
# HYDROGEN SAFETY: A COMPARATIVE ANALYSIS OF LEAK DETECTION SENSORS

O. Petrella[1], A. Martucci[1], P. Caruso[1], L. Travascio[1], A. Vozella[1]

[1] CIRA- Italian Aerospace Research Centre, Capua (CE), Italy

## Abstract

Current research worldwide is investigating potentialities, limitations and constraints associated with the use of hydrogen as an energy source. A thorough investigation is especially needed to mitigate risks to the environment and human health related to hydrogen usage. Indeed, hydrogen can be the cause of various accidents leading to different risk scenarios, due to potential physical and chemical phenomena depending on specific environmental conditions. Some of the main risks include: asphyxiation, freezing, shock waves from explosions, thermal hazards from flame releases and combustion. However, these risks can be reduced by adopting specific mitigations and safety measures which can be identified since the design phase. Careful prevention and a detailed risk assessment, combined with an accurate analysis by monitoring sensors are absolutely necessary for the safe use of hydrogen systems. It is worth noting that Hydrogen has very fast dynamics due to its low molecular weight and high diffusivity. This means that it can quickly disperse and accumulate in confined spaces, potentially leading to hazardous situations. Its high flammability and wide range of explosive concentrations in air make even small leaks dangerous. Therefore, promptly detecting any leakage becomes crucial and monitoring sensors can represent an enabler for Hydrogen safe adoption.

This work reports on the analysis carried out on the most suitable sensors [1], for the risk mitigation, in particular related to hydrogen leakage.

Different kinds of sensors have been analyzed and compared, such as optical, electrochemical, semiconductors and SAW (Surface Acoustic Wave) sensors, according to the requirements provided by the DOE (Department of Energy in the United States) for an efficient hydrogen detection sensor.

A preliminary comparison for the main parameters (Response Time, Measurement Range and Sensitivity) has been made among the previous categories.

Finally, the SAW sensor, since it appears to be the ideal candidate in terms of response time (compared to the other categories), has been characterized metrologically. This sensor has initially been analysed in its two physical components, the sensing and the transduction parts. Later, among all the theoretical models for SAW operating mode, the formula related to adsorption [3] has been chosen for the simulations (in Python environment) to evaluate the uncertainty measurements.

Moreover, in MATLAB environment, the sensitivity of SAW sensor has been studied in order to evaluate its operating limits.

**Keywords:** Sensors; Hydrogen; Aerospace; Metrology; Safety;

## 1. Sensors' description

In this chapter the characteristics and of different types of sensors will be analyzed. The most commonly sensors used for the detection of gases and in particular of hydrogen have been chosen:

- Optical Sensors
- Electrochemical sensors
- Semiconductor sensors
- SAW Sensors

## 1.1 Optical Sensors

Optical sensing technologies for hydrogen monitoring are becoming increasingly important following the need to make a transition to the use of propulsion systems with high environmental compatibility for different application sectors.

This is due to their excellent characteristics of immunity to electromagnetic interference, high sensitivity (gas detection at levels lower than a few units of ppm) and wide applicability.

Figure 1 shows the types of optical sensors used for hydrogen detection [4],[5],[6].

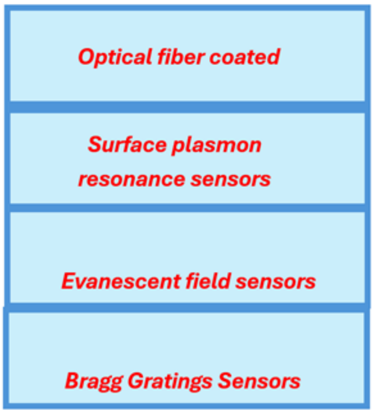


*Figure 1 – Optical sensors used for hydrogen detection.*

The coating of the sensing element of optical sensors, used for hydrogen capture, plays an important role. It has been proven that Palladium, Palladium alloys and tungsten oxide are the best candidates to increase the performance of such sensors. In presence of hydrogen, the response of optical sensors changes due to a change in the optical characteristics of the substance with which the sensitive elements are coated.

Indeed, considering one of the simplest schemes for detecting hydrogen, as an optical fiber coated with palladium and ethylene-vinyl acetate (hollow fiber sensor), it is possible to detect the presence of hydrogen. This is because the transmission spectrum of the sensor has a shift towards the red as the hydrogen concentration increases, due to the changes in the optical characteristics of the involved materials [4].

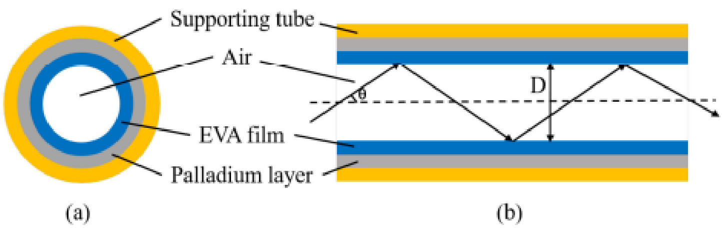


*Figure 2– Optical fiber coated with palladium*

Compared with other fiber optic hydrogen sensors, the considered sensor offers advantages of simple structure, easy fabrication, low cost, high sensitivity and good safety performance.

### *1.1.1* Surface plasmon resonance sensors

The Surface Plasmonic Resonance (SPR) is the propagation of a coherent oscillation of surface conduction electrons, which therefore generates an oscillation (plasmon) of the charge density in a metallic material when it is hit by electromagnetic radiation and comes into contact with a material having a dielectric constant of opposite sign (i.e.,a dielectric) [7],[8],[9],[10].

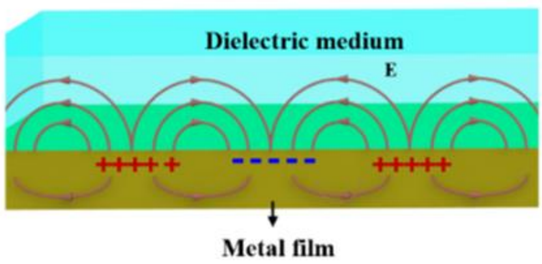


*Figure 3- Interaction between the Dielectric and Metal Film*

This phenomenon regards both the oscillation of the charges in the metal (i.e. the actual plasmon) and the one relative to the electromagnetic waves in the dielectric. This is named Surface Plasmon Polariton (SPP) shown in figure 3.

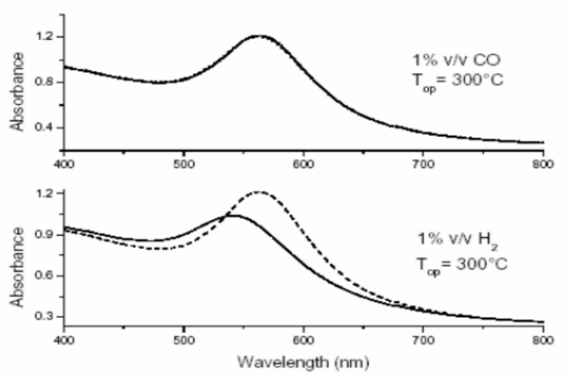


*Figure 4 : UV-visible absorption spectra measured in air (dotted line) and after the exposure to an air atmosphere containing 1 vol% CO and 1 vol% H2 (solid line) for a gold-containing sample*

The surface plasmonic resonance sensors have extremely high sensitivity and selectivity for hydrogen detection.

Below the main characteristics of plasmonic sensors are reported:

- Extremely high sensitivity and possibility to detect even low concentrations of hydrogen
- Almost instantaneous response to changes in hydrogen concentration
- Specific detection of hydrogen without responding to other gases
- Stability over time.

Table 1: Response and recovery times for the best SPR performing samples

| Sensing Material | Platform | Detection Range | Sensitivity | Response Time |
|---|---|---|---|---|
| Au-IRMOF-20 | MMF | 0–50% | NA | 5 s–10 s |
| Ag/SiO2/Pd | MMF | 4% | NA | - |
| Ag/SiO2/PdY | MMF | 4% | NA | NA |
| Ag/ZnO(1-x) Pdx | MMF | 4% | NA | 1 min |
| Au/silica/Pd | MMF | 0.5–4% | NA | 15 s |
| Au/Ta2O5/Pd | Hetero core | 4% | NA | 15 s |
| Au/Ta2O5/Pd | MMF | 4% | NA | 25 s |
| Pd75Au25 | MMF | 0–4% | NA | Response time 90 s/Recovery time 10 s |
| Au/Ta2O5/Pd | Hetero-core | 4% | NA | 40s |
| Ag/Si/Pd | Plastic clad | 4% | NA | - |
| Ag/Si/WO3/Pt | MMF | 2% | NA | - |
| Au-Pd nano cube | Fiber bundle | 4% | NA | Response time 30 s/Recovery time 4 s |
| Ag/SiO2/Pd | MMF | 0–4% | NA | - |
| Ag/TiO2 | MMF | 14.7% | 523 nW/% | - |
| Graphene -Au-PDnanofilm | FBG | 0–4.5%, | 290 pm/% | - |

Surface Plasmon Resonance is a phenomenon that occurs when polarized light hits a metal film at the interface of media with different refractive indices. SPR techniques excite and detect collective oscillations of free electrons (known as surface plasmons). When an incident beam hits a metallic surface after passing through a prism, the light is completely reflected. In presence of hydrogen the reflected beam is partially absorbed by metallic film. Consequently, the resonance peak has a directly proportional shift to hydrogen percentage. The reflected image shows a dark line due to SPR.

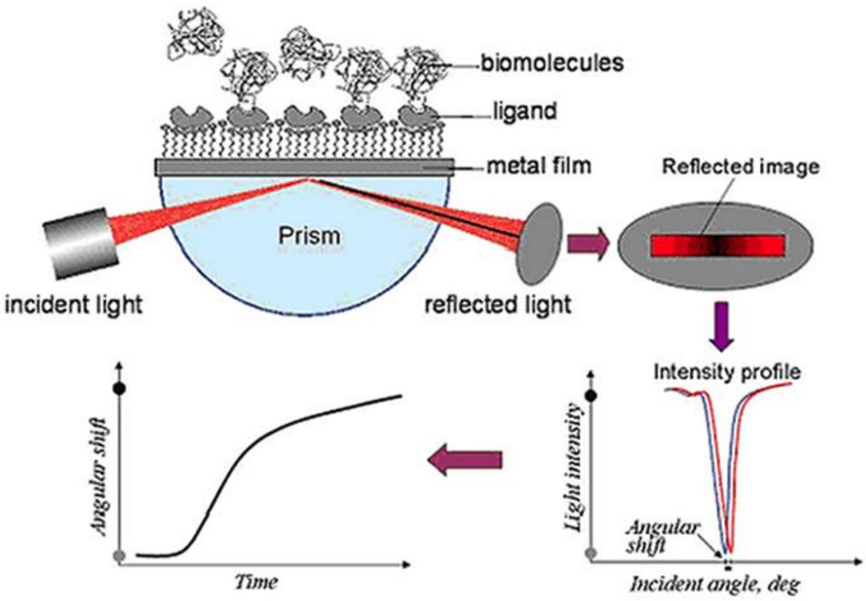


*Figure 5 - Surface Plasmonic Resonance Phenomenon description*

### *1.1.2* Evanescent Field Sensors

Inside the optical fiber, total reflection occurs only if the incidence occurs at a certain angle. If this condition does not occur, the light ray will still be reflected inside the fiber but a small part of it will enter the medium surrounding the fiber, decreasing exponentially [4].
This phenomenon is called the Evanescent Field. The basic working principle of the considered sensor is the interaction between the hydrogen and the evanescent field.
The smaller the thickness of the fiber cladding, the more efficient this sensor is, so as to make the evanescent field to exit outside of the cladding and therefore enhancing the interaction with the hydrogen to be detected [15].

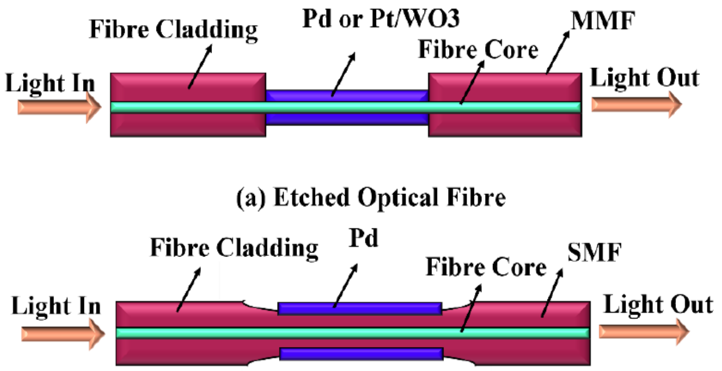


*Figure 6- Tapered Optical Fiber*

This sensor becomes more sensitive when the manufacturing technology allows the creation of a thin shell. Furthermore, its sensitivity also depends greatly on the wavelength of the light radiation.

Table 2: Evanescent field sensors for hydrogen detection

| Sensing Material | Sensor | Detection Range | Sensitivity | Response Time |
|---|---|---|---|---|
| Pd film | Etched MMF | 0.2%<br>0.6% | NA | 30 s<br>20 s |
| $Pd/WO_3$ | Etched MMF | 100% | NA | 10–20 min |
| Pd film | Tapered SMF | 0–10% | NA | <100 s |
| Pd film | Polished SMF | 4% | NA | Response time 100 s recovery time 150 s |
| Pd/Au film | SMF sandwiched by 2 MMFs | <4% | NA | 15 s |
| Pd/Au multilayer stack | Hetero core | 4% | NA | Response 4.5 s/ recovery 13 s |
| Pd particle embedded in PMMA | Tapered SMF | 0.2–1% | 5.58 nm/% | 5 s |
| Molybdenum Trioxide | Tapered MMF | 0.125–2.00% | 11.96 vol/% | 220 s |
| Pd particle | Tapered MMF | 2% | NA | Response 50 s/ Recovery 230 s |
| Pd | Tapered SMF | 1.8–10% | NA | <100 s |
| $Pt/WO_3$ | Etched MMF | 1% | NA | 5 min |
| Pd/Au | Etched D-shape fiber | 0.25–20% | NA | ≈30 s |
| Au capped with Pd | MMF | 0.8–4% | NA | 116 s |

### *1.1.3* Bragg Gratings

The optical sensor with Bragg Grating (FBG) is a particular type of optic fiber. On its surface a certain number of incisions make it able to filter only certain wavelengths [4].

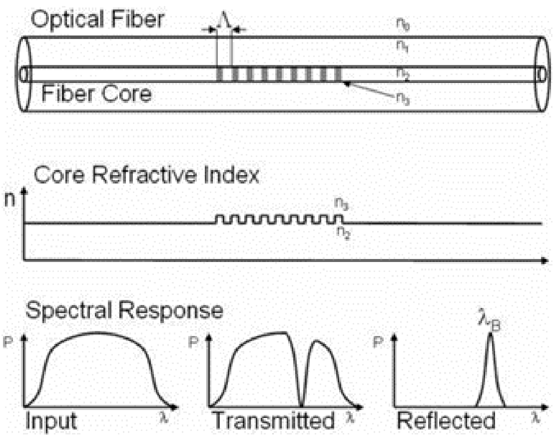


*Figure 7 Bragg Grating Sensor*

These elements have a particular spectral characteristic in resonant reflection, i.e. characterized by a "peak" centered at a specific characteristic wavelength, called Bragg Wavelength (λB).
In case of fiber deformation due to the temperature variation, a shift of the central wavelength peak occurs. Variations over time constitute the sensor response.
The peak location varies in presence of hydrogen, allowing the detection of the gas percentage.
In order to improve the real-time sensing response, an alternative approach was developed. In this case the sensor was created by inscribing 1 cm long gratings in high attenuation fiber (HAF). Choosing the gratings area properly, the sensor has its performances improved, indeed it is able to detect 1% hydrogen at -150°C as fast as 2 minutes. However, response time still remains the limit for this technology [12].

Table 3: FBG based optical hydrogen sensor

| Sensing Material | Sensor | Detection Range | Sensitivity | Response Time |
|---|---|---|---|---|
| Pd:Ag = 76:24 | Etched FBG | 4% in volume | 10 pm/% | 280–300 s |
| Pd:Ni = 91:9 | Etched FBG | 0.5–4% | 36.5 pm/% | 5–6 min |
| Pd film | LPFG | 4% | NA | NA |
| Pd film | LPFG | 4% | −0.29 nm/min | NA |
| Pd film | FBG/w HAF | 1–10% | 27 pm/% | - |
| Pd | Tapered FBG | 0.1–1% (*v*/*v*) | 81.8 pm/% | 30 s |
| Pd/Ti/polyimide | FBG | 0.25–2% | 13.5 ppm/pm | ≈1 h |
| Pd/Ti/polyimide | FBG | 1791.46 ppm | 0.042–0.044 pm/ppm | - |
| $Pd_{91}Ni_9$ | Etched FBG | 1% | 15 pm/% | 5 min |
| Pd/Ag | FBG | 0–2000 μL/L | 0.055 pm/(μL/L) | 24 min |
| Pd:Cr = 58:42 (with $TiO_2$) | Standard FBG | 0–650 ppm | NA | 10 min |
| $Pd/WO_3$ | Polished FBG | 0–8% | 6.5 pm/% | 40–90 s |
| $Pd/WO_3$ | Polished FBG | 0.2–1.4% | 196 μL/L | - |
| Pd | FBG | 1%/5% | NA | Response 20–30 min/ recovery 50 min |
| Pd foil | Etched FBG | 1–5% | 212.6 pm/% | 4 h |
| Pd membrane | Titled FBG | 1–4% | NA | 5 min |
| Pd film | FBG | 4% | NA | 2 min |
| $Pt/WO_3$ | FBG | 1500–20000 ppm | NA | 55–80 s |
| Pd/Ag | Side-polished FBG | 0.08% | 4770 pm/% | <1 h |
| Pd | Two Etched FGBs | 1% | 20 pm/% | 2 min |
| $Pd_{75}Ag_{25}/Ni$ | FBG/w microgroove | 0–4% | 16.5 pm/% | 10 min |
| Pd | Tapered FBG | 5% | 216 pm/% | 1 min |
| $Pd_{91}Ni_9$ | FBG | 0–1% | 0.01 pm/ppm | ≈200 s |
| $Pt/MoO_3$ | FBG | 1500–15000 ppm | 0.022–0.031 pm/ppm | Response 100 s/ recovery 110 s |

## 1.2 Electrochemical sensors

An electrochemical sensor is made by a sensing electrode (also called working electrode) and another one, separated by the first by means of a thin film of electrolyte. The gas reaches the working electrode surface, and an oxidation-reduction process takes place. If the two electrodes are electrically connected by means of a resistance, a current proportional to the gas concentration flows from the anode to the cathode [7], [13].
The electrochemical sensors have a high sensitivity and are not contaminated by other gases.

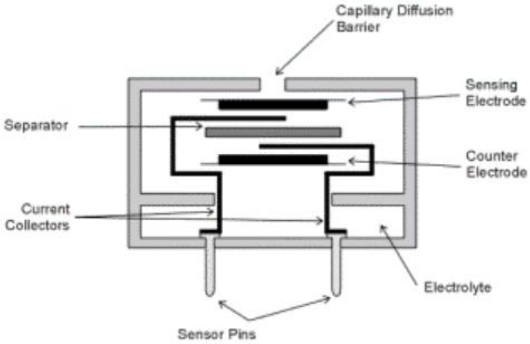


*Figure 8 Electrochemical Sensor Scheme*

Electrochemical sensors are divided into:
- Potentiometric Sensors: where the response of the transducer is a potential difference dependent on the analyte concentration
- Voltmetric - Amperometric sensors: where the response of the transducer is a current
- Conductometric Sensors: where the response of the transducer is the change in resistance of a material when it comes into contact with the analyte

The main features of this kind of sensors are:
- Not expensive
- Usable for hydrogen detection
- Linear response (current generated directly proportional to the gas concentration)
- High sensitivity. They can also reach a minimum detection range of 1-10 ppm [13]
- Operating temperature range of -30˚C to +50˚C
- Ideal operating humidity and temperature is 20°C and 60% RH.

These sensors require periodic maintenance, which may include replacement of the working electrode or calibration of the sensor to ensure accurate measurements over time, regular maintenance and calibration significantly contribute to the sensor maintaining optimal performance.

An electrochemical sensor detects changes, in charge transport or electrical properties, due to the electrochemical reactions that occur in the element sensitivity of the electrode. There are generally two types of electrochemical sensor.

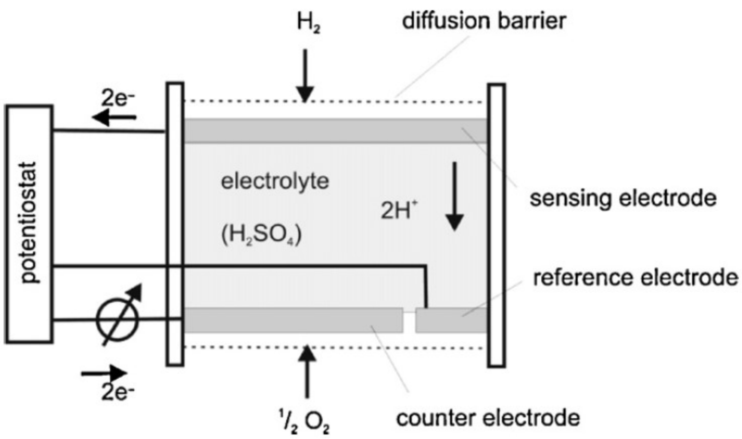


*Figure 9 Scheme of an electrochemical sensor for hydrogen detection*

The **Amperometric Electrochemical Sensors** work at a constant applied potential and signal is given by the limitation to the diffusion of the current. The main components of these sensors are the electrodes. They are usually composed of a noble metal (for hydrogen, the platinum) and generally they are two: a measuring and a counter electrode.
Alternatively, a single electrode and a potentiometer can be used to apply a constant voltage. Then there is an electrochemical cell which contains a solid (preferred in hydrogen sensing) or liquid electrolyte which allows the transport of ions between the two electrodes. The Nafion is often used, while ceramic materials are preferred for high-temperature applications. Finally, a permeable gas covers the electrode surface by limiting the diffusion of other gases. Hydrogen diffuses through this gas and ends up oxidizing at the electrode, generating 2H+ + 2el by modifying the potential of the sensitive electrode.

The **Potentiometric Sensor** differs from the amperometric sensor because it works at current approximately zero and evaluates the hydrogen concentration by means of the voltage generated between the measuring electrode and that of reference. The potential of the measuring electrode is related to the concentration of $H_2$ from Nernst's law:

$$E = E_0 \left[\frac{RT}{Fz}\right] ln\left(\frac{a}{a_0}\right) \quad (1)$$

with: E electrode potential, E0 standard electrode potential, R universal gas constant, T temperature, F Faraday constant, z number of electrons taking part in the reaction, a is the chemical activity (a measure of the effective concentration of species in a mixture) of the electrode analysed, a0 the chemical activity of the reference electrode. The mechanism of diffusion, in order to accurately represent the potential, must achieve the balance. The response times of this sensor is lower than 2s.

## 1.3 Semiconductor sensors

Semiconductor gas sensors are devices that use an element sensitive to the gas concentration (called heater).
Sensitive materials such as SnO2 are used to create this heater. When the SnO2 crystal is heated to high temperatures, it adsorbs oxygen from the air and oxidizes. This causes a potential barrier on the upper face of the material.
In presence of an electrical current, the potential barrier is detected as an electrical resistance (Rs) that is proportional to the gas concentration.
The response of the sensor is proportional to the concentration of the gas in the air, following a relationship such as:

$$R = R_0 \cdot e^{(-kC)} \quad (2)$$

The conductivity variation is detected via electronic circuits embedded in the sensor. An increase of the conductivity and a decrease of the resistance are caused by an increase of the hydrogen concentration of the semiconductor material [13].
The sensor converts this change of conductivity into an electrical signal, that can be viewed on a display or used to trigger alarms or control safety devices.
Semiconductor sensors for hydrogen detection have good performances and very fast response time to changes of concentration.
These sensors are used in a wide range of applications, including industrial safety, hydrogen fuel cell monitoring, vehicular emissions control, and detecting hydrogen leaks in critical environments. The choice of the most suitable sensors depends on the specific needs of the application.
Other features are:

- Sensitivity to a single element
- Wide range of detectable concentrations
- Rapid response to changes in hydrogen concentration

- Stable over time
- Very sensitive to temperature and humidity
- Suitable for domestic uses.

The sensitivity of semiconductors sensor is affected by changes in temperature and humidity. In addition. these sensors may require a "break-in" period before reaching maximum efficiency. The semiconductors sensor must be subject to continuous calibration.
Another limit is the selectivity. MOS (Metal Oxide Semiconductors) sensors can be sensitive to multiple types of gases. All of this can lead to a false positive. However, with technological innovation and the use of advanced materials, the selectivity and accuracy of these sensors continue to improve.
The following table shows the principal characteristics of different kinds of semiconductor sensors:

Table 4: Summary of sensing performance of Silicon Carbide (SiC) based sensors for Hydrogen Detection Sensors.

| Materials | Gases | Concentration (ppm) | Response/recovery time (s) |
|---|---|---|---|
| Pd/SiC NC | H2 | 100 | 10/18 |
| Pt–PSiC | H2 | 30 | 55/160 |
| Pd-Pt/SiC/PSi | H2 | 100 | 21/35 |
| Pt NC @SIC NS | H2 | 500 | 72/101 |
| Pd decorato SIC | H2 | 100 | 7/13 |
| Nanofilo SIC | H2 | 4% | 3/45 |
| Nanofilo SiC decorate Pt | H2 | 100 | 15/40 |
| Pd/AIN/SiC | H2 | 100 | 85 |

## 1.4 Surface Acoustic Wave Sensors

The **Surface Acoustic Waves** are mechanical waves whose energy remains confined mainly on the surface of the material within they propagate, penetrating for one wavelength inside it. This confinement leads to a high sensitivity in detecting perturbations that occur on the surface itself.
In the presence of H2 gas, the acoustic wave has a propagation delay along the sensitive surface. From this delay, it is possible to easily calculate the percentage of H2 gas present in the environment.
The **SAW Sensor** operating principle is based on the propagation of surface acoustic waves. The propagation of elastic waves involves different physical properties of the medium. It can be influenced by environmental conditions as temperature, pressure, electric and magnetic field, as well as by the chemical-physical characteristics of the surface.
From the interaction of the surface, the acoustic propagation medium, the environment and the acoustic wave, it is possible to increase the sensor sensitivity towards chemical and biological quantities.
They are successfully used in several applications such as the electrical signals processing in the radar field, telecommunications and civil electronics.
The characteristics of the SAW sensors make them very suitable in several applications [12]:

- Low cost
- Small size
- High sensitivity
- Good stability
- Good response time
- Linear response
- High signal/noise ratio
- High Adaptability.

Depending on the phenomena to be measured, the mechanical wave is transduced in an electrical signal (i.e. the hydrogen percentage).
Changes in amplitude, phase, frequency, or time-delay between the input and output electrical signals

can be used to measure the concentration of the interested gas [14].
By means of a suitable set of electrodes, it is possible to generate the acoustic wave in one part of the material and detect an electrical signal in another part related to the mechanical deformation. The most common mode of propagation is the Raleigh mode, the propagation speed of the wave depends on the conditions of the medium.
Interdigital electrodes act as electro-mechanical transducers (IDTs). The electric field under the IDTs induces a mechanical deformation that propagates as an acoustic wave within the medium.

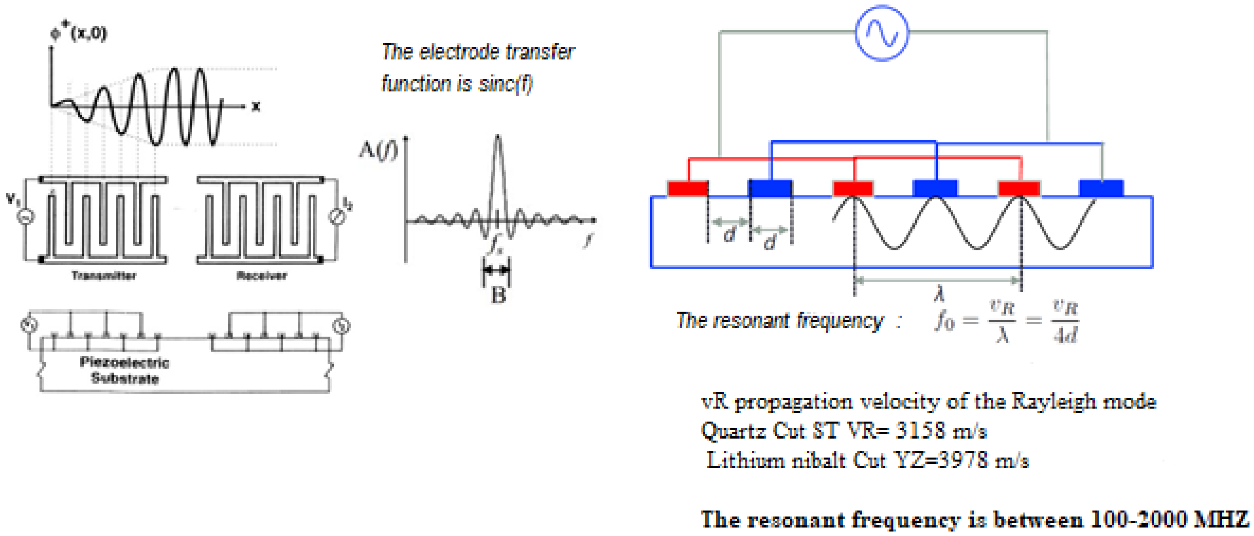


Figure 10 - SAW Sensor Operating Principles

High frequencies are obtained with micrometric interdigital translators that can only be realized with photolithographic techniques [RD13]. This type of sensors generally consists of a delay line or a resonator.
The Surface Acoustic Wave sensors have a wide sensing range and a short response time (about 1 s, [15]).

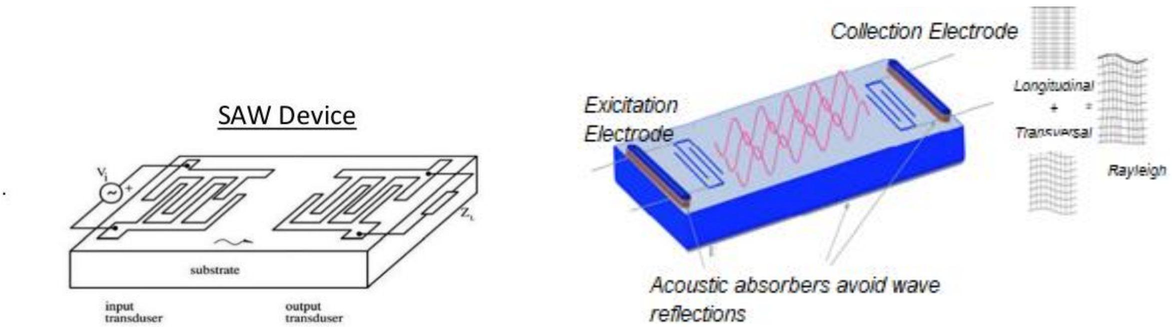


Figure 11 – SAW Sensors

## 2. Hydrogen sensor requirements for safety

All types of sensors described so far are essential to guarantee the safety in the case of hydrogen leakage events. In this regard, the Department of Energy (DOE) in the United States has provided a short list (in Tab. 5) of the requirements necessary to design suitable sensors [1], [2].
Obviously, there is no sensor that is suitable for all applications and the environment also significantly affects the choice of a device. Indeed, there are some sensors that can be influenced by temperature, others by pressure. The final choice will be made by the designer of the hydrogen system, based on the requirements of the project which will also encompass constraints related to the operative environment.

Table 4: Requirements for hydrogen detection sensors (provided by DOE)

| Parameter | System Safety Requirements |
|---|---|
| Detection range | 0.1 to 10 vol% |
| Operating temperature | −30 °C to 80 °C |
| Gas environment | Ambient air, 10% to 98% relative humidity |
| Accuracy | 5% of full scale |
| Response time | <1 s |
| Life time | 10 years |

The Safety Sensor Testing Laboratory of the NREL (National Renewable Energy Laboratory) has carried out, by means of a particular bench, tests on the sensors for the hydrogen detection that currently exist on the market, taking into account some important characteristics:

Table 5: Characteristics taken into consideration by NREL

| *Metrological Characteristics* |
|---|
| **Detection limit, Selectivity, Linear Range, Response Time, Repeatability, Effects of the environment** |
| *Physical characteristics* |
| **Maturity level, Size, Maintenance, Life cycle** |

The evaluations have not been made taking into account a particular application, but only considering the comparison between the performances of the various sensors. The result of this analysis considering a rating ranging from 0 to 5 is shown in the Table 6.

For SAW sensors these parameters have not been evaluated yet except the response time. However, since the response time is a crucial parameter for selecting hydrogen detectors and, in this regard, the SAW sensor has better performance than the others, this paper has opted to explore additional aspects of the sensor and in particular its sensitivity and the evaluation of its metrological performance. Indeed, a parametric analysis has been carried out in order to realize which parameters mostly influence the uncertainty of the SAW.

Table 6: Evaluation of sensor characteristics performed by NREL

| | **Electrochemical** | **Semiconductor** | **Optical** |
|---|---|---|---|
| ***Analytical Metrics*** | | | |
| Detection limit | 4 | 4 | 4 |
| Selectivity | 3,5 | 3 | 4,5 |
| Linear Range | 4,9 | 3 | 3 |
| Response Time | 4 | 3 | 3 |
| Ripetibility | 3,5 | 4 | 4 |
| Environmental Effect | 3,5 | 3,5 | 4 |
| | | | |
| Level of maturity | 5 | 5 | 3,5 |
| Size | 4 | 4 | 4 |
| Power | 4 | 3 | 4,5 |
| Maintenance | 3,5 | 3,5 | 5 |
| Lifetime | 3,5 | 4 | 4 |

## 3. SAW Sensitivity

To investigate the SAW sensitivity, a Graphene Oxide (GO) Sensor with Palladium (Pd) coating was considered [13]. The sensitivity was evaluated by its transfer function derivative. The transfer function is shown in Fig 12:

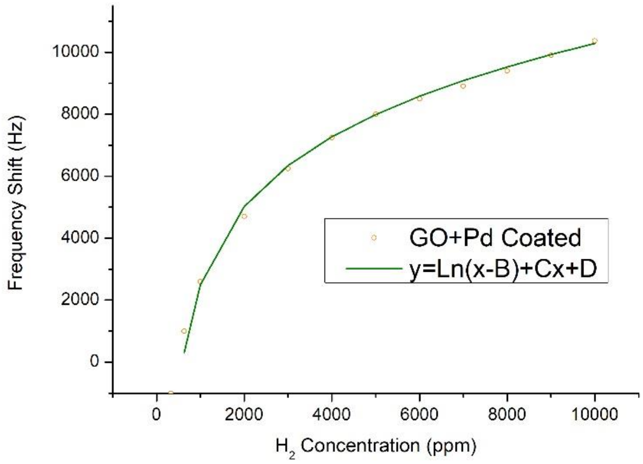


Fig12. SAW GO+Pd Coated

By means of the differentiation of the transfer function, it is possible to obtain the sensor sensitivity:

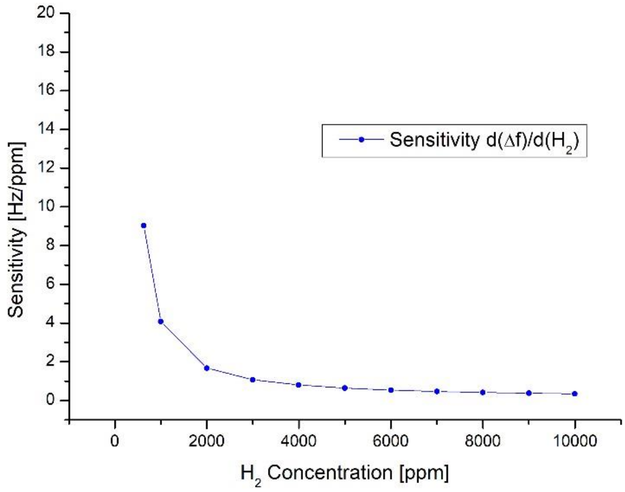


Fig13. Sensitivity SAW GO+Pd Coated

As the figure shows, the sensitivity of GO+Pd Coated considered sensor decreases as the hydrogen percentage increases. This is easily explainable with the sensor sensing element saturation.
Therefore, it must be taken into consideration when choosing the sensor in the presence of high hydrogen concentrations.

## 4. SAW Metrological Behaviour Analysis

As previously reported, some simulations for the evaluation of the metrological behaviour of the sensor, by means of Python programming language, have been carried out. Since the variables that contribute to the uncertainty are independent of each other, according to [19],[17] the standard uncertainty of a function of multiple variables (equation 3) can be evaluated by means of the equation (4):

$$f = f(x_1, x_2, \dots, x_n) \qquad (3)$$

$$u_f = \sqrt{\left(\frac{\partial f}{\partial x_1}\right)^2 \cdot u_{x_1}^2 + \left(\frac{\partial f}{\partial x_2}\right)^2 \cdot u_{x_2}^2 + \dots + \left(\frac{\partial f}{\partial x_n}\right)^2 \cdot u_{x_n}^2} \qquad (4)$$

In [20] a correlation between P/P0 ratio (where P is the pressure of the gas to be detected and P0 is the saturated vapor pressure at the adsorption temperature) and the measured frequency shift by means of the sensor (Δf) is shown. This involves a second order equation, with one only acceptable solution (the discarded solutions give a negative pressure value). The quantity taken into account (P/P0) is related to the gas concentration, and it is indicated as x in equation (5).

$$\frac{\Delta f}{\Delta f_1} = \frac{ckx}{(1-kx)[1+(c-1)kx]} \qquad (5)$$

where k is an adjustable constant decided by the nature of the adsorption system, Δf1 is the frequency offset of the SAW oscillator caused by a monomolecular layer covering the detector surface and c is an adsorption characteristic parameter (depending also by geometric characteristics of microstrip material), which is decided by the temperature, the average adsorption heat of the first monolayer and the gas liquefaction heat. The parameters of $\Delta f_1$ and c in Equation (5) can be determined by means of fitting experimental data.
The equation (5) can be manipulated, and it is possible to obtain it in the form of a second order algebraic equation as in equation (6).

$$Ax^2 + Bx + C = 0 \qquad (6)$$

With:

- $A = \frac{\Delta f}{\Delta f_1}(1-c) \cdot k$
- $B = \left[\frac{\Delta f}{\Delta f_1}(c-2) - c\right] \cdot k$
- $C = \frac{\Delta f}{\Delta f_1}$

Solving equation (6) two solutions are found, but as mentioned only one is admissible because not negative.
Applying equations (3) and (4) to the solution of equation (6), some evaluations can be carried out in order to obtain the uncertainty of the parameter x with respect to:

- The frequency shift Δf
- The uncertainty of Δf
- The value of the parameter c
- The uncertainty of the parameter c

The following plots report these data respectively.

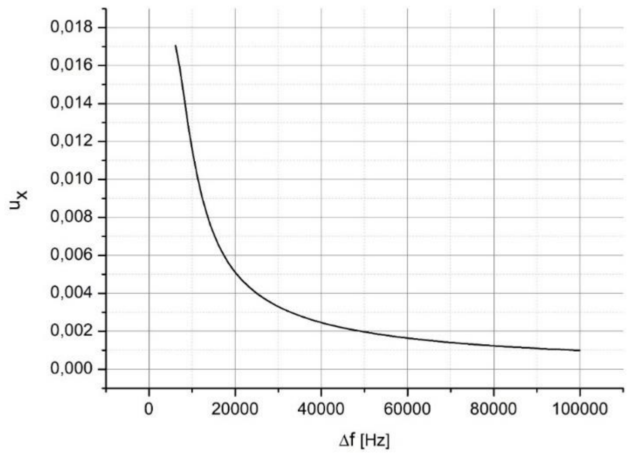


Figure 14: Uncertainty of P/P0 versus the frequency shift Δf

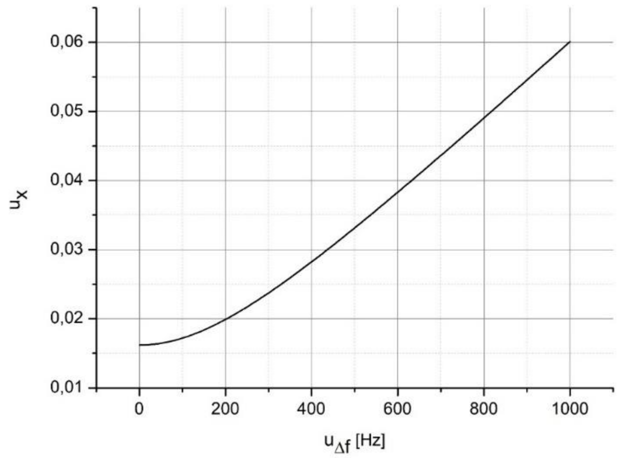


Figure 15: Uncertainty of P/P0 versus the uncertainty of Δf

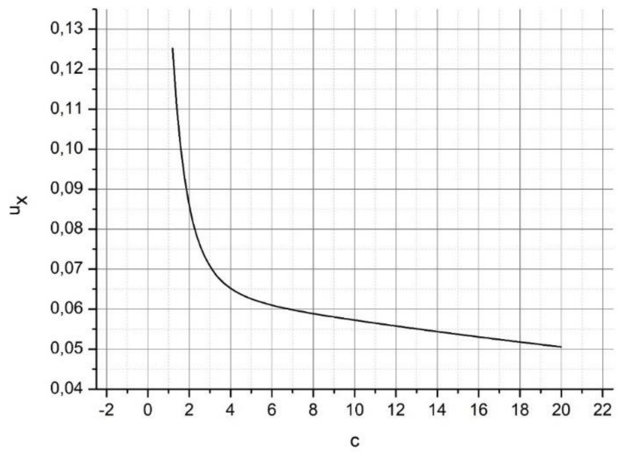


Figure 16: Uncertainty of P/P0 versus the parameter c

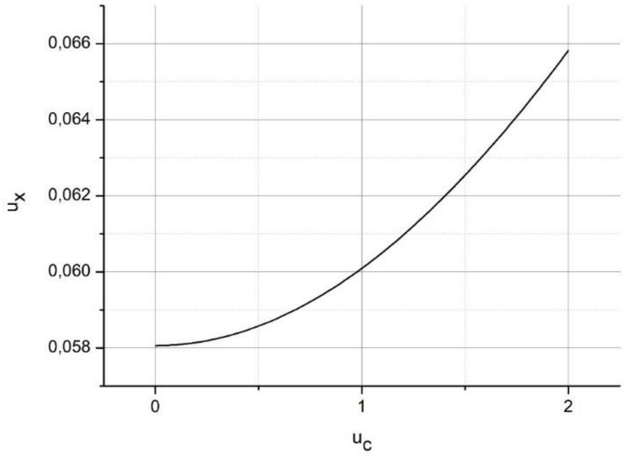

Figure 17: Uncertainty of P/P0 versus the uncertainty of c

The parameter Δf (Fig.14) has high influence on the metrological performance. In fact, when the frequency shift between the generated and the detected wave increases, the uncertainty decreases. This is due to the fact that the Δf increasing is directly proportional to the absorption increasing that in turn generates a growth in measurement uncertainty.
The evaluations made show that the greater the uncertainty on (Δf), the greater the measurement uncertainty of the sensor (Fig.15).
Another interesting result is that the uncertainty of the SAW sensor has a good sensitivity to its adsorption characteristics and geometric characteristic of microstrip material (represented here by the parameter c). The parameter c depends on the absorption characteristics of the material used and on the geometric characteristics (width and thickness) of the microstrip. In fact, the smaller the parameter c, the smaller the width of the microstrip, the greater the edge dispersion effect, and the greater the uncertainty. Conversely, the greater the width of the microstrip, the smaller the edge effect, and the smaller the uncertainty. (Fig.16)
Furthermore, the evaluations made show that the greater C uncertainty, as can be easily understood, the greater the measurement uncertainty of the sensor (Fig.17).
Since the frequency shift increases proportionally to the value of the hydrogen concentration, it is clear that this sensor is suitable for measuring high concentrations of hydrogen.

## 5. Conclusions

A comparison among different kinds of sensors (Optical, Electrochemical, Semiconductor and Surface Acoustic Wave Sensors) has been made in order to assess their capability for hydrogen leaks monitoring. Some simulations of the metrological behaviour have been carried out by means of simulations in MATLAB and Python environment. For these simulations an analysis of the uncertainty of the sensor as a function of different parameters has been done. As a result, the uncertainty is clearly sensitive to the frequency shift, as conceivable. In addition, a significant sensitivity to the physical properties of the sensor has been found.
Following the guidelines provided by the New York Department of Energy, the analysis of the sensors has been focused on one of the most important parameters indicated by the DOE: the response time.
Regarding this parameter, it has been seen that the SAW sensor has the best characteristics, because its response time is within 2 seconds. The other sensors are characterized by a response time that varies between a few tens of seconds and a few minutes.
For this reason, it has been decided to investigate the metrological behaviour of this sensor. The first characteristic evaluated is the sensitivity, in order to evaluate its operating limits a SAW sensitivity was investigated.
Since sensitivity decreases with increasing hydrogen percentage, it is recommended to use this sensor for hydrogen quantities up to 2 parts per million.
In order to understand if the measurement carried out has a good accuracy, the SAW uncertainty was analysed. From these analyses, it has been derived that the uncertainty of the device under

examination is influenced by the adsorption characteristics of the device itself and strongly influenced by the frequency shift between the generated and the received wave.
This difference depends proportionally on the concentration of hydrogen present in the environment. Therefore, the higher the concentration of hydrogen, the lower the measurement uncertainty of the sensor.
In conclusion, we can state that, despite its low response time, it is not recommended to use the SAW sensor at all, for the identification of small leaks, but it is more suitable for the monitoring of leakages characterized by higher amount of hydrogen concentrations.
A global evaluation can be made following further analyses carried out in the same way for the other parameters indicated by the DOE and for the other sensors to be taken into account.

**Copyright Statement**



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