INTERNATIONAL JOURNAL OF HYDROGEN ENERGY 40 (2015) 11740–11747

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Selectivity and resistance to poisons of commercial hydrogen sensors

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ARTICLE INFO

Article history:
Received 19 November 2014
Received in revised form
23 February 2015
Accepted 25 February 2015
Available online 20 March 2015

Keywords:
Hydrogen sensors
Hydrogen safety
Cross-sensitivity
Poisons
Inhibitors
Interferents

ABSTRACT

The resistance of several models of catalytic, workfunction-based metal-oxide-semiconductor and electrochemical hydrogen sensors to chemical contaminants such as SO_2, H_2S, NO_2 and hexamethyldisiloxane (HMDS) has been investigated. These sensor platforms are among the most commonly used for the detection of hydrogen. The evaluation protocols were based on the methods recommended in the ISO 26142:2010 standard. Permanent alteration of the sensor response to the target analyte (H_2) following exposure to potential poisons at the concentrations specified in ISO 26142 was rarely observed. Although a shift in the baseline response was often observed during exposure to the potential poisons, only in a few cases did this shift persist after removal of the contaminants. Overall, the resistance of the sensors to poisoning was good. However, a change in sensitivity to hydrogen was observed in the electrochemical platform after exposure to NO_2 and for a catalytic sensor during exposure to SO_2. The siloxane resistance test prescribed in ISO 26142, based on exposure to 10 ppm HMDS, may possibly not properly reflect sensor robustness to siloxanes. Further evaluation of the resistance of sensors to other Si-based contaminants and other exposure profiles (e.g., concentration, exposure times) is needed.

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Introduction

Hydrogen sensors are an important enabling technology for the safe implementation of the emerging hydrogen infrastructure. Hydrogen sensors are deployed to increase safety in applications such as hydrogen production, storage, distribution and use. The market acceptance of emerging hydrogen and fuel cell technologies depends directly on their perceived safety. Therefore hydrogen safety measures have been developed to ensure the safe use of hydrogen, including guidelines for mitigation of fault and accidents. Hydrogen safety sensors can indicate hydrogen concentrations before the lower flammability limit (LFL) of 4 vol% in air is reached. Sensors are used to trigger an alarm, which may be followed by additional measures such as closing off the hydrogen

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http://dx.doi.org/10.1016/j.ijhydene.2015.02.120
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supply, increasing ventilation or initiating system shutdowns. This is a significant contribution to the safe use of hydrogen. To facilitate the reliable and proper use of hydrogen sensors sensor testing facilities were independently established by the European Commission's Joint Research Centre - Institute for Energy and Transport (IET) [1] and by the US Department of Energy (DOE) at the National Renewable Energy Laboratory (NREL) [2].

Many types of hydrogen safety sensors are commercially available, based on different mechanisms to detect hydrogen. These sensors generally provide for a reliable detection of hydrogen under a broad range of ambient conditions, however, performance gaps have been identified regarding some applications [3]. Hydrogen sensors are widely implemented in industrial applications [4], but the deployment of hydrogen safety sensors in novel applications may lead to different and more challenging performance requirements. Sensor selectivity and robustness against poisons are especially important in applications where numerous chemical species could be present and the exposure of the hydrogen sensor to a different species, i.e. contaminants, can lead to false alarms. As an example, sensors deployed in hydrogen refueling stations are likely to be exposed to NOx and SOx from the internal combustion engines of conventional vehicles. The lubricants and sealants used in warehouses may be harmful to sensors mounted close to indoor refueling points for materials handling vehicles. Contaminants may also temporarily or permanently alter the sensor's response to hydrogen, which could have serious safety consequences as leaked hydrogen may go undetected.

Selectivity describes the ability of a sensor to respond to the target analyte without influence from the presence of contaminants. A gas sensor developed for a specific target analyte (e.g. hydrogen) should not respond to other species that may be incidentally present at the point of use. The sensitivity of the hydrogen sensor to other gases is referred to as cross-sensitivity. When the presence of a chemical other than the target gas induces a temporary change in the sensor response, it is termed an interferent, whereas chemicals which permanently affect a sensor response to the target analyte are termed poisons. A hydrogen sensor fails the requirement of ISO 26142 when its response to hydrogen varies by more than 20% as a result of exposure to a contaminant [5]. It is noted that a contaminant may be a poison on one sensor platform but may be an interferent or even inert on another. In this paper we report the resistance to poisoning of catalytic, metal-oxide-semiconductor and electrochemical hydrogen sensor platforms evaluated to procedures and requirements laid out in ISO 26142. This work was initiated under the auspices of a JRC-NREL Memorandum of Agreement [6].

There are a great variety of commercially available hydrogen sensing platforms. The most commonly deployed platforms are electrochemical (EC) and catalytic pellistor (CAT) sensors [7]. A relatively new platform for hydrogen sensing is the workfunction-based metal-oxide semiconductor sensor (MOS). While these platforms have distinctively different hydrogen detection mechanisms, they all share a common feature: all use a catalyst material for the dissociation or combustion of hydrogen. The electrochemical oxidation of hydrogen in EC sensors typically takes place on a Pt/C catalytic layer [8]. The Pd or Pt catalyst of CAT sensors is commonly coated onto the alumina bead containing the filament. MOSFET hydrogen sensors use platinum, palladium or an alloy containing these metals as the catalytic gate material deposited as a thin film on an insulating oxide layer.

This catalyst may be susceptible to contaminants, which may influence the response of the sensor to hydrogen. The sensors tested, as listed in Table 1 were selected based on their proven robust performance, high level of development, and widespread deployment.

In this work, the performance of these sensors during exposure to potential poisons is evaluated. This is a continuation of previous work, which analyzed the effect of potential interferents on these and other sensor types [9]. Detailed descriptions of the detection principles of the various hydrogen detection platforms has been presented elsewhere, e.g. Ref. [7]. The specific contaminants used in this study were chosen because they are listed in ISO 26142 as species to which the resistance to poisoning of hydrogen detection apparatus needs to be evaluated for certification (see Table 2) [5].

Sensors based on catalyzed chemical reactions (such as CAT and EC) make use of noble metal catalysts (e.g. Pd, Pt) which may be susceptible to catalyst poisoning. A poisoning effect on the catalyst may be due to blocking of an active site, affect the adsorption of other species, or the chemical nature of the catalyst through the formation of new compounds [10]. The interaction between a potential poison and the catalyst depends in part on the electronic configuration of the species involved, which controls both the formation and orientation of chemical bonds between a poison and the catalyst. Elements of the nitrogen (N, P, As, Sb) and oxygen (O, S, Se, Te) groups act as poisons on platinum group metal catalysts [10]. The availability of electrons for bonding can also explain the order of increasing poisoning activity for sulphur species, as H_2S has a stronger effect that SO_2 [11].

The effect of catalyst poisons on the performance of gas sensors is well known and counter-measures have been developed by sensor manufacturers. Different design strategies have been employed by sensor manufacturers to minimize cross-sensitivity and improve sensor resistance to poisons (e.g. Ref. [12] for metal-oxide conductometric sensors). The sensor stability will depend on the properties of the catalyzing material and on the presence of filters or protective membranes such as molecular sieve coatings. The interferents would otherwise attach to and block the active sites of the catalyst inhibiting the hydrogen oxidation reaction, which corresponds to the basic detection principle of a catalytic sensor. A physical barrier can protect the catalyst material by preventing poisoning species from reaching it. For example, hydrogen-permeable films of polytetrafluoroethylene [13] or fluorinated ethylene propylene [14] deposited on or above the catalytic surfaces have been used to prevent the diffusion of potential poisons and interferents to the catalyst. An outer zeolite layer has been proposed for a catalytic sensor to trap larger molecules before reaching the gas sensing element [15], as well as active charcoal or other filter materials [16]. For electrochemical sensors, membranes or diffusion barriers have been used to improve selectivity as

Table 1 – Overview of tested sensors.

Sensor technology	Acronym	Reported measuring range	Reported cross-sensitivity
Catalytic	CAT-1	0–1.4 vol%	Response to combustible gases
(Combustible gas sensor)	CAT- 2	1–4 vol %	
Electrochemical	EC	0 – 4 vol %	No response to NO_2, H_2S and SO_2
Workfunction based semiconductor-metal-oxide	MOS	0–4.4% vol %	No response to H_2S, NO_2

well as reduce the effect of poisons [8]. Such physical barriers are usually based on a size exclusion effect, but chemical barriers have also been proposed. The use of a secondary catalyst material, providing strong redox sites to react with poisons, but not catalysing gas combustion is described in a US patent [17]. In general sensor manufacturers treat the identity and nature of the catalyst as well as the protective measures as proprietary.

Experiments and procedures

The impact of exposure to SO_2, H_2S, NO_2 and HMDS on the performance of several hydrogen sensor platforms is reported in this work. Four representative commercial sensor platforms.

(4 sensor models total) were selected. Two representative models of the catalytic platform were tested, with CAT-1 corresponding to a low-cost model and CAT-2 to a more complex model of combustible gas sensor. Neither model was listed by the manufacturer as being poison resistant.

Cross-sensitivity testing procedure

The impact of chemical species as potential poisons on hydrogen sensors was evaluated in a dedicated test fixture, which was designed and built for testing the performance of hydrogen sensors exposed to contaminants. The tests are performed by exposing the sensors to gas flows alternating between hydrogen (1 vol%) and the contaminants as well as a combination of hydrogen with the contaminant at controlled concentrations. Environmental parameters in the test chamber were maintained at 25 °C ± 2 °C and 100 kPa ± 2 kPa. Dry test gases were used in experiments so that the relative humidity was typically less than 5%. The total gas flow rate in the test chambers was 1000 sccm. The desired test gas mixtures were generated by dynamic mixing of synthetic air, 2 vol% H_2 in air and certified mixtures of the contaminant gas in air. The concentration of all test gases was calculated from the ratio of the respective gas flow rates as controlled by mass flow controllers.

Table 2 – Concentration of contaminants.

Gases	Concentration [ppm]
Sulphur dioxide	500
Hydrogen sulphide	50/40[a]
Nitrogen dioxide	20
HMDS	10

[a] Due to a change in gas bottle, the concentration of H_2S was 40 ppm for the test on the EC sensor.

The exposure profile used for the cross-sensitivity test is illustrated in Fig. 1 and consists of the following stages:

(a) Operation in clean air, followed by exposure to 1 vol% H_2 in air and subsequent recovery in clean air (initial response test based on ISO 26142). The sensor response to this initial exposure to hydrogen was scaled so as to indicate 1 vol% in the following plots.
(b) Exposure to the contaminant at the concentration specified in Table 2 followed by simultaneous exposure to 1 vol% H_2 in air and subsequent recovery in the contaminant gas mixture (poisoning test based on ISO 26142).
(c) The exposure sequence in stage (a) was repeated to highlight any short term influence on the sensor's response to hydrogen following exposure to the contaminant (final response test based on ISO 26142).

Table 2 indicates the concentrations of potential poisons used in this study. The concentrations were selected close to the levels specified in the ISO 26142 standard. Hydrogen concentration was set to 1 vol%, which is 25% of the LFL and a common alarm set point.

Cross-sensitivity/poisoning assessment

The effect of the contaminants on the sensor response was evaluated by comparing the sensor response to air (baseline response) and to 1 vol% hydrogen in air in the presence and absence of the contaminant. In order to quantify the cross-sensitivity and the poisoning effect of the different sensors tested, the cross-sensitivity factors, X_0 and X_H, and the poisoning factor X_P were defined, X_0 was defined as the ratio of net sensor response to the contaminant and the net sensor response to 1 vol% H_2 in air and is given by formula (1). This factor captures the increase or decrease of the sensor response (as an apparent vol% H_2) caused by the presence of the contaminant. The X_H factor is defined as the ratio of the difference in sensor response to 1 vol% hydrogen in air in the presence and absence of the interferent to the net sensor response to hydrogen in air and is given by the formula (2).

The second factor reflects the change in sensitivity to hydrogen in the presence of the interferent.

The third factor, X_P is defined as the ratio of net sensor response to 1 vol% H_2 in air before and after the exposure to the contaminant and the net sensor response to 1 vol% H_2 before the exposure. It is given by the formula (3).

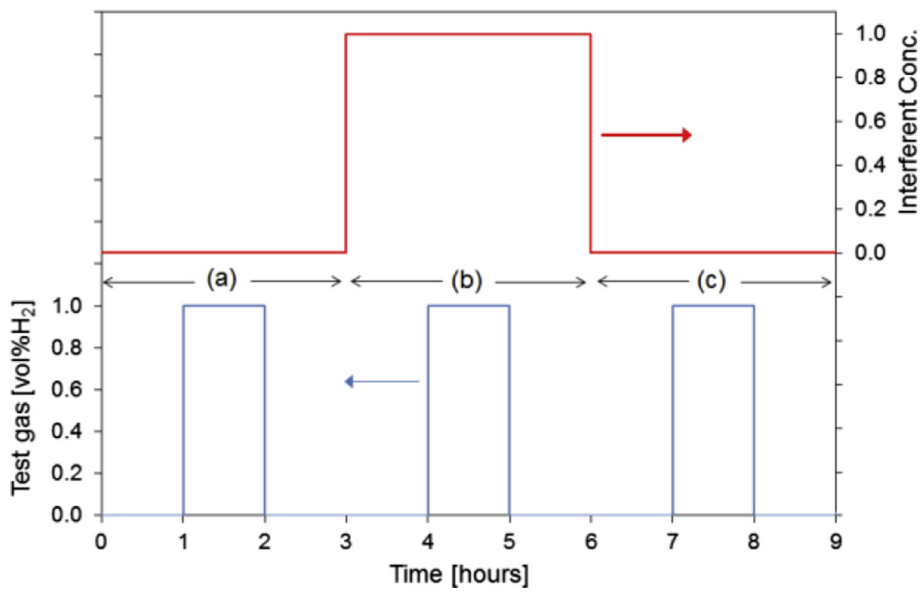

Fig. 1 – Exposure profile for the cross-sensitivity test showing hydrogen concentration (vol% in air) and contaminant concentration (arbitrary units). The letters a – c correspond to the different stages of the test as described in the text.

$$X_0 = \frac{R_i - R_0}{R_H - R_0} \quad (1)$$

$$X_H = \frac{R_{H,i} - R_i}{R_H - R_0} - 1 \quad (2)$$

$$X_P = \frac{R_{H,final} - R_0}{R_H - R_0} - 1 \quad (3)$$

R_0 represents the sensor response in clean air; R_H is the sensor response to 1 vol% hydrogen in air; R_i is the sensor response in the presence of the interferent "i" (at concentrations listed in Table 2); $R_{H,i}$ is the sensor response to 1 vol % hydrogen in air in the presence of the interferent "i". These values are determined at the end of each exposure period. $R_{H,\ final}$ is the sensor response to 1 vol% hydrogen in air in stage (c) as described in section Cross-Sensitivity Testing Procedure.

Results and discussion

X_0, X_H, and X_P calculated for all the sensors tested are tabulated in Table 3. According to the definitions, the contaminant has no influence on the sensor response when the values for X_0 and X_H are both equal to zero. The error of the cross-sensitivity factors was evaluated case by case considering the noise on the sensor response and the sensor resolution. In case of X_H, the error on the actual hydrogen concentration was also taken into account. Both the sensor resolution and the

Table 3 – Cross-sensitivity factors and poisoning effect.

Species	Sensor code	X_0	X_H	X_P
50/40 ppm H_2S	Cat 1	−0.06 ± 0.01	−0.05 ± 0.02	−0.05 ± 0.01
	Cat 2	0.02 ± 0.02	0.00 ± 0.02	−0.03 ± 0.01
	EC	0.04 ± 0.03	0.35 ± 0.05	0.04 ± 0.03
	MOS	0.00 ± 0.03	−0.01 ± 0.04	0.00 ± 0.03
500 ppm SO_2	Cat 1	−0.84 ± 0.02	0.08 ± 0.04	−0.45 ± 0.02
	Cat 2	0.00 ± 0.01	−0.03 ± 0.02	−0.03 ± 0.01
	EC	0.07 ± 0.03	0.38 ± 0.05	0.11 ± 0.03
	MOS	0.00 ± 0.03	0.01 ± 0.03	0.00 ± 0.03
20 ppm NO_2	Cat 1	0.00 ± 0.01	0.01 ± 0.02	0.00 ± 0.01
	Cat 2	–	–	–
	EC	0.00 ± 0.03	0.01 ± 0.03	−0.05 ± 0.03
	MOS	0.00 ± 0.03	−0.01 ± 0.03	0.00 ± 0.03
10 ppm HDMS	Cat 1	0.00 ± 0.02	0.05 ± 0.03	0.04 ± 0.02
	Cat 2	0.03 ± 0.01	−0.03 ± 0.03	0.03 ± 0.01
	EC	0.00 ± 0.03	−0.01 ± 0.03	0.00 ± 0.03
	MOS	0.00 ± 0.03	−0.01 ± 0.03	0.00 ± 0.03

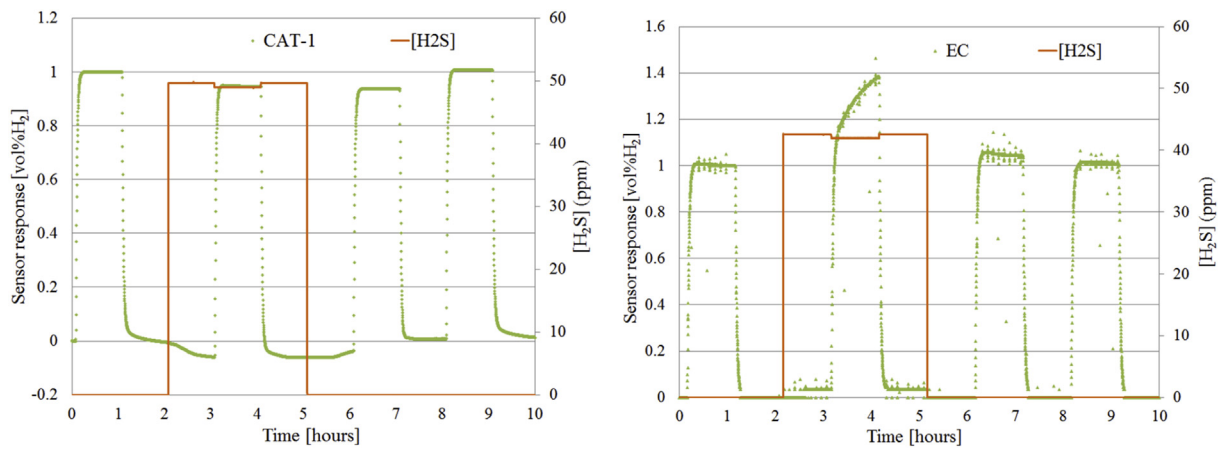

Fig. 2 – Effect of 50 ppm H_2S on the response of the catalytic sensor CAT-1 (left) and the electrochemical sensor EC (right).

sensor lower detection level were determined experimentally. X_P factors greater than 0.2 would be out-of-compliance with the requirements of ISO 26142.

Sulphur-containing compounds

Sulphur-containing species such as sulphur dioxide (SO_2) and hydrogen sulphide (H_2S) can be present as impurities either in hydrogen or in air, as sulphur is a common constituent in many hydrocarbon fuels.

For the catalytic sensor CAT-1, the exposure to H_2S resulted in a decrease of the baseline (see Fig. 2(left)). The effect was, however, not permanent, as the sensor baseline returned to the value prior to the H_2S exposure after one exposure to H_2 in clean air. The model CAT-2 was not affected by the exposure to H_2S. For these sensors, at the given H_2S concentrations, the poisoning effect is negligible. The impact of H_2S exposure on an electrochemical sensor is shown in Fig. 2 (right). The presence of H_2S induced an increase in the baseline of the EC sensor due to a positive cross-sensitivity to H_2S. Remarkably, the response of the sensor to a mixture of hydrogen and H_2S was much greater than the response observed for hydrogen only (more than 30% increase of sensitivity). A pronounced drift of the signal can be observed.

The MOSFET sensor response was not affected by the exposure to H_2S (see Table 3).

Fig. 3 (left) shows the exposure profiles of the catalytic sensors CAT-1 and CAT-2 to 500 ppm of SO_2. A marked decrease of the baseline was observed for CAT-1, which recovers only partially following the removal of SO_2. As a consequence of the exposure to the contaminant, the sensor response to hydrogen decreases by 45% implying failure of the sensor according to ISO26142. A minor increase of the net response to H_2 was found during the exposure to SO_2. Different behavior was observed for the other catalytic sensor model. The sensitivity to H_2 of CAT-2 was slightly decreased due to the exposure to SO_2, but in this case the baseline was unaffected.

The effect of SO_2 on the electrochemical sensor was similar to that of H_2S (see Fig. 3 (right)). Both the baseline and the response to hydrogen increased. As observed for the presence of H_2S, the sensor signal is subject to drift. The effect on the

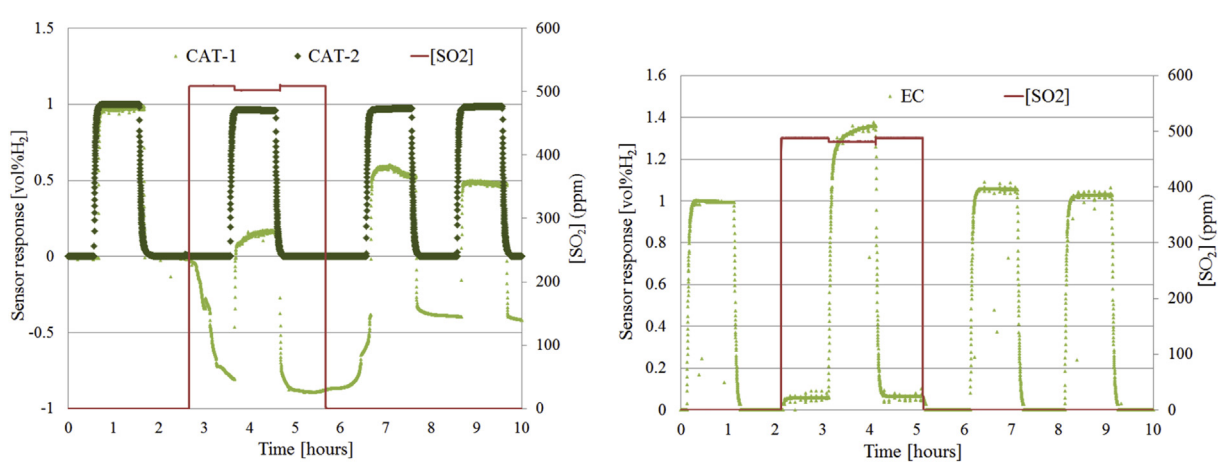

Fig. 3 – Effect of 500 ppm SO_2 on the responses of the catalytic sensors CAT-1 and CAT-2 (left) and electrochemical sensor EC (right).

sensor response X_H of 0.35 ± 0.05 for 500 ppm SO_2 is close the value of that 0.38 ± 0.05 for 50 ppm H_2S. This is a remarkable result as the concentration of H_2S is only 1/10th that of SO_2.

The response of the MOSFET platform to hydrogen was unchanged during exposure to SO_2 (data not shown).

Both H_2S and SO_2 can cause poisoning of the sensor catalyst by blocking the active sites of the sensing element. The reactants, oxygen and hydrogen, are prevented from being adsorbed on the catalyst surface, which will influence the response of the sensor. The higher poisoning activity of H_2S compared to SO_2 has been explained by the electronic configuration of the SO_2 molecule, which is attributed to the shielding of the sulphur ion by oxygen [10,11]. The reaction of a sulphur containing compound with catalysts is the subject of a significant research effort and has been described as a complex phenomenon involving both electronic and morphological changes [18].

Among the sensor platforms studied, EC sensors as well as one model of the CAT sensors (CAT-1) were affected by sulphur-containing species. The design of the CAT sensor models may be different with respect to the materials and protective measures. While the exact nature of these are not known (proprietary information), the observed difference in response to SO_2 suggests more effective protective measures for the sensor model CAT-2. This engineering solution is also reflected in the much higher price of the sensor. Another option could be the use of a different composition of catalyst, or substrate material. The noble metal catalysts used on hydrogen sensors have different susceptibilities to poisoning. The bonding of sulphur with metal withdraws electron charge, which reduces the sticking probabilities and coverage of reactants on the catalyst [19]. The magnitude of this effect depends on the participation of the metal atom d-orbitals in metal bonding (Pt < Pd), which indicates that Pd would be more affected by sulphur poisoning than Pt. The effect of the catalyst support has been shown to be important, as some materials may act as SO_2 sinks [20]. A Pd catalyst deposited on a carrier material capable of adsorbing SO_2 tolerates higher concentrations of SO_2 than on other types of material [21].

To understand the poisoning mechanism of EC sensors, studies on the effect of fuel impurities on the performance of PEM fuel cells can be useful (e.g. Ref. [22]). PEM fuel cell electrodes as well as the membrane are affected by poisoning species, this could also be the case for EC sensors.

The investigation of H_2S chemisorption on Pt electrodes has revealed that H_2S adsorbs as two types of sulphur species and, depending on the applied potentials, undergoes further electro-oxidation to elemental sulphur and sulphur dioxide [23,24]. For PEM fuel cells, transient concentrations of pure hydrogen may result in partial recovery of the cell performance [22] after exposure to sulphur-containing compounds. Although largely reversible, sulphur poisoning has been shown to be cumulative, as not all species of the adsorbates may be completely removed or could be further oxidized [25]. Chemical degradation of Nafion-type membranes can take place through formation of peroxide radicals, which form due to the presence of impurity cations. A report on an amperometric H_2S sensor with a composite Pt electrode also states that electro-oxidation products of H_2S depend on the local electrode potential at the time of adsorption [26]. It was also found that the deposition of elemental sulphur on the Pt electrode was the main cause of sensor degradation. This effect was reversible, i.e. the sensor recovered to its normal sensitivity once H_2S was removed. These findings may help explain the pronounced, but temporary effect of H_2S on the EC sensor. The gradual increase, or drift of the signal could be indicative of a slow, secondary electrochemical reaction taking place. The reversibility of the effect is in line with reports regarding the effect of H_2S on PEM fuel cells and on the H_2S sensor. Further investigation into the long term effects of the poisoning of EC sensors is necessary.

Nitrogen dioxide (NO_2)

NO_2 is a toxic gas produced in power plants, heavy industry, and combustion processes including biomass burning. The poisoning effect of NO_x species on catalysts is subject to debate and not yet well understood [27]. Numerous studies on the effect of NOx on the performance of PEM fuel cell have been published (e.g. Ref. [22]), which employ Pt-based catalyst materials. It has been proposed that NO_2 is not poisoning the catalyst surface but rather affects the membrane or the catalyst–membrane interface [28].

The sensor CAT-1 showed a decreased baseline and a minor increase in sensitivity to H_2 during exposure to NO_2 (data not shown). The sensitivity of the sensor to hydrogen almost fully recovered once exposure to NO_2 was terminated. The sensor CAT-2 was not exposed to NO_2.

The response of the electrochemical sensor was affected by the presence of NO_2, with the sensitivity to hydrogen permanently reduced by about 5%. While NO_2 can be considered as a poison for this platform (see Fig. 4), nevertheless the 5% change in sensitivity is within the allowable tolerances for poison resistance specified in the ISO 26142.

A slight effect of NO_2 on the sensitivity to hydrogen of the MOSFET sensor was observed (data not shown), but the magnitude of this effect is lower than the measurement uncertainty (see Table 3) and therefore should not be viewed as significant.

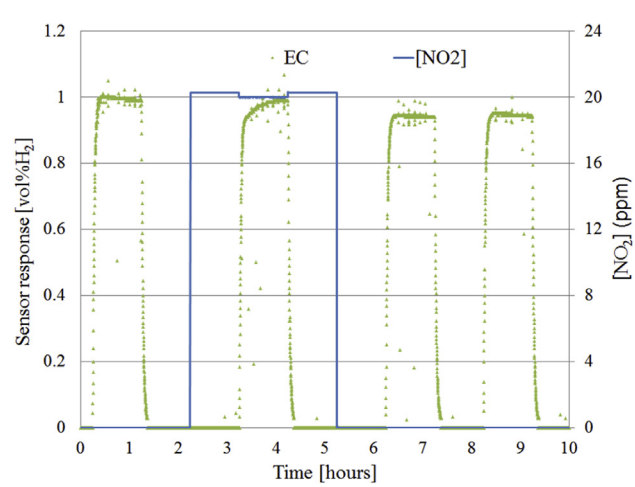

Fig. 4 – Effect of 20 ppm NO_2 on the response of the electrochemical sensor EC.

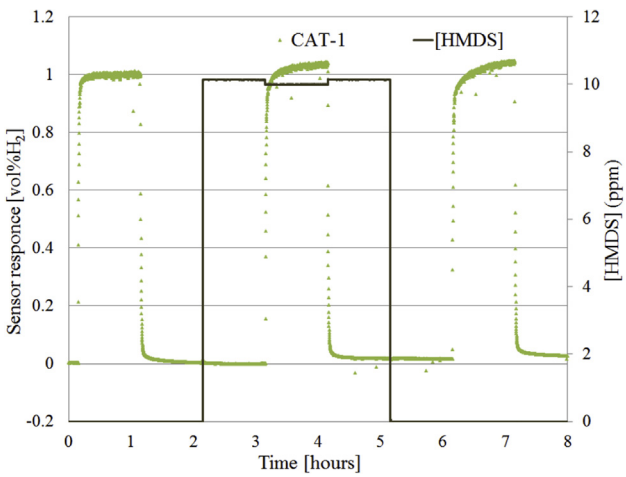

Fig. 5 – Effect of 10 ppm HMDS on response of catalytic sensor CAT-1.

Hexamethyldisiloxane (HMDS)

Silicon-based compounds are used as lubricants, sealants, and often as so-called inert ingredients in a variety of consumer products. These compounds are recognized as poisons on several sensor platforms, including CAT. As mentioned above, the poisoning of catalytic sensors may be avoided through the use of filters, such as molecular sieves or activated charcoal. Thicker filter layers prolong the lifetime of the sensor, but also lead to longer response times. As filter materials only have limited capacity to absorb contaminants, other methods have been developed, such as a means to desorb silicon adhering to the detection element. The hydrogen sensor is exposed to a high concentration of hydrogen, raising the temperature of the sensing element in order to remove any silicon compounds and recover full sensitivity [29]. The effect of HMDS on the sensor performance has been shown to depend on the temperature, time and concentration of HMDS. Poisoning of the sensor occurs through the formation of a SiO_2 layer the Pt/Pd surface [30]. Although Si-based compounds such as HMDS are often reported as catalyst poisons, none of the sensors investigated show a significant degradation of performance upon exposure to HMDS at the concentration level and exposure time prescribed by ISO 26142. HMDS is chosen as a suitable representative Si-containing species because of its availability, volatility and ease of use. Only in the case of the catalytic sensor CAT-1 was a minor change (increase) in the in the sensitivity to H_2 observed (see Fig. 5).

During and after the exposure to HMDS, the response to hydrogen exhibited an increased drift. Longer exposures or higher concentrations of HMDS are expected to be harmful to this sensor. Further investigations are needed to determine a specific threshold concentration and exposure duration.

Conclusion

The catalytic sensor platforms tested here were found to be robust towards most poisons identified in the ISO 26142 standard, including siloxane and the sulphur compounds. The exposure of the CAT-1 sensor to 500 ppm of SO_2 did, however, result in a marked lowering of the baseline, with potentially serious safety consequences. Moreover, this sensor model fails the resistance to poisoning test according to the ISO 26142 specifications. A recalibration of the sensor after exposure to SO_2 may be necessary. In all other cases the resistance to the selected species was good.

During exposure to H_2S and SO_2 the electrochemical sensor shows a remarkable increase of the sensitivity to hydrogen, i.e. by 35% and 38% respectively. This effect is notable even for a 50 ppm concentration of the sulphur compound H_2S. Sensor users should take this susceptibility of electrochemical sensors into account as it could lead to a false alarm. Also the drift of the sensor response to hydrogen during simultaneous exposure to either H_2S or SO_2 warrants further investigation. As the response of the sensor to hydrogen was not permanently affected nor did the response even decrease during the exposure to sulphur compounds, these chemicals cannot be properly classified as poisons for EC sensors. Exposure to NO_2 at 20 ppm level caused a permanent decrease of the sensitivity to hydrogen, in which case NO_2 does act as a poison. Note, however, that the sensor does not fail according to the requirement of the ISO 26142 standard.

The MOSFET sensors seem to be the most robust sensor type with respect to poisons. This may be due to an advanced sensor design, including use of filters and selective layers.

A more significant impact on the sensor response was expected for the tests with HMDS, as siloxanes are known to be harmful to sensors, especially the catalytic and electrochemical platforms [30]. The impact observed on the catalytic sensor, however, is well within the tolerance limits defined in the ISO 26142 standard, and the effect on the other platforms was negligible with regards to the experimental error. The siloxane resistance test prescribed in ISO 26142, based on exposure to 10 ppm HMDS, may possibly not properly reflect sensor robustness to siloxanes. Further work on other Si-based contaminants and other exposure profiles (e.g., concentration, exposure times) will be performed to evaluate the resistance of sensors and to assess the relevance and suitability of HMDS as representative species for Si-containing compounds.

In general, these initial results of resistance to poisons shown by the sensors are encouraging, as in almost all cases the response to hydrogen is ultimately not affected. It should be noted, however, that the exposures were of short duration, for single contaminants, and at a dry humidity (<5% RH). Increased humidity levels may result in a stronger effect of contaminants due to the formation of new species and moisture facilitated chemical reasons. Repeated or chronic low-level long-term exposures to poisons can be expected for sensor applications such as hydrogen refueling stations. An on-going study has revealed significant differences in the performance of sensors deployed in the fields as compared to those tested in the laboratory [31]. As the test parameters should be representative of the working environment of the sensors, further testing protocols should be developed to ascertain the suitability of hydrogen sensors for more challenging environments.

Future work will focus on further assessment of the resistance of sensors to contaminants by varying the testing

protocols, e.g. the type of contaminant, concentration, exposure time and environmental conditions. The long-term effects of poisons may not be accurately reflected by comparing the response of the sensor before and immediately after exposure to the contaminant; therefore the definition of sensor durability and resistance to poisons needs further discussion.

Acknowledgements

This work was performed as part of an on-going collaboration between NREL and JRC and supported by the FCH JU project H2Sense, GA number 325326 and Hyindoor for CAT sensors, GA number 278534. The NREL Sensor Laboratory is supported by DOE-EERE Fuel Cell Technologies Office.

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