Optical sensor for carbon dioxide gas determination, characterization and improvements

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ABSTRACT

A study of different alternatives to improve the stability and lifetime of sensors for the determination of gaseous CO_2 has been performed. It includes the characterization of different sensing membranes, a discussion of the results obtained and possibilities for the future. The solid sensor membrane for gaseous CO_2 based on changes in the luminiscence of a luminophore immobilized on O_2-insensitive film, concurrent with the displacement of a pH indicator, has some drawbacks, such as the loss of efficiency over time and the need to maintain the sensor in special atmospheric conditions. As a solution to these drawbacks, two alternatives were tested, the first alternative was replacing the newly proposed tetraoctyl ammonium hydroxide (TOAOH) phase transfer agent with other basic agents that did not undergo a Hoffman degradation reaction, and the second alternative was the use of hydrophilic polymers that could retain water needed for CO_2 sensing more efficiently. The different membranes tested indicated that the use of tetramethyl ammonium (TMAOH) instead of TOAOH as the phase transfer agent produced better results regarding stability and sensitivity. In addition, replacing the membrane polymer with hydrophilic polymers improved the sensing characteristics in terms of response time and stability over hydrophobic polymers. With a detection limit of 0.006%, the response time is 19 s and the recovery time is 100 s. The lifetime of the sensing membranes, which do not need to be held in any special atmosphere other than darkness, is longer than at least 300 days for membranes with TMAOH in hydrophilic polymer and 515 days for membranes with TMAOH in ethyl cellulose.

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1. Introduction

The determination of CO_2 gas is of considerable interest in different areas including clinical [1,2], environmental [3], biological [4], biochemical and industrial fields [5], such as wastewater treatment, biotechnological process control and modified atmosphere packaging [6]. Conventional optical sensors for CO_2 gas are based on the measurement of IR absorption extending from 4200 to 4400 nm, but they are bulky and expensive, and the interference from CO is serious, because CO has very similar absorption behaviours to CO_2 in the IR spectral region. Further, optical monitoring of CO_2 concentration based on its acidic nature, using the colorimetric or luminescence changes in acid–base indicators located in a membrane in an aqueous hydrogen carbonate buffer, has been studied [7,8]. The limitations of this design due to the need to maintain the moisture level in the membrane enable the production of solid sensor membranes [7] that can replace the aqueous buffer system with a quaternary ammonium hydroxide, typically TOAOH. This base performs various functions: 1) ion

pairing of the basic form of the pH indicator, depending on the charged groups of the indicator; and 2) providing needed water from the hydrated ionic pair for the uptake of CO_2 from the atmosphere by forming a lipophilic hydrogencarbonate buffer [9].

The main problems with this type of sensor are the limited number of fluorescent indicators that allow for such measures [10]. In order to eliminate this problem, different strategies have been devised such as fluorescence resonance energy transfer [11] and inner filters like photoinduced electronic transfers [12] and protonic transfers [13–15].

Other problems related to the poor photostability of the indicators, variability of the excitation source and the leaching of reagents have been addressed through lifetime measurement [16] instead of the intensity measurement, by methods of ratios of signals or ratiometric using, for example, two excitation wavelengths of luminophore [4,17], and a dual luminophore referencing technique (DLR) [18].

The membrane polymer used plays an important role in the sensitivity and stability of gas sensors, with ethyl cellulose [19], sol–gels [11], silicones [4] and composite materials [20] being common. The sensing material can also be placed on a rigid and optically transparent support [18] or directly attached to the tip, at the end or in the core of an optical fibre [1]. The problems of

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stability with membranes, especially with regard to dehydration, have been addressed through the replacement of a quaternary ammonium cation with room-temperature ionic liquids [21,22]. The use of ionic liquids in gas sensor carbon dioxide helps to retain water [23]. The most recent modification with this type of sensor is the use of upconverting nanoparticles (UCNOs) [24] that exhibit high penetration depth with the excitation power, with the advantage of avoiding any autofluorescence from biomolecules because of the excitation by infrared radiation.

In this paper, we report on some strategies to reduce the inconvenience of solid phase sensors, exemplified by a phosphorescent inner filter-based sensor for CO_2 [25]. The sensor works by quenching a luminescent dye using one of the chemical forms of a non-fluorescent pH indicator, α-naphtholphthalein [26] containing the ammonium quaternary hydroxide TOAOH as an internal buffering system. The change in the position of the acid–base equilibrium by CO_2 in the membrane and the consequent change in colour is transduced in luminescence change due to the overlapping of the absorbance spectrum of the pH indicator and the emission of the long-lifetime luminophore platinum octaethylporphyrin (PtOEP). The first alternative tested was replacing the widely-used TOAOH by other basic agents, since these did not undergo Hoffman degradation, and the second alternative was the use of hydrophilic polymers [27] that could retain water molecules needed for CO_2 sensing more efficiently.

2. Experimental section

2.1. Materials

The polymers used for the membrane preparation were: poly (vinylidene chloride-co-vinyl chloride) (PVCD, particle size 240–320 μm), ethyl cellulose (EC, ethoxyl content 49%) from Sigma-Aldrich Química S.A. (Madrid, Spain), and hydroxypropyl methylcellulose polymers (Methocel E-5, LV USP/EP premium grade) from Dow Chemical Iberia S.L. (Tarragona, Spain).

The other reagents used were platinum octaethylporphyrin complex (PtOEP) obtained from Porphyrin Products Inc. (Logan, UT, USA), α-naphtholphthalein, tetraoctyl ammonium hydroxide (TOAOH) (0.335 M in methanol), tetramethylammonium hydroxide pentahydrate (TMAOH), 1,8-diazabicyclo[5.4.0] undec-7-ene, n-butilamine, ethanolamine, pyridine, cetyltrimethylammonium bromide (CTAB), polyoxyethylene lauryl ether (Brig 35), dioxane, tetrahydrofuran (THF), tributyl phosphate (TBP) and Tween 20, all from Sigma-Aldrich Química S.A; Mighty PSP from Kao Chemical GmbH (Emmerich am Rhein, Germany) and Melflux 2651 from Basf Chemical Company (Tarragona, Spain). Sheets of Mylar-type polyester from Goodfellow (Cambridge, UK) were used as a support for membranes. CO_2, O_2 and N_2 gases used were of high purity (> 99%) and were supplied in gas cylinders by Air Liquid S.A. (Madrid, Spain). The water used was reverse-osmosis type quality from Milli-RO 12 plus a Milli-Q purification system (Millipore, Bedford, MA, USA).

2.2. Instrumentation

A Cary Eclipse fluorescence spectrometer (Varian Australia Pty Ltd.) was used for steady-state luminescence measurements of the sensing films with a homemade cell holder [28], measuring the membrane at 45° angle in the cell to minimize light scattering with 2.5/5.0 nm excitation and emission slits. Double membranes on the same or opposite sides of the plastic support were irradiated with excitation light from the luminophore side and the luminescence was collected from the indicator side.

Standard mixtures of CO_2 (up to 100%) in N_2 were prepared by controlling the flow rates of gases, which entered a mixing chamber using a computer-controlled mass flow controller (Air Liquid España S.A., Madrid, Spain) operating at a total pressure of 760 Torr and a flow rate between 100 and 500 $cm^3 min^{-1}$. For the preparation of gas mixtures with a CO_2 concentration lower than 0.40%, a standard of 5% CO_2 in nitrogen was used, with the lowest CO_2 concentration tested being 0.02%. All the emission intensity measurements were carried out at room temperature. All measurements were made in triplicate, except when stated otherwise, to check for experimental errors.

2.3. Procedures

2.3.1. Sensing membrane preparation

The membranes were produced on the non-luminescent Mylar polyester substrate using a spin-coating technique. All cocktails were prepared weighing the chemicals in a 4 mL flask with a DV215CD balance (Ohaus Co., Pine Brook, NJ, USA) with a precision of ± 0.01 mg. Cocktail 1 was prepared by adding 0.5 mg PtOEP into a solution of 100 mg PVCD in 1 mL of freshly distilled THF. Cocktail 2 in all cases contained the indicator α-naphtolphthalein along with different polymers and phase transfer agents (Table 1). Different sensing films were prepared from cocktails 1 and 2 in two different configurations on the Mylar support (12 mm × 35 mm × 0.5 mm thick): a) double-membrane configuration, one over another prepared with 15 μL of cocktail 1 and, after drying in saturated THF atmosphere for 1 h, depositing 25 μL of cocktail 2 on top of the membrane and drying under vacuum for 12 h. This configuration was used in membrane B4; b) double membrane on opposite side support configuration, prepared with 20 μL of cocktail 1 and 25 μL of cocktail 2 but each one on opposites sides of the Mylar support. This was used for membranes B1 to B3. As usual, the membranes containing PtOEP in PVCD were stored in darkness for 9 days to cure them before their use [25]. The thickness of the dried membranes was calculated to be 0.8 μm for the membrane formed using cocktail 1 and 2 μm for the membrane formed using cocktail 2.

The measurement of sensing membranes phosphorescence was performed with a gate time t_g of 10 ms and a delay time t_d of 0.15 ms, with excitation and emission slit widths of 2.5 and 5 nm at $\lambda_{em} = 537$ under a stream of a mixture of dry gas.

Table 1
Composition of the different sensor membranes tested.

Membrane	TBP (%)	α-naphtolphthalein solution[a] (%)	Ethyl cellulose solution[b] (%)	TMAOH (%)	DBU solution[c] (%)	HPMC (%)	Tween 20 (%)
Membrane B1	4.9	0.56	4.8	0.97	–	–	–
Membrane B2	4.9	0.56	4.8	–	5.48×10^{-3}	–	–
Membrane B3	4.9	0.56	–	0.97	–	60	–
Membrane B4	–	0.56	–	0.97	–	2	0.31

[a] 2 mL toluene and ethanol in ratio 80:20 v/v.
[b] In 1 mL toluene.
[c] In 200 μL methanol.