Sensors and Actuators B 184 (2013) 281–287

Contents lists available at SciVerse ScienceDirect

Sensors and Actuators B: Chemical

journal homepage: www.elsevier.com/locate/snb

A new highly sensitive and versatile optical sensing film for controlling CO_2 in gaseous and aqueous media

Paulina K. Contreras-Gutierrez [a], Santiago Medina-Rodríguez [a,b], Antonio L. Medina-Castillo [c],
Jorge F. Fernandez-Sanchez [a,*], Alberto Fernandez-Gutierrez [a]

[a] Department of Analytical Chemistry, Faculty of Sciences, C/Fuentenueva s/n E-18071, Granada, Spain
[b] Department of Signal Theory, Networking and Communications, CITIC-UGR, University of Granada, C/Periodista Rafael Gómez 2, E-18071, Granada, Spain
[c] NanoMyP®, Nanomateriales y Polimeros S.L., Spin-Off Company of the UGR, BIC Building, Avd. Innovacion 1, E-18100, Granada, Spain

ARTICLE INFO

Article history:
Received 18 January 2013
Received in revised form 16 April 2013
Accepted 18 April 2013
Available online 26 April 2013

Keywords:
CO_2
Luminescent polymers
Gas analysis
Water analysis
Medical application
Breath-by-breath analysis.

ABSTRACT

We describe a CO_2-selective sensing film based on the incorporation of a phase-transfer agent, tetraoctylammonium hydroxide (TONOH), into a fluorescence pH-sensitive functionalized polymer. This film can be used for CO_2 determination in gaseous and aqueous media. We have investigated the effect of the concentration of TONOH, and the influence of external parameters such as flow rate, humidity and interfering gases (O_2, CO and NO_2). The sensing films respond to CO_2 concentrations in the gas phase between 7.7 and 40% CO_2 (v/v) and between 4.4 and 60% CO_2 (v/v) in aqueous media, with detection limits of 2.3 and 1.3% CO_2 (v/v), respectively. The covalent immobilization of the fluorescence pH-indicator on the polymer chains provides lower probability of aggregation and no leaching of the optical pH-sensitive dye. In addition, the developed sensing film quick response time ($t_{95} = 5$ s from 0 to 20% CO_2 (v/v) in gas phase), good opto-thermal stability and high versatility. In order to demonstrate this claim, we have developed an optical fiber sensor. It shows good analytical properties (linear dynamic rage of 1.4–40% CO_2 (v/v) with a detection limit of 0.4% CO_2 (v/v).

1. Introduction

Carbon dioxide is one of the most important compounds on earth. Produced by living beings, CO_2 is dangerous to them at high concentrations. Apart from environmental monitoring [1,2] because of its role in global climate change, a variety of other applications exist where determining CO_2 concentration is essential. The quantitative detection of CO_2 is of interest to the food [3,4], beverage [5], biotechnological [6,7], and health [8–10] industries.

Analysis of CO_2 in gas phase is commonly accomplished by nondispersive infrared (NDIR) sensors which are an inexpensive alternative to traditional FT-IR [5]. These sensors cannot be used for analysis of aqueous CO_2, where the Severinghaus electrode is considered as standard [11,12]. Nevertheless, this electrode, or modified versions, is expensive, bulky, susceptible to interferences and slow [13]. The use of optical sensors for quantitative CO_2 analysis offers potential advantages over other analytical methods such as, for example, electrical isolation, reduced noise interference, the possibility of miniaturization and remote sensing, and when coupled to optical fibers it provides a non-invasive monitoring system that is free from electromagnetic interferences [14]. In addition, they are often inexpensive and can be mass-produced as disposable materials [13].

Optical CO_2 sensing is normally based on the pH change due to protonation of a pH indicator when exposed to acidic CO_2 gas. This involves either a colorimetric [10,14–18] or fluorescent [19–22] pH indicator which is incorporated, either covalently [23] or physically, in a liquid polymeric membrane [1,14,24,25] or sol gel matrix [3,13,26–28] in the presence of a transfer agent such as tetraoctylammonium hydroxide (TONOH). Changes in the optical properties of either colorimetric or fluorescent dyes rely on the protonation of the dye counterion (D-) by bicarbonate ion formed by the interaction of CO_2 with the transfer agent [8,13,14,21,29].

Most of the studies utilize the colorimetric dye α-naphtholphthalein (NAF) or the luminescent dye 1-hydroxypyrene-3,6,8-trisulfonate (HPTS or pyranine) physically immobilized in polymer or sol gel matrix, respectively. The incorporation of a dye into a polymer matrix may involve some drawbacks such as aggregation and/or precipitation of the dye into the liquid membrane, and lixiviation of the pH-sensitive dye. In addition, the physical immobilization of a dye into a sol-gel matrix provides a decreasing on its sensitivity compared with its immobilization in polymeric matrices [1], and they are prone to aging caused by structural evolution of the sol-gel, which in turn severely can affect sensitivity to CO_2 [30]. Thus, the development of

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* Corresponding author. Tel.: +34 958 240451; fax: +34 958 243328.
E-mail address: jffernan@ugr.es (J.F. Fernandez-Sanchez).
URL: http://www.ugr.es/local/fqm297 (J.F. Fernandez-Sanchez).

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http://dx.doi.org/10.1016/j.snb.2013.04.074

alternative materials is still of much interest. Hence, we propose to use a matrix which contains the pH-indicator covalently attached to the polymeric matrix. This approach maintains the advantages of the polymeric matrices and solves some of its drawbacks: avoid both the lixiviation and agglomeration of the pH-sensitive dye.

Nowadays new polymers which contain luminescent pH-sensitive dyes chemically attached to their structures are commercially available. One of them is called Polym-H7 and is supplied by nanoMyP®. It is perfectly compatible with aqueous media and is based on the co-polymerization of fluorescein o-acrylate (FOA), methylmethacrylate (MMA) and hydroxymethylmethacrylate (HEMA) in the presence of 3-methacryloylaminopropyl-trimethylammoniumchloride (MAPTAC) by reverse atom-transfer radical polymerization (ATPR). The pH fluorescent probe (FOA) covalently attached on the copolymer chains shows an apparent pKa of 7.8. Polym-H7 has been tested for the development of pH-sensitive sensing films [31].

The aim of this work is to demonstrate that these kinds of copolymers can be used for developing CO_2-sensing films for gas and aqueous samples and that these sensing films can be easily implemented in a optical fiber sensor.

2. Experimental details

2.1. Chemical reagents and materials

Polym-H7 (nanoMyP®, Spain, www.nanomyp.com) and tetraoctylamonium hydroxide (TONOH, 20% in MeOH, Fluka Chemie AG, Buchs) were used as received.

Dry N_2, quality 5.5, was supplied from a 50 L bottle at 200 bar (Air Liquide). CO_2, quality 4.8, from 10 L bottle at 49.5 bar (Abello Linde), NO_2 10 ppm and CO 1000 ppm in N_2 from 10 L bottles at 200 bar (Abello Linde) was also used.

2.2. Preparation and characterization of sensing films

The cocktails were prepared in sealable 4 mL flasks containing 50 mg mL^{-1} of Polym-H7, 125 mg mL^{-1} of TONOH and MeOH.

The sensing films were prepared by spin-coating using a Laurell spin-coater model WS-400B-6NPP/LITE (North Wales, PA, USA). 200 μL of the cocktail was injected onto a rotating glass plate of a spinning device at 300 rpm. All the membranes were transparent and allowed visible light to pass through. The thickness of the layer was optimized for this concrete application. It should be re-optimized for other applications and/or deposition methods. The sensing films were characterized by measuring $(I_0 - I_x)$ at $\lambda_{exc/em}$ = 480/520 nm, with a detector voltage of 650 V and excitation and emission slit width of 5 nm where I_0 is the fluorescence emission of the film in absence of CO_2 and I_x is the luminescence emission on exposure to different percentages of CO_2. Although the excitation and emission wavelengths were quite close, problems with dispersed light were not observed due to the small width of the excitation and emission slits.

In gas analysis the concentration of CO_2 was set balancing the target analyte with N_2 and providing a gas carrier stream with a 40% relative humidity (RH) and a flow rate of 100 mL min^{-1}.

The concentration of CO_2 in aqueous phase was set by bubbling an accurately controlled mixture of CO_2 and N_2 trough the carrier of the FIA system.

All measurements were made in triplicate to check experimental error and all the results are expressed as the average of 3 replicas ± error $(s \cdot t/\sqrt{n})$, where s is the standard deviation, t is the student t and n is the number of replicas.

2.3. Measurement setup

Fluorescence was measured on a Cary Eclipse luminescence spectrometer (Varian Inc.) using a specially designed flow-through cell. CO_2-sensitive films were fitted in the cell and a gas or aqueous stream was applied. Copper and stainless-steel tubing was used for the connections.

For gas analysis, dry N_2 was split into two lines before two mass-flow controllers (MFCs) Bronkhorst. One branch was humidified by guiding the N_2 over water in a 2-neck glass flask, thus avoiding the formation of water droplets. A relative humidity (RH) of up to 85% was obtained. This was monitored with a hygrometer (Rotronic, Bassersdorf) coupled after the measurement cell. The two lines of N_2 were merged to provide the desired carrier gas stream, to which additional lines could be connected. The responses of the CO_2-sensing films were normally investigated using a flow of N_2 humidified to 40% RH. The percentage of CO_2 was varied by using mass-flow controllers to balance CO_2 with humidified N_2. To investigate the effect of interference by other gases such as humidity, O_2, NO_2 and CO a constant concentration of CO_2 was mixed with different flow rates of these gases using mass-flow controllers.

For aqueous determination, a gas station was coupled with a flow injection system (FIA). The gas station consist in two MFCs (one for N_2 and other for CO_2) which bubbling an accurately controlled mixture of CO_2 and N_2 through the carrier solution of the FIA system. A Minipuls 3 Gilson peristaltic pump (Gilson, Villiers Le Bel, France) was used for carrier delivering and flow regulation. PTFE connecting tubing (0.8 mm id) were used to connect the carrier with the flow-cell. Fig. 1 shows the scheme of both devices.

Both gas stations (for gas and aqueous analysis) were controlled by home-made LabVIEW programs which fully control the MFCs via RS-232. The luminescence measurements were controlled by Cary Eclipse software for Windows 95/98/NT system.

For the development of the optical fiber sensor, a 470 nm blue LED (Ocean Optics, USA) was used to excite the sensing film. This LED device was installed in a LS-450 HOLDER (Ocean Optics, USA) which is equipped with a SMA-905 connector for an optical fiber and a bandpass optical filter $\lambda_{central}$ = 469 nm BW = 35 nm (Thorlabs GmbH, model MF469-35).

A bifurcated optical fiber probe, ½" Industrial Fluorescence Probe (Avantes BV) was used to focus the light emitted by the LED to the sensing film and also to collect the fluorescence emission from the cell to the detector. A branch of the probe which has 12 UV/VIS fibers of 200 μm-external diameter (called the illumination branch) was connected via SMA-905 to the LS-450 HOLDER. The other branch, which is equipped with a 600 μm-external diameter fiber (called the detection branch) was also connected via SMA-905 with the CCD spectrometer. The end of the probe consists of a stainless steel cylinder, ½" diameter, containing a 10 mm diameter × 1 mm thick sapphire windows with anti-reflection coating and the 12 illuminating 200 μm-fibers round surrounding the single 600 μm-fiber which is in the middle of the tip.

The measurement cell used was specially designed for this work. It allows the use of gaseous or aqueous streams, and contains the sensing film and the end of the optical fiber probe perfectly coupled.

The Fiber Optic Spectrometer AvaSpec-2048 was used as detector. It was used to record the emission fluorescence. It is based on the AvaBench-75 symmetrical Czerny-Turner design with 2048 pixel CCD Detector Array. The spectrometer has a SMA fiber-optic entrance connector, a collimating and focusing mirror and a UB (UV/VIS; 200–800 nm) diffractional grating with a blaze at 0 nm and a slit of 500 μm. Avasoft-Full software controls the spectrometer and saves the emission spectra. The software also permits the recording of 8 different time-drive functions simultaneously, thus permitting the recording of the emission intensity at 8 different wavelengths versus time simultaneously,