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Experimental investigation of the effect of polymer matrices on polymer fibre optic oxygen sensors and their time response characteristics using a vacuum testing chamber and a liquid flow apparatus

Rongsheng Chen[a], Federico Formenti[a], Hanne McPeak[a], Andrew N. Obeid[b], Clive Hahn[a,*], Andrew Farmery[a]

[a] Nuffield Division of Anaesthetics, Nuffield Department of Clinical Neurosciences, University of Oxford, John Radcliffe Hospital, Oxford OX3 9DU, UK
[b] Oxford Optronix Ltd, 19-21, Central 127, Olympic Avenue, Milton Park, Oxford OX14 4SA, UK

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ABSTRACT

Very fast sensors that are able to track rapid changes in oxygen partial pressure (PO_2) in the gas and liquid phases are increasingly required in scientific research – particularly in the life sciences. Recent interest in monitoring very fast changes in the PO_2 of arterial blood in some respiratory failure conditions is one such example. Previous attempts to design fast intravascular electrochemical oxygen sensors for use in physiology and medicine have failed to meet the criteria that are now required in modern investigations. However, miniature photonic devices are capable of meeting this need. In this article, we present an inexpensive polymer type fibre-optic, oxygen sensor that is two orders of magnitude faster than conventional electrochemical oxygen sensors. It is constructed with biologically inert polymer materials and is both sufficiently small and robust for direct insertion in to a human artery. The sensors were tested and evaluated in both a gas testing chamber and in a flowing liquid test system. The results showed a very fast T_{90} response time, typically circa 20 ms when tested in the gas phase, and circa 100 ms in flowing liquid.

1. Introduction

Ultrafast sensors are needed to follow rapid changes in the partial pressure of oxygen (PO_2) in both gas and liquid phases in medicine, physiology and biology [1–4]. In particular, there is an increasing interest in monitoring very fast changes in the PO_2 of arterial blood in some respiratory conditions [5–8], and only photonic devices are capable of meeting this need in terms of miniaturisation, robustness and rapid response time. Previous attempts to design electrochemical (e.g. Clark electrode) oxygen sensors for routine intravascular use in physiology or medicine have all failed to meet the required criteria [2].

Oxygen analysis in the gas phase has been traditionally achieved by electrochemical sensing, paramagnetic analysis, mass-spectrometry and more recently by fluorescence/luminescence based optical devices exploiting the Stern–Volmer relationship [9,10]. Conventional electrochemical sensors are relatively slow, often with up to 60 s response times [11]. Although both mass spectrometry and paramagnetic devices have potentially much faster response times of 100–500 ms, they are both bulky and costly and their ultimate response times are limited by gas transport, sampling and signal processing issues. They also tend to be restricted to measurements in the gas phase only.

In contrast, optical sensors based on the well-established technique of oxygen quenching of excited luminescent dyes and optical fibre based chemical sensor (OFCS) technology overcome these limitations. In principle, a luminophore (the luminescent dye or reagent) is solubilised into a polymer matrix and coated onto the tip of an optical fibre. The immobilised luminophore is excited by an LED light source of fixed wavelength which has been transmitted through the optical fibre to the sensor tip. The (oxygen) quenched emission is then also transmitted back through the same optical fibre and measured by a sensitive photodetector. The decay rate of the luminescence from its chemically excited state is

* Corresponding author.
E-mail address: clive.hahn@nda.ox.ac.uk (C. Hahn).

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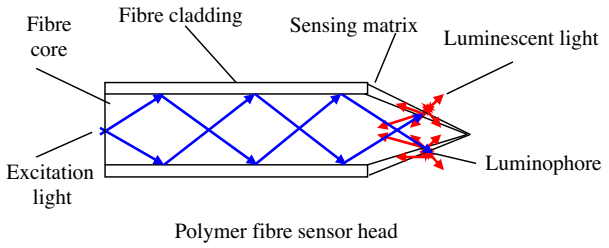

Fig. 1. Schematic illustration of the tapered-tip design.

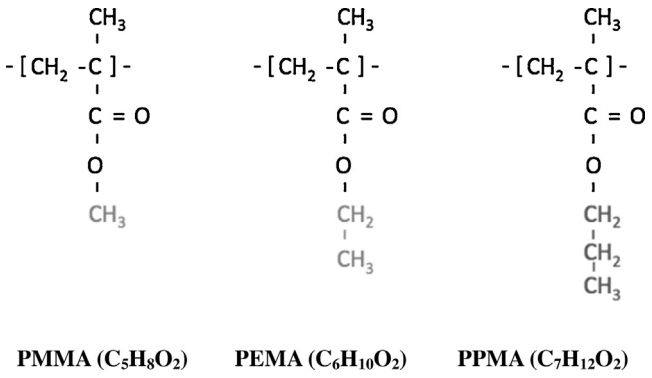

Fig. 2. Molecular structures of the different polymer matrices.

dependent upon the concentration of oxygen and can be calculated from the Stern–Volmer relationship [9,10]. Sensors based on OFCS technology are relatively easy and inexpensive to manufacture and crucially, allow measurement in both gas and liquid phases. In addition, OFCS sensors can have lengths of many metres, do not suffer interference from electromagnetic fields (such as MRI) and can have response times of much less than 1 s [12,13]. Typically, OFCS sensors are constructed by depositing a suitable sensing film on the blunt, distal end of a fibre using a dip-coating process which needs to be sufficiently thick to generate a strong, detectable, luminescence signal [14,15]. OFCS sensors based on evanescent light wave transport through an optical fibre, have also been reported [16,17]. In such cases, the sensing film (which has a low refractive index relative to the fibre core) is coated along the sides of the optical fibre. The evanescent excitation light (which represents only a fraction of the overall excitation energy) penetrates the surrounding, thin-coated film to excite the embedded luminophore. With this technique, the light interaction length needs to be typically several centimetres along the fibre in order to generate enough detectable luminescence, because the luminescent excitation efficiency is relatively poor.

To improve the overall signal to noise (S/N) ratio of the detectable luminescent light, several reported studies have focused on using large-diameter, polymer type optical fibres (e.g. PMMA) for oxygen sensing [18,19], which due to their larger surface area, provide improved S/N performance and are also suitable for invasive medical applications due to their inherent robustness when compared with standard silica fibres. Tapered-tip polymer fibre based oxygen sensors have also been investigated [20,21]. In these studies, a tapered-style sensing tip was used to achieve high luminescent signal level and increased S/N performance of the sensing system. However, these sensors were only evaluated in a gaseous environment and the results showed the sensors to be both relatively insensitive and with slow response times to changes in PO_2. We propose this may have been due to the low oxygen permeability of the type of sensing matrix used in the studies and the possibility that oxygen may have diffused and become trapped in the polymer fibre itself, thereby creating a 'reservoir effect' which would effectively limit the overall response time of the sensor.

Here, we present a small, sensitive and ultra-fast response time oxygen sensor also constructed from polymer type optical fibre. Fig. 1 shows the schematic of a polymer fibre optic sensor head.

We investigated the influence of using different polymer matrix materials in our previous study [1] in which three different polymer materials were compared in terms of oxygen (PO_2) sensitivity and T_{90} time response in a series of sensor tests in the gaseous phase. Our experimental results revealed that oxygen sensors constructed with a PPMA based luminophore matrix provided higher sensitivity and faster time responses than those made with either PMMA or PEMA matrices in our PO_2 range of interest (approx. 5–30 kPa).

2. Principle and sensor fabrication

2.1. Principle

The optical oxygen sensor presented here is based on luminescence quenching by oxygen of a fluorophore immobilised in the matrix material. Assuming dynamic quenching only, the luminescence intensity and luminescence life time are directly related to the oxygen concentration according to the Stern–Volmer relation [9]:

$$I_0/I = \tau_0/\tau = 1 + \mathrm{Ksv}[O_2] = 1 + k\tau_0[O_2] \quad (1)$$

where I_0 and I are the intensities of the luminescence in the absence and presence of oxygen respectively; τ_0 and τ are the lifetime of the excited state luminescence in the absence and presence of oxygen respectively; Ksv is the Stern–Volmer quenching constant; $[O_2]$ is the oxygen concentration; k is the bimolecular rate that describes the efficiency of the collision between the luminophore and oxygen molecules. Under ideal conditions, the plot of $(I_0/I - 1)$ or $(\tau_0/\tau - 1)$ against $[O_2]$ is linear with a slope equal to Ksv, and can be used for simple sensor calibration.

2.2. The polymers

To examine the influence of the oxygen diffusivity on sensor time response, the oxygen quenching luminophore, (PtOEP, a Platinum (II) complex) was first immobilised and then tested in a series of several different acrylate type polymers. Acrylate polymers are generally considered biologically inert and therefore potentially safe for medical applications [22]. In most polymer materials, the larger pendant groups prevent the polymer chains closing and packing together, so polymers with larger pendant groups will tend to have higher oxygen solubility and higher diffusion coefficients [23,24]. In this study we tested three acrylate polymers: poly(methyl methacrylate) (PMMA), poly(ethyl methacrylate) (PEMA) and poly(propyl methacrylate) (PPMA) as matrix materials to immobilise the Platinum (II) complex. These three polymers have similar main structures but different pendant group sizes (see Fig. 2) and hence different oxygen permeability. Theoretically, a sensor using PPMA as the matrix should have both higher sensitivity and a faster time response [1].

2.3. Sensor preparation

Matrix polymer materials of poly(methyl methacrylate) PMMA, poly(ethyl methacrylate) PEMA, and poly(propyl methacrylate) PPMA and the solvent of dichloromethane were obtained from Sigma–Aldrich (USA). The Platinum-Octaethyl-Porphyrin (PtOEP) luminophore was purchased from Porphyrin (USA). All reagents were analytical grade and used as received. Three