Measurement of CO_2 using refractometric fiber optic sensors

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Abstract: - An indicator free optical fiber sensor for determination of carbon dioxide is presented. The sensing layer is based on the acid-basic equilibrium of phenol and of its derivative p-nitro-phenol that, in the presence of CO_2, are prone to protonation introducing refractive index changes. The new sensitive layer is characterized and tested in different refractometric fiber optic sensor configurations. Using a fiber based interferometric setup, a CO_2 dependent refractive index change of ~0.05 RIU is observed, in the 10%-90% CO_2 concentration range, demonstrating the membrane viability. Preliminary results are presented for an all-fiber LPG-based carbon dioxide sensor.

Key-Words: - Optical fiber sensor, carbon dioxide, refractometry, LPG-Long-period grating

1 Introduction

The measurement of chemical parameters using optical sensors is an expanding area of research with growing importance, especially in environmental applications. The combination of optical fibre technologies with the development of new sensitive membranes, has greatly contributed to the progress of optical chemical sensors suitable for environmental monitoring [1].

Carbon dioxide sensing techniques are applied in diverse fields, such as chemical and clinical analysis, food and beverages industry and environmental monitoring. Especially, the measurement of CO_2 concentration in seawater is growing in importance due to the need to map out and understand the CO_2 fixation processes in oceans [2].

Several fibre optic based solutions have been proposed for carbon dioxide detection. Amao and Nakamura [3] demonstrated CO_2 sensor based in luminescence intensity changes of tetraphenylporphyrin (TPP) due to absorption change of a pH indicator dye. Other solutions based in pH indicators have been proposed using luminescent schemes. Nevertheless configurations using indicator dyes suffer from leaching and photobleaching effects. In addition, working in the visible range imposes some limitations in applications where remote and multipoint detection are a priority. Using direct spectroscopy at 1.57 μm, carbon dioxide concentration could be measured using an evanescent field sensor based in a quartz glass multimode fibre [4]. However, this approach needs DFB laser sources, relatively long interaction lengths and is very sensitive to contamination of the fiber surface.

In this work, a new approach is presented where fiber optic refractometric configurations are combined with polymeric layers that experience

refractive index changes in the presence of CO_2. A new sensitive membrane is fabricated and characterized using fiber optic configurations based in standard telecom optoelectronic components.

2 Experimental Results

2.1 Sensing layer chemistry

The sensing chemistry was based on the acid-basic equilibrium of phenol and of its derivative p-nitro-phenol. They were kept into their deprotonated form in the sensing membrane. In the presence of carbon dioxide, hydrogen carbonate was formed that partly protonated the phenols. The hydroxylic group is involved in protolitic reactions that modify the charge distribution in the molecule. As result of the interaction with carbon-dioxide a change in their refractive index was expected due to the delocalized electrons in the aromatic ring of these compounds. A quaterner ammonium compound, didodecyl-dimethyl-ammonium hydroxide (DDMA) was used to deprotonate the phenols, preparing them for being protonated by the analyte.

The sensing layers were prepared of a 5% (m/m) polyurethane hydrogel (D4) dissolved in ethanol solution. 10 µl-s of 0.1 M ethanolic p-nitrophenol and 20 µl-s of 0.1 M ethanolic DDMA solution was added to 1 ml polymer solution.
20 µl of the cocktail was spread by a micropipette on the sensitive surface of the LPG-s. In other configurations coating by dip-coating or casting methods was applied. After 3 hours of gelation, the layers were ready for sensing applications.

2.2 Characterization of sensing membrane

Prior to the thin film deposition, some tests were made with the sensing layer precursor cocktail. In order to determine the refractive index difference of the solution in its protonated (when submitted to CO_2 bubbling) and deprotonated states (bubbling with Argon), a Fiber Bragg Grating (FBG) Fabry-Perot refractometer was used [5].
Fig. 1 shows the experimental setup. The refractometric fiber probe was immersed in the solution and fixed in rigid support while the visibility of its interferometric output was monitored using a scanning laser unit from Fibersensing (FS-4200, 1520-1590 nm, 1 pm max. resolution) with modified software. In each case, refractive index was measured after some minutes of bubbling with the corresponding gas.

The results showed a consistent visibility difference of 1% between the two states, meaning that there was a refractive index decrease of ~0.005 RIU (refractive index unit) induced by the increase in CO_2 concentration. While it is expected that these refractive index changes will be different after film deposition and membrane solidification, these result demonstrate, nevertheless, an effective response to CO_2.

Fig 1 Setup used to evaluate refractive index changes of the polymer precursor solution.

In order to test the response of the sensing chemistry in the solid state, some glass slides where coated with a sensing layer using a casting method. The films produced in this fashion where then tested in an interferometric setup.
The coated glass substrates were placed in a test chamber and attached to the end face of an optical fiber inserted into a ceramic ferrule as shown in Figure 2. To avoid undesirable reflections the interface between the fiber and the sample was filled with index matching oil.

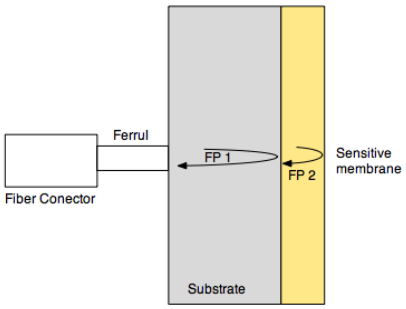

Fig 2 Interferometric setup for evaluating the sensing film refractive index taking advantage of the Fabry-Perot cavities formed by the substrate and the sensitive layer.

In this situation two low-finesse Fabry-Perot cavities are formed by the different material interfaces. The first cavity is produced by the reflections in the fiber/substrate and substrate/film interfaces. It has a thickness of approximately 1 mm and a refractive index of 1.489 at 1550 nm. The second cavity is formed by the reflections in the substrate/film and film/external medium interfaces. It has a thickness of ~30µm. This setup results in two-overlapped interferometric spectra at the fiber output. In the

example shown in Fig 3, the larger substrate cavity results in a very short period (0.80 nm) modulation while the thinner film cavity displays a much larger periodic modulation (~30 nm).

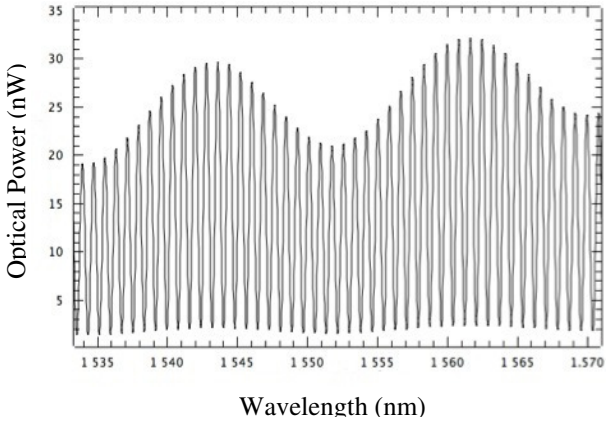

Fig 3 Typical Interferometric output spectrum of the dual cavity setup

In this particular application for signal acquisition and processing a new LabView™ application was developed for the FS4200 unit. The software separates the signal of the sensing film (longer period) using an envelope detector. Filtering and averaging was also implemented. Because the membrane refractive index variations will result in changes in the wavelength of this interferometric pattern, the software was designed to monitor the peaks and valleys related to the sensing signal. The membrane RI changes can also vary the fringe period, but the effect of wavelength shift is much more significant, around 50 times higher, as confirmed by a theoretical model. Fig 4 shows the channeled spectrum, after filtering, obtained with the film submitted to different CO_2 concentrations. It is visible a negative wavelength shift of the interferometric pattern of about 35nm, which was observed when increasing the CO_2 concentration from 10% to 30%. A smaller change is also noticeable between 0% and 10%. The negative change in the interferometric pattern is well correlated with the decrease in the refractive index of the film.

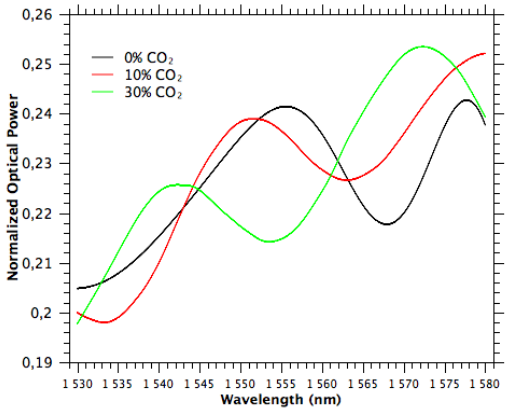

Fig 4 Interferometric channeled spectra related to three different CO_2 concentrations

Using this setup the sensing film was tested in the concentrations raging from 0% to 90% CO_2. This was achieved by using a flow control system fed with CO_2 and Argon inlets. At this point, and to avoid any cross-sensitivity with humidity, both gases were thoroughly bubbled trough water to become saturated with humidity.

A nonlinear response was observed that is show in Fig 5. A second order polynomial fit could be obtained considering the 10-90% concentration range. A high sensitivity range could be established between 10-60%, in which it is noticeable a wavelength shift of 51 nm. Above 70% the membrane response becomes saturated.

From this data, assuming that the membrane thickness remains unchanged and using a two wave interferometer approximation, it is possible to estimate roughly a refractive index variation of 0.045 RIU for the 10-90% CO_2 range. Response time and reversibility were also studied. The best response time observed was approximately 3 min. Also it was observed that refractive index change was not fully reversible, probably due to much larger recovery times. In this configuration, the response time and the stability of the response were not optimal due to the increased thickness of the layer (~30 um) that increased the diffusion time of the gas in the hydrogel matrix.

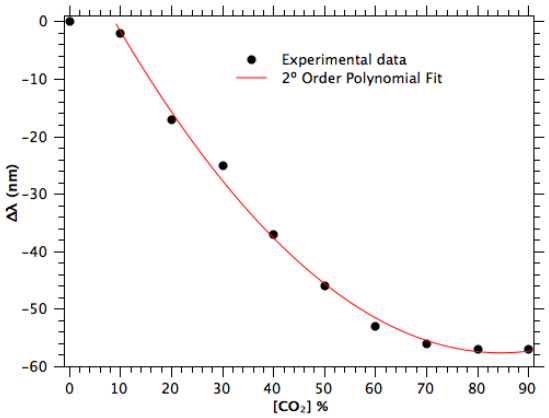

Fig 5 Calibration curve obtained with a glass slide coated with the sensitive layer, for a CO_2 concetration range between 10-90%.

These initial setup and tests were used to perform optimization of the sensing layer by introducing some adjustments in its composition and fabrication process. In addition, knowledge of the magnitude of refractive index changes observed allow us to choose which fiber optic refractometric configuration would suit best each application. Sensing layers with most promising characteristics were then chosen to coat some fiber probes.

2.3 LPG based CO_2 fiber probe

To implement an all fiber based configuration, it is needed a design where the guided radiation can interact through its evanescent field with the external medium. For this purpose a Long period grating (LPG) was used.
LPG is created by a periodic modulation of the refractive index in the fiber core. The arc-induced and photo-induced techniques are the most common fabrication processes. The consequence of this refractive index modulation is the coupling of the fundamental mode propagating in the fiber core with forward-propagating cladding modes, creating as a result, a series of attenuation bands in the fiber transmission at discrete wavelengths. The sensitivity of LPG to external refractive index is well known [6]. Coating the LPG with the sensitive layer, whose refractive index depends on CO_2 concentration, will therefore enable its quantification by evaluating the spectral response of the grating.

A sensing head was fabricated consisting in a LPG written on standard SMF-28 optical fiber by the electric arc technique. The period of the grating was 395 μm, and the resonance depth 20 dB. The LPG was coated with the sensing chemistry and cured at room temperature. Due to the high sensitivity of the LPG to the external refractive index, some adjustments had to be made in order to ensure that the resonant behavior was maintained after coating. In practice, it was verified the coating from the original solution eliminated the resonance, meaning that the refractive index change was too high. Therefore, the original cocktail was diluted by 50%.
The Fig 6 and Fig 7 show the changes of the resonance wavelength and of its optical power during the coating process with the diluted cocktail. A negative wavelength shift of ~ 5.2 nm is clearly visible while the attenuation is decreased by ~7 dB. From this data and considering previous studies [6] it is possible to establish that, after deposition, the LPG is still operating in a refractive index sensitive regime.

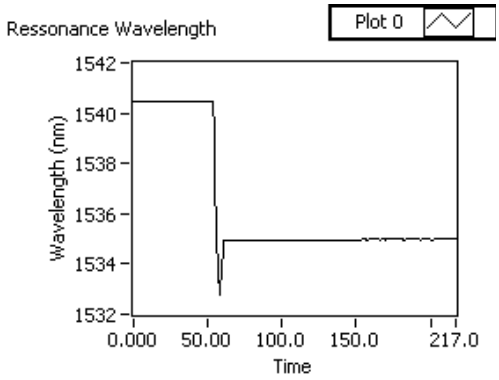

Fig 6 Resonance wavelength changes during the film deposition process.

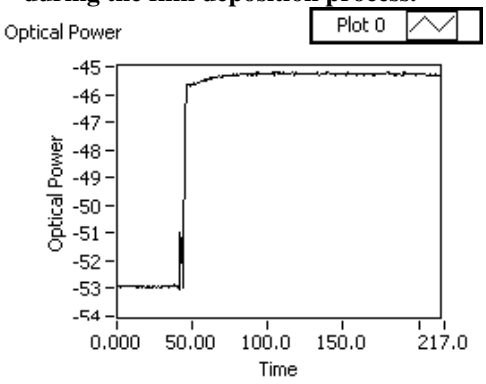

Fig 7 Resonance depth changes during the film deposition process.

For characterization of this sensing head, the setup showed in fig 8 was used. The LPG was well fixed in a proper gas sealed chamber. Because the FS4200 interrogation unit only operates in reflection, a silver mirror coating was applied in the distal end of the fiber. In this way, the radiation crossed the LPG twice increasing sensitivity. Interferometric effects were avoided, at this stage, by ensuring the mirror was set at a distance that established an unbalance much larger than the source coherence length.

Because the LPG sensitivity to temperature can induce a measurement error, a FBG was placed into the chamber to simultaneously measure temperature. This way, while temperature was kept approximately constant (~25 ºC), compensation of small fluctuation could be operated in real time. For such signal acquisition and processing, a new LabView™ application was developed for FS4200.

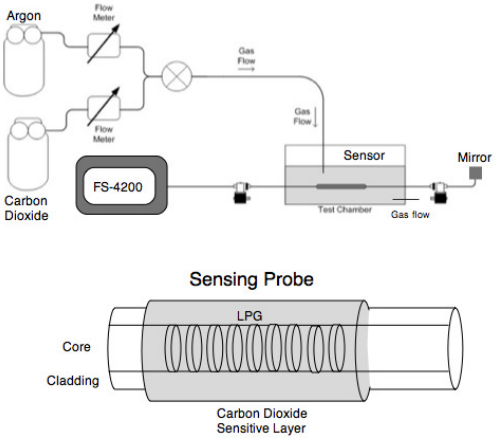

Fig 8 Setup used to test the LPG based CO_2 sensor.

The sensing head showed sensitivity to variations in CO_2 level by changing the LPG resonance wavelength. This behavior was quantified by changing progressively the gas concentration in the chamber from 0 to 50%. Fig 9 shows the results obtained. The sensor showed a non linear response where the wavelength shift for the full concentration range was ~65 pm. For concentrations above 50% the sensor response rapidly saturated. A positive change in the resonant wavelength with increasing concentration agrees well with the typical response of an LPG to the decrease in refractive index of the sensing layer. The combination of the non linear response of the sensing layer with the LPG non linear response to refractive index changes resulted in the logarithmic response displayed in figure 5.

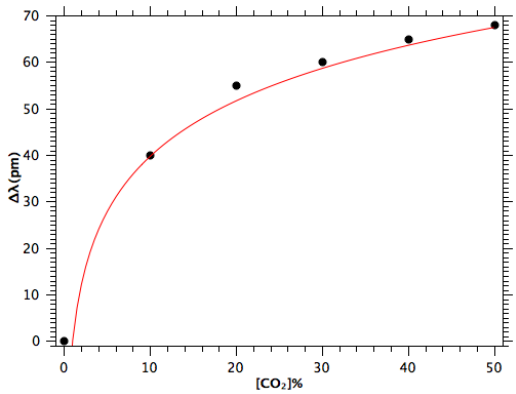

Fig 9 Response to CO_2 variations of the coated LPG.

While a reversible response was observed, there was never a complete recovery of the membrane to previous levels when it was submitted to repeated cycles of CO_2 concentration.
At this point several optimization procedures are needed. The wavelength shift observed was much smaller than expected, indicating that the dilution and coating procedures had an important impact on the sensing layer properties. Furthermore, in face of the fact that LPG sensitivity depends strongly on the refractive index range of operation, it is imperative to make a fine tuning, perhaps using an intermediate buffer layer between the LPG and the sensing film.

3 Conclusions

In this work a new principle for measuring carbon dioxide concentration was described and demonstrated. A hydrogel based sensitive layer whose refractive index depends on CO_2 concentration, was combined with fiber optic based refractometric probes. The results obtained are preliminary but nevertheless indicate several optimization routes and demonstrate the viability of implementing label free carbon dioxide sensors compatible with standard telecom technology.

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