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Fiber optic hydrogen sensor for a continuously monitoring of the partial hydrogen pressure in the natural gas grid

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ABSTRACT

The development of reliable hydrogen sensors will facilitate the introduction of hydrogen to the natural gas infrastructure. One of the most promising configurations for such a device is a thin film based fiber optic sensor. We demonstrate that with such a device not only the measurement of a specific threshold partial pressure is possible, but also allows for a quantitative determination of the partial hydrogen pressure measured real-time and in-situ in the gas stream. The changing hydrogen pressure, up to 200 mbar partial pressure, can be measured optically using a Pd–Au alloy thin film. However for the daily use of the sensor in the natural gas infrastructure it is important to determine the hydrogen sensing abilities under non-ideal conditions i.e. in gas mixtures containing high concentrations of CH_4, C_2H_6, and C_3H_8.

It is found that, the type of carrier gas (i.e. Ar (clean-conditions), CH_4, C_2H_6, and C_3H_8) has hardly any influence on the measured hydrogen concentration and switching kinetics of the sensor. The sensor response times (hydrogenation kinetics) are comparable to those for clean H_2 flows.

1. Introduction

The increasing desire to regulation regarding CO_2 emissions and enhance the sustainability of the energy supply result in a trend toward the use of hydrogen. To avoid the necessity of large investments, a (cost-) effective way to transport and deliver hydrogen to end-users (industrial, commercial and residential) is to inject it into the natural gas grid. However, since the combustion properties of hydrogen differ in many respects to those of natural gas [1–3], the allowable fraction of hydrogen in natural gas is strongly limited by the deteriorating performance of gas combustion equipment such as spark-ignited engines, burners and turbines to hydrogen-enriched natural gas [4,5]. To enable the introduction of hydrogen on a large scale, extra measures are required to guarantee the safety and performance of end use equipment when substantial fractions of hydrogen are present in natural gas. For example, when the hydrogen fraction in natural gas is known the control system of the appliance can automatically adjust the fuel/air ratio to obtain an optimal combustion. For this purpose, the development of reliable and cheap gas sensors with fast response times and high selectivity in gas appliances and gas quality meters is a key issue.

More general, there is a huge interest in developing accurate, cheap and reliable hydrogen sensors due to the flammable and highly explosive nature of hydrogen. Here we use metal thin films as quantitative hydrogen sensors in a micro-mirror fiber optic sensor configuration [1–7]. This measurement method has the advantage of being intrinsically safe in an explosive environment due to the lack of electric leads in the sensing area [6–12].

Our fiber optic hydrogen sensor is a chemical sensor and is based on a $Pd_{81}Au_{19}$ alloy thin film. This $Pd_{81}Au_{19}$ alloy changes its optical properties upon hydrogen absorption and desorption due to a metal–metal hydride phase transition [13–16]. In the literature, pure Pd is often used as hydrogen sensing material due to its high sensitivity and selectivity toward hydrogen. The absorption of hydrogen causes an upward shift of the Fermi level and as a result the real and imaginary part of the dielectric function decreases and thereby lowering the reflection of the Pd. Furthermore, below the critical temperature of the Pd–hydrogen system (i.e. bulk: 556–566 K [17,18], thin films: 528–568 K [14,19,20]), a first order phase transition from the solid solution α phase, to a metal hydride β phase, $PdH_{0.7}$, is observed at a well-defined hydrogen pressure. Therefore, it can be used as hydrogen detector. However, this phase transition is accompanied by a hysteresis

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between the absorption and desorption pressure, see Ref. [26], which results in an uncertainty in the reading of this detector. Alloying Pd with other metals like for example Au, suppresses the α–β phase transition by lowering the critical temperature [26]. Alloying results in a distribution in the energy of the interstitial sites and instead of having a single plateau pressure, one observes a sloping plateau pressure and thus gradual change of the optical reflection as a function of the hydrogen pressure. Furthermore, when $T > T_c$ a hysteresis-free behavior is expected, which allows for the design of a quantitative hydrogen sensor.

The change in optical properties of the Pd–Au based sensor is proportional to the amount of hydrogen absorbed in the alloy, which is governed by the thermodynamics of the Pd–Au–H_2 system. Therefore at any given temperature the optical change depends on the partial pressure of hydrogen in the system. Furthermore, this Pd-alloy should have a high hydrogen sensitivity independent of other gas components present in natural gas [21–23] and selectivity toward only H_2. Therefore, in this research we investigate the hydrogen sensing properties of the $Pd_{81}Au_{19}$ alloy as function of temperature and for H_2–CH_4, H_2–C_2H_6 and H_2–C_3H_8 gas mixtures.

It is found that the partial hydrogen pressure can indeed be monitored quantitatively in $CH_4 + H_2$, H_2–C_2H_6 and H_2–C_3H_8 gas mixtures with H_2 partial pressure up to 200 mbar H_2. The observed sensor response is reproducible, independent of the carrier gas and the response time (hydrogenation kinetics) is less than 30 s for all investigated gas mixtures.

2. Experiments

2.1. Experimental setup

Pd–Au thin films with a typical thickness of 60 nm are deposited at room temperature on the end of optical fibers (with a fiber core of 200 μm in diameter) in an ultrahigh-vacuum (UHV) DC/RF magnetron sputtering system (base pressure 10^{-8} mbar, deposition pressure 0.003 mbar). To prevent delamination of the sensing thin film we deposit a 3 nm thick Ti intermediate layer between the Pd-alloy film and the optical fiber surface [13]. The sensor is capped with a sputtered polytetrafluorethylene (PTFE) coating of 50 nm to improve the hydrogenation kinetics and to reduce the influence of gas species other than hydrogen.

To obtain the correct Pd–Au alloy composition, pure Pd and Au thin films are prepared and from the deposition time and the deposited thickness of the films, as determined by a profilometer (DekTak^3), the deposition rate is obtained. Subsequently the composition is calculated by using the atomic volumes of Pd (8.85 cm^3/mol) and Au (10.2 cm^3/mol).

The light of a tungsten halogen light source is guided onto the sensing thin film (micro-mirror) using a multimode optical fiber. The reflected light from the Pd–Au thin film is measured with a multi-mode optical fiber system. The reflected light is coupled to a second optical fiber which is connected to an Ocean Optics USB4000 spectrometer, see Fig. 1. The spectrometer measures the light reflected by the hydrogen-sensitive $Pd_{81}Au_{19}$ layer in the entire wavelength range from visible to near infrared. However here, the data is mainly given at 635 nm, because most of the standard LEDs and photodiodes operate at this wavelength. To a first approximation of scaling the optical response to the hydrogen partial pressure, we normalize the measured optical response in reflection by the reflection value in the unloaded state.

A flow setup that includes a solenoid valve and mass flow controllers is used to characterize the optical response of this Pd–Au film in reflection mode during gas loading experiments. The Pd–Au sensor is subjected to a controlled flow while mass flow controllers

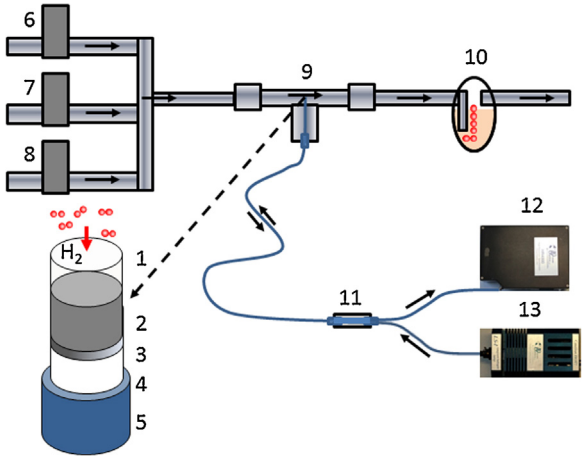

Fig. 1. Schematic representation of the optical fiber sensor layout with (1) PTFE coating, (2) Pd–Au sensing layer, (3) Ti adhesion layer, (4) multimode fiber, (5) fiber jacket, (6) Ar–H_2 flow controller, (7) carrier gas flow controller, (8) Ar flow controller, (9) hydrogenation cell, (10) bubble glass container with silicon oil, (11) bare fiber adapter, splice bushing, and bifurcator, (12) Ocean Optics USB4000 spectrometer, (13) Ocean Optics tungsten halogen light source.

regulate the relative amount of hydrogen, argon, methane, propane and ethane in the feed flow. The flow ranges of the mass-flow controllers (Bronkhorst, EL-FLOW) were selected to provide an accuracy of better than 5%. All gasses used in this study were supplied in cylinders with purity better than 99.9%. A flow between 200 and 500 mL/min is used during the gas mixture experiments and the outlet of the flow cell is vented. After each experiment the flow cell is flushed before preparing the next experiment to ensure identical starting conditions for the next cycle. Subsequently the solenoid valve, which is positioned at the end of the gas filling line near the flow cell, is closed and the gas line is filled with the hydrogen/carrier gas fraction under investigation. By opening the solenoid valve instantaneously the methane/hydrogen mixture flows into the flow cell and the response time of the senor is measured. The typical temperature of the gas feed is room temperature while the loading cell can be heated to probe the influence of temperature. To investigate the influence of each natural gas component on our hydrogen sensor we use gas mixtures of only H_2–methane, H_2–ethane, and H_2–propane.

3. Results

3.1. Optical response in H_2 gas mixtures

A quantitative hydrogen sensor is only practically applicable when it has a well-defined relation between the optical response and the partial H_2 pressure with a negligible influence of other gas components present in natural gas, such as methane, ethane and propane. Therefore we investigated the influence of H_2–CH_4, H_2–C_2H_6, and H_2–C_3H_8 gas mixtures on the optical response of our fiber optic hydrogen sensor. The change in reflection as function of hydrogen partial pressure is measured and the reflection levels are normalized by the unloaded reflection intensity for scaling purposes. The effect of the gas mixtures on the sensor's response is investigated for gas mixtures with up to 200 mbar H_2 and in a 200–500 mL/min flow. Unloading is performed with a 200–500 mL/min flow without H_2.

It is interesting to observe that, the optical response does not depend on the type of carrier gas but only on the partial hydrogen pressure, see Fig. 2. Only a small random variation between the different measurements can be observed. To assure the reproducibility of the sensor we measured the partial hydrogen pressure