Development of thermostable FBG optical sensor for oil and gas applications

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Abstract— **Important progress has been made towards the expanding of the limits of applicability of Fiber Bragg Grating optical sensors. The development of new thermostable coatings has opened up the possibility towards the use of this technology under extreme conditions, i.e. at high temperatures and pressures. The developed sensors have been tested for adsorption of a range of gaseous analytes and exhibit a sensitivity towards linear alkanes. Preliminary tests at high temperature in liquid phase indicate a high thermal stability.**

Keywords- optical sensors, FBG, thermostable coatings

I. INTRODUCTION

For improving the control of chemical processes, enhancing oil recovery and improving the quality of the environment, chemical sensing is becoming increasingly important. Several factors play a role in the implementation of chemical sensors: reliability under extreme conditions, sensitivity, and costs. Optical sensors based on Fiber Bragg Gratings (FBG) (Figure 1) have been known for a long time for measuring physical parameters like temperature and strain.[1] In recent years, the Materials Solutions group at TNO, Eindhoven, the Netherlands, has been developing chemical sensors based on FBG technology.

The principle on which a FBG chemical sensor is based is an axial strain of the fiber, as a result of an environmental chemical effect that is to be detected, for example by using a polymeric coating on the fiber that deforms in the presence of a chemical compound (analyte). When the FBG stretches or shrinks under such strain, the spectral pattern of reflected light changes (Figure 1) and a shift in reflected wavelength ($\Delta\lambda$) is observed. The changes in reflected wavelength provide quantitative information on the environmental effect [2]. The challenges in the design of such optical chemical sensors are the design and synthesis of chemically selective responsive coatings, the processing of these coatings onto the optical fibers and the development of an optimal configuration of fiber packaging and interrogator system with sufficient sensitivity. Typically, FBG chemical sensors are stable at temperatures of up to 100 degrees Celsius and pressures of up to 100 bar. The limiting factor is the chemically responsive coating, which until now consists of polymers such as polyacrylates or polyimides. For use in oil and gas applications, the chemical sensors must withstand higher temperatures (up to 300 degrees Celsius) and pressures (up to 200 bar). Thus, extending the application range of these systems is essential. Recently, important progress has been made towards the expanding of the limits of applicability of FBG optical sensors. The development of new thermostable coatings has opened up the possibility towards the use of this technology under extreme conditions, most importantly at high temperatures and high pressures.
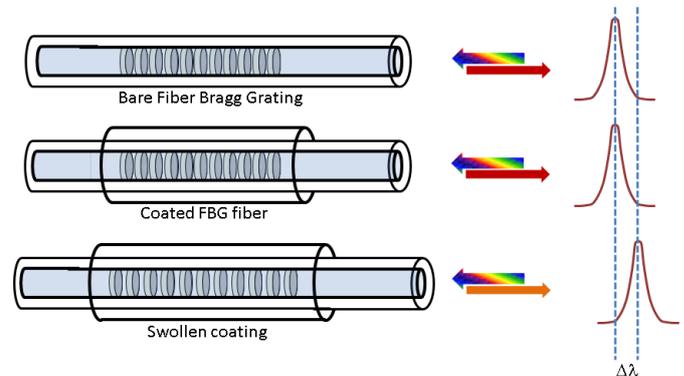

Figure 1. Working principle of a Fiber Bragg Grating based chemical sensor

II. RESULTS AND DISCUSSION

A. Gas Adsorption Measurements

Measurements to assess gas adsorption characteristics of the developed sensors were performed using a purposely built Gas Exposure System (GES) (Figure 2). The fibers were inserted into an airtight, custom-made glass measuring chamber (Figure 3). The fibers were connected to an interrogator which analyses the wavelength of light reflected by the FBG. With this setup, it was possible to continuously measure the reflected wavelength as a function of exposure to a certain gas. The gas flow was controlled by the Gas Exposure System, which is equipped with software controlled gas flow meters and a humidity sensor. The measurements were performed at room temperature. The influence of temperature fluctuations was determined by measuring the signal of a bare FBG over a period of time and was found to have a maximum deviation of around 5 pm.

Prior to starting each measurement, a flow of 500 mL/min nitrogen was applied for 30 min to remove possible traces of moisture or other gases and to establish a baseline signal. Subsequently an equal flow of the probe gas was applied until the measured signal became stable. This process was repeated several times to assess the reversibility and reproducibility of the observed effects.
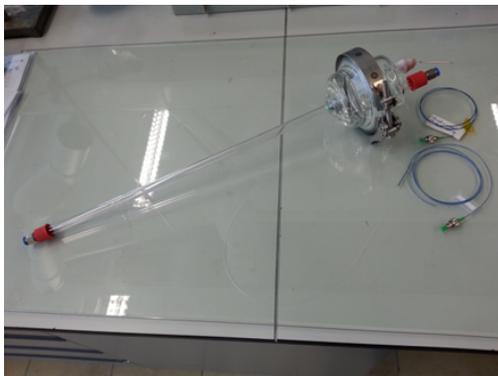

Figure 2. Gas exposure system

Figure 3. Custom-made glass measuring chamber for FBG sensors

Three fibers with different coating thicknesses, *i.e.* 7, 12 and 18 μm, were prepared and tested for their gas adsorption characteristics.

For fiber A (7μm coating), the probe gases were CH_4, C_2H_6, CO_2, H_2O (85% relative humidity in N_2) and isopropanol (prepared by bubbling a stream of N_2 through liquid isopropanol). The data are presented in Figure 4 and Table 1, which show the shift in reflected wavelength (in pm) upon exposure to each of the different gases. In all cases presented in Figure 4, the shift has been considered with respect to the signal observed for pure N_2. The data are averages of several measurements. For fiber A, the only two gases that gave a significant response were C_2H_6 and isopropanol. For fiber B (12 μm coating), the probe gases were CH_4, C_2H_6, C_3H_8, C_4H_{10}, CO_2 (pure gases), H_2O (85% relative humidity in N_2), octane, mesitylene and isopropanol (prepared by bubbling a stream of N_2 through the liquids). Going to a thicker coating layer, *i.e.* comparing fibers A and B, a much larger response was observed for all gases except CH_4 and H_2O, which still barely gave any response. The response curve as measured for exposure of fiber B to C_2H_6 is shown in Figure 5. Upon exposure to C_2H_6, a shift in the reflected wavelength of 90 pm

is observed. Upon flushing the system with N_2, the signal returned to its starting value, indicating that the effect is fully reversible. Several repeats of this process showed a good reproducibility.

Subsequently, a fiber with an even thicker coating of 18 μm was tested (fiber C). The observed responses for this fiber were in general comparable to those observed for fiber B (Figure 4). Apparently, no further increase of signal results from increasing the coating thickness beyond 12 μm. A possible explanation for this observation is that a thicker coating may not be able to efficiently transfer the strain due to swelling to the surface of the glass fiber and thus to the grating segment of the sensor.
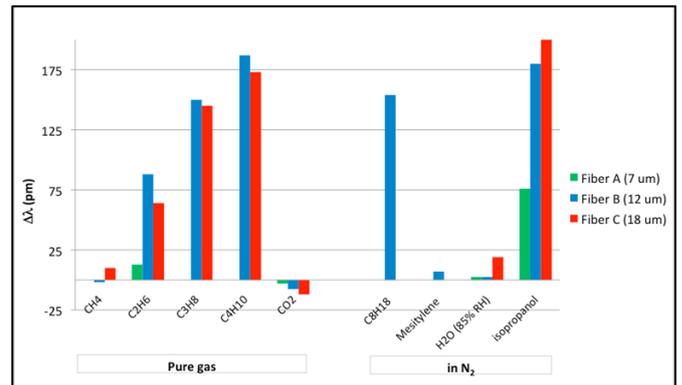

Figure 4. FBG responses measured for exposure to gases for fibers coated with thermostable coatings.
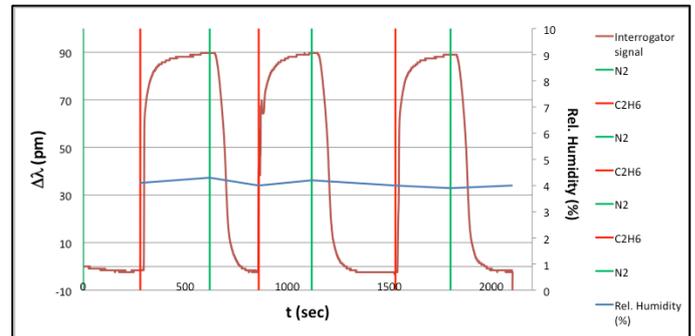

Figure 5. Response curve measured for exposure of fiber B (12 μm thermostable coating) to C_2H_6.

The FBG response as a function of the concentration of C_2H_6 in N_2 was measured for concentrations starting from 1% (Figue 6), for fiber B. These measurements showed a very sharp increase for concentrations lower than 10%, while higher concentrations only lead to a small further increase of the signal. Clearly, the sensor is very sensitive to low concentrations of C_2H_6, but much less sensitive to high concentrations.

Further measurements were performed in the liquid phase, by immersing the thermostable coated FBG sensor (measurements only performed for fiber B) in a beaker containing stirred H_2O at room temperature. The data are

presented in Table 1. The shift in wavelength upon addition of 1M NaCl as well as to changes in the pH (by addition of either concentrated HCl or KOH solutions) was measured. It could be concluded that the sensor has a very low sensitivity for salt and pH. Only at very high or very low pH, a significant shift was measured.

Table 1. FBG responses ($\Delta\lambda$ in pm) measured for exposure to gases or liquids, for fibers containing thermostable coatings.

	Fiber A	Fiber B	Fiber C
Coating layer thickness (μm)	6.9	11.8	18.3
CH_4 [a]	0	-1.9	10
C_2H_6 [a]	13	88	64
C_3H_8 [a]	n.d.	150	145
C_4H_{10} [a]	n.d.	187	173
CO_2 [a]	-3.0	-7.6	-12
C_8H_{18} [b]	n.d.	154	n.d.
Mesitylene [b]	n.d.	7	n.d.
H_2O (85% RH) [b]	2.5	2.5	19
isopropanol [b]	76	180	215
1 M NaCl [c]	n.d.	-4	n.d.
pH 13 [c]	n.d.	17	n.d.
pH 12 [c]	n.d.	0	n.d.
pH 2 [c]	n.d.	2	n.d.
pH 1 [c]	n.d.	10	n.d.
0.2 vol% decane [d]	n.d.	170	n.d.

a). Pure gas (data with respect to N_2 baseline signal). b). In N_2 (data with respect to N_2 baseline signal). c). In H_2O (data with respect to H_2O baseline signal). d). In mesitylene, at 150 °C. (data with respect to mesitylene baseline signal at 150 °C).
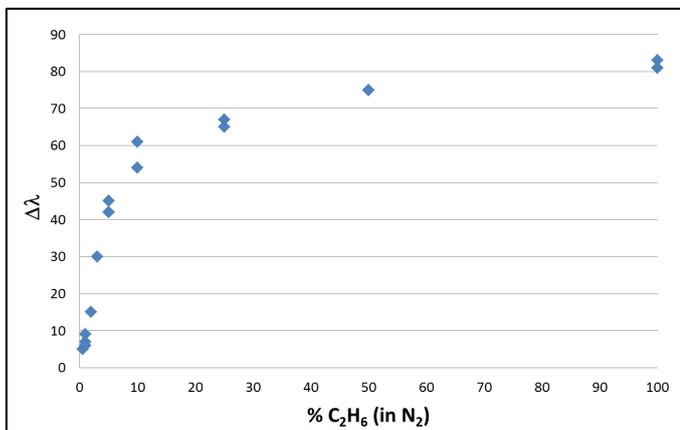

Figure 6. FBG response as a function of the concentration of C_2H_6 in N_2.

Finally, in order to assess the temperature stability of the sensor, fiber B was immersed into mesitylene at 150 ºC. As was established in previous experiments, mesitylene itself does not lead to a significant response. After the signal had become stable, a small quantity (0.2 vol%) of liquid decane was added to the stirred mixture. Immediately a large increase of the

reflected wavelength was observed, indicating that the coated FBG still functioned at 150 ºC. Adding higher concentrations of decane (tested up to 1.5 vol%) did not lead to a further change in the signal, suggesting that the coating was saturated after exposure to 0.2 vol% decane.

For fiber B, the response times and regeneration times were estimated from the obtained response curves for all gases (Table 2). The response time was defined as the time required until no further change of the signal was observed. Some variation between the different gases was observed and in general, the response times were 300 s or less. The regeneration times were defined as the time required for full recovery of the baseline signal. In several cases the regeneration took longer than the response time. For butane and octane, the regeneration was very slow and was in fact not achieved within the timeframe that was used for the experiment. In those cases, as well as for exposure to liquid decane, heating of the coated segment was required for full regeneration.

Table 2. Response times and regeneration times for fiber B (12 μm coating).

Gas	response time (s)	regeneration time (s)
CH_4	60	60
C_2H_6	200 - 300	200
C_3H_8	150 - 300	600 - 800
C_4H_{10}	200	2000 <
C_8H_{18}	250	4000 <
CO_2	100 - 200	100 - 200
IPA	100	700

III. CONCLUSION AND OUTLOOK

In the current project, important progress has been made towards the expanding of the limits of applicability of FBG optical sensors. The development of new thermostable coatings has opened up the possibility towards the use of this technology under extreme conditions. The gas adsorption characteristics of the thermostable coated FBG sensors were tested in a custom built gas exposure chamber. It was found that the coated FBG sensors exhibited strong responses to C_2H_6, C_3H_8, C_4H_{10}, octane and isopropanol, but negligible responses to CH_4, H_2O, CO_2 and mesitylene. Comparing the responses of three sensors containing varying coating thicknesses indicated that an optimum in terms of response magnitude existed around a thickness of 12 μm. Tests were also carried out in liquid water for the sensor with a 12 μm thick coating. The sensors proved to be insensitive to salt or pH changes. Finally, a test was carried out at a temperature of 150 ºC in liquid phase, i.e. in mesitylene. Under these circumstances the sensor exhibited a strong response to exposure to liquid decane, proving that the sensor works at 150 ºC. The response times were in general less than 300 s; regeneration times were less than 800 s, except for butane and octane, for which heating is required for full regeneration. Further research will focus on extending the scope and

selectivity of this new type of FBG sensor by exploring different types of thermostable coatings with different properties. Secondly, further testing under extreme conditions, including higher temperatures up to 300 ºC, is anticipated. To this end, we are currently realizing a second generation gas exposure system which allows testing of the sensors for exposure to flammable gases at high temperatures and pressures. Details of the synthesis, chemical composition and characterization of the developed thermostable coatings have been deliberately omitted from this paper in view of a pending patent application. Full details will be disclosed during the presentation of the paper at the ICST2014 conference.

REFERENCES

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