

Investigation of interaction of carbon dioxide with ionic liquid filled photonic crystal fiber

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In this study, we proposed a new carbon dioxide (CO₂) gas sensor based on an ionic liquid filled photonic crystal fiber (PCF). 1-ethyl-3-methylimidazolium tetra fluoroborate (EMIMBF₄) was selected to fill the PCF as the ionic liquid because carbon dioxide can easily dissolve in it. Optical transmission differences, depending on the carbon dioxide in the medium, was investigated. The optical transmission spectrum was measured between wavelengths of 500 to 850 nm. It was observed that the light transmission decreased under the influence of CO₂; however the decrease was considerably less between wavelengths of 650 to 850 nm. The transmission changes observed under the influence of CO₂ at 550 and 850 nm were %60 and %28 respectively.

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1. Introduction

Optical fibers have been deployed worldwide since 1970's and have revolutionary changes in communication technologies with their advantages on copper lines with properties such as electrical isolation, very large bandwidth, low transmission loss, low weight, and signal security [1]. Fiber optic sensor technologies with high sensitivity feature have worldwide widespread in 20 last years [2]. Photonic crystal fiber (PCF) is a subset of optical fibers. It was produced in the second half of 1990's and spread throughout commercial technologies rapidly [3, 4]. PCF is made of a single material and its cladding consists of a microstructured array of air holes elongating around the fiber axis. PCF has several geometric parameters which can be manipulated for larger flexibility of design which gives it different important features such as dispersion tailoring[5], nonlinearity, high birefringence. PCF sensor systems are more sensitive than classical fiber systems. It gives excellent results when sensing temperature, strain, pressure, bending and refractive index changes. It also has a wide range of research field uses such as spectroscopy, metrology, biomedicine, imaging, telecommunications, industrial machining and military applications [6-8].

Several studies about using PCF as a gas sensor have been implemented since its proliferation [9, 10]. PCF is an alternative to classical gas sensors since their features include small sample volumes, low transmission loss, electromagnetic immunity, chemical inertness and high flexibility. Additionally, the air holes provide the possibility to insert materials needed to initiate the refractive index change under the external physical parameters. Generally in these studies, a hollow core fiber

is used and gas was directly inserted into the holes of the PCF [9, 10].

The ionic liquids are salts soluble at room or lower temperatures. Although ordinary liquids like water are electrically neutral, ionic liquids contain too many ions and transient ion pairs. According to several studies, ionic liquids have more CO₂ holding capacity than polymeric materials and CO₂ can be reversibly dissolved in imidazolium based ionic liquids [11]. Since ionic liquids are very powerful solvents, 1-ethyl-3-methylimidazolium tetra fluoroborate (EMIMBF₄) was chosen to fill the PCF.

In this study, we studied the CO₂ response of EMIMBF₄ filled PCF in both the Near IR and part of VIS regions by using optical transmission based experimental setup. To the best of our knowledge the filling of ionic liquid to PCF and investigation of its interaction with CO₂ has never been investigated before. Therefore, we feel our study is going to provide a valuable aspect to use of PCF as a gas sensor.

2. Experimental

2.1 Materials

The PCF used is LMA-20 fiber from Thorlabs which shows endlessly single-mode properties. It is a solid core fiber and its core diameter is 20 μ , air hole diameter is 6.4 μ . (LMA-20: $d=6.4\mu\text{m}$; $\Lambda=13.2\mu\text{m}$). 1-ethyl- 3-methylimidazolium tetra fluoroborate (EMIMBF₄) was of analytical grade and purchased from Sigma-Aldrich. Carbon dioxide and nitrogen gases of 99.99% purity were obtained from Linde Gas, Izmir, Turkey.

2.2 Instrumentation and gas measurements

The system includes a light source, a lens system, a spectrometer, PCF, and a CO₂ source (Fig. 1). A Halogen lamp was used as the light source. Light was guided into the PCF's core utilizing the lens system. Then the light, which was transmitted through the PCF, was guided into the spectrometer. A PCF with a length of 12 cm was used in our experiments. Before CO₂ was sent into the system, the system was set to maximize the light transmission by sending light into the PCF. The reference spectrum was then recorded. The CO₂ tube was switched on and the gas inlet to the initially air filled system was gradually delivered for one hour. The effect of CO₂ was measured when the PCF was both empty and filled with the ionic liquid. Since the air of the medium is set as the reference spectrum, the changes which occur from the gas can be clearly observed. While the gas was diffusing through the fiber, the transmission data was recorded periodically to obtain the spectrum. Afterwards, the CO₂ inlet was closed and the outlet opened while a N₂ tube was switched on to remove remaining CO₂ from the chamber.

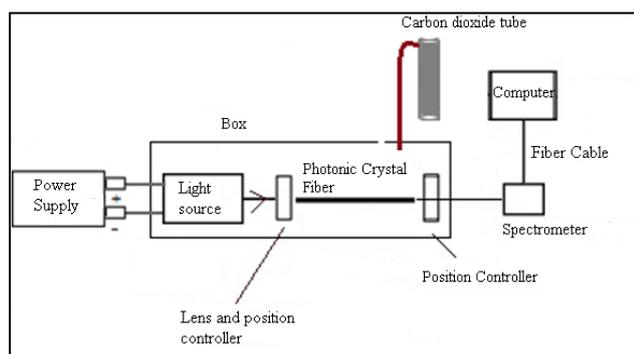


Fig. 1. Schematic representation of the experimental setup.

3. Results and discussion

The first experiment was conducted while the PCF was empty to observe the CO₂ sensitivity of the PCF without ionic liquid. We also wanted to observe if any external factors existed which can cause errors during the transfer of CO₂ into the system. The PCF was placed into the testing apparatus and the reference spectrum was recorded. We began to insert CO₂ into the system and the initially recorded spectrum was used as a reference. Since there was no significant absorption at visible and near infrared wavelengths, and the refraction index of CO₂ was close to the refractive index of air, no change in light transmission was expected during the gas' entrance into the system. After one hour in the overall spectrum, the maximum transmission change was 2%. This result exposed that the effect of external factors on transmission was around 2%.

As a next step, the experiment was repeated by using the ionic liquid filled PCF. CO₂ was injected into the

system via the CO₂ tube for 60 min to provide the pure CO₂ medium and afterwards N₂ gas injected for another 60 min. The changes in the spectrum were observed throughout this process. Since the chemical structure changes by CO₂ solution in ionic liquid it is expected to cause change in refractive index. It is clear that this refractive index change results the change in transmission characteristics of PCF [12]. As expected, the overall transmission began to decrease considerably after 25 min. Also, a step was observed in the transmission spectrum as shown below in Fig. 2 and Fig. 3a. Three distinct transmission characteristics were observed at wavelengths around 500-620 nm, 620-650 nm and 650-850 nm. The intensity variation can be explained by reviewing the excitation-emission results detailed in the studies of Oter et al. and Zhang et al [13, 14]. In their study, Oter et al. observed the emission intensity decreased depending on increased amounts of CO₂ in the wavelength interval of 300-600 nm under the maximum excitation of 518 nm [13]. Our results show that the transmission decrease is less above the 600 nm where the emission of liquid is less effective. The decrease of transmitted intensity observed between 500-600 nm verifies the increase of CO₂ in the medium. It's evident that the step observed on the transmission spectrum in our measurements was due to the fluorescence behavior [15] of the liquid.

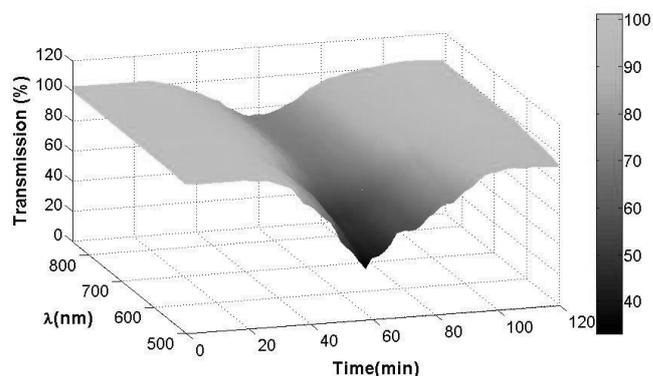


Fig. 2. Time and wavelength dependent transmission (%) change ($t=0-60$ min CO₂, $t=60-120$ min N₂)

At the end of 60 minutes, CO₂ injection into the system was halted and N₂ injection was initiated. As can be seen in Figs. 2 and 3, the transmission intensity slowly began to return back to its initial value. At the end of 120 minutes the light transmission reached to nearly 100% of its initial value at wavelengths above 650 nm (Fig. 2 and 3). To acquire more descriptive information, a light transmission graph according to time and wavelengths between 500-850 nm was sketched as Fig. 3a. Return of transmitted intensity to almost initial conditions (Fig. 3a, $t=0$) by replacement of CO₂ with N₂ (Fig. 3a, $t=120$) in the system proves that the observed effects completely arise from CO₂.

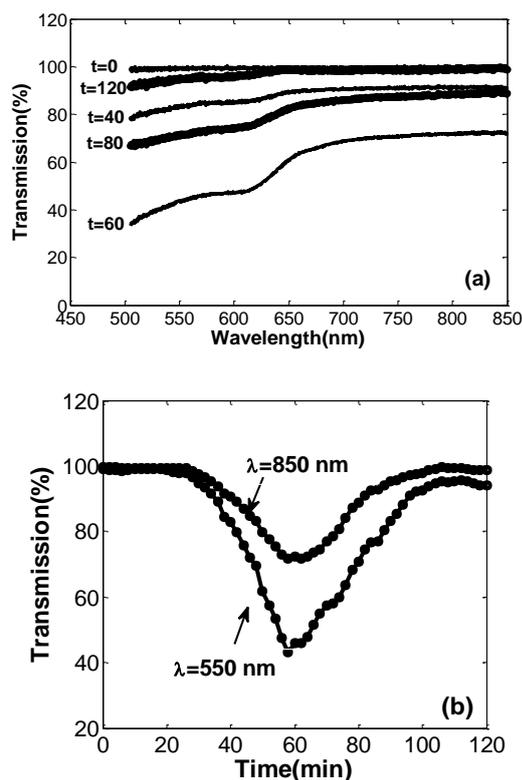


Fig. 3. a) Wavelength dependent light transmission change: bold lines corresponds to N_2 medium, b) Comparison of the time dependent light transmission at wavelengths 550 nm and 850 nm ($t=0-60$ min CO_2 , $t=60-120$ min N_2)

Our measurement system saturates after 60 min within a CO_2 environment. The main reasons for such a long saturation time can be attributed to the small sized PCF holes ($6.4 \mu m$) and relatively long PCF length (12 cm). Although the response time is relatively long, the 60% transmission change occurring at 550 nm and the 28% transmission change at 850 nm prove that it is possible to construct sensitive CO_2 sensors by utilizing ionic liquid filled PCF.

The transmission difference in spectrum between 500-620 nm and 650-850 nm constitutes another usage of the system. It is possible to reduce external alignment or light source intensity variation errors by taking measurements at two different wavelengths selected from different regions. Thus, comparing the data from two different wavelengths, such as 550 nm and 850 nm (Fig. 3.b), gave us a clear and measurable difference. Therefore, it is entirely possible to set up a simpler system which can work at two different wavelengths instead of a wide spectrum. The occurrence of two different transmission mechanisms shows that this system can be used as a viable CO_2 sensor.

The changes observed according to the amounts of CO_2 used proved that this system can be used as a sensor. Although the usage of PCF with a length of 12 cm increases the interaction of light with liquid and thereby increases the sensitivity of the system, it also decreases the

response time. However, there are several ways to speed up the response time. One of the approaches is to use a hollow core PCF or shorter PCF to decrease the diffusion time. Another approach could be using parallel or several consecutively placed short PCFs with open ends [9]. By using these methods it is possible to increase both response time and sensitivity. Finally, according to presented results, CO_2 gas can be detected with the system we set up by using a PCF filled with ionic liquid. This system can be improved upon after further research.

4. Conclusion

In this study, in order to observe the effects of CO_2 gas in a simpler manner, trials were carried out by filling the PCF with ionic liquid ($EMIMBF_4$), in which CO_2 is able to easily dissolve. It is observed that in CO_2 mediums transmissions change like a step for different wavelength regions. Benefiting from the observance of the step like transmission change, the presence of CO_2 in the environment can be easily detected. It is observed that the response time of our system is relatively long. In various studies it is shown this kind of slow response time of PCF sensors and alternative ways to prevent such disadvantage were produced [9, 15]. As an advantage since the interaction of light with ionic liquid is higher %67 (at 500 nm) to %28 (at 850 nm) transmission change observed under the influence of CO_2 . As a result, a simple system capable of performing CO_2 gas measurement was developed by filling the holes of photonic crystal fiber with the ionic liquid.

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