Available online at www.sciencedirect.com
SCIENCE DIRECT®
Sensors and Actuators B 103 (2004) 284–289
SENSORS AND ACTUATORS B CHEMICAL
www.elsevier.com/locate/snb

Exploitation of a pH-sensitive hydrogel disk for CO_2 detection

S. Herber*, W. Olthuis, P. Bergveld, A. van den Berg

Laboratory of Biosensors, Faculty of Electrical Engineering, MESA+ Research Institute, University of Twente, P.O. Box 217, 7500 AE Enschede, The Netherlands

Available online 15 June 2004

Abstract

In this paper is described how hydrogel is exploited as sensor material for the detection of carbon dioxide (CO_2). A pH-sensitive hydrogel disk, which swells and deswells in response to pH changes, was clamped between a pressure sensor membrane and a porous metal screen together with a bicarbonate solution. CO_2 reacts with the bicarbonate solution resulting in a pH change, which is converted into a pressure by the enclosed hydrogel. This pressure is a measure for the partial pressure of CO_2. The main advantage of this sensor principle is the fact that a reference electrode as required for potentiometric sensors is no longer needed.

Keywords: Hydrogel; pH-sensitive; Stimulus-sensitive; P_{CO_2} sensor; Severinghaus

1. Introduction

Hydrogels are cross-linked hydrophilic polymers that can contain a large amount of water [1,2]. By incorporating functional groups, a hydrogel can be made stimulus-sensitive. Such stimulus-sensitive hydrogels can undergo volume changes in response to changes in stimuli [3–7]. These stimuli can be pH, temperature, light, ion concentration or electric field. Applications for stimulus-sensitive hydrogels have been mostly proposed in the biomedical field [3,4], e.g. for controlled drug delivery, but also for sensors and actuators [5]. Hydrogel-based sensors usually consist of a particular stimulus-sensitive hydrogel, which is used as sensing element, and a transducer to convert the swelling of the hydrogel to the optical or electrical domain. Conductometric, amperometric, optical and mechanical methods have been explored to measure the hydrogel swelling [5].

In this paper, a CO_2 sensor is presented which makes use of a pressure sensor as transducer and a pH-sensitive hydrogel as sensing material. Fig. 1 shows a schematic representation of the sensor. A pH-sensitive hydrogel is placed in a bicarbonate solution enclosed by a porous cover and a pressure sensor. CO_2 reacts with the bicarbonate solution, resulting in a pH decrease according to the Severinghaus principle [8]. In response to the pH decrease the pH-sensitive hydrogel starts to swell but since its volume is fixed by the porous cover, a pressure will be generated (isometric conditions). This pressure is a measure for the partial pressure of carbon dioxide. The advantage of this sensor is that a reference electrode, showing typical problems like drift, leakage and fouling, is no longer needed. In future, a CO_2 permeable membrane must be added to complete the sensor.

The main application of the proposed sensor is to measure the partial pressure of carbon dioxide in the stomach. High P_{CO_2} levels can indicate that a person has gastrointestinal ischemia caused by occlusion of arteries or veins, or by general circulatory failure resulting in splanchnic hypoperfusion (insufficient blood circulation in stomach and/or intestines) [10]. Because the CO_2 measurements takes place in situ, miniaturization is required to be able to insert the sensor, applied on a catheter, in the stomach through the nose. Further possible applications are in the automobile industry, in horticulture and for environmental monitoring instruments.

2. Optimization

Recently, initial results of the proposed CO_2 sensor with pH-sensitive hydrogel microspheres have been presented [9]. The present paper reports the continuation of this research, where the microspheres are replaced by a thin layer of pH-sensitive hydrogel. Further miniaturization of the sensor is obtained by using a micro pressure sensor. The replacement of the microspheres by a thin layer was a done for several reasons. Hydrogel microspheres are difficult to handle, hard to dose and difficult to confine, all due to their

* Corresponding author. Tel.: +31 53 489 2724/2760; fax: +31 53 489 2287.
E-mail address: s.herber@el.utwente.nl (S. Herber).

0925-4005/$ – see front matter
doi:10.1016/j.snb.2004.04.113

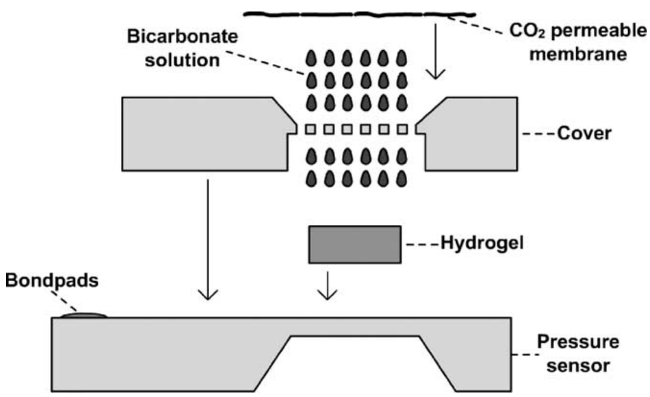

Fig. 1. Schematic representation of the hydrogel-based P_{CO_2} sensor.

small size of a few micrometers. Another disadvantage was that an additional membrane with small pores (<2 μm) was required to enclose the microspheres. Diffusion of ions to the hydrogel was slowed down by this membrane which resulted in a relative longer response time of the sensor. Furthermore, the microspheres moved during swelling, resulting in noise and hysteresis in the measurement signal. Using a thin layer of hydrogel has many advantages—ease of handling, well-defined dimensions and it can be confined by a cover with large pores. Larger pores allow faster diffusion and consequently a decrease in the sensor response time.

The sensor should be able to measure CO_2 levels from 22.5 to 135.0 mmHg for the medical application. The relation between the $[H^+]$ and the partial pressure of CO_2 (mmHg) is given by the following equation [8,9]:

$$P_{CO_2} = \frac{[H^+]^2 + [NaHCO_3][H^+] - K_w}{SK_1K_h(1 + (2K_2/[H^+]))} \tag{1}$$

where S is the Henry's coefficient (M/mmHg; representing the solubility of CO_2 in water), K_h the Henry's law constant, K_w the water dissociation constant and K_1 and K_2, the first and second dissociation constants of H_2CO_3. When the clinical CO_2 values are substituted in Eq. (1) for a 100 mM bicarbonate solution, the pH range of the bicarbonate solution can be calculated and is between pH 7.48–8.25. Consequently, the hydrogel should swell in this range. It is known that hydrogels swell around the pK_a of the titratable monomers that are used [7]. So, a hydrogel has to be used with a pK_a in the basic region around 7.8. For our sensor we used a hydrogel consisting of dimethylaminoethyl methacrylate (DMAEMA), because the pK_a of the protonable monomer is approximately 8. The sensitivity of the sensor can be defined as the change in generated pressure per change in CO_2 partial pressure:

$$S = \frac{\Delta P}{\Delta \log P_{CO_2}} = \frac{\Delta P}{\Delta pH}\frac{\Delta pH}{\Delta \log P_{CO_2}} \tag{2}$$

The pH response to a change in CO_2 ($\Delta pH/\Delta \log P_{CO_2}$) depends on the concentration of bicarbonate used and is theoretically optimal at 1 mM or higher (8). The pressure response to a change in pH ($\Delta P/\Delta pH$) is optimal when the pK_a is near the centre of the range where the pH varies.

3. Experimental

3.1. Materials

Hydroxyethyl methacrylate (HEMA) and DMAEMA were purchased from Acros. Tetraethyleneglycol dimethacrylate (TEGDMA) was obtained from Fluka and 2,2-dimethoxy-2-phenylacetophenone (DMPAP) from Aldrich. The HEMA and DMAEMA were purified by distillation. The other chemicals were used as received.

The pressure sensor was obtained from Honeywell (26PC series). The metal screen, used to enclose the hydrogel, was cut out of a fine-mesh gas filter.

3.2. pH-sensitive hydrogel disk preparation

A pH-sensitive hydrogel disk was prepared from HEMA and DMAEMA by UV-polymerization. A monomer mixture of HEMA and DMAEMA was made with a mole ratio of 95:5 and to the total mole amount, 1.5% cross-linker TEGDMA and 3% photoiniator DMPAP was added. Silicon moulds were prepared in the cleanroom. With reactive ion etching a square cavity was created with 2000 μm sides and a depth of 50 μm. An amount of hydrogel monomer mixture was pipetted in the cavity and covered with transparent Mylar foil, which prevents oxygen to interfere with the polymerization, but allows UV light to pass. By pulling the foil over the mould, abundant solution is removed until the cavity is exactly filled with the monomer mixture. A mask was placed on top of the foil with a circular aperture (diameter 750 μm) through which UV can pass. The hydrogel was polymerized by 366 nm UV light for 90 s. The principle is shown in Fig. 2. By using this method a hydrogel disk with a diameter of 750 μm and a thickness of 50 μm was created. The disk was removed from the mould by placing the mould in a pH 6 buffer, which makes the hydrogel to swell, and carefully extracting the swollen disk with a scalpel.

3.3. Sensor fabrication

The Honeywell 26PC pressure sensor consists of a silicon pressure sensor chip and a plastic housing. The housing can easily be removed to obtain the sensor chip. A hole was drilled in a PCB stick and the pressure sensor chip was glued at all four sides in it in such a way that the bondpads and front and back side of the pressure sensor membrane were kept free. The bondpads on the chip were connected to the electrode tracks on the PCB by wirebonding. The wirebonds and electrode tracks were then isolated with two-component glue. The cavity of the pressure sensor chip was filled with silicone rubber. After hardening of the rubber, a thin layer of Teflon coating was applied to prevent sticking of the