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A new optical sensor for sensing oxygen based on phase shift detection

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ABSTRACT

A simple signal processing, low-cost technique for the fabrication of an optical oxygen sensor based on phase shift detection is described. The sensing film is based on the oxygen-sensing dye platinum tetrakis pentrafluoropheny porphine (PtTFPP) embedded in a polymer matrix. The feasibility of coating a photodiode with the oxygen-sensing film to fabricate an optical sensing device is investigated. The optical oxygen sensor is tested with regard to monitoring excitation voltage and oxygen concentration. The experiment results show that the maximum phase difference between 0% and 100% gaseous oxygen is 26°.

A preparation procedure for coating photodiodes with the oxygen-sensing film that produces repetitive and reliable sensing devices is proposed. The developed optical oxygen sensor is low-cost, has simple signal processing, and lacks optical filter elements. The proposed sensor is a cost-effective alternative to traditional electrochemical-based oxygen sensors and provides a platform for other optically based sensors.

1. Introduction

Oxygen (O_2) is involved in many chemical and biochemical reactions as either the reactant or the product. Considerable effort has thus been devoted to the development of suitable techniques for measuring O_2 concentration. Optical oxygen sensors overcome the limitations of the conventional Clark electrode and are widely applied in chemical [1], clinical [2], and environmental monitoring [3] fields. In such sensors, the oxygen concentration is determined based on the reduction in fluorescence intensity caused by the oxygen quenching of the emitting state. The optical oxygen sensors presented in the literature invariably embed the fluorescent indicator in either a polymer [4–7] or a sol–gel matrix [8–14].

Typically, these optical oxygen sensors measure luminescence intensity [15–24] or lifetime [5–7]. Luminescence intensity measurements are typically made by monitoring the emission intensity of the oxygen sensing material at various oxygen concentrations. The level of oxygen concentration changes the luminescence intensity. However, luminescence-intensity-based oxygen sensors are sensitive to interference from factors such as the power drift of the light source, turbidity of the gas sample, background or auto fluorescence of the samples, and photobleaching of the fluorescent dye itself. As a result, it is difficult to build a luminescence-intensity-based oxygen sensor with long-term stability. These difficulties can be minimized by measuring the luminescence lifetime, which is an intrinsic property of luminophores. Therefore, lifetime-based measurement methods are often preferred for the design of reliable luminescence-based optical oxygen sensors. Although time domain methods are ideally suited to eliminate the auto fluorescence of samples, an extremely complicated and expensive instrument setup that combines a pulsed laser (usually a pico or femto second pulsed laser), high-speed data acquisition electronics, and specific signal processing devices are required, making this approach rather expensive.

Optical oxygen sensors based on phase shift measurements do not generally require such sophisticated instrumentation [25–27], and can be implemented using inexpensive light-emitting diodes (LEDs) and electronic devices. These sensors are thus promising for simple and low-cost optochemical measurement systems. Phase fluorometric optical sensors require the optical excitation source to be modulated with a sinusoidally modulated light at a fixed frequency, producing a modulated luminescence emission signal at this frequency. The luminescence signal exhibits a phase shift relative to the excitation signal that can be measured. This shift is related to the lifetime, which can then be related to oxygen concentration. The phase fluorometric method offers several advantages over intensity and lifetime measurement techniques, including relative simplicity and simpler signal detection and processing

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instrumentation, and insensitivity to changes in the optical path and drift due to degradation or leaching of luminophores. Therefore, low-cost approaches with simple signal processing for the phase detection of optical oxygen detection systems are desirable

The present study describes a cost-effective, robust, and reliable phase measurement device with simple signal processing based on an LED and photodiode (PD) configuration. The device can be easily assembled without the need for an extensive background in electronics, signal processing, and optical engineering. The sample is excited with sinusoidally modulated light and the phase shift between the excitation and luminescence emission is measured. The proposed optical sensor provides a versatile instrumentation platform for other phase-based analytical methodologies.

2. Principles of phase fluorometry

In a homogeneous microenvironment, quenching follows the Stern–Volmer equation:

$$\frac{I_0}{I} = \frac{\tau_0}{\tau} = 1 + K_{SV}[O_2] \quad (1)$$

where I_0 and I represent the steady-state fluorescence intensities in the absence and presence of O_2, respectively; τ_0 and τ represent the steady-state fluorescence lifetimes in the absence and presence O_2, respectively; K_{SV} is the Stern–Volmer quenching constant; and $[O_2]$ is the oxygen concentration. In the ideal case, a plot of τ_0/τ versus $[O_2]$ is linear with a slope equal to K_{SV} and an intercept of unity, allowing the application of a simple single-point sensor calibration scheme.

For phase shift detection, luminophores are excited with a sinusoidally modulated light at a fixed modulation frequency. Therefore, the modulated luminescence emission signal has a phase shift relative to the sinusoidally modulated signal at the same frequency. The relationship between the lifetime, τ, and the corresponding phase shift, θ, is [25]:

$$\tan\theta = 2\pi f\tau \quad (2)$$

where f is the modulation frequency. Fig. 1 shows the phase shift between the modulated luminescence emission signal and the luminescence emission signal. Therefore, from Eqs. (1) and (2), measurements of the phase shift, θ, provide a convenient way to monitor analyte/quencher concentrations.

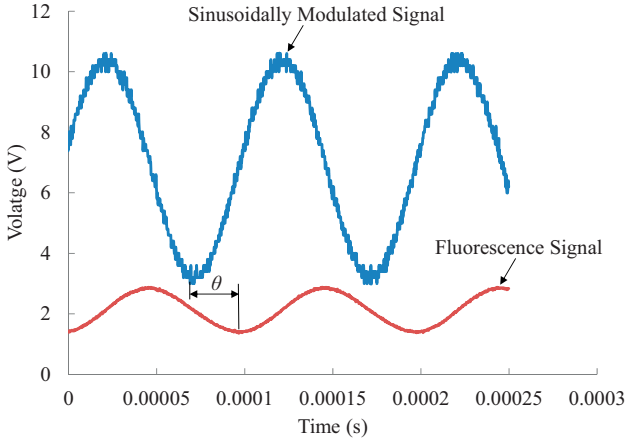

Fig. 1. Principle of phase fluorometric method.

3. Experiments

3.1. Polyvinyl alcohol and mixing processes

Polyvinyl alcohol (PVA) is a low-toxicity, biocompatible polymer employed for a wide range of biomedical applications [29]. Chemical crosslinking with bifunctional compounds capable of reacting with the hydroxyl groups of the polymer is often used to enhance resistance to dissolution in water and to improve the mechanical properties of the polymer. The PVA solution was prepared as follows [30]. White PVA powder (1 g) was dissolved in de-ionized water (10 mL), and after 2 h of magnetic stirring at 50 °C, a 10 wt% transparent PVA aqueous solution formed. The oxygen-sensitive dye solution was prepared by dissolving 2 mg of PtTFPP into 10 mL of tetrahydrofuran (THF). The luminophore-doped PVA aqueous solution was then prepared by mixing the PtTFPP/THF solution (1 mL) into the PVA aqueous solution. The resultant PVA composite solution was stirred mechanically for 10 min; subsequently, a PVA matrix was prepared at room temperature. Then, the dye/polymer solution was deposited by drop-coating onto the active area of the PD (with an active area of about 6.6 mm^2). The membrane (wet layer thickness: 500 μm) on the active area of the PD was left to dry at room temperature for 1 week. The full details of the oxygen indicator preparation process can be found elsewhere [6].

3.2. Instrumentation

Fig. 2 shows a schematic illustration of the experimental arrangement used to characterize the performance of the proposed optical oxygen sensor. In the sensing experiments, the fluorescence excitation was provided by an LED (LED405E, Thorlabs, Inc.) with a central wavelength of 405 nm. The optical oxygen sensing system consisted of a coated PD and an electronic circuit. Various oxygen concentrations were obtained by mixing oxygen and nitrogen fed by gas flow controllers. The mixed gas was heated to temperatures ranging from 25 to 55 °C in a hot circulator standard oven (RISEN Co., Ltd., D9LR-RHD452), the temperature of which was measured with a thermometer (Lutron Electronic Co., Ltd., Model TM-925).

3.3. Phase measurement electronics and signal processing

Fig. 3(a) and (b) shows the signal processing algorithm and electronic circuits of the optical oxygen sensor system, respectively. The LED is modulated with a sinusoidal signal at a frequency of 10 kHz. The modulated luminescence emission signal from the PD is converted via an amplifier to a voltage signal. The modulation

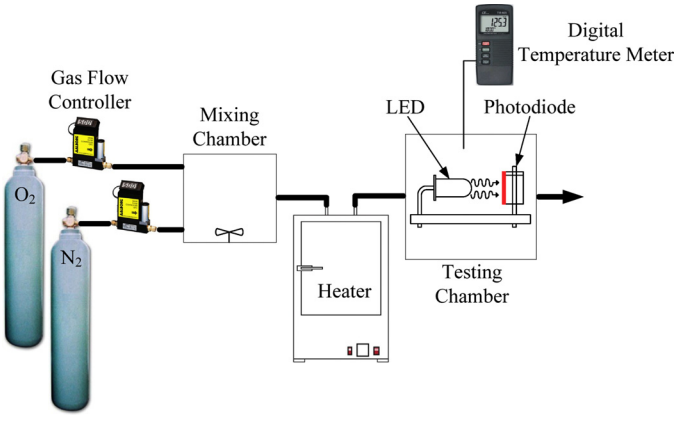

Fig. 2. Schematic diagram showing experimental arrangement used for characterization.