Response changes of thin film palladium based optical fibre hydrogen sensors over time

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Abstract. Results are presented of a Palladium optical fibre sensor utilising a thin film as the sensing element as a transmission based sensor for the detection of hydrogen. Different thicknesses of Palladium between 8-13nm thick were deposited onto glass slides and tested by repeatedly exposing them to 5% Hydrogen gas in a nitrogen atmosphere. Initially the test samples had response times as low as 4-5 seconds with a change in spectral output up to 15%. Results are presented comparing the initial testing of the palladium slides to tests carried out 6 months later. A change in response for some sensing elements is demonstrated whereas others remain consistent to repeated exposures of Hydrogen gas.

1. Introduction
There is an increasing need for research and development in the use of hydrogen as the next generation energy source, which is clean and renewable, to ease or replace our dependence on fossil fuels. There are however certain technological barriers to be overcome before hydrogen can be used to replace fossil fuels as an energy source. Hydrogen gas ($H_2$) is a highly combustible substance with a Lower Explosive Limit (LEL) of 4.65% at room temperature and pressure. Since it is the lightest element one of the main barriers to overcome is hydrogen leak detection. Palladium (Pd) was used in this experiment as the active sensing layer of the sensor as the optical properties of palladium are known to change when in contact with hydrogen as a function of hydrogen concentration [1]. In this paper, a transmission based optical fibre sensor utilizing thin Pd films, 8-13nm thick, as the sensing layer for the detection of 5% hydrogen ($H_2$) in a nitrogen ($N_2$) atmosphere is discussed. The change in the spectral signature of the transmitted optical signal for the palladiums reaction from 0% $H_2$ to 5% $H_2$ is presented along with the response time of the sensor as it was exposed to 5% $H_2$ and as $H_2$ was flushed from the system. A comparison between experiments carried out when the thin Palladium film sensing elements were first deposited onto glass substrates and experiments carried out 6 months after the initial deposition is discussed. The degradation of the response of some of the Palladium sensing elements tested is discussed along with evidence that other Palladium thin films tested remained consistently repeatable and reversible over this time period.

2. Principal Operation
Palladium has the unique property of selectively and reversibly reacting to hydrogen by absorbing it to form a binary hydride. When palladium is exposed to hydrogen the palladium absorbs the hydrogen and forms a reversible palladium hydride. Hydrogen molecules are converted into hydrogen atoms ($H_2 \rightarrow 2H$) at the palladium surface with an efficient dissociation rate. The hydrogen atoms diffuse rapidly through the palladium film leading to the reversible hydrides of the form PdHx where x is the atomic ratio H/Pd.
The palladium hydride film (PdHx) has different mechanical, electrical and optical properties than those of a hydrogen free palladium film. The formation of PdHx causes an increase in the Fermi level and subsequent decrease in both the real and imaginary parts of the dielectric function, resulting in a decrease in the reflectivity of the thin films as a function of hydrogen concentration [2]. PdHx has two different phases, namely α and β depending on the Pd/H composition. The reversible α-phase is found at low hydrogen concentration. Without hydrogen, Pd exists in the α phase. As the hydrogen concentration increases Pd is transformed to the β-phase. The hydrogen concentration at which the phase transition takes place depends on the film thickness and temperature and it introduces a hysteresis in the optical and mechanical parameters of the palladium film. Pd in the β-phase has the same face centred cubic symmetry of pure palladium but with the lattice parameter expanded up to 3.5%. Transition from the α-phase to the β-phase for a thin Pd film (10nm-100nm) occurs at a wider hydrogen concentration range than the transition in the thicker Pd films (>10um) which occurs at around 4% concentration.[3]

3. Experimental Set-Up
Thin films of palladium were deposited onto highly polished glass slides using a BOC/Edwards E305A vacuum thermal coating system. This system contains an Edwards FTM5 quartz crystal to monitor the rate of film deposition and to measure the film thickness. The quartz crystal was positioned directly above the evaporation source. The mass deposited on the quartz crystal during the evaporation alters its natural frequency of vibration. This frequency change was recorded on the meter of the film thickness monitor connected to the quartz crystal. Using this system the thickness of the deposited palladium films were grown to thicknesses between 8-13nm.

![Experimental set-up for hydrogen detection](image)

Figure 1. Experimental set-up for hydrogen detection

The experimental set up is shown in figure 1. A gas cell was specially constructed to hold the Pd coated glass slide. It is made from aluminium and consists of two collimating lenses, which are aligned at an orientation of 180 degrees, and gas inlet and outlet connectors. Broadband visible light was transmitted into the gas cell from a DH-2000 UV-VIS-NIR deuterium-halogen light source from ocean optics using the halogen lamp only. The received light was detected by an S2000-TR spectrometer from ocean optics and the data from the spectrometer is acquired and stored using a personal computer running Labview™. The light source and detector were optically coupled to the gas cell using multimode polymer optical fibres (Fibre data A19A15A0) via the collimating lenses.
The gas supply component consists of a 5% Hydrogen-95%Nitrogen (H₂) mix and Nitrogen zero grade (N₂) from BOC gases. They were connected to the gas cell using stainless steel piping and the gases could therefore be mixed together or used separately using shut-off valves.

4. Results

Figure 2 shows an increase in the transmitted intensity in the visible region produced by a thin Palladium film when exposed to 5% Hydrogen in a Nitrogen atmosphere, which is as expected from the literature [4]. A series of experiments were undertaken to test the signal response, response time and repeatability of the sensor utilising the different Palladium film thicknesses. A comparison between the experiments carried out when the thin Palladium samples where initially formed and experiments carried out after six months was made to determine the repeatability of the sensor’s response with different palladium thicknesses on a glass substrate.

![Figure 2. Increase in Transmission spectrum from exposure of 0-5% H₂ in N₂](image)

Figure 3 shows 2 such experiments and compares the transmitted intensity of a sensor that initially had a fast response time with a strong signal response to the same sensor tested 6 months later whose response time has decreased and whose signal amplitude has also decreased. During both experiments the sensor was repeatedly exposed to 5% H₂ in a nitrogen atmosphere and subsequently flushed with 100% Nitrogen over a series of cycles. Several wavelengths were monitored and it was found that the wavelength of 625nm gave the strongest signal response in the visible spectrum. The response and recovery times are defined as the time required to achieve 90% of the signal change for the adsorption and desorption of hydrogen respectively. After 90% of the signal change there is a hysteresis effect on the reaction of the adsorption and desorption of hydrogen by the palladium thin film as the time response characteristic levels off to reach its settling value for the concentration of H₂ to which it has been exposed.

From figures 3(a) and (b) there is an 11.5% increase in the transmitted intensity upon exposure to 5% H₂ with a response time of 8 seconds and recovery time of 45 seconds when flushed with N₂. Comparing this to that of figure 3(c) and (d), where there is only a 10.1% increase in the transmission spectrum with a response time of 18 seconds and a recovery time of 80 seconds, there is a clear decrease in the transmitted intensity of the sensor after 6 months of the fabrication of the sensor. This degradation in the sensor’s response can be attributed to the peeling and blistering of the thin film Palladium glass slide due to constant expansion and contraction of the Pd as it adsorbs and desorbs hydrogen and expands and contracts to and from the α-phase and β-phase [5], [6] and [7]. The solid glass substrate does not...
accommodate the expansion of the Pd slide and due to its thickness of only 8-9 nm the sensing element cracks and peels thus slowing down its ability to absorb hydrogen.

![Graphs showing sensor response](image)

**Figure 3.** Comparison of sensors response at a wavelength of 625nm for repeated exposure of 5% H₂ in N₂ from when the palladium-sensing element was initially deposited to tests carried out 6 months later. (a) Percentage change in the transmission spectrum for the sensor when the Palladium sensing element was initially deposited. (b) Rise time of the sensor. (c) Signal response 6 months after initial testing. (d) Rise time of the sensor 6 months later.

The degradation of the sensor’s transmission did not occur for all Palladium sensing elements tested. The thicker Palladium slides of 12-13nm remained repeatable and consistent from the initial experiments undertaken to experiments carried out 6 months afterwards. Figure 4 shows the comparison of one such sensor whose transmission remained consistent throughout the experimentation. The transmitted intensity
showed an increase of 10.7% with a response time of 5 seconds to 5% H2 and a recovery time of 30 seconds for both the initial experiments and the experiments carried out 6 months after the Palladium slide was formed. This indicates that the thicker the Palladium sensing layer is, in the low nanometre scale, the more resistant it is to cracking or peeling when it has been deposited onto a solid glass substrate.

Figure 4. Comparison of H2 sensor with a 12-13nm thick Palladium sensing element. (a) Results recorded after sensing element had originally been deposited. (b) Results recorded 6 months after initial deposition

5. Conclusion

An experimental transmission based optical fibre hydrogen sensor utilizing thin Palladium films that can measure up to 5% Hydrogen in a Nitrogen atmosphere has been presented. The ageing of the sensors over a 6-month period has been discussed and the degradation of some of the sensors has been demonstrated. The decreased transmission is attributed to the cracking of thinner sensing elements due to consistent expanding and contracting of the Palladium sensing element due to the adsorption and desorption of hydrogen into the Palladium sensing element. Each of the sensors responses has been demonstrated to be completely reversible. It has also been shown that some of the sensor’s transmitted response did not degrade and were consistently repeatable to continuous cycles of 5%H2 over a 6 month period.

Future work will continue to investigate the ageing of the different thicknesses of the Palladium sensing element. Different substrates for the Palladium sensing elements to be deposited onto will also be investigated to increase the lifetime of the sensor as well as different thicknesses of Palladium to improve the ageing characteristics of the sensor. Different optical embodiments of the sensor will also be investigated along with the sensors response to varying concentrations of hydrogen below and above 5% H2.
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