Compact and multiplexible hydrogen gas sensor assisted by self-referencing technique

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Abstract: We have experimentally implemented a multiplexible but compact fiber sensor system suitable for multipoint sensing of hydrogen gas leakage. By making dual cavities along an optical fiber and coating a palladium film only at the end of the fiber tip, the measurement errors induced by the optical source power fluctuation and the mechanical perturbation in the lead fiber could be compensated. By adjusting the length of the dual-cavity, the capability of multiplexing several hydrogen sensors could be achieved. The experiment results showed that the response speed of the sensor was increasing with temperature, but at a low temperature the response amplitude became large.

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1. Introduction

Hydrogen has attracted considerable interest due to the possibility of alternative energy to fossil fuels in various applications such as hydrogen-fueled cars. The hydrogen, however, is dangerous since it is volatile, flammable, and highly diffusible. Hydrogen has wide flammability and explosion ranges of 4-75% and 18-59% (concentration in air), respectively. In addition, it has low ignition energy of about 0.02 mJ compared to gasoline vapor and natural gas which have 0.2 mJ and 0.29 mJ, respectively. Therefore, many of electrical sensors are not suitable for hydrogen gas sensing because of the potential of causing flame and explosion, mainly due to electric sparks. However, fiber-optic sensors do not have the risk of explosion but have several advantages including compactness, flexibility, electromagnetic immunity, multiplexity, and remote-operation capability.

Several types of fiber optic sensors have been developed for hydrogen gas detection using fiber Bragg grating [1], hybrid fiber grating [2,3], long period fiber grating [4], Raman scattering [5], tapered multimode fiber [6-8], surface plasmon resonance [9,10], cantilever [11], side-polished fiber [12] and palladium mirror [13,14]. Among them, the micro palladium mirror-based hydrogen sensor has great simplicity in fabrication and compactness in packaging the sensor head; however it has the problem of susceptibility to the optical source power fluctuation and the mechanical perturbation in the lead fiber [15], which reduces the resolution, dynamic range, and remote-sensing ability of the sensor. To remove these problems related with the intensity-based sensors, self-referencing techniques based on fiber loop ring resonators [16] or Fabry-Perot cavities [17,18] have been reported. However, the ring resonator was relatively bulky and the Fabry-Perot cavity-based sensor needed two detectors [17]. The other extrinsic Fabry-Perot cavity-based hydrogen sensor had a very long response time, unfortunately, because of using mechanical stress on the fiber [18]. Also, multiplexing capability of hydrogen sensors is another important factor for multipoint monitoring or distributed sensing.

Several reports have been made to address the self-referencing techniques and multiplexing issues [19,20]. However, so far, no intensity-based hydrogen sensor with both self-referencing and multiplexing abilities has been demonstrated yet. In this work, we propose and experimentally demonstrate a compact self-referencing intensity-based hydrogen sensor suitable for multipoint monitoring. To achieve both goals at a time, the dual-cavity fiber interferometer scheme is introduced and the spatial frequency domain analysis is utilized. By using the inner cavity of the dual-cavity, the self-referencing could be accomplished, and by adjusting the cavity lengths, the multiplexing capability could be achieved. The sensor response speed and amplitude are experimentally examined in terms of temperature.
2. Fabrication of the hydrogen gas sensor head

The sensor head is composed of a dual-cavity, which is formed by splicing two difference fiber pieces in series to the lead-in fiber as shown in Fig. 1. We chose a hollow optical fiber (HOF) as the first fiber to maximize the index-difference and hence to enhance the reflectivity at the interface. The HOF was drawn with a conventional fiber drawing tower and had the inner and outer diameters of 50 and 125 μm, respectively. The second fiber was a single mode fiber (SMF) with palladium coating on the surface of its free-end, which acted as the transducer for hydrogen gas sensing. We used a commercial fusion splicer (S183PM, FITEL Co.) for splicing the fibers, while we employed a specially designed in-house tool [21] to cleave the fiber with a required length of an accuracy of about 5 μm.

The fabrication process involves splicing of a HOF to the lead-in fiber and then cleaving the other end of the HOF with the cleaving tool to obtain the HOF cavity, cavity 1, of a required length L1. By using the similar procedure, a SMF is fusion spliced to the HOF and then cleaved at a length of L2, which forms the cavity 2. The length of the HOF in the sensor head should be kept below 1.5 mm, above which the interference fringe contrast reduces rapidly [21]. Finally, by using an e-beam evaporator only the free-end of the SMF piece is coated with nickel and palladium of thickness 2 and 20 nm, respectively. While the palladium coating acts as the hydrogen transducer, the nickel coating acts as a buffer for better adhesion of the palladium. When exposed to hydrogen gas, palladium absorbs hydrogen molecules and becomes palladium-hydride, which gives refractive index reduction. The hydrogen absorption also increases the volume, thus it causes damage and reduces the lifetime of the palladium layer. Therefore, a thin buffer layer (Ni) is essential to enhance the performance of the sensor head [22,23].

![Fig. 1. Schematic of the sensor head having a dual-cavity. Cavity 1 is a short piece of hollow optical fiber (L1 = 35 μm), and cavity 2 is just a piece of single mode fiber (L2 = 604 μm). R is the reflectivity at each surface. The end face of cavity 2 is coated with nickel (2 nm) and palladium (20 nm) in series.](image)

2. Operating principle of the hydrogen gas sensor

The light beam returned from the sensor head is composed of mainly three parts, reflected from the three interfaces with the Fresnel reflection coefficients of \( R_0 \), \( R_1 \), and \( R_2 \). The returned three beams make interference with each other. When the multiple reflections are neglected, since the reflection coefficients are not so big, we have the intensity of the total reflected light as [24]

\[
I = |E_0|^2 \left( R_0^2 + \eta_1^2 R_1^2 + \eta_2^2 R_2^2 + 2 \eta_1 R_0 R_1 \cos(kL_1) + 2 \eta_1 R_0 R_2 \cos(kn_0 L_2) + 2 \eta_2 R_1 R_2 \cos(kn_1 L_2) \right) \tag{1}
\]

where \( E_0 \) is the amplitude of the incident beam. The round trip coupling coefficient \( \eta_i \) means how much of the beam emitting from the lead-in fiber is guided through the HOF and then returned to the lead-in fiber when the reflection at the end of the first cavity is perfect. The
coefficient \( n_2 \) is the same one but from the lead-in fiber to the end of the second cavity. It is noted that mainly due to the large core of the HOF composing the first cavity, the coupling between SMF and HOF is not appreciably big in general. Further, the returned beams make interference with each other according the optical path lengths of cavities. In Eq. (1), \( L_1 \) is the length of the HOF cavity having the air core, while \( L_2 \) is the length of the SMF cavity having the silica core of an effective refractive index of \( n_{eff} \). Where, \( k \) is the wavenumber. We can see from the equation that the last two interference terms are related with the reflectance at the palladium coating, and the interference fringes are affected by the corresponding cavity length. In other words, by choosing the proper combination of \( L_1 \) and \( L_2 \), we can identify the sensor among many multiplexed sensors.

Figure 2 shows the experimental setup, which consists of a broadband light source (SLED, \( \lambda: 847 \) nm, INPHENIX Co.), a spectrometer (HR4000, OCEAN OPTICS Co.), and a signal processing part. The current controller intentionally modulates the input current to BBS for the experiment in section 3, compensation of input power fluctuation. The transmission loss is also arbitrarily agitated by bending the transmission fiber for the same purpose.

![Fig. 2. Schematic of the experimental setup for the detection of hydrogen gas.](image)

Figure 3(a) shows the interference spectrum experimentally obtained from the sensor head composed of 35 \( \mu \)m and 604 \( \mu \)m cavities. The slowly varying fringe pattern is originated from the short HOF cavity of 35 \( \mu \)m, while the fine fringes shown in the inset come from the long SMF cavity of 604 \( \mu \)m. To make it clear, fast Fourier transform (FFT) on the data of Fig. 3(a) was made and we got Fig. 3(b). There are four dominant peaks. The peak at zero OPD (Optical path length difference) comes from the DC terms of Eq. (1), mainly due to the power

![Fig. 3. (a) The interference spectrum of the sensor having HOF cavity of a length 35 \( \mu \)m and SMF cavity of 604 \( \mu \)m, and (b) its Fast Fourier transformed (FFT) spectrum. A peak in the Fourier spectrum gives the OPD (optical path length difference) of the corresponding cavity.](image)
spectrum of the light source. Peaks 1 and 2 are originated from the cavities 1 and 2 of lengths $L_1$ and $L_2$, respectively. The composite cavity formed by HOF and SMF with a length $L_3$ gives the last one, peak 3.

When the sensor head is exposed to hydrogen gas, the intensities of peaks 2 and 3 become decreased due to reduction in the refractive index of the palladium [13]. The right inset of Fig. 3(b) shows the experimentally obtained response of peak 3 to hydrogen gas. However, as the left inset of Fig. 3(b) shows, peak 1 is not affected by the hydrogen gas. It is noted that cavity 1 is located between two SMF pieces, thus cannot be exposed to hydrogen gas. Therefore, peak 1 can be used to trace and compensate unwanted intensity variations in the system, including the power loss perturbation in the transmission fiber and the power fluctuation of the light source.

3. Compensation of light power fluctuation

If there is power fluctuation in the light source, all peaks in the Fourier spectrum would be fluctuated with the same ratio. However, since peak 1 is not affected by the hydrogen gas, we can compensate the fluctuation of peak 2 or 3 by simply taking ratio with peak 1 as

$$S_{\text{compensated}} = \frac{S_{\text{measured}}}{S_1}$$

In order to check the compensation of the source power fluctuations, we have measured 4% concentration (lower explosive limit, LEL) of hydrogen gas with intentional power fluctuation in the optical source. By using a current controller (SourceMeter 2440 5A, KEITHLEY Co.), the power of the BBS in Fig. 2 was fluctuated. The current to the BBS was modulated in a saw-tooth shape by repeatedly sweeping it from 70 mA to 65 mA with a step of 1 mA per every five seconds. The gas chamber used in the experiment was alternatively connected to 4% hydrogen gas and pure nitrogen gas for purging. The reflection spectrum of the sensor head in the gas chamber was measured for every 5 seconds. The flow rates of both gases were kept as 100 cc/min.

The intensity of peak 1 is measured and shown with Fig. 4(a), while peak 3 is shown with Fig. 3(b). By taking the ratio between them, we have the compensated signal of Fig. 4(c). We can see that the rapid oscillation in peak 3 of Fig. 4(b) is almost completely removed in Fig. 4(c). Thus, Fig. 4(c) shows the sensor response only to the hydrogen gas. With the turn-on of the hydrogen gas, the peak intensity was reduced quickly and then saturated. On the other hand, with the purging gas of nitrogen, the peak intensity was recovered rather slowly. The response time of the sensor to hydrogen gas and the recovery time with nitrogen gas were measured as 65 and 100 seconds, respectively.

To check the sensor response to another real situation, second experiment was made with mechanical perturbation at the lead-in fiber. We made bending loss with about maximum $-0.3$ dB in the lead-in fiber continuously during the measurement of hydrogen gas. Likewise with the first experiment, the intensities of peak 1 (Fig. 4(d)) and peak 3 (Fig. 4(e)) were simultaneously fluctuated with the bending perturbation. However, after the compensation the intensity fluctuation was clearly eliminated as shown in Fig. 4(f).

In our experiment, the background noise and the measurement error of the system were 0.102% and 0.198%, respectively. However, with the intentional perturbation, the error ratio increased slightly. In principle, the perturbation compensation should be immediate, because the air cavity (HOF cavity giving peak 1) does not have any time delay to any optical input power variation. However, in practical case, the spectrometer needs appreciable integration time to get a set of data, during which the sensor system should be stable. In our case, the integration time was 100 ms, which means the fluctuation faster than 10 Hz cannot be properly compensated. The error associated with the Fourier domain signal was already addressed in other article [25].
4. Sensors multiplexing

To demonstrate the multiplexing or multipoint sensing capability, we have designed the setup for a four-point detection system as shown in Fig. 5. The multiplexing was done by using the spatial frequency multiplexing technique [26]. In order to distinguish the peaks from each sensing point, the cavity parameters were set differently among each other. The HOF and SMF lengths need to be different to be able to distinguish peak 1 and peak 3 from each sensor head. The spectrum of the multiplexed system with four sensors and the corresponding Fourier spectrum showing the corresponding peaks are shown in Figs. 6(a) and (b), respectively. The (HOF and SMF cavity) lengths of each sensor head was made as (35 μm, 604 μm), (58 μm, 550 μm), (78 μm, 475 μm), and (117 μm, 347 μm), respectively. The peaks corresponding to each sensor head are labeled 1 to 4 in Fig. 6(b). It can be seen that each peak...
is clearly distinguished in the frequency domain. Since each sensor has its own reference peak 1, power fluctuations from optical source and mechanical stress of lead-in fibers can be compensated by tracking the intensity variation of each peak 1.

In our setup, only four sensors are multiplexed due to the concern of the loss when HOF length becomes too long. The main factors that limit the number of multiplexible sensors are 1) Loss in the HOF cavity, 2) Power reduction due to the number of couplers, and 3) Sensitivity and resolution of the spectrometer. Considering the availability of high power sources and the high sensitivity of CCD spectrometers, the main issue to be addressed is the loss that increases with the HOF length. We believe this can be easily addressed by replacing HOF with air-core photonic band gap fibers.

Fig. 6. (a) The reflection spectrum measured with four multiplexed sensors and (b) its Fourier spectrum. In the reflection spectrum, the contribution from each sensor cannot be distinguished; however in the Fourier spectrum, the peaks from each sensor are well separated.

5. Temperature characteristics of the sensor

Finally, we have also measured the response of the sensor to 4% hydrogen gas exposure at different temperatures. Generally, palladium hydride film has two solid phases called α and β phases, depending on the atomic H/Pd ratio. At room temperature, palladium film always is in α phase, which provides short response time and small response amplitude. When palladium is exposed to hydrogen, the phase transition from α phase to β phase always occurs. However, at this time, the transition time depends on the film thickness and the surrounding temperature. According to the pressure composition isotherm graph [27], the lower surrounding temperature is, the faster transition time from α phase to β phase comes. Therefore, the sensor provides long response time and large response amplitude at a low temperature. To make sure the performance of the hydrogen sensor, the response time and the response amplitude of the sensor were measured at five different temperatures. As before, 2 nm nickel and 20 nm palladium were coated. The nickel before palladium coating enhanced the adhesive strength of the palladium coating and increased the repeatability of the system.

The responses of the compensated intensity of peak 3 at various temperatures are shown in Fig. 7(a). The response of the sensor becomes faster with temperature. The response time was about 65 seconds at room temperature (25°C). It became shorter as 45 and 40 seconds at 35°C and 40°C, respectively. On the other hand, at low temperatures, slow responses were observed as 75 and 83 seconds at 15°C and 6°C. The similar behaviors were observed in the recovery time with pure nitrogen gas; the recovery became faster at higher temperature. However, as Fig. 7(b) shows the hydrogen reaction time of palladium was about 2 times faster than that of nitrogen at the same temperature. Another interesting thing was that the response amplitude was dependent on temperature also. With respect to time, the signal amplitude was reduced with hydrogen and then saturated. The ratio of the saturated signal intensity to the intensity without hydrogen is plotted at Fig. 7(c), which shows that the response amplitude is larger at lower temperature.
Fig. 7. (a) Sensor responses to hydrogen gas measured at different temperatures, (b) the response time to hydrogen and nitrogen gases plotted in terms of temperature, and (c) the response amplitude plotted in terms of temperature. The response of the sensor was faster with temperature but the response amplitude became small at a high temperature.

In all experiment, 2 nm nickel coating was made before 20 nm palladium coating. Without the nickel coating, it was observed that the adhesive strength of the palladium coating was not strong enough, thus the repeatability of the system was not good. In our previous work [28], the response time of the palladium was investigated in terms of the thickness of palladium coating. The thicker coating gave the slower response. Even though we are not sure of the most proper condition, the coating of 2 nm nickel and 20 nm of palladium was good enough as a sensor. However, more intensive work is necessary to get the best condition. The response time and the response amplitude at other temperatures, especially at very low ones, are also important. We are planning a more systematic experiment equipped with a proper gas chamber of a wider temperature control range in near future.

6. Summary

We have proposed and demonstrated the fiber-based hydrogen gas sensor system that could multiplex four sensors in the Fourier frequency domain. By adapting a dual-cavity structure and utilizing Fourier domain analysis, we could make the intensity-based multipoint hydrogen sensor system that was not appreciably affected by the power fluctuation of the light source and the loss perturbation in the transmission fibers. By coating 20 nm thin palladium on a piece of single mode fiber (SMF) the sensor cavity was formed, while by inserting a short piece of hollow optical fiber (HOF) between the sensor fiber and the lead-in fiber the reference cavity could be fabricated. Simply by splicing both cavities in series with a conventional fusion splicer and a special homemade cleaving tool, the sensor head could be implemented. The hydrogen-induced refractive index variation of the palladium film gave the variation in the interference contrast of the sensor cavity. Taking the Fourier spectrum allowed separating the signal only from the reference cavity, which was utilized to compensate the power fluctuation of light source and the transmission fiber loss perturbation in the system. By connecting several sensor heads having different cavity lengths, we could multiplex several
sensors and retrieve the signal of each sensor in the Fourier domain. The proposed sensor showed the faster response to hydrogen at the higher temperature, but the response amplitude was larger at the lower temperature.

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