



## Optimizing the sensitivity of palladium based hydrogen sensors

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### ABSTRACT

This paper reports on the sensitivity optimization of palladium based hydrogen sensors. The transduction mechanism is the volumetric expansion of palladium, leading to induced strain in a strain sensing element. Absorption of hydrogen in the palladium lattice causes expansion, which can be measured using strain sensors attached to the palladium. The strain transduced from the expanding palladium is dependent not only on the hydrogen partial pressure and temperature, but also the geometry of the palladium and the mechanical transfer of strain to the sensor. In this paper we demonstrate the design and validation of a sensor for defined hydrogen concentration ranges, selection of a working temperature, and selection of a palladium geometry to achieve a desired sensitivity. We show that operating temperature and concentration range are critical in order to avoid the phase change region, which can cause hysteresis, as well as degradation of the palladium itself and the adhesive interface. In order to quantify the strain transfer between palladium and the sensor, a coefficient of strain transfer  $k_{st}$  is introduced. Two empirical methods are demonstrated to calculate  $k_{st}$ : (a) via calibration for hydrogen sensitivity, (b) via calibration for temperature sensitivity. Three sensor designs, with fiber Bragg gratings as a strain sensor, are used to correlate the theoretical design assumptions with experimental data.

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### 1. Introduction

The development of hydrogen ( $H_2$ ) sensors is of increasing research interest for asset health monitoring [1–3] and safety applications [4–6]. Several sensing concepts have been reported in the literature [7]; one group of concepts is based on fiber optic sensing principles. Fiber optic  $H_2$  sensors have the advantage of being intrinsically safe in explosive gas mixtures, and to some degree, offering the potential of distributed sensing [7]. These aspects make fiber optic sensors an ideal candidate for sensing in high voltage environments, e.g. distribution and power transformers [2,8].  $H_2$  is generated in transformers during standard operation and increasingly during faults. The hydrocarbons of the insulating mineral oil in the transformer are broken down during partial discharge and several other faults [9,10]. The  $H_2$  generated by this decomposition dissolves into the oil and the transformer health status can be assessed according to the dissolved concentration following a dissolved gas analysis (DGA). DGA classifies the transformer health into 4 categories according to the dissolved  $H_2$  concentration ranging from <100 ppm to >1800 ppm. In the gas phase this correlates

to 2300–41800 ppm [9]. Therefore, a  $H_2$  sensor covering this range is desirable.

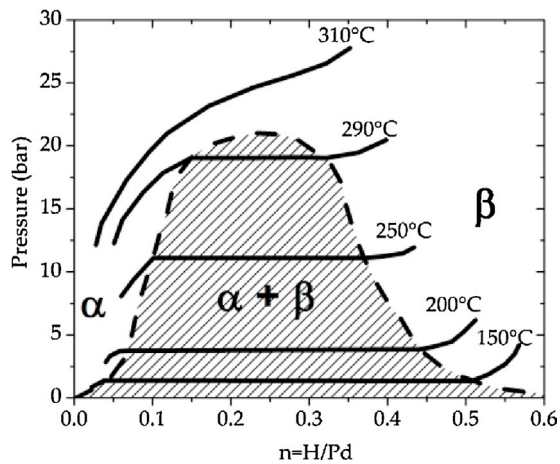
One  $H_2$  sensing technique is to transfer the volumetric expansion of palladium (Pd) due to  $H_2$  absorption to a strain within a fiber optic strain sensor. Concepts based on Fabry-Perot [11] and fiber Bragg grating (FBG) [12–16] have been reported.

Pd is popular for  $H_2$  sensing since it selectively absorbs  $H_2$  [17,18]. However, several other gases can have an inhibiting effect on the hydrogen absorption:  $O_2$ , CO,  $CO_2$ ,  $H_2O$ ,  $H_2S$ , and  $SO_2$  have been reported to affect the absorption [19–23]. Of these CO and  $H_2S$  have the most significant impact, but only CO is present in a transformer. CO can slow down the  $H_2$  response time of Pd based sensor, but does not affect its sensitivity [22].  $H_2O$  has been reported to have a reduction of less than 5% on the permeation of hydrogen through Pd-based membranes with thicknesses >75  $\mu m$ . However, partial delamination of Pd-based thin film sensors with thicknesses below 200 nm have been reported when the sensor is exposed to high humidity levels [24,25]. To mitigate the effect of humidity on the sensors PTFE membranes proved to be effective [24]. In general,  $H_2O$  is not a major concern in transformer oil since the solubility is only around 100 ppm [26].

The  $H_2$  absorption process in Pd is as follows:  $H_2$  molecules are dissociated into atomic H on the Pd surface. Subsequently, the H atoms are absorbed by the Pd causing a volumetric expansion

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**Fig. 1.** Phase diagram of Pd hydride: H<sub>2</sub> partial pressure vs. concentration. (Using data from [29]).

[27]. The volumetric expansion increases linearly with increasing H concentration ( $n < 0.7$ ) [28]. H<sub>2</sub> absorption of Pd results in two different phases for temperature below 293 °C: the so called  $\alpha$ - and  $\beta$ -phases. Both phases are solid phases.

The  $\beta$ -phase has a significantly larger lattice constant and increased hydrogen solubility. The formation of these phases depends on the temperature, as well as H<sub>2</sub> partial pressure (see phase diagram-[Fig. 1](#)). Initially the  $\alpha$ -phase is exclusively present, until the  $\beta$ -phase starts to coexist at  $n = \alpha_{\max}$  [29].

This  $\alpha$ -  $\beta$  phase change poses several challenges in a H<sub>2</sub> sensing application:

- (1) In the  $\alpha$  - phase the ratio  $n$  increases with increasing H<sub>2</sub> partial pressure. In the miscibility gap the ratio  $n$  increases with constant H<sub>2</sub> partial pressure. Since the volumetric expansion increases linearly with increasing  $n$ , measuring over the phase change region would cause a non-continuous signal to be generated.
- (2) Cycling between the phases can cause irreversible deformation of the Pd [29].
- (3) The large expansion of the Pd due to the phase change could stress severely the interface between the Pd and the sensor. This could degrade the interface and damage the sensor.

Since longevity is one of the core demands for hydrogen sensors in many applications, the phase change needs to be avoided [7]. Other core demands are high sensitivity and signal to noise ratio (SNR) [7]. Previously, we presented sensors designs with increased sensitivity by using large cross-sectional area palladium foils attached to an FBG [30]. However, the experimentally determined sensitivity differed partially considerably from the calculated sensitivity.

Different ways to calculate the sensitivity of Pd based H<sub>2</sub> sensors using fiber optic strain sensors have been presented [12,13,30–32]. All assume a perfect strain transfer between the Pd and the fiber. However, the strength of adhesion between the Pd and the strain sensing element critically affect the sensitivity of the resultant mechanical sensors [7]. A coefficient of strain transfer can quantify this effect for surface bonded FBGs used for strain measurements. This coefficient is the ratio of strain measured with an FBG to strain measured with a strain gauge [33]. This coefficient has not previously been applied to Pd based H<sub>2</sub> sensors.

In this paper, we introduce a method to select the working temperature of a Pd based H<sub>2</sub> sensor to avoid the phase change region. We provide guidance to easily select a geometry that achieves a required sensitivity. Furthermore, we introduce a coefficient

of strain transfer, which quantifies the strain that is transduced from the expanding Pd into the fiber, and which therefore directly describes the sensitivity and accuracy of the sensor. This coefficient is derived from experimental values and theoretical calculations. We report two methods to obtain the coefficient: (a) via calibration for H<sub>2</sub> sensitivity, and (b) via calibration for temperature sensitivity. The theoretical assumptions are verified with experimental data from 3 different sensor designs, which were previously presented in [30].

## 2. Material and methods

### 2.1. Design principle 1: selecting appropriate working temperature to avoid phase change

When designing a reliable Pd based H<sub>2</sub> sensor the phase change region must be avoided. This can be achieved by selecting an appropriate working temperature so the maximum expected H<sub>2</sub> concentration does not lead to a phase change, i.e.,  $n$  does not exceed  $\alpha_{\max}$ . Simons et al. [34] show  $\alpha_{\max}$  as a spinodal curve with  $n$  versus temperature. For sensor design purposes, this diagram can be improved by display of the spinodal curve of H<sub>2</sub> partial pressure (or concentration calculated as  $c = \frac{p_{\text{partial}}}{p_{\text{total}}}$ ), versus temperature. Therefore, the partial pressure is calculated with (1) [34] for given  $n$  and  $T$ .

$$\ln(p) = 13.04 - \frac{2327}{T} - \frac{11110n}{T} + 2 \ln\left(\frac{n}{1-n}\right) \quad (1)$$

This leads to a new diagram with extended information content and improved usability (see [Fig. 2](#)). Now, temperature and H<sub>2</sub> partial pressure, or concentration can be directly correlated to the phase change, without an additional step of converting  $n$  to the H<sub>2</sub> partial pressure, or concentration.

[Fig. 2](#) can be utilised as follows: In the region below the spinodal curve the Pd hydride is in the  $\alpha$ -phase; in the region above the curve the miscibility gap is entered. Selecting the working temperature is now easy and intuitive: The minimum working temperature is the abscissa corresponding to the intercept of the maximum expected H<sub>2</sub> partial pressure, or concentration with the spinodal curve. For example, if we want to sense up to 5 % H<sub>2</sub> at 1 bar (50 mbar partial pressure) we have to set the working temperature of the sensor to at least 50 °C to avoid a phase change. Conversely, the selection of a working temperature can be used to determine the maximum H<sub>2</sub> concentration to which the sensor can be exposed before entering the phase change region.

For the purposes of the investigation reported here, the measurements were conducted at 30, 60, 90, and 120 °C leading to maximum H<sub>2</sub> partial pressures of 25, 100, 300, and 800 mbar respectively before entering the phase change region. Therefore, the H<sub>2</sub> partial pressure for each experiment was chosen below those values.

The working temperature should be selected to avoid the phase change region, but not significantly higher, since increasing the working temperature decreases the sensitivity (see [Fig. 3](#)).

### 2.2. Design principle 2: designing sensor geometry to achieve required sensitivity

A practical Pd based H<sub>2</sub> sensor should achieve a required sensitivity, and the design process is outlined here. First, calculate the maximum possible sensitivity of the sensor, neglecting the influence of (a) the strain sensor itself limiting the expansion of the Pd, and (b) imperfect strain transfer between Pd and sensor. Both of these factors influence the sensitivity negatively.

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