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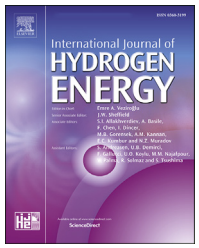

Test methodologies for hydrogen sensor performance assessment: Chamber vs. flow-through test apparatus

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ABSTRACT

Certification of hydrogen sensors to meet standards often prescribes using large-volume test chambers [1,2]. However, feedback from stakeholders such as sensor manufacturers and end-users indicates that chamber test methods are often viewed as too slow and expensive for routine assessment. Flow-through test methods are potentially an efficient and cost-effective alternative for sensor performance assessment. A large number of sensors can be simultaneously tested, in series or in parallel, with an appropriate flow-through test fixture. The recent development of sensors with response times of less than 1s mandates improvements in equipment and methodology to properly capture the performance of this new generation of fast sensors; flow methods are a viable approach for accurate response and recovery time determinations, but there are potential drawbacks. According to ISO 26142 [1], flow-through test methods may not properly simulate ambient applications. In chamber test methods, gas transport to the sensor is dominated by diffusion which is viewed by some users as mimicking deployment in rooms and other confined spaces. Conversely, in flow-through methods, forced flow transports the gas to the sensing element. The advective flow dynamics may induce changes in the sensor behaviour relative to the quasi-quiescent condition that may prevail in chamber test methods. The aim of the current activity in the JRC and NREL sensor laboratories [3,4] is to develop a validated flow-through apparatus and methods for hydrogen sensor performance testing. In addition to minimizing the impact on sensor behaviour induced by differences in flow dynamics, challenges associated with flow-through methods include the ability to control environmental parameters (humidity, pressure and temperature) during the test and changes in the test gas composition induced by chemical reactions with upstream sensors. Guidelines on flow-through test apparatus design and protocols for the evaluation of hydrogen sensor performance have been developed. Various commercial sensor platforms (e.g., thermal conductivity, catalytic and metal semiconductor) were used to demonstrate the advantages and issues with the flow-through methodology.

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Introduction

Hydrogen has been broadly used in many industrial applications from chemical and refining to metallurgical, glass and electronics [5]. New environmental requirements are extending the use of hydrogen to other fields, for instance as an alternative fuel in transport applications or for energy storage purposes, supporting the integration of renewable energy sources in the energy mix. It has to be considered that hydrogen presents some issues regarding safety. Its broad flammability range in air, together with its small molecular size that increases the potential for leaks, requires special safety measures to avoid hazardous situations. One main approach for the assurance of safety is the use of hydrogen sensors to detect it before it reaches dangerous concentrations. It is often required that these sensors are certified to ensure safe and reliable operation. For this purpose, test protocols are described in performance standards [1,2] to verify various sensor parameters, such as accuracy, repeatability, lifetime, impact of environmental parameters (e.g., T, P, RH) cross-sensitivity to other gases, etc.

The above mentioned extended use of hydrogen means that potentially more sensors will be deployed. This increase of sensor deployment makes necessary the development of large scale sensor production through advanced manufacturing methods. An efficient means of performance verification is necessary to maintain the economy-of-scale manufacturing. Although performance standards often prescribe using large-volume test chambers, this method is viewed by some as too slow and expensive for some applications such as qualification testing by an end-user for their specific application or as a QA/QC screen for sensor manufacturers. Flow-through test methods have numerous advantages relative to chamber methods, including shorter test times and smaller quantity of test gas. An additional advantage of the flow-through method is that it can simulate conditions in specific applications (where the gas is flowing, i.e. pipelines) better than the chamber method. However, it may not properly simulate ambient applications.

The goal of the work presented here is to define the conditions for which flow-through method is comparable to the chamber method for hydrogen sensor evaluations, while showing its advantages in terms of shorter test duration and potential for simultaneous sensor testing. Flow-through test apparatus design and operation strategies are described that allow for assessment of the impact of the gas composition and changes in environmental parameters. The discussion will address pitfalls that may be encountered if inadequate controls or improper test conditions are implemented. Sensors with different operating principles (thermal conductivity (TC), catalytic combustion (CC), and metal oxide (MOX)) were tested using both methods to compare the results and to identify the potential advantages that the flow-through method can offer. The tests performed were: accuracy, short-term stability, pressure dependence and flow rate dependence. The flow rate dependence test was performed only with the flow-through apparatus. Details on the test protocols have been described elsewhere [6]. The sensor testing was performed at the Sensor Testing Facility (SenTeF [7]), which is one of several hydrogen technologies laboratories of the Joint Research Centre - Directorate for Energy, Transport and Climate [8].

Experimental setup

The experimental setup is part of the JRC laboratory SENTEF [3]. The sensors were evaluated using both chamber and flow-through test apparatus. The chamber test apparatus is schematically illustrated in Fig. 1. Each gas line is connected to a gas cylinder of known composition (±2% relative uncertainty). Flow from each gas cylinder to the sensor test fixture is regulated by a mass flow controller (MFC) that had been calibrated for the specific gas. The maximum uncertainty for the MFCs after calibration is ± 0.1%. Regulating the relative flow rates of the gas supply MFCs ensures proper control of the test gas composition. Multiple gas lines are fed into a single pneumatic line for mixing. A back pressure regulator and vacuum pump maintain a constant pressure within the test chamber, which can be less than or greater than the ambient pressure (the actual pressure range was 80–120 kPa). Chamber pressure was measured with a pressure transducer that had an uncertainty after calibration of ± 0.1%.

Sensors are placed in the test chamber, which has an internal volume of around 3.1 L. Sensor performance testing is done at a fixed flow rate of 1000 Nml/min and consists of a series of exposures to different gas compositions ranging from 0 to 2 vol% H2 in dry air at the indicated pressure. Testing is performed at ambient laboratory temperature (except in the temperature dependence test) and dry air. The duration of each exposure step has been set to 1 h to assure purging of the chamber with the proper test gas and to assure that the sensor has reached a stable final indication. Control and data acquisition is done via Labview® software installed on a PC. The logging frequency of the sensor response was 1 point each 5 s. A second chamber test apparatus was used for tests to analyse temperature dependence of sensor response. The chamber of this instrument has bigger internal volume (around 3.9 L) and also a double wall. The space between the two walls is filled with heating/coolant fluid coming from a thermal bath, controlling in this way the temperature inside the chamber. This configuration can also be seen in Fig. 1.

For the flow-through method, the chamber was removed and the sensors are placed in a custom-built interface, directly connected in-line with the gas supply line, in a series configuration. This configuration brings some advantages over parallel configuration as, for instance, a lower number of MFCs to control flow rate and gas composition during sensor testing. Due to the reduction of the internal volume of the flow-through apparatus relative to the chamber apparatus, internal pressure fluctuations induced by the pressure regulation system (i.e., the back-pressure regulator and vacuum pump) impact the stability of the gas flow-through the MFCs. In order to avoid these flow, and corresponding pressure, oscillations, two buffer tanks are placed between the back pressure regulator and the vacuum pump. A schematic of the flow-through test apparatus is depicted in Fig. 2 (without thermostatic chamber). As with the chamber test apparatus, control and data acquisition is done via Labview® software installed on a PC. For sensors with analogue output a multimeter was used to

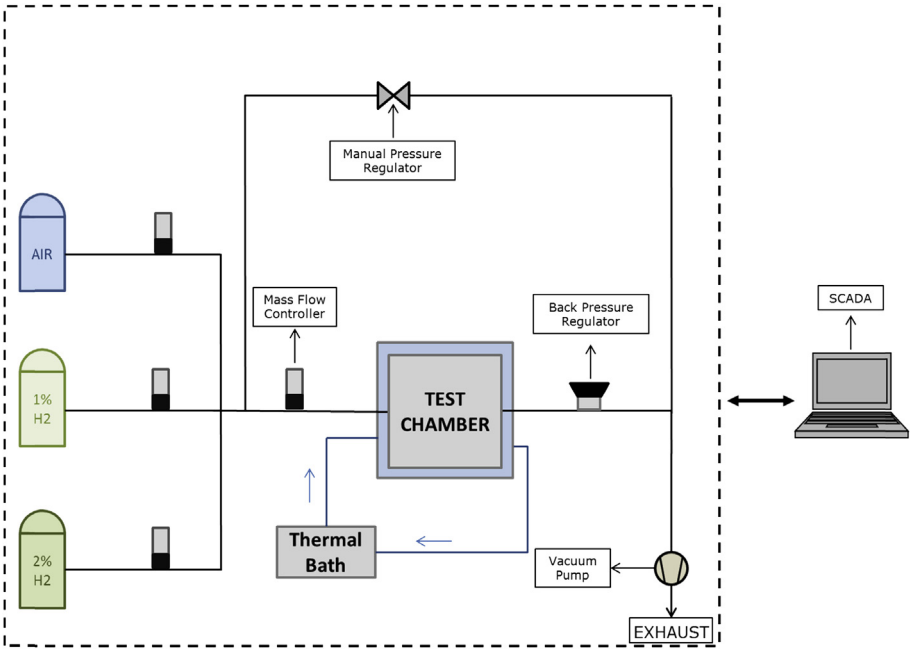

Fig. 1 – Scheme of the experimental setting for the chamber method.

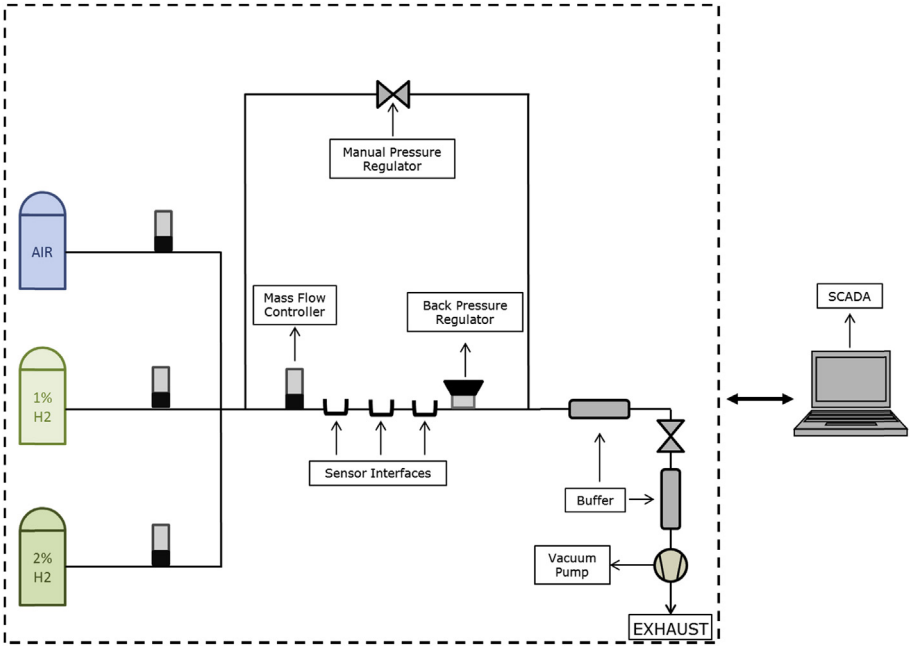

Fig. 2 – Scheme of the experimental setting for the flow-through method.

measure the response. During the calibration of these multimeters an uncertainty of less than 0.01% was determined.

When performing test at different temperatures in flow-through method, the sensors and part of the gas supply line are placed inside a thermostatic chamber that controls the temperature of the test (Fig. 3). It can provide temperatures from −40 °C up to +180 °C, with a deviation from the set point between 0.1 and 0.3 °C. Maximum thermal gradient inside the chamber is 3 °C.

Different sensor technologies were used to test the impact of chamber vs. flow-through test methods on performance. These sensors or sensing elements were based upon the following principles: thermal conductivity (TC), catalytic combustion sensor (CC), and semiconducting metal oxide sensor (MOX), and all of them are commercially available. TC sensors respond to changes in the thermal conductivity of the gas mixture. The TC sensor responds to a change in the composition of a gas mixture, but does not change the composition. The sensor response can be correlated to the concentration of a specific gas provided the sensor has been calibrated for that specific gas relative to a reference mixture [9]. Catalytic combustion sensors detect hydrogen and other

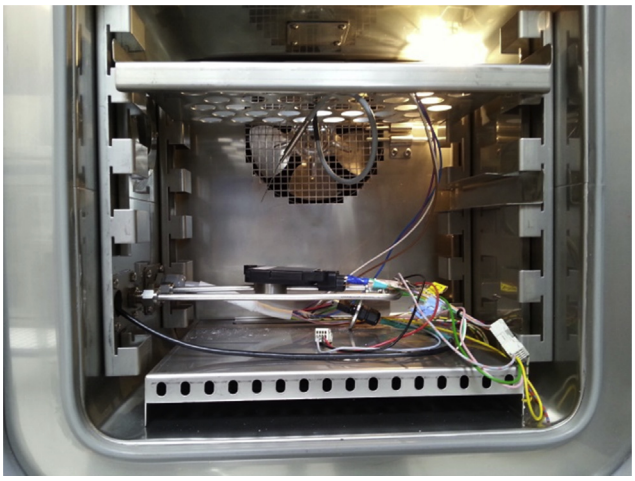

Fig. 3 – Gas sensor and gas supply line inside thermostatic chamber for flow-through temperature tests.

combustible gases calorimetrically, that is through the heat released from the catalytic combustion reaction of the analyte [9]. Semiconducting metal oxide sensors are one type of conductometric sensors. The operating principle of the MOX sensor is based on the change of electrical conductivity or resistance of a metal oxide material induced upon exposure to a reducing or oxidising gas that then increases or depletes the mobile charge carrier density within the conduction or valance bands of the semiconducting material [9]. Both the CC and MOX sensor react with hydrogen, and therefore change the test gas composition.

Table 1 lists the sensors and sensing elements tested in this study (according to the definition of ISO 26142 [1], a hydrogen sensing element *is the component that provides a measurable, continuously changing physical quantity in correlation to the surrounding hydrogen*, while a sensor *is an assembly, which contains one or more hydrogen sensing elements and may also contain circuit components associated with the hydrogen sensing elements, that provides a continuously changing physical quantity or signal in correlation to the physical quantity provided by the hydrogen sensing element(s)*). Multiple models of a given sensor platform were used in this study, as indicated by the numeric value added to sensor code indicated in Table 1 (e.g., TC-101 and TC-201 refers to two different thermal conductivity sensor models).

Except for CC-201, the TC and CC sensors output a response in units of vol% H_2 or an analogue (current or voltage) response that is readily converted to vol% H_2 using a nominal manufacturer-supplied calibration expression. The CC-201 sensor and MOX sensing element are integrated into an electronic circuit that outputs a voltage response that can be correlated to the hydrogen level; the circuit designs and operation were based upon standard designs for the sensor type. The electrical outputs for the MOX sensors used in this study, however, were relatively insensitive to changes in hydrogen concentration (i.e. the electrical signal was nearly saturated). For this reason the MOX sensors results were analysed separately from the results obtained with TC and CC sensors.

In the flow-through testing apparatus it is necessary to hermetically seal the interface of the sensors to the gas line to assure proper gas composition and control of sensor test parameters, especially for pressure dependence test, where dilution of hydrogen by air leaking into the testing apparatus, has been observed at pressures lower than the ambient. In general, a specific sensor interface design was necessary for each sensor model. A different sensor interface type was required for TC-101 and the MOX sensors since their physical design renders it unfeasible to assure a leak-tight seal between the gas line and the sensor head. These sensors were placed inside a micro-chamber (internal volume around 50 ml), where flow-through conditions were simulated. Photographs of both sensor interface types (a representative sensor holder and micro-chamber) are shown in Fig. 4.

The sensors were subjected to various test protocols to assess sensor performance. The tests were: accuracy, short-term stability, pressure dependence, flow rate dependence and temperature dependence [6] and were performed in the order indicated. Each of these test protocols was performed in both the chamber (Fig. 1) and flow-through apparatus (Fig. 2). Except in the flow dependence test, all testing was performed with a total fixed gas flow rate of 1000 Nml/min. For the chamber method tests, a step duration of 1 h was used, which gave sufficient time to allow the chamber to purge and for the sensor to reach a stable final indication. Alternatively, in tests performed with flow-through method, a step time of 10 min was sufficient. Descriptions of these tests as well as the results obtained are described in the following section.

Due to the different measuring range of the sensors, the chamber method tests were performed sequentially with two different sets of measurements. In the first set, the thermal conductivity and catalytic combustion sensors were mounted within the test chamber. In the second set, the metal oxide sensors were installed in the test chamber. Once the chamber method tests were completed, the sensors were transferred to the flow-through apparatus and retested. As mentioned

Table 1 – List of sensors/sensing elements tested.

Sensor Code Name	Operating principle	Sensor/Sensing element	Output Signal Type	Hydrogen concentration range (vol%)
TC-101	Thermal conductivity	Sensor	H2 ppm	0–100
TC-201	Thermal conductivity	Sensor	H2 ppm	0–2.4
CC-101	Catalytic Combustion	Sensor	0.5–4.5 VDC	0–4
CC-201	Catalytic Combustion	Sensor	analogue V	0–4
CC-301	Catalytic Combustion	Sensor	0.5–4.5 VDC	0–4
MOX-101	Metal Oxide	Sensing element	analogue V	0–1
MOX-201	Metal Oxide	Sensing element	analogue V	0.05–1

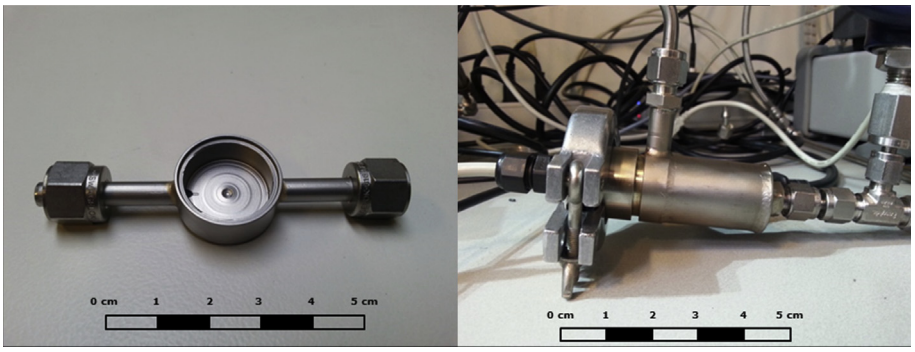

Fig. 4 – Sensor holder (left) that fits directly over the gas interface of a hydrogen sensor and micro-chamber (right) into which the sensor/sensing element were placed. The holders were used to perform tests in the flow-through apparatus.

above, the tests performed in the flow-through apparatus were identical to the ones performed in the chamber apparatus, except for the shorter time step and the addition of the flow rate dependence tests.

One of the advantages of the flow-through method is the possibility of testing a large number of sensors simultaneously, however most of the experiments were performed with individual sensors. The individual testing was chosen to prevent any influence of the sensors' particular location within the test fixture on the results. Additionally, in order to assess the influence of a series configuration on the test results the TC-101 and CC-201 sensors were tested simultaneously. The transduction mechanism of the TC does not change the chemical composition of the test gas, unlike the CC sensor, which chemically reacts with hydrogen. Therefore the order in which the sensors are placed in the test fixture in a series configuration may have an effect on the sensor response. Testing was conducted to quantify the effect of sensor position in a series configuration as well as that of the flow rate.

The sensor signal was logged into an electronic data file at a measurement frequency of 1 point each 5 s. The sensor final indication to a test gas was taken as the average of the last 100 s (20 data points) taken at the end of step. The final indication for the sensor response was either already provided in units of vol% H2 or converted to vol% H2 using a manufacturer supplied calibration expression. The output signal of the MOX sensing element is in units of volts, which was not converted into vol% H2 since the calibration expression was not available neither an experimental expression could be accurately determined. Sensors have been tested under test protocols that have been adapted from the ones present in ISO 26143 [1]. Sensor responses were compared to the tolerances specified in ISO 26143 [1] for the correspondent test protocol. The results obtained with the two configurations were compared to determine the impact of test method on sensor behaviour.

Sensor testing protocols and results

Specific details on the testing protocols and the results obtained, as well as the comparison of the test methods on sensor performance assessments, are presented in this section. The sensor responses determined in the various tests were in general within the tolerances defined in [1] for both the chamber and flow-through test method. This indicates that the flow-through method can provide comparable performance data as that obtained with the chamber method, but with the advantages of shorter testing time and less gas consumption. However, some appreciable differences in the sensor responses from the flow-through method as compared to those from the chamber method were observed, as shown in the following.

Accuracy test

In the accuracy test, the sensor final indication is compared to the various concentrations of a hydrogen test gas. The hydrogen concentration is controlled by in-line mixing of certified calibration gases of 1.0 ± 0.02% hydrogen in air (for concentrations up to 1 vol% H2) and 2.0 ± 0.02% hydrogen in air (for concentrations between 1 and 2 vol % H2) with synthetic air. The hydrogen concentration is increased and then decreased in discrete steps, according to the following sequence: 0, 0.2, 0.5, 0.8, 1.0, 1.2, 1.5, 2.0, 1.5, 1.2, 1.0, 0.8, 0.5, 0.2, and 0 vol% in air. Each concentration step is maintained for 1 h in the chamber test versus 10 min for the flow-through testing. Environmental conditions were maintained at ambient laboratory temperature, 100 kPa pressure and dry humidity (e.g., the test gas as obtained directly from the gas cylinder without humidification or drying, typically < 5% RH). In the case of MOX sensors (MOX-101 and MOX-202) the test protocol was slightly modified, since the manufacturer specified range is only up to 1 vol% H2 in air, with tests performed using 0, 0.2, 0.5, 0.8, 1, 0.8, 0.5, 0.2, 0 vol% H2 in air. To generate these hydrogen concentrations, a certified calibration gas 1 vol % hydrogen in air was mixed with synthetic air.

The initial comparison between sensor test methods was performed using data from the accuracy test. The data points in the following graphs show the sensor final indication in response to the test gas. Results from accuracy test in chamber and flow-through method for TC and CC sensors are shown in Figs. 5 and 6, respectively. The sensor response for both the ascending and descending hydrogen concentration steps is depicted, but the symbols overlap, which means there is no hysteresis. For comparison, the accuracy tolerance, as specified in ISO 26142 [1], is presented as well. In general, the results for the sensors tested in the chamber method show a

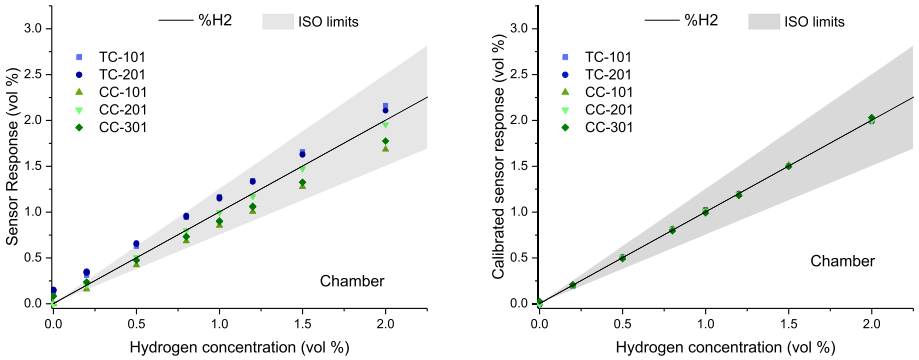

Fig. 5 – Accuracy test results for TC and CC sensors with chamber method. Left: Final indication (vol% H2) using the factory supplied calibration. Right: Normalised sensor response.

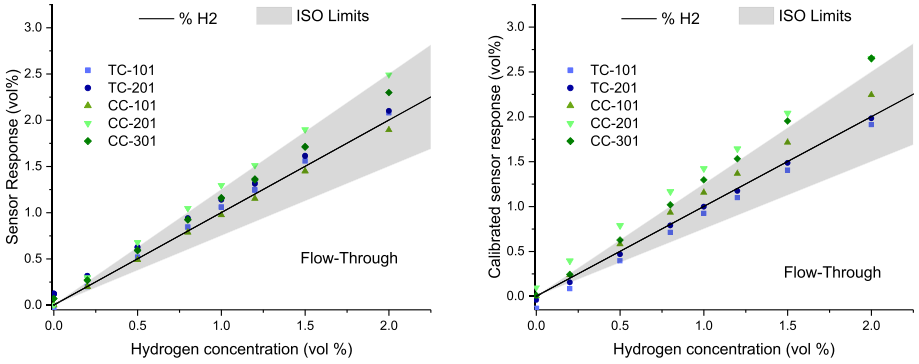

Fig. 6 – Accuracy test results for TC and CC sensors with flow-through method. Left: Final indication (vol% H2) using the factory supplied calibration. Right: Transformation of the final indication using normalisation as obtained from the chamber accuracy test.

good accuracy, within the limits established by ISO 26142 [1], where the allowable sensor response in vol% is ± 20% of the hydrogen test gas concentration (grey area in Figs 5 and 6). The only deviations from the ISO specifications are for the TC sensors at low hydrogen concentrations.

In order to better highlight the differences induced by the test method, the sensor response was normalised to the sensor response obtained during the accuracy test with the chamber method. This normalisation removes the variability in sensor to sensor behaviour, and also allows easier visualization of the impact of the test method on sensor performance. On the right side of Figs 5 and 6 the normalised sensor response is provided for comparison with the values obtained with the manufacturer provided calibration expression. It can be observed in Fig. 5 that the calibrated values fall, logically, in the black line that represent the actual hydrogen concentration of the test gas. For the flow-through method (in Fig. 6, right side) it can be seen that catalytic sensors deviate slightly from the values obtained in the chamber method, whereas the responses of TC sensors were nearly identical in both methods.

As stated above, the MOX sensing elements were subjected to a testing protocol with a maximum hydrogen concentration in air of 1% vol. The results of the accuracy tests on the MOX sensors are shown in Fig. 7 for both the chamber and flow-through methods. The MOX sensor final indication shows a low sensitivity within the hydrogen concentration range tested, meaning that the change of the resistance of the sensing element with changes in hydrogen concentration is small, even though this test is performed within the range as specified by the manufacturer. The extremely small change in electrical response with a change in hydrogen concentration makes it difficult to generate a useful calibration expression for these specific MOX sensors. Accordingly, in the following analysis, the analogue voltage was used for the sensor response. When comparing results with both methods, it can be observed that MOX-101 response has a slight increase in the flow-through method compared to chamber method, whereas MOX-201 obtains similar results in both methods. Both sensors show negligible hysteresis.

Short-term stability test

In the short-term stability test, the sensors are exposed to the hydrogen profile depicted in Fig. 8 (0, 1.0, and 2.0 vol% hydrogen in air). This exposure sequence was performed 9 times in order to assess the sensor short-term signal stability. Test conditions are maintained at ambient laboratory temperature, 100 kPa pressure and dry humidity. For the MOX sensors the hydrogen concentration steps were changed to 0, 0.1 and 1 vol% in air. Certified calibration gases of 0.1 and 1 vol % hydrogen in air were used. Same procedure was follow in the pressure and flow dependence tests.

All sensors tested in this study exhibit very good stability for both the chamber and flow-through test method as

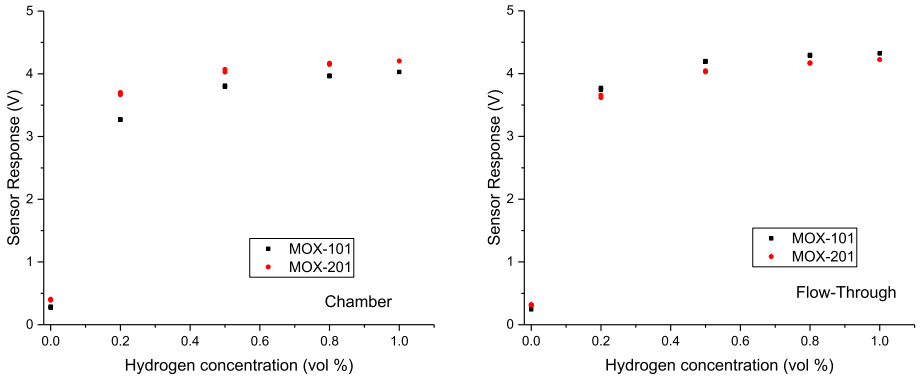

Fig. 7 – Accuracy test results for MOX sensors with chamber method (left) and flow-through method (right).

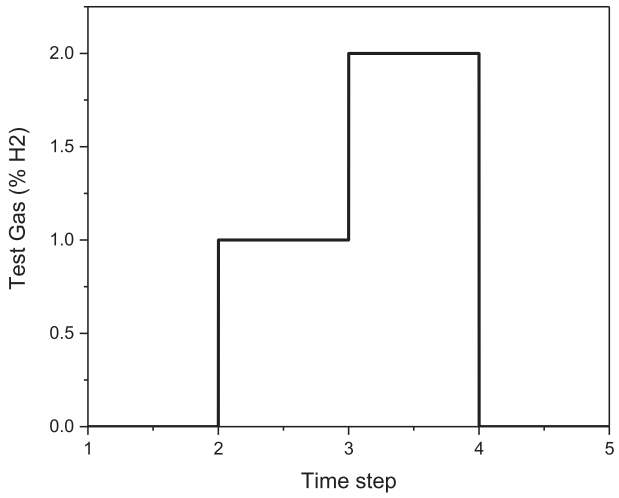

Fig. 8 – Hydrogen concentrations for each step in Short-term Stability test.

indicated by the results obtained from the short-term stability test (see Table 2). The values shown in this table are the maximum deviation in percentage observed within the 9 cycles performed in the short-term stability test, for every sensor and hydrogen concentration. This maximum deviation is calculated following equation (1).

$$Deviation = MAX\left(100*\frac{SR_i - Av}{Av}\right),\ Av = \frac{\sum_{i=1}^{9} SR_i}{9} \quad (1)$$

where SR_i is the sensor response in cycle i (i from 1 to 9).

The responses remain within the limits specified in ISO 26142 [1] for a similar test (±10% deviation in sensor response). As observed in the accuracy test, the CC sensors showed a slight increase in their response in the flow-through method compared with the chamber method.

In the short-term stability test MOX sensors responses to hydrogen are quite repeatable in both methods. Maximum deviations in chamber method are below 2%, whereas in flow-through these deviations never surpass 1%. As mentioned before, in the case of MOX sensors the sensor response analysed is the voltage output. From the results from the accuracy test (see Fig. 8) it is possible to observe that the sensor responses for 0,5% and 1% hydrogen concentration differ less than 3%. Given the limited sensitivity of the MOX sensors it is difficult to assess if the small deviations in the sensor responses observed in the short-term stability test fall outside the ISO 26142 limits when translated into hydrogen concentration.

Pressure dependence test

The pressure dependence test was performed in order to determine the influence of pressure on sensor response. In addition efforts were undertaken to establish the design requirements for a flow-through sensor test fixture to accommodate the pressure dependence test. Gas exposures were performed at pressure set points of 80, 100 and 120 kPa. For each pressure set point, the sensors were subjected to the following exposures, 0, 1.0, and 2.0 vol% hydrogen in air. Fig. 9 shows the evolution of pressure and hydrogen concentration during the test.

Fig. 10 depicts the results from the pressure dependence tests. It can be observed that the sensor response generally increases with increasing pressure (except for TC-201) for the same hydrogen concentration in the test gas. This effect is stronger in the case of the CC-101 and CC-301 sensors. When comparing results between chamber and flow-through method, it can be seen that the influence of the pressure on

Table 2 – Maximum percentage deviation from the average sensor response observed in short-term stability test for TC and CC sensors in chamber and flow-through methods.

	Chamber method					Flow-through method				
	TC-101	TC-201	CC-101	CC-201	CC-301	TC-101	TC-201	CC-101	CC-201	CC-301
0%H_2	4.9	2.0	0.0	0.3	1.1	6.3	3.9	0.0	0.0	0.5
1%H_2	0.5	0.6	0.3	0.3	0.8	0.1	0.8	0.1	0.0	0.4
2%H_2	0.2	0.4	0.2	0.7	0.5	0.1	0.5	0.2	0.0	0.3

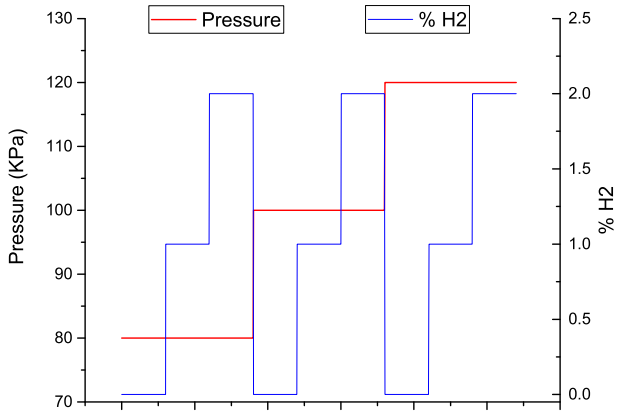

Fig. 9 – Pressure and hydrogen concentration evolution during pressure dependence test.

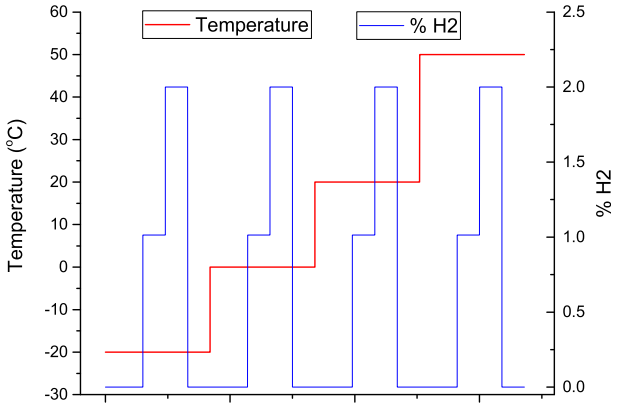

Fig. 11 – Temperature and hydrogen concentration evolution during temperature dependence test.

the sensor response is smaller for the flow-through method. According to ISO 26142 [1] for the equivalent test, the values obtained for 80 kPa and 120 kPa should not deviate more than 30% from the value obtained at 100 kPa. The sensors tested fulfil this requirement for both testing methods. Only CC-301, for 1 vol% hydrogen, 80 kPa, when tested in the chamber method has fallen outside this limit.

In the case of MOX sensors the pressure dependence tests showed that their response is barely affected by changes in the pressure in the range 80–120 kPa. Sensor responses (in volts) for 80 kPa and 120 kPa deviate less than 1% compared to the sensor response at 100 kPa. This lack of pressure dependence is observed both in chamber and flow-through methods.

Temperature dependence test

The temperature dependence test was performed in order to determine the influence of temperature on sensor response. It was also performed to develop the design requirements for a flow-through sensor test fixture that can accommodate the temperature dependence test. Gas exposures were performed at temperature set points of −20 °C, 0 °C, 20 °C, 50 °C. For each temperature set point, the sensors were exposed to 0, 1.0, and 2.0 vol% hydrogen in air. The evolution of temperature and hydrogen concentration during the test is shown in Fig. 11. All the sensors have been operated within their temperature operational range. MOX sensors were not tested under this protocol.

In Fig. 12 the results from the test on temperature dependence are presented. According to ISO 26142 [1] for the equivalent test, the values obtained for −20 °C, 0 °C and 50 °C should not deviate more than 20% from the value obtained at 20 °C. For the test performed with chamber method, all sensors fulfil the requirements of ISO 26142. For sensor CC-101 the results at −20 °C reveal an erratic response which may have to do with the placement of the sensor in the chamber and needs to be investigated further. These results are therefore not shown. There is no clear trend in the response of the sensors when changing the environmental temperature. For some sensors the response decreases with the temperature (CC-201 and CC-301), others show an increase of their response up to 20 °C and then a decrease when tested at 50 °C (TC-201 and CC-101). In the case of TC-101 the highest response is obtained at 0 °C. Also the baseline is affected by temperature.

Tests performed with flow-through method (Fig. 12, right) gave a similar qualitative result, the sensors do not deviate more than 20% from the value obtained at 20 °C, as required by [1]. As with the test performed with chamber method, CC-201 and CC-301 responses decrease when increasing the temperature. In the case of CC-301, the response is significantly

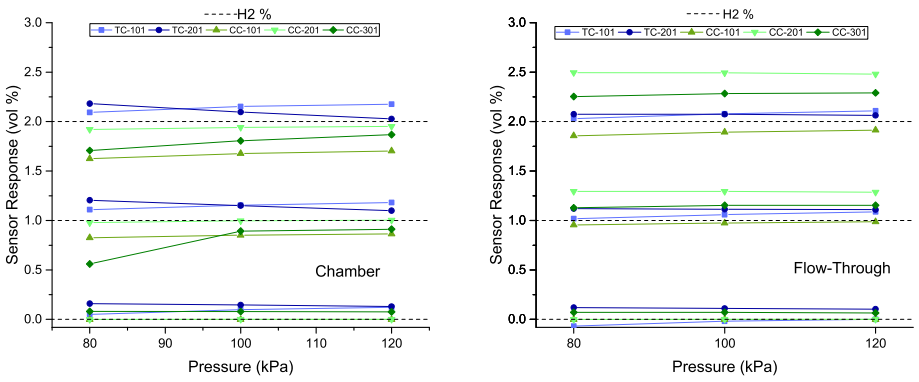

Fig. 10 – Pressure dependence test results for TC and CC sensors with chamber method (left) and flow-through method (right).

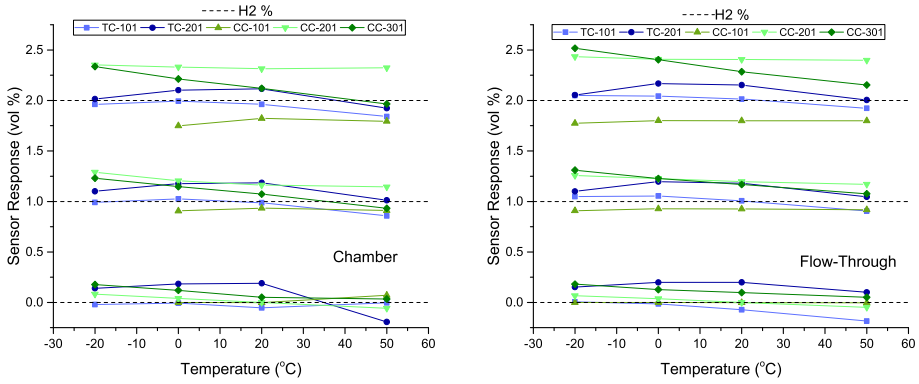

Fig. 12 – Temperature dependence test results for TC and CC sensors with chamber method (left) and flow-through method (right).

higher when tested in flow-through compared to the results obtained with the chamber method, as also observed in accuracy and pressure dependence tests. TC-101 shows a similar behaviour than CC-201 and CC-301, the sensor response decreases with higher temperatures. This dependence is also observed in chamber method, but in the range from 0 °C to 50 °C, since from −20 °C to 0 °C the response slightly increases.

In general the two methods lead to very similar results for the sensors. However, for CC-101 it was observed that sensor response was barely affected by the temperature when tested in flow-through and more strongly in chamber method. TC-201 results in flow-through method are similar to the ones obtained in chamber method. It can also be observed that its response decreases considerably when tested at 50 °C.

Flow rate dependence test

This test is performed only in flow-through testing apparatus. Sensors are exposed to total gas flow rates of 100, 500, 1000 and 2500 Nml/min. For each flow rate set point, the sensors were subjected to the exposure profile 0, 1.0, and 2.0 vol% hydrogen in air. The evolution of gas flow and hydrogen concentration during the test is shown in Fig. 13.

A characterisation of flow rate dependence is depicted in Fig. 14 for TC and CC sensors. It can be seen that, in the case of CC sensors, the response of the sensors increases with increasing flow, especially at small flows. This effect is not observed for TC sensors, for which the flow rate has a negligible effect on the sensor response. Comparing the sensor responses for the two methods, it can be observed that for CC sensors, the values obtained at low flows (100 Nml/min) in the flow-through method are similar to the ones of the chamber method with a flow of 1000 Nml/min. In the case of TC 101 sensor, the chamber method generally produces higher responses than flow-through for any flow considered, but the difference is not deemed significant. The MOX sensors do not show a strong dependence on the flow rate since the differences observed in the sensors responses between minimum and maximum flow rate were around 0.5%.

A nominal flow rate set for the chamber method does not mean that this flow rate is actually reaching the sensing element, which may help to explain the flow rate dependence observed in the CC sensors. Depending on the configuration inside the chamber, an area of local hydrogen depletion may form around the CC sensor, even for the flow rate of 1000 Nml/min. Further experiments are planned to verify this effect.

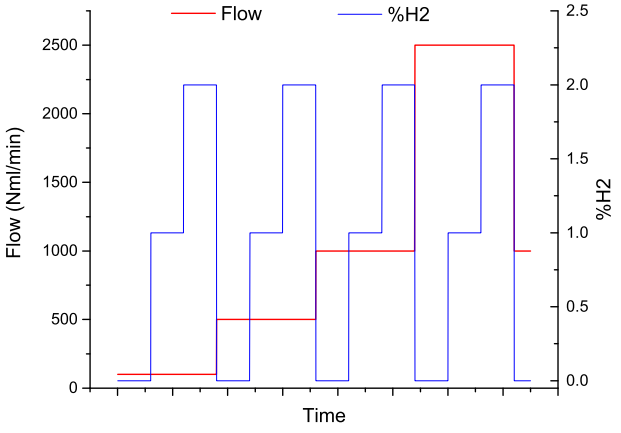

Fig. 13 – Flow rate and hydrogen concentration evolution during flow rate dependence test.

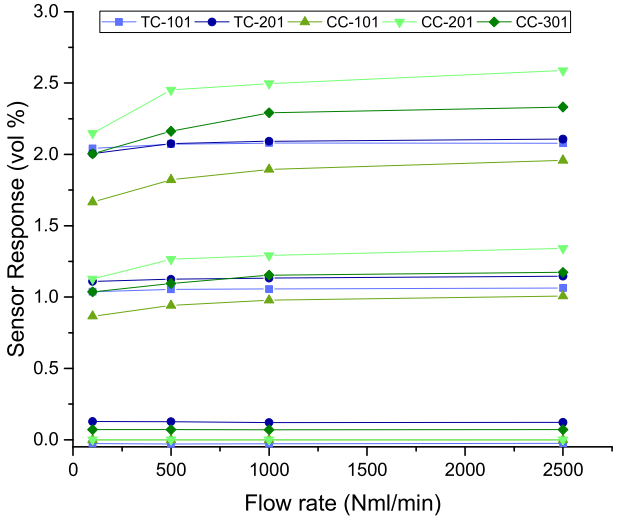

Fig. 14 – Flow rate dependence test results in flow-through method for TC and CC sensors.

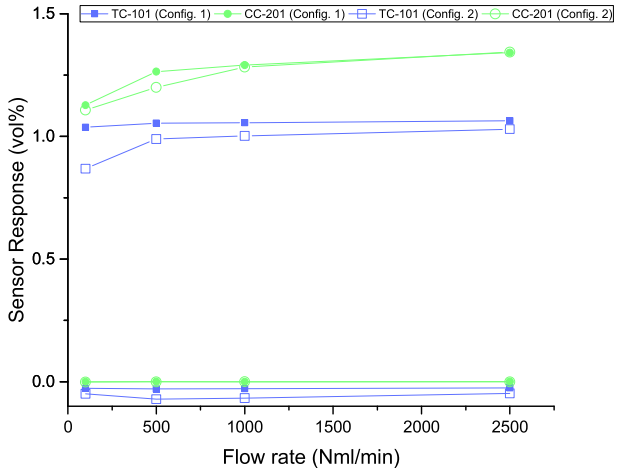

Fig. 15 – Influence of sensor location in flow-through apparatus for sensors arranged in series.

Importance of sensors placement during flow-through test

Flow rate dependence tests were also performed with two sensors configured in series in the flow-through apparatus. As previously mentioned, some sensor platforms such as catalytic combustion or metal oxide, consume hydrogen as part of the specific detection mechanism. This means that the hydrogen level in the test gas is depleted through the operation of those sensors. Therefore the placement of sensors consuming hydrogen in a series configuration has to be considered carefully, as the sensors downstream may not be exposed to the same hydrogen concentration as the sensors upstream. In order to assess the magnitude of this effect, TC-101 and CC-201 were installed in two different configurations. In the first configuration (config. 1 in Fig. 15), TC-101 is placed upstream relative to CC-201. In the second configuration (config. 2 in Fig. 15) the sensors' positions were reversed. If the CC sensor is measurably depleting hydrogen in the test gas, the TC sensor should give a lower reading in the second configuration compared to the first. In Fig. 15, the sensor responses obtained for different flows of 0 vol% H2 and 1 vol% H2 in air are shown for the two configurations. It can be observed that TC-101 has a significantly lower response when placed downstream from CC-201 (configuration 2, open black square symbols), demonstrating that the CC sensor changes the composition of the gas. This effect is, as expected, more pronounced at lower rates. The results suggest that this influence can be reduced by increasing the flow rate. In the current set-up the effect of hydrogen depletion is minimal at 2500 Nml/min, but this is expected to depend on the test apparatus used and the sensors used.

Results summary

The performance of the different sensors, were similar with both methods, thus demonstrating that changing the test methodology will not fundamentally yield different results. Sensors performances fall within the limits stated in the ISO standard [1] (in the case of TC and CC sensors) for the equivalent tests regarding accuracy, short-term stability and pressure dependence. Similar conclusions can be reached from the results obtained with MOX sensors.

From a quantitative aspect, the TC sensors results obtained in the chamber method are better replicated in flow-through method. However CC sensors show a higher response when exposed to the same hydrogen concentration in flow-through relative to that obtained in chamber method. Perhaps this is due to the reaction of hydrogen on the CC surface, which lowers the local concentration of hydrogen at the sensor, an effect that is offset by higher flow rates. In the case of MOX sensors, results obtained in both methods are more comparable for MOX-201 than for MOX-101, within the experimental error.

The main advantage of the flow-through testing is that the experiments can be performed much faster (a factor of 10 seems feasible) than the chamber method. This also means that, for the same flow rate, the volume of test gas will be lower. For both methods, multiple sensors can be tested simultaneously. For the chamber method, there is a limitation to the number of sensors based on the space in the chamber. For the flow-through fixture, in principle a large number of sensors can be placed in series or parallel. Therefore flow-through testing instruments can be recommended for the performance testing of sensors, as long as some general guidelines are adhered to, which are presented in the correspondent section.

Conclusions

The aim of this work was to validate the flow-through method as a faster and more economical alternative of the traditional chamber method to assess hydrogen sensors performance. Accuracy, short-term stability and pressure dependence tests were performed on several sensor platforms (Thermal Conductivity, Catalytic Combustion and Metal Oxide) in experimental apparatus based on chamber and flow-through methods [1].

A new flow-through apparatus was designed and built to perform the tests mentioned above. During the implementation of this system several potential pitfalls were encountered. In order to enable the accurate characterisation of sensors on flow-through test apparatus, guidelines are presented on the design and testing protocols.

Of the issues encountered for the test apparatus, the most challenging was working out a well-functioning flow/pressure control of the system and the ability to maintain a leak proof interface between the sensor and gas supply line. A leak proof interface was particularly troublesome for some sensor designs. Solutions to these problems were implemented in the design features of the flow-through apparatus. For example, some sensors required a micro-chamber (Fig. 2).

For a series configuration for the testing of sensors, there is a potential influence on a sensor response due to the presence upstream of sensors that have an operating principle based on hydrogen consumption (Catalytic, MOX). This effect has been demonstrated. The response of the TC sensor was lower when placed downstream the CC sensor than the one obtained when the TC sensor was placed upstream the CC sensor. This effect can be minimized with higher flow rates or avoided when sensors are placed in parallel.

Regarding the testing methodology itself, the flow rate dependence needs careful consideration. The response of the CC sensors tested shows marked flow rate dependence and, correspondingly, a higher response in the flow-through method than for the chamber method, for all flow rates above 100 Nml/min. The TC sensors did not exhibit significant flow rate dependence.

Guidelines

Some guidelines for the design and operation of a flow-through method test apparatus have been developed and include:

General

- Pressure control (above and below ambient) is feasible with a vacuum pump and pressure controller as shown in Fig. 3. The apparatus should be fitted with a back-pressure controller plus a buffer tank, as otherwise pressure control may cause flow fluctuations through the MFCs. The effect is most pronounced if there is a small internal volume of the experimental system.
- Temperature control (above and below ambient) can be reached by different ways. In our experimental set-up a thermal bath in the case of chamber method (Fig. 1) and a thermostatic chamber for the flow-through (Fig. 3) have been used. In the case of the flow-through it was also considered the possibility of wrapping the supply lines with electrical heaters, however this solution would only work for testing at temperatures above room temperature. In addition, the thermostatic chamber provides a better control of the cooling/heating process.
- The interface of the sensor (or sensing element) to the gas manifold needs to be leak tight, which is not always easy to achieve. For some types of sensors, the construction of a micro-chamber containing the entire sensor may be the only option to ensure a tight seal. In particular pressure dependency tests require a good level of leak tightness.

Testing methodology

- The same testing protocols as for the chamber method can be performed. However, for the pressure dependence testing, the results should be checked carefully as abnormally low responses of the sensors may indicate leaks at lower than ambient pressures (i.e. dilution of hydrogen by air leaking into the testing apparatus).
- Flow rate dependence of sensor response should be taken into account when choosing the flow rate. Not all sensor platforms are affected by flow rate changes. In the case of the CC sensors tested, their responses increase with the flow. It was also observed that the CC sensor responses are closer to the responses obtained with the chamber method when they are tested at low flows (100 Nml/min). To identify the minimum testing flow that provides sensor responses and/or behaviour comparable to the chamber method will be important to make the flow-through method more cost-effective.

Placement of sensors

- Series configuration may cause problems if the sensors operation is influencing the test gas composition. The detection mechanism of some platforms is based on the consumption of hydrogen (e.g. combustible gas sensors, MOX sensors), therefore sensors downstream may be exposed to less hydrogen than those upstream. Setting an appropriately high flow rate may circumvent this issue. The relationship between flow rate and hydrogen consumption must be quantified. It may be necessary to implement an independent verification of the hydrogen concentration in the incoming and exhaust gas lines to verify that hydrogen consumption was not significant.
- Parallel configuration calls for the placement of multiple MFCs in order to ensure that all the sensors will be exposed to same flows and hydrogen concentrations. Although this may lead to additional complexity of the testing apparatus, in case of testing CC and MOX sensors, this configuration is recommended.

Evaluation of sensor performance

- The experiments have shown that the flow rate can have an influence on the response of the sensors. In particular the CC sensors show a significantly higher response with higher flow rates, which can be explained by their mode of operation. The response for these sensors may even be outside the ISO 26142 limits if the sensors were calibrated at a lower flow rate. For evaluation of sensor performance the deployment conditions should be considered and the flow rate chosen accordingly.

Acknowledgments

The work presented in this paper is the result of an on-going collaboration between the sensor laboratory at the National Renewable Energy Laboratory (NREL) [4] in the U.S. and the Joint Research Centre (JRC) of the EC. The JRC-NREL collaboration was formalized under a Memorandum of Agreement that was signed in 2010 [10]. There have been additional collaboration agreements between NREL and the JRC, including work performed within the framework of a common call between the European Fuel Cell and Hydrogen Joint Undertaking (FCH JU) and the U.S. Department of Energy; one aspect of this agreement was the project H2Sense [11]. Presently, the NREL-JRC collaboration is under the auspices of a program-level agreement between the U.S. Department of Energy and the JRC [12]. A round-robin testing of the respective laboratories (Sensor INTerlaboratory COMparison, SINTERCOM [6]), together with numerous scientific publications [13–18] as well as a book on hydrogen sensors [9] resulted from the NREL-JRC sensor laboratories collaboration.

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