LPG Based Fiber Optic Sensor for Carbon Dioxide

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ABSTRACT

In this work a novel optical-fiber sensor for carbon dioxide measurement is presented. A polymeric sensitive layer based on the acid-base equilibrium of phenol and of its derivative 4-nitro-phenol is used for carbon dioxide determination. The sensitive material presents changes in color and in its refractive index. Colorimetric and refractometric measurements were performed. The results show the sensor is more sensitive for lower concentrations and a saturation effect occurs for higher levels. For the colorimetric response, a resolution of ±0.15% was estimated and a response time of 30s was measured. For the refractometric measurements, a resolution of ±0.50% could be estimated and a response time of 12s was measured. Reversibility and reproducibility were also demonstrated.

Keywords: Carbon dioxide, long period grating, absorption, chemical sensors.

1. INTRODUCTION

Optical chemical sensors are an appealing alternative for on-line monitoring of critical parameters in many in environmental and industrial applications [1]. The development of new sensitive membranes, with analyte dependent optical properties, in combination with fiber optic technologies enable powerful tools for in situ and real time monitoring of chemical and biological species [2]. Real time determination of CO_2 concentration is an important issue in diverse fields, such as chemical and clinical analysis, food industry and environmental monitoring [3-5]. Specifically in aquaculture systems, the level of CO_2 is an important issue for fish health and development. Elevated dissolved carbon dioxide concentration (dCO_2) in the water will induce stress responses in fish causing significant physiological disturbances that can result in reduced growth and poor feed conversion. In spite of its critical nature in fish farms, presently existing systems for CO_2 determination, still do no satisfy the industry needs [6, 7].

Several fiber optic based configurations have been proposed for carbon dioxide detection mostly relaying in either colorimetric or fluorescence based methods. Segawa et al [8] presented a CO_2 fiber sensor based on the pH indicator dye thymol blue, immobilized in a sol-gel matrix. The optical attenuation varied according with the CO_2 concentration due to absorption change of an indicator dye induced by the carbon dioxide induced acidification. Amao and Nakamura [9], on the other hand, demonstrated a CO_2 sensor based in luminescence intensity changes of tetraphenylporphyrin (TPP) due to absorption changes of a co-immobilized pH indicator dye. Nevertheless, configurations using indicator dyes are prone to 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 absorption spectroscopy of the gas absorption lines in the mid infrared is also a reliable sensing mechanism. Nevertheless for remote multipoint sensing at these wavelengths (~4,6 μm) special chalcogenide glass optical fibers are needed [10]. Using higher vibrational harmonics it is possible to detect CO_2 also at 1.57 μm. Orghici et al [11], showed that CO_2 concentration could be measured using an evanescent field sensor based on a quartz multimode fiber in this wavelength range. However, this approach required DFB laser sources, relatively long interaction lengths and was very sensitive to contamination of the fiber surface.

In this work, a CO_2 optical fiber sensor is proposed using standard optical fiber technology. In particular a polymer layer sensitive to CO_2 is interrogated using a long period grating (LPG). The sensing layer is based on the acid-base equilibrium of phenol and of its derivative 4-nitro-phenol, which, in the presence of CO_2, are protonated introducing absorption and refractive index changes. The new sensitive layers were first casted on glass slides and characterized by absorption spectroscopy in the visible range (410 nm). The layer refractive index was also evaluated 1550 nm using a LPG based sensing head. The dual effect observed demonstrates the possibility of CO_2 determination using either mechanism. Therefore, it is possible to use this sensitive layer with fiber optics in visible range using standard

colorimetric arrangements or in refractometric configurations based in standard telecom optoelectronic components. The latter approach is quite promising in terms of multiplexing and remote monitoring capabilities.

2. PRINCIPLE AND EXPERIMENT

The CO_2 sensitive layer is based on the acid-basic equilibrium of phenol and of its derivative 4-nitro-phenol. They are kept in their deprotonated form in the sensing membrane. In the presence of carbon dioxide, hydrogen carbonate is formed that partially protonates the phenols. The hydroxyl group is involved in protolitic reactions that modifies the charge distribution in the molecule. As result of the interaction with carbon dioxide, a change in absorption and in refractive index is expected due to the delocalization of the electrons in the aromatic ring of these compounds. A quaternary ammonium compound, didodecyl-dimethyl-ammonium hydroxide (DDMA) was used to deprotonate the phenols, preparing them for being protonated by the analyte.

The sensing polymer layers were prepared of a 5% (m/m) polyurethane hydrogel (D4) dissolved in ethanol solution. Then 50 µl of 0.1 M ethanolic 4-nitro-phenol and 100 µl of 0.1 M ethanolic DDMA solution were added to 500 µl of polymer solution. The response of the new sensitive material to CO_2 was characterized by absorption spectroscopy and its refractive index was also monitored using a fiber optic long period grating scheme.

For absorption spectroscopy characterization, the setup showed in figure 1 was used. Several glass slides were coated by a casting method. The coated samples, which presented a yellow color, were homogeneous, and were placed in a test chamber and illuminated by violet LED (λ_c at 410 nm) through a 4 mm-diameter fiber bundle. The transmitted signal was collected through identical fiber bundle and carried for detection. An Ocean Optics USB4000 spectrometer, connected to a PC, was used for the absorption measurements. The membrane thickness was approximately 1µm.

Figure 2 shows the schematic setup used to evaluate the CO_2 induced refractive index changes in the polymer layer using a LPG as the sensing probe. LPGs are well known fiber refractometers [12]. Coating the grating with the CO_2 sensitive membrane, it is possible to quantify the gas concentration as function of the resonance wavelength. For the experiment, a 40 mm long LPG with period Λ=396 µm (fabricated by the electric-arc technique) and center wavelength λ=1572 nm was used. This resonance wavelength corresponds to the 6th-order cladding mode. Prior to fiber coating, the fiber was cleaned with 5 M HCl solution and silanized using fresh 10% 3-aminopropyl-triethoxysilane (APTS). This procedure allows a better attachment of the sensing material to the silica surface. After drying, the fiber was coated using drop-coating technique (withdraw velocity~0.5 mm/s). The sensing element was evaluated using a FS 2200 Braggmeter (Fibersensing, SA), with 1pm resolution, working in the 1500-1600 nm range, operating in transmission mode.

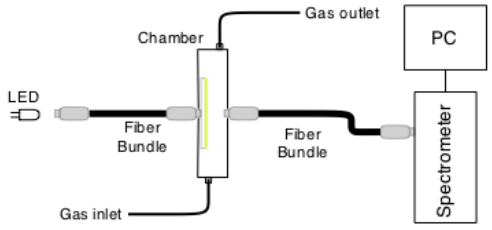

Figure 1 Absorption measurement setup

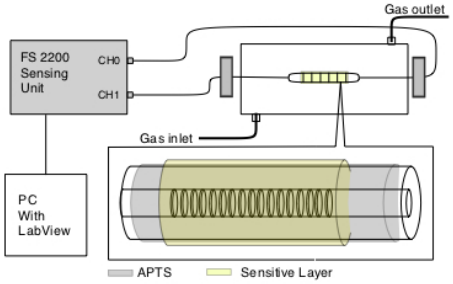

Figure 2 LPG based CO_2 sensing system

Using the schemes described above, the sensors were tested in the concentrations range from 0% to 100% CO_2. This was achieved by using a flow control system fed with CO_2 and N_2 inlets. At this stage, measurements were made in saturated moisture environment, to avoid cross sensitivity with humidity level. All the measurements were made at room temperature (23ºC). The pressure and the flow rate were kept constant.

3. RESULTS AND DISCUSSION

3.1 Absorption measurements

In figure 3 the response of the sensor to dynamic changes in CO_2 concentration can be observed. The inset shows the transmitted spectrum after crossing the test chamber for three different CO_2 concentrations, it is noticeable the dependence of the transmittance with the gas concentration. From the dynamic behavior a calibration curve for the lower

range of CO_2 levels, <15%, could be obtained and is showed in figure 4. The results present a clear increase of transmittance with the increment of the CO_2 concentration showing that, indeed, the presence of the gas in the membrane is causing changes in the electronic distribution of the sensitive membranes through protonation induced by the presence of carbonic acid. Observing the calibration curve in figure 4, it can be seen that the sensor is more sensitive in the lower concentration range and that a saturation effect occurs at higher concentrations. The transmittance variation for the range between 0% and 15.25% was approximately 60%. In this range, the highest sensitivity was observed between 0% and 8%, where a transmittance variation of ~52% was noticeable. A full range response was also evaluated. From 0% to 100%, the transmittance increased by a factor of 2, confirming the saturation of the membrane. From the dynamic behavior displayed in figure 3, a response time of 30s for lower concentrations could be estimated. Also from this data, a resolution of ±0.15% was calculated considering a minimum detectable signal of two times the standard deviation. In figure 3 is also noticeable the reversibility of the response from 15.25% to 0% and from 100% to 0%. The repeatability of the response was evaluated by performing the same experiment three times, the results agreed within the measured standard deviation.

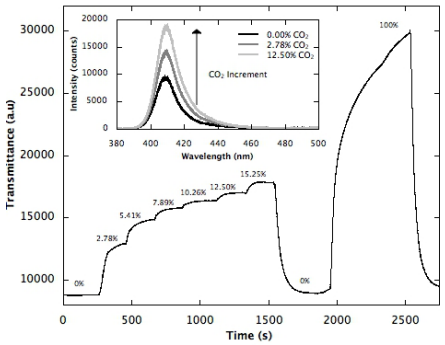

Figure 3 Dynamic response of the sensor in absorbance

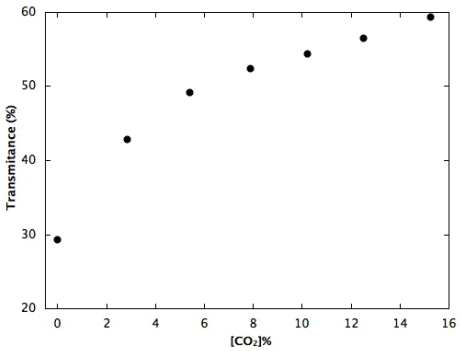

Figure 4 Calibration curve from 0-15%.

3.2 LPG based fiber CO_2 sensing probe

Figure 5 shows the sensing probe transmission spectrum during the different stages of the fabrication. In the inset, the time evolution of the resonance wavelength during the coating process is presented. It is possible to appreciate a wavelength shift of 1.5 nm and 6.4 nm after the silanization and coating, respectively. In figure 6(a) the response of the sensing probe to dynamic changes in CO_2 levels can be seen. From this data a calibration curve can be obtained that is showed in figure 6(b). The results show that the presence of CO_2 increases the refractive index of the layer, shifting the LPG resonance to shorter wavelengths. Observing the calibration curve in figure 6(b) it is appreciable that similarly to what was seen in the colorimetric measurements, the sensor is more sensitive in the lower concentration range. The wavelength shift for the range between 0% and 30% was approximately 180 pm. On the other hand, in the full 0% to 100% concentration range, the wavelength shift observed was around 300pm. From the dynamic behavior, a response time of 12s for a concentration change from 0-57% can be estimated. Also from this data, a resolution of ±0.50% was calculated considering a minimum detectable signal of two times the standard deviation. In figure 6(a) it is also noticeable the reversibility of the response. The repeatability of the response was also observed by performing the same experiment three times, the results obtained agreed within the measured standard deviation.
The difference between the response time between colorimetric and the refractometric experiments are related with the thickness of the layers and difference in the volumes of the used chambers.

4. CONCLUSION

In this work, a new optical fiber sensor for carbon dioxide measurement was proposed. The sensing layer was based on the acid-base equilibrium of phenol and of its derivative p-nitro-phenol which, in the presence of CO_2, are prone to protonation introducing absorption and refractive index changes. Thin films casted on glass slides were characterized using a LED source (λc at 410 nm) and an Ocean Optics USB4000 spectrometer. The layers were tested in the full concentrations range. The results show the increase of transmittance with the increment of the CO_2 level. The membrane presents a non-linear response. The transmittance variation for the range between 0% and 15.25% was approximately 60%. The dynamic behavior was also analyzed in this range. The determined response time was 30s and a resolution of ±0.15% was estimated. For refractometric measurements an LPG coated with the new sensing layer was used. The

resonance of the LPG varies according with the CO_2 concentration indicating a refractive index change in the layer. A wavelength shift of 180pm for a variation in the range between 0% and 30% was noticeable. A resolution of ±0.50% was calculated and a response time of 12s was determined. These results show the viability of a carbon dioxide optical measurement using the phenol-based membrane with the application of colorimetric or refractometric based configurations.

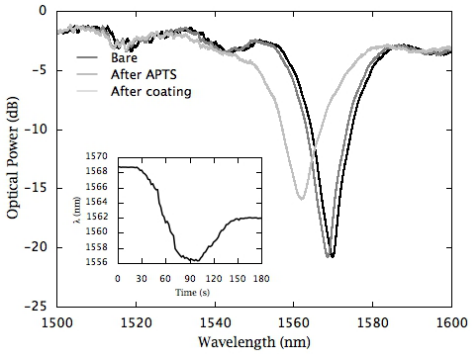

Figure 5 Spectrum of the sensing head during the different stages of fabrication.

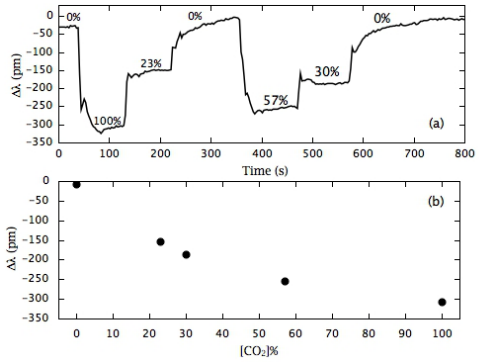

Figure 6 (a) The dynamic response of the LPG CO_2 sensor to gas changes and the resulting calibration (b).

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