able to measure not only the sensor response time but also the recovery time. As with both previously described methods a sealed 30L aluminium diffusion chamber was used. A smaller chamber (0.39L), used as the sensor holder, was attached to a flange on one face of the diffusion chamber. The two volumes were separated by a fast acting solenoid gate valve.

During response time measurements, the sensor holder was flushed with clean air and the diffusion chamber with test gas. When the desired gas concentration in both volumes was confirmed by GC all flows were stopped. The valve was then opened electronically. This was recorded as two signals corresponding to the gate contact at the start and at the finish of valve opening, which takes 0.4–0.6 s. The start time of the experiment was taken as halfway between the two contact times. A fan was used to direct gas flow from the diffusion chamber towards the sensor. The procedure for carrying out recovery time measurements was identical to this, except that in these tests the diffusion box was filled with clean air, while the sensor holder was filled with test gas.

**Sensors:** Two commercial sensors were chosen to evaluate the four test methods. The first is a MOSFET sensor capable of measuring hydrogen concentration in the range 0–4.4 vol% hydrogen in air with an accuracy of ± 3000 ppm. The t(90) and t(10) specified by the manufacturer are <3s and <10s respectively. The second sensor is a thermal conductivity sensor (TCD) with a measuring range of 0–100 vol% and an accuracy of ±1 vol%. Both t(90) and t(10) are quoted as <20s, with a typical value of 10s. The reaction times of these sensors were measured at different hydrogen concentrations using all methods except the Membrane method, to highlight any influence this may have on the measurement.

## 3 Results and Discussion

Reaction times were measured over the concentration range 0.5–2 vol% hydrogen and results are shown in Table 1 averaged over all concentrations tested. All response time results are shown graphically in Figs. 1 and 2 for the MOSFET and TCD respectively.

### 3.1 Flow-through method

In the case of response time measurements on the MOSFET sensor, it was found that a plateau often occurred in the response curves. At lower concentrations, this plateau tended to occur before the 90% value had been reached, therefore influencing the measured t(90) and causing greater scatter in the measurements, as shown in Fig. 1. Above 1 vol% hydrogen this scatter is significantly reduced and the apparent influence of concentration disappears. In experiments on the TCD sensor, it was found that the flow rate had an influence on its response. As the flow rate increased, both the zero reading and the reading in hydrogen increased. This may be explained in terms of its mode of operation – the faster the flow the greater the effective thermal conductance of the gas as it cools the heating element. This did not affect the measured reaction times however, as the flow affected the zero reading and the reading in hydrogen equally. No apparent influence of concentration on the response time of the TCD could be discerned. However, considering that the measuring range of this sensor is 0–100 vol% and that tests were performed at a maximum of 2 vol% hydrogen for safety reasons, it is likely that any effect of concentration would not be observed. Interestingly, the measured t(90) is significantly shorter than that given by the manufacturer of 20s and typically <10s.

Recovery time measurements were performed within the same concentration range. No plateau occurred in the sensor signal as it decreased, and so the recovery time results for the MOSFET sensor show less scatter than the response time results, Table 1. A slight steady decrease was observed in the t(10) values with decreasing concentration as fewer hydrogen molecules are required to desorb from the sensor surface. Similar to the response time results, recovery times of the TCD sensor are shorter than stated by the manufacturer and show no influence of concentration within the range tested.

### 3.2 Membrane method

During initial testing, the repeatability of the Membrane method was found to be extremely low, giving an average response time for the MOSFET sensor of 12.8 ± 12.1s. For this reason, it was used only to test the MOSFET sensor at concentrations of 0.5 and 1 vol% and was modified to give improved repeatability and shorter response times using the Lid method. This lack of repeatability can be principally attributed to lack of consistency in opening of the rubber membrane and to imprecision in marking the start time using the manual switch.

### 3.3 Lid method

The shortest response times for both sensors were measured using the Lid method and these results also show good repeatability. In addition to addressing the difficulties with the Membrane method as outlined above, this method also reduces the potential for diffusion of hydrogen into the sensor holder prior to the start of the experiment. It was found that where the sensor holder was sealed with the rubber membrane, diffusion of hydrogen occurred after 315s, as indicated by a non-zero sensor signal. When the membrane was replaced with the metal lid, diffusion into the sensor holder was found to occur after 1200s.

### 3.4 Gate valve method

The Gate valve method was designed in order to allow for recovery time measurement using a diffusion-based method. However, in the case of the MOSFET sensor, it was found that t(10) could not be measured at concentrations above 1 vol% hydrogen because the final homogenised concentration did not drop below the detection limit of the sensor. The test gas was not replaced by clean air, but instead highly diluted, and although the final concentration had fallen well below 10% of the initial hydrogen concentration, the MOSFET was found to overestimate the hydrogen concentration at such low values, making measurement of t(10) impossible. Recovery time tests were performed on the TCD without difficulty because the experimentally determined detection limit of this sensor is higher than that of the MOSFET, 0.15 vol% versus <0.03 vol%. Response time measurements gave reasonable results, but the necessity of using a fan to direct gas flow towards the sensor raises the possibility of this perpendicular gas flow (as distinct from the parallel flow used in the Flow-through method) influencing the sensor response.

### 3.5 Summary and recommendations

Each method has its own advantages and limitations. The method that results in the shortest response times is the Lid method, which also demonstrates good repeatability and is therefore recommended for response time measurement. However, the Flow-through method is recommended for recovery time measurement as it is the only method in which the test gas is really switched to clean air rather than being highly diluted.

**Table 1: Average response and recovery times using the 4 test methods.**

| Method | MOSFET t(90) | | MOSFET t(10) | | TCD t(90) | | TCD t(10) | |
|---|---|---|---|---|---|---|---|---|
| | Average | σ | Average | σ | Average | σ | Average | σ |
| Flow through | 4.4 | 1.2 | 10.2 | 0.7 | 5.2 | 0.6 | 9.7 | 2.0 |
| Membrane | 12.8 | 12.1 | – | – | – | – | – | – |
| Lid | 2.3 | 0.3 | – | – | 3.6 | 0.8 | – | – |
| Gate valve | 3.0 | 1.2 | 9.2 | 2.6 | 5.2 | 1.2 | 5.3 | 1.2 |

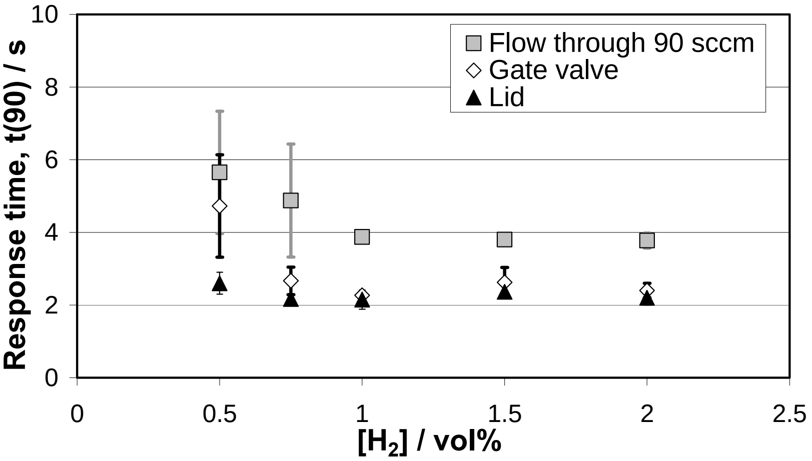

**Figure 1: Average response time of MOSFET sensor using three test methods; error bars represent standard deviation. Membrane results omitted for clarity.**

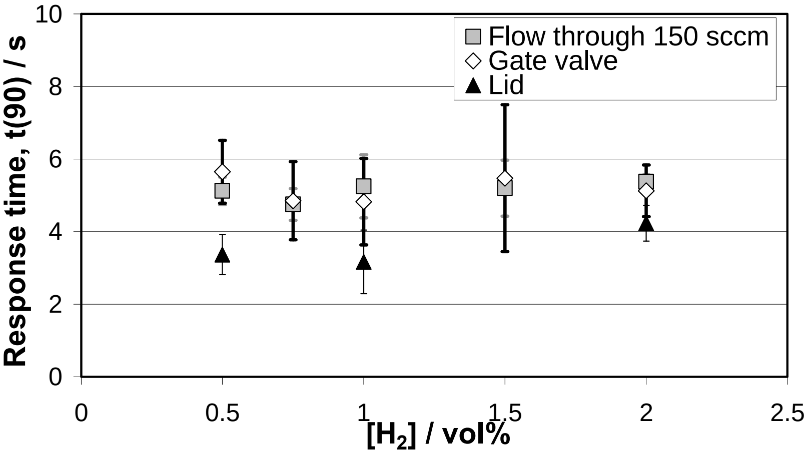

**Figure 2: Average response time of TCD sensor using three test methods; error bars represent standard deviation. Membrane results omitted for clarity.**

## Resferences

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