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# Cross-sensitivity of hydrogen sensors to relative humidity

***Abstract**. The influence of the relative humidity of hydrogen-air mixture on the most commonly used types of hydrogen sensors, based on catalytic combustion, metal oxide semiconductor, and thermal conductivity is discussed, and compared. The cross-sensitivity of these types of hydrogen sensors to relative humidity is discribed and exemplified with experimental data, as well as approaches to mitigate that cross-sensitivity are characterised.*

***Streszczenie.** Przedstawiono i porównano wpływ wilgotności względnej mieszaniny wodór-powietrze na najbardziej rozpowszechnione typy sensorów wodoru: katalityczne, półprzewodnikowe z tlenków metali, i termokonduktancyjne. Opisano czułość skrośną tych typów sensorów wodoru na wilgotność względną i podano przykłady jej wyznaczania, oraz scharakteryzowano sposoby zmniejszania tej czułości. (**Czułość skrośna sensorów wodoru na wilgotność względną**).*

**Keywords:** hydrogen sensors, cross-sensitivity to relative humidity, mitigation of cross-sensitivity.
.**Słowa kluczowe:** sensory wodoru, czułość skrośna na wilgotność względną, zmniejszanie czułości skrośnej.

## Introduction

First devices for measuring hydrogen concentration in gas mixtures emerged around 1900 (used in airship filling systems) [1]. Intensive research on hydrogen sensors has begun in 1960s, and at present several electrical or electronic operating principles are well established and implemented in technologically advanced hydrogen-sensing devices. More than 400 models of hydrogen sensors are offered by about 100 manufacturers located mainly in Europe (ca. 50 %), North America (ca. 35 %), and East Asia (ca. 15 %). One of the reasons for that growing interest in hydrogen sensors is the long-term policy of the European Union and the USA to develop low-carbon energy technologies, including hydrogen as one of the most promising alternative sources of clean energy, till 2050 [2].

The biggest obstacle to the further progress in use of hydrogen in domestic life and automotive applications is the danger of explosion when the hydrogen concentration in air exceeds 4 vol% $H_2$. Moreover, the hydrogen molecules are the smallest and the lightest of all gas molecules, and in the case of leakage they spread very fast in ambient air, forming an hydrogen-air mixture of very low ignition energy (0.02 mJ [3]). Reliable, fast and robust hydrogen-specific safety sensors are required. Some regulations allow to use oxygen sensors for quantifying hydrogen releases in vehicles, but this approach is disputed [4].

The most popular commercially available types of hydrogen safety sensors are: catalytic (ca. 30 %), electrochemical (ca. 30 %), thermal conductivity (ca. 15 %), and resistive (ca. 15 %). Market pull among the greatest car manufacturers imposed more stringent technical performance requirements for automotive hydrogen sensors than for the use in stationary systems [5]. The question of determining the cross-sensitivities of hydrogen sensors to various gases and vapours is one of the current research topics [6], but it is focused mainly on the interferent species which are mentioned in standards (e.g. [7]). However, as relative humidity is a common factor in many gasous environments, and its level can vary within wide range, it may cause variations in sensor output signals which at low concentrations of hydrogen may also affect the reliability of the sensing system.

In this paper, the interaction of water vapour with different types of hydrogen sensors is discussed, and compared. The cross-sensitivity of catalytic combustion type, metal oxide semiconductor-based, and thermal conductivity-based hydrogen sensors to relative humidity was illustrated using experimental data. (The electrochemical sensors are not included because the relative humidity fluctuations in ambient air have negligible effect on this type). The ways to evaluate that cross-sensitivity and methods for its possible reduction or correction are also characterised.

## Theoretical background for the cross-sensitivity of hydrogen sensors

The (main) sensitivity of a hydrogen sensor can be defined as the ratio of the net change produced at the sensor's output to the known net change in volume fraction of hydrogen gas in air. Ideally, the sensor should only be sensitive to hydrogen and not to any other gas or vapour, i.e. no other gas or vapour should cause sensor's response. In reality, although the response to hydrogen dominates, also some other gases or vapours produce slight output signals. Those gases or vapours are called "cross-sensitive species", and their (unwanted) influence on the sensor's response is referred to as "cross-sensitivity" in order to be distinguished from the (wanted) "main" sensitivity to the target gas, $H_2$.

The cross-sensitivity to water vapour for a given type or model of hydrogen sensor can be defined individually, but in order to compare cross-sensitivities of various sensor types, a relative measure independent of the kind of the sensor's output signal is needed. Such quantitative measure can be evolved from the notion of selectivity, defined as the response of hydrogen sensor to hydrogen compared with its response to water vapour. If the conversion function of the sensor is: $y=f(c_{\mathrm{H2}},\varphi)$, where: $c_{\mathrm{H2}}$ is the volume concentration of hydrogen, and $\varphi$ is the relative humidity, then the ratio of sensor's responses to $H_2$ and to $H_2O$ vapour can be expressed as the $SRR$ (Sensor's Responses Ratio) factor:

$$SRR = \frac{f(\varphi) - f(0)}{f(c_{\mathrm{H2}}) - f(0)} \cdot 100\% , \tag{1}$$

where: $f(0)$ is the sensor response in clean ($H_2$-free) dry air, $f(\varphi)$ is the sensor response in clean ($H_2$-free) humid air, and $f\,(c_{\mathrm{H2}})$ is the sensor response to a certain $c_{\mathrm{H2}}$ hydrogen concentration in dry air [8]. Assuming linear dependencies between sensor output signal and both $c_{\mathrm{H2}}$ and $\varphi$, a change in sensor response caused by a certain value of relative humidity can be calculated. That cross-sensitivity may experimentally be determined by exposing the sensor consecutively to clean dry air, clean humid air, and dry air-hydrogen mixture.

Another procedure of determining the cross-sensitivity is to keep the sensor in the mixture of dry air with a known hydrogen concentration, when the relative humidity increases stepwise with defined step of e. g. 10 %RH. Then the cross-sensitivity factor ($CSF$) can be expressed as:

$$CSF = \frac{f(c_{\mathrm{H2}},\varphi) - f(c_{\mathrm{H2}})}{f(c_{\mathrm{H2}}) - f(0)} \cdot 100\% \cdot \quad (2)$$

The cross-sensitivity is often reported as an equivalent additional apparent percentage of hydrogen concentration read by the sensor. In general, $CSF$ can be positive or negative. The former can lead to false alarms while the latter is regarded as more dangerous because the lower explosion limit for $H_2$ can be exceeded without triggering an alarm.

## Working principles of hydrogen sensors and the influence of relative humidity

The idea of catalytic combustible hydrogen sensor is based on the property of flammability of hydrogen gas. Spontaneously, under atmospheric pressure hydrogen gas starts to burn in air at or above the autoignition temperature of 585°C [1]. That type of sensor localises the hydrogen oxidation reaction to a very small area of the sensing element by the use of a catalyst of a high catalytic activity towards hydrogen and oxygen [9]. At low hydrogen gas concentrations, the amount of the heat released in the exothermic reaction is small, and the catalyst surface must be heated to a temperature high enough to keep high rates of adsorption of the hydrogen and oxygen molecules, fast surface reaction, and fast desorption of water molecules. The catalyst which exhibits the highest catalytic activity to hydrogen is palladium (Pd).

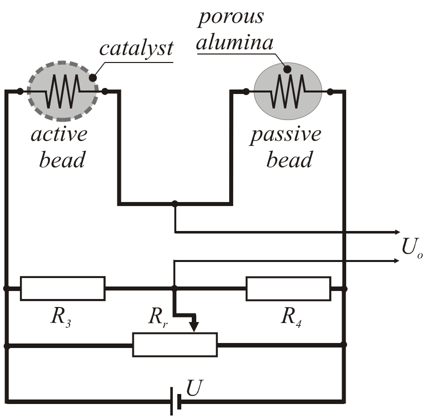

Fig.1. The schematic of the catalytic combustion bead sensor: $R_3$ and $R_4$ - bridge balancing resistors, $R_r$ - bridge-balancing potentiometer, $U_o$ - output voltage

In order to drive the reaction of hydrogen oxidation, the current is passed through the coil of the active bead, and the heat generated in the coil is conducted to the bead surface coated with the catalyst. The operating temperature of the beads varies from 300 to 500°C in different devices.

The task of the passive bead is to compensate the measuring signal from the active bead for changes in ambient conditions. The role of the platinum wire coils is threefold: they act both as heaters and supporting structures of the beads, as well as resistance temperature detectors (RTD) for the measurement of beads temperature, and temperature-to-resistance converters in the arms of Wheatstone bridge.

The active bead forms one arm of the bridge, and the passive one constitutes the adjacent arm. The other half of the bridge is formed of two balancing resistors (Fig.1). If no hydrogen gas flows in the vicinity of the catalytic surface on the electrically heated active bead, then no combustion occurs, and both beads – active and passive – have the same temperature; the Wheatstone bridge is balanced.

After the arrival of hydrogen gas molecules with ambient air to the catalyst surface on the active bead, the exothermic oxidation reaction is initiated and supported by the heat flow from the coil. The release of combustion heat, although small at low concentrations, gives an increase of the temperature of the sensing bead by a few centigrade. The amount of generated heat is proportional to both the enthalpy of hydrogen (285,8 kJ/mol) and its concentration.

The thermal conduction of a part of combustion heat to the coil of the active bead raises its temperature a few centigrade above the temperature of the other coil, so that the resistance of the "active" coil raises proportionally. On the other hand, the combustion heat is proportional to the hydrogen concentration. So, the bridge's output voltage is an indirect measure of the concentration of the flammable gas burning on the catalytic surface of the active bead.

The presence of water vapour in the gaseous mixture $H_2$-air, passing through the catalytic combustible gas sensor, results in a slight increase in sensor's reading (positive cross-sensitivity to water vapour). That means a slight increase in the temperature of the active bead if compared with the oxidation reaction of hydrogen in dry air. That additional increase in temperature could be explained twofolds. Firstly, the desorption and convection of the water vapour molecules produced on the active bead is retarded by the increase in the partial pressure of the water vapour in the air around the bead; that involves a bit slower heat loss from that bead and its slight increase of temperature. Secondly, some water vapour molecules from the vicinity of the active bead could reach the catalytic surface and dissociate producing hydroxyl groups which support a multistep autocatalytic reaction, simultaneous with the main hydrogen-oxygen catalytic reaction. The retardation of desorption of water molecules from the active bead could lead to a reverse reaction: $H_2O \rightarrow H^+ + OH^-$, and then atomic hydrogen can react with the oxygen from air.

The influence of the relative humidity on the performance of catalytic combustible gas sensors was investigated, and the results are presented in Table 1.

Table 1. The cross-sensitivity of catalytic combustible hydrogen sensors to relative humidity

<table>
<tr><th rowspan="2">$\varphi$</th><th rowspan="2">$c_{\mathrm{H2}}$</th><th colspan="2">Sensor No. 1</th><th colspan="2">Sensor No. 2</th></tr>
<tr><th>$c_{\mathrm{H2}}$</th><th>$CSF$</th><th>$c_{\mathrm{H2}}$</th><th>$CSF$</th></tr>
<tr><td>%RH</td><td colspan="2">vol%$H_2$</td><td>%</td><td>vol%$H_2$</td><td>%</td></tr>
<tr><td rowspan="2">0</td><td>0</td><td>0</td><td>–</td><td>0</td><td>–</td></tr>
<tr><td rowspan="4">0.30</td><td>0.32</td><td rowspan="2">6.2</td><td>0.30</td><td rowspan="2">6.7</td></tr>
<tr><td rowspan="2">30</td><td rowspan="2">0.34</td><td rowspan="2">0.32</td></tr>
<tr><td rowspan="2">12.5</td><td rowspan="2">13.2</td></tr>
<tr><td>60</td><td>0.36</td><td>0.34</td></tr>
</table>

The metal oxide semiconductor sensors convert a chemical stimulus to an electric response; they are mostly of conductive type, often denoted in short as the "MOX sensors". An exemplary design is shown in Fig. 2. The sensing materials for hydrogen sensors are the broad band-gap polycrystalline semiconducting metal oxides. The electrodes are made chiefly from noble metals: Pt, Ag/Pd or Au. The heaters are made from Pt, and separated from the sensing MOX layer and the electrodes by a thick substrate layer of a good insulator [10]. The amount of energy supplied to the sensing material during technological process is of crucial importance for the grain size, which in turn limits the amount of grain boundaries [11].

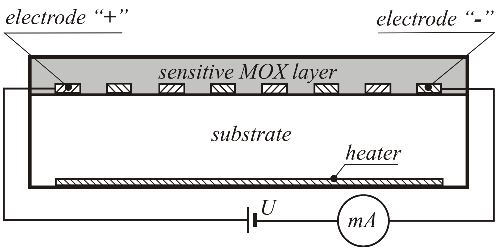

Fig.2. The schematic of the metal oxide semiconductor gas sensor

If the heated MOX sensor is placed in a flow of clean air, the surface of the sensing film is covered with chemisorbed oxygen ions $O_2^-$. In MOX sensors operating at temperatures higher than 150°C, the $O_2^-$ ions are transformed into more reactive ions $O^-$ [12]. The chemisorbed oxygen ions on the grain surfaces capture electrons from the conduction band. Assuming that the metal oxide is an *n*-type semiconductor with electrons as charge carriers, then a depleted region emerges. That results in a certain decrease of the electric conductivity of the MOX sensing layer, proportional to the concentration of oxygen ions on the grain surfaces.

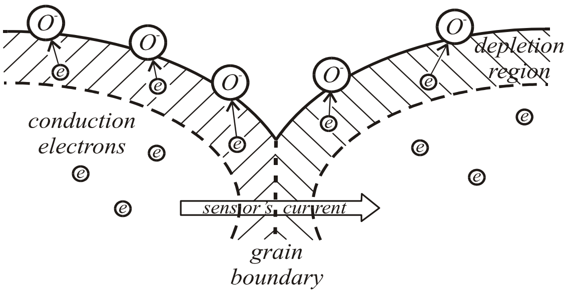

Fig.3. The schematic of the metal oxide semiconductor gas sensor working principle in the absence of hydrogen gas (in ambient air)

Hydrogen is a reducing gas; if its molecules appear in the vicinity of the sensing layer surface covered with oxygen ions, the interaction between $H_2$ molecules and $O^-$ ions occurs. $H_2$ molecules are adsorbed and dissociate to atoms: $H_2 \rightarrow 2H$. Ions $O^-$ and atoms H combine into hydroxyl groups: $2\,H + 2\,O^- \rightarrow 2\,OH^-$, which in turn react with other hydrogen atoms to produce water vapour molecules. The $H_2O$ molecules desorb from the surface, leaving oxygen vacancies and free electrons. That results in a reduction of the width of the depleted region, and an increase in conductivity proportional to the concentration of hydrogen.

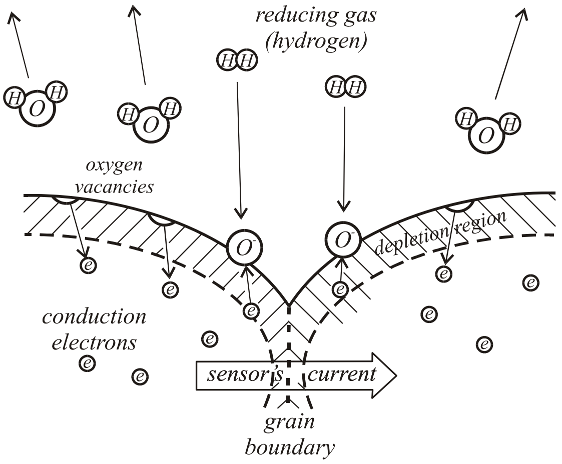

Fig.4. The schematic of the metal oxide semiconductor gas sensor working principle in the presence of hydrogen gas

The MOX materials developed for MOX ionic-type *humidity* sensors are similar (e.g. $SnO_2$) to that for $H_2$-sensors but the sensing mechanisms are different [13]. In commercial MOX $H_2$-sensors, mainly $SnO_2$ doped with other MOXs and catalysts like Pd nanoparticles are used. $SnO_2$ exhibits oxygen vacancies which can donate electrons to the conduction band. Water molecules adsorbed on the surface of a MOX gas sensing layer can dissociate and cause its hydroxylation [14, 15] inhibiting sorption of both oxygen and hydrogen. The details of these complex processes between oxygen- and water-related species are still investigated, but two final effects induced by humidity are reported.

Firstly, in the absence of hydrogen gas, water molecules adsorb on the MOX surface and diminish the surface area available for the adsorption of oxygen molecules. Therefore, the baseline conductance of the MOX hydrogen sensor is decreased. Secondly, after exposing the MOX layer to a hydrogen-air mixture, water molecules compete with $H_2$ for oxygen species and further diminish the surface available for the adsorption of $H_2$ molecules. Hence, the sensitivity of a MOX sensor to hydrogen is decreased, too.

As an example, the cross-sensitivity to relative humidity can be characterised for the sensor TGS 2600 (Figaro Inc.) developed for hydrogen detection (and some other gases [16]). Its datasheet contains two charts illustrating the influence of relative humidity and hydrogen on the sensor performance. The reference value is the sensor's resistance $R_0$ in clean air at 20°C and 65 %RH. If at these conditions a hydrogen concentration of 35 ppm is mixed into the ambient air, the sensor's resistance will decrease to $0.2R_0$. On the other side, if the ambient humidity increases to 95 %RH, the sensor's resistance will decrease to $0.8R_0$. The value of $SRR$ of 25% is obtained.

In thermal conductivity (TC) hydrogen sensors the change in sensor's signal is caused by variations in thermal conductivity, which is a physical property. Thermal conductivity characterises the ability of a given material to conduct heat, described by TC coefficient usually dendoted as $\lambda$ and often called "thermal conductivity" itself. Generally, the smaller the molecules of a given gas, the greater its value of $\lambda$. For hydrogen (at 300 K) $\lambda_{H2} \approx 187$ W/(m·K), which is around 7 times greater than $\lambda_a$ of the air.

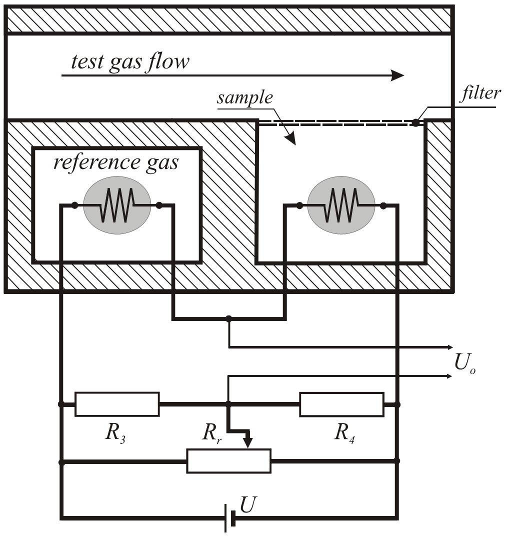

Fig.5. The schematic of the TC hydrogen sensor

The TC sensor comprises two passive pellistors. The matched pellistor coils work simultaneously as both heaters and RTDs, connected to form two legs of a Wheatstone bridge. One of the pellistors is placed in a chamber through which the tested gas is flown. The other pellistor is located in a reference chamber filled with air (Fig. 5). After introducing a mixture of air and hydrogen gas of low concentration, the $\lambda$ of the mixture in the test chamber is greater than $\lambda_a$ of air, and the pellistor in that chamber is cooled more intensively than the pellistor in the reference chamber. That implies an out-of-balance output voltage of the bridge, which is proportional to the drop in the resistance of the "test-chamber" pellistor, and to the hydrogen concentration to be measured.

The thermal conductivity of hydrogen relative to air $\lambda_{H2r}$, decreases quasi-linearly with temperature rise: from 7.37 at 0°C to 6.34 at 500°C [17]. On the other hand, the thermal conductivity of water vapour relative to air within the same temperature interval increases from 0.97 to 1.49. For the binary mixture hydrogen-air, the mean thermal conductivity $\lambda_m$ is calculated as follows:

$$\lambda_{\mathrm{m}} = X_{\mathrm{a}} \cdot \lambda_{\mathrm{a}} + X_{\mathrm{H2}} \cdot \lambda_{\mathrm{H2}}, \tag{3}$$

where: where: $X_a$ is the molar ratio of air, and $X_{H2}$ - of hydrogen. As the reference gas is the air, the relative thermal conductivity of hydrogen $\lambda_{H2r} = \lambda_{H2}/\lambda_a$ is used. Then the output sensor signal for hydrogen concentration is: $S_H = X_{H2}\ (\lambda_{H2r} - 1)$. In the case of an additional component of the hydrogen-air mixture, the sensor's output signal $S_{HWV}$ contains a sum of terms: $S_{HWV} = X_{H2}\ (\lambda_{H2r} - 1) + X_{WV}\ (\lambda_{WVr} - 1)$. For the concentration of 1 vol%$H_2$ in air, the change in heat transfer is about 2 % [18]. The addition of 100 %RH water vapour causes a contribution to the heat transfer of 0.5 % - that is equivalent to the effect of 0.25 vol%$H_2$. So, the $CSF$ calculated following Eq.(2) is 25 %.

## Discussion

The thermal conductivity-based hydrogen sensor differs from the two other types in that it uses a physical operating principle, and does not need oxygen for sensing hydrogen concentrations properly. The catalytic and MOX-based sensors both work on chemical principles, and require oxygen. Their cross-sensitivities to relative humidity are positive, and for MOX sensors at high relative humidities the sensor's output signal can rise considerably [19].

In order to reduce the influence of relative humidity on the operation of the hydrogen sensors, several precaution approaches can be applied. Firstly, the hydrogen-air mixture can be passed through a dehumidifying facility before reaching the sensor. Secondly, active filters could be applied, but filters may hinder the access of $H_2$ and $O_2$ molecules to the sensing layer, and the kinetic diameter of $H_2O$ molecules is close to that of $O_2$ molecules. Another mitigating approach against the water vapour influence is to apply the sensing materials less cross-sensitive to relative humidity (e.g. to dope $SnO_2$ with $TiO_2$ [14]). Yet another approach is to apply additional temperature and relative humidity microsensors and a microprocessor that calculates the corrections for hydrogen concentration readings.

As a rule, the calibration of $H_2$ sensors is performed using gases obtained from gas cylinders (e.g. synthetic air) at less than 5 %RH. So, if the user knows the humidity levels at which the sensor would be working, the best solution seems to be the calibration of the sensor with hydrogen-humid air mixtures.

## Conclusions

For the three types of hydrogen sensor discussed in the paper, the positive cross-sensitivity to relative humidity influences the output signals of all of them; the most cross-sensitive are the semiconducting metal-oxide sensors. The best approach to mitigate the effect of cross-sensitivity to relative humidity seems to calibrate the sensors in hydrogen-humid air mixtures of given levels of humidity, corresponding to the levels encountered in the working conditions of these sensors, especially for measurements of low hydrogen concentrations.

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