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Hydrogen sensor based on a palladium-coated fibre-taper with improved time-response

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Abstract

We report an experimental study of the response of a hydrogen sensor, based on a palladium-coated tapered optical fibre, at different temperatures in the range −30 to 80 °C. We have studied the transmission, the time-response and the initial response velocity, being able to correlate these measurements with the pressure–composition isotherms of the Pd–H system and its phase transitions. Heating of the palladium layer optically with an auxiliary laser diode permits to improve the sensor's time-response at low temperatures.

Keywords: Fibre-optic sensors; Hydrogen sensors

1. Introduction

The development of aeronautics, sustainable energy systems and sustainable surface transport technologies drives the use of hydrogen as energy carrier. Hydrogen as combustible has superior characteristics over conventional fuels and it is clean. Thus, future developments in surface transport technologies based on hydrogen should lead to a reduction of contamination and earth heating.

The dangers associated with the use and storage of hydrogen have always been a tremendous problem. A leak of gaseous hydrogen in air, at room temperature and atmospheric pressure, leads to an easily ignited explosive atmosphere for hydrogen concentrations by volume of more than 4%, the lower explosive limit (LEL). Consequently, security systems operating in hydrogen environments demand fast, sensitive and reliable hydrogen sensors.

In the last years, many hydrogen sensors, using palladium as transducer, have been reported; most of them are based on electrical techniques of detection [1]. Optical techniques seem to be more attractive in hazardous atmospheres owing to the lack of sparking possibilities. The optical properties of palladium change when it interacts with hydrogen [2]. Moreover, optical sensors can provide very high sensitivity and fibre-optic hydrogen sensors in particular add multiplexing and remote sensing capabilities [3–10]. A wavelength multiplexed hydrogen sensor has been reported, based on a Pd-coated fibre Bragg grating (FBG) [6]. However, this device shows little sensitivity and requires thick layers of Pd, which makes the device's time-response too long for many applications.

In previous works, we reported a hydrogen sensor based on a Pd-coated single-mode tapered optical fibre [7,8]. The attenuation change of the fibre-mode when the device was exposed to hydrogen was exploited to detect and to measure hydrogen concentration in gaseous atmospheres. The device showed high sensitivity to low concentrations of hydrogen and a fast time-response. We have also demonstrated a wavelength multiplexed hydrogen sensor that employs a Pd-coated tapered fibre combined with a fibre Bragg grating [9] and, more recently, we developed a time-domain fibre-laser sensor [10].

In this paper, we report an extensive experimental study of the temperature effects on the response of Pd-coated tapered fibre hydrogen sensors and a solution is proposed to enhance

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the sensor response-time at low temperatures. The hydrogenation reaction of a palladium film is highly dependent with temperature [11]; hence, it is expected that the response of this type of sensor also change with temperature. Here, the transmission and the response-time are measured in the range of temperature −30 to 80 °C. The initial velocity of the response has also been investigated as a function of temperature. This parameter can play an important role when hydrogen leaks fast detection is required. First, we explain the working principle of the sensor. Second, we present the experimental results obtained when the sensors were exposed to a fixed hydrogen concentration at various temperatures. Finally, we show that the response of the sensor at low temperatures can be modified and optimised for a fast detection of hydrogen leaks by heating optically the palladium film.

2. Operation principle

When palladium is exposed to hydrogen, hydrogen molecules are converted into two hydrogen atoms ($H_2 \leftrightarrow 2H$) at the palladium surface with very efficient dissociation rate. The hydrogen atoms then diffuse rapidly through the palladium film, leading to reversible hydrides of the form PdH_x, where x is the atomic ratio H/Pd. The palladium hydride film has different mechanical, electrical and optical properties than those of a hydrogen-free palladium film.

Typical pressure–composition isotherms of the Pd–H system are shown in Fig. 1 for palladium films of ∼100 nm thickness. The data corresponding to the 75 and 25 °C isotherms have been obtained directly from Ref. [11], while the isotherm of −30 °C is an interpolation from data provided by the same reference. In this figure, we can observe that each isotherm has an isopressure zone that corresponds to a crystallographic phase transition of palladium upon adsorption of hydrogen. The width of the isopressure zone decreases drastically for thinner palladium films (see Ref. [12] for a comparison between films of 6 and 120 nm). Approximately, we can say that an H/Pd ratio below 0.1 corresponds to the limit of the α-phase, above a ratio of 0.5 we find the β-phase and, in between both phases coexist without miscibility. Without hydrogen and at low hydrogen concentrations, palladium is entirely in the α-phase. Increasing the H/Pd atomic ratio leads progressively to the β-phase, which has a larger lattice parameter than the α-phase. In the β-phase, the palladium film is swelled, and consequently, the volume density of free electrons decreases. This, in turn, causes that both the real and imaginary parts of the complex permittivity of palladium decrease. Bevenot et al. [4] introduced an empirical simple equation to describe this effect, in which the complex permittivity of the palladium hydride film ε_{PdH} is expressed as:

$$\varepsilon_{PdH} = h\varepsilon_{Pd} \quad (1)$$

where ε_{Pd} is the complex permittivity of the hydrogen-free palladium film and h is a non-linear function decreasing with hydrogen concentration and taking values inferior to one.

The device studied in this paper exploits the changes in the imaginary part of the refractive index of palladium, when it is exposed to hydrogen. Tapering of the fibre allows the interaction of light with the palladium coating. The propagation constant of the fundamental mode of the Pd-coated tapered optical fibre exhibits an attenuation coefficient, γ, different from 0 since the palladium refractive index is complex. When the device is exposed to a certain concentration of hydrogen, the complex refractive index of palladium changes and the attenuation constant of this mode decreases an amount $\Delta\gamma$. The power transmission P of the device can be obtained from:

$$P = P_0 \exp[2\Delta\gamma L_{in}] \quad (2)$$

where P_0 is the power transmission when no hydrogen is present, and L_{in} is the interaction length. Thus, measuring the changes of light transmitted through the sensor, one can obtain the hydrogen concentration.

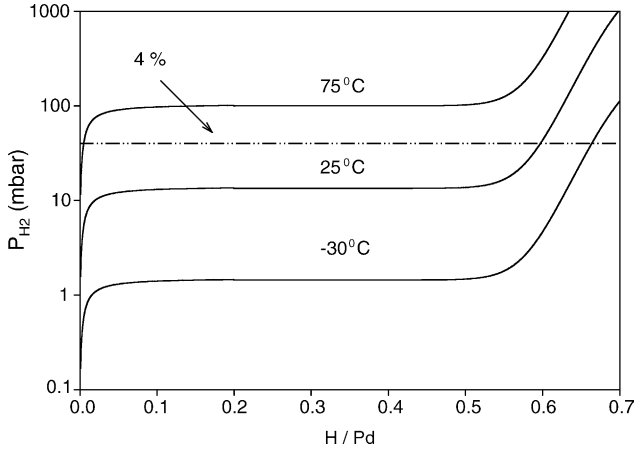

Fig. 1. Pressure–composition isotherms of palladium vs. the adsorption of molecular hydrogen (from Ref. [11]). The dashed line is the pressure level (40 mbar) that corresponds to the LEL (i.e., 4% of hydrogen concentration at atmospheric pressure).

3. Experimental results and discussion

The devices were fabricated in standard optical fibre-tapered adiabatically using the travelling-burner technique [13]. This optical fibre-tapering technique is a well-established fibre processing technique that allows fabricating tapers with submicrometric accuracy and excellent reproducibility. The tapered fibre used for fabricating the hydrogen sensor had a uniform waist of 25 μm diameter and 8 mm length. We chose such dimensions in order to get a compact device, with good response and easy handling [7,8]. Finally, a palladium layer of 8 nm thickness was evaporated onto the taper waist (Fig. 2(a)). The sensors that we fabricate using our laboratory facilities have a reasonable degree of reproducibility. However, each individual sensor requires a specific calibration.