Optik 124 (2013) 6799–6802

Contents lists available at ScienceDirect

Optik

journal homepage: www.elsevier.de/ijleo

Temperature effect on fluorescence of PtOEP embedded in sol–gel membrane used in oxygen sensor☆

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ARTICLE INFO

Article history:
Received 11 January 2013
Accepted 23 May 2013

Keywords:
PtOEP
Spectrum properties
Temperature effect
Oxygen sensor

ABSTRACT

PtOEP has been used in dissolved oxygen sensors as excellent indicators for its good fluorescent properties. In this paper, we mainly studied the temperature effect on the PtOEP embedded in sol–gel film after confirming that the fluorescence emitted from PtOEP can be quenched by oxygen, and found the fluorescence intensity of PtOEP decreased with the rise of temperature. Then a quadratic polynomial which can be a good description of the relationship between the fluorescence intensity and temperature was given out. At last, analysis of the temperature influence on the dissolved oxygen sensor precision was presented.

1. Introduction

Many techniques have been developed over the past years to detect dissolved oxygen and the optical oxygen sensors based on the quenching of fluorescence or phosphorescence emitted from oxygen-sensitive dyes have long been the focus of many research works [1–6]. Hydrophobic PtOEP (2,3,7,8,12,13,17,18-Octaethyl-21H,23H-porphine platinum(II)) is a kind of excellent performance fluorescence indicator, with high luminescence quantum yield and large Stokes shifts, which is used for the sensitive material on dissolved oxygen sensors.

The spectral character of PtOEP has been much reported [7]. Chu and Lo recorded the absorption spectra of PtOEP doped in Octyl-riEOS/TEOS composite xerogels using a spectro fluorometer in 2011. The curve of spectrum showed that there was a Soret band at 384 nm and two Q bands between 500 nm and 534 nm, and when detecting its emission spectrum used CCD spectrometer, a strong fluorescence was shown at 646 nm [8]. The exist of dissolved oxygen in water can quench the fluorescence emitted from PtOEP and the quenching of fluorescence was taking place in accordance with the Stern-Volmer equation, which is the principle to detect dissolved oxygen [9].

There are some advantages of the sensors using indicator of PtOEP that with quick response time, high sensitivity and high resolution, and whose greatest merit is no consumption of oxygen. Comparing with ruthenium (II) complexes, the other indicator widely applied on oxygen sensors, PtOEP has higher oxygen quenching efficiency and larger fluorescence lifetime. At room temperature, the I_0/I value of the PtOEP-doped sensor is as high as 82.5, the Stokes shifts are about 100 nm, and the longest excited-state lifetime is more than 100 μs. These are the key reasons for PtOEP being a good candidate as optical oxygen sensor materials [10].

In 1997, Lee and Okura [11] used PtOEP as fluorescence dye to detect oxygen concentration, found that the maximum value of I_0/I was 8, and the response time could be as short as 5s. In the same year, they respectively compared PtOEP with ruthenium (II) complexes in polymer matrices and in sol–gel matrices, and gave the differences. They found that the PtOEP immobilized in sol–gel matrices showed better performance at the value of I_0/I, which was as high as 40. When the oxygen concentration changes from 0% to 100%, the corresponding changes of response time were ranging from 1 min to 9 min [12].

Usually, the influencing factors of an optical oxygen sensor are following several points; (i) influence result from the property of the solid carrier; (ii) impact from the membrane material; (iii) effects of the spectral character and optical stability of the

☆ *Financial support*: National Natural Science Foundation of China (31101748, 31271614, 61134011) and Innovation Building Program of Beijing Academy of Agriculture and Forestry Sciences (KJCX201102001).

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http://dx.doi.org/10.1016/j.ijleo.2013.05.096

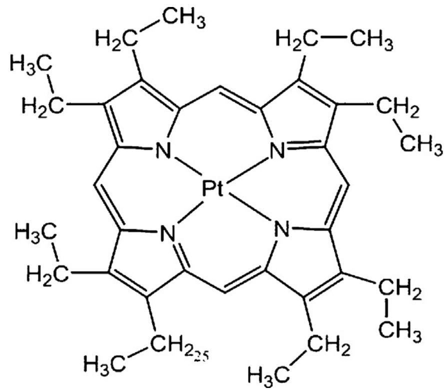

Fig. 1. Chemical structure of PtOEP platinum complexes.

indicators [13]. However most studies before were carried out at room temperature, but the changing of temperature can also impact the sensitivity of oxygen sensors through increasing or decreasing the fluorescence intensity of the indicator. Research has shown that the fluorescence property of PtOEP can affected by temperature. Chu and Lo [9] have reported in 2007 that when the temperature increased from 25 to 74 °C, the fluorescence intensity of the PtOEP-doped oxygen sensor which was exposed in a nitrogen-only environment reduced by approximately 78%.

The water temperature changes in the natural environment will not beyond the range of 0–40 °C, for the field of environmental protection or aquaculture, the temperature compensation of dissolved oxygen sensors should be adapted to the changing range of water temperature in a natural environment. So we studied the fluorescence intensity variation of PtOEP embedded in sol–gel matrices with the water temperature change in the range of 0–40 °C.

This paper firstly confirmed the oxygen quenching ability to the fluorescence of PtOEP in sol–gel matrices, and then studied the fluorescence property with temperature changing, which may give a reference on temperature compensation to the future sensors based on this material. The paper is organized as follows. In Section 2, the experimental section gives the design of a method that detects the fluorescence properties with the change of dissolved oxygen concentration or temperature. In Section 3, the results of the experiment are presented. The discussion about the results is also presented in Section 4. Finally, our work of this paper is summarized in the last section.

2. Experimental sections

2.1. Materials and instrumentation

Firstly the oxygen sensor dye was prepared. The chemical structure of PtOEP was shown in Fig. 1. Unlike $[Ru(dpp)_3]^{2+}$, PtOEP is very hydrophobic and not well dispersed in EtOH. However, it dissolves into tetrahydrofuran (THF) very well. Dissolved 2 mg of PtOEP into 10 mL of THF, we got a highly homogenous dye solution. Then, the luminophore-doped sol solution was prepared by mixing the PtOEP/THF solution into the sol solution. The sol mixtures were capped and magnetically stirred for 10 min prior to dip-coating. Subsequently a xerogel film was formed by dip-coating on a piece of glass that had been cleaned by soaking in NaOH for 24 h, and rinsed with copious amounts of deionized water and EtOH [10].

The spectrometer used in this experiment is AvaSpec-2048 (Avantes USA) whose main technical data is shown in Table 1.

The light source is AvaLight-DHS(Avantes USA) and its wavelength range is 210–2500 nm. The reflected fluorescence optical fiber is customized whose length is 1m and diameter is 1 mm. The temperature control cabinet is YSL GDW-225 which is purchased from Beijing Yashilin Test Equipment Co. LTD. Its temperature adjustment range from −20 °C to 150 °C and its temperature fluctuation is ± 0.5 °C.

Table 1
Main technical data of AvaSpec-2048.

Parameter	Value
Wavelength range	200–1100 nm
Resolution	0.04–20 nm
Stray light	<0.1%
Sensitivity (AvaLight-HAL, 8 μm fiber)	20,000 counts/μW per ms integration time
Signal/noise	200:1
Sample speed with on-board averaging	1.1 ms/scan

2.2. Method

It is generally acknowledged that the solubility of oxygen is impacted by the concentration of sodium sulfite in water. And the oxygen dissolved in solution of saturated sodium sulfite is approximate zero. So the influence of oxygen on the fluorescence film can be eliminated through adding sodium sulfite in water until saturated. In this way, we confirmed the dissolved oxygen quenching ability to the fluorescence of PtOEP in sol–gel matrices.

The measuring system is illustrated in Fig. 2. A small beaker was poured in some water and the PtOEP membrane was dipped into the water. Subsequently, sodium sulfite was put into the beaker and dissolved in the water which evicted out the dissolved oxygen. In this process, the change of fluorescence was recorded. Sodium sulfite is a material easily soluble in water. In this experiment, enough sodium sulfite was prepared to make the water in the beaker saturated. We averaged the sodium sulfite into ten shares, each time put one share into the water and stirred until dissolved, recorded the fluorescence intensity this time. With the increase of sodium sulfite, oxygen dissolved in the water was gradually reduced. Until the sodium sulfite solution was saturated, the dissolved oxygen concentration was 0, and the fluorescence intensity avoided the interference of oxygen. The fluorescence quenching ability of dissolved oxygen was obtained from this measuring system. The integration time of the spectrometer was set at 80 ms in this case.

After confirming the dissolved oxygen quenching ability on the fluorescence of PtOEP in sol–gel matrices, the temperature effect of the PtOEP film dipped in a saturated sodium sulfite solution and exposed in the air was studied respectively. The integration time of the spectrometer was set at 120 ms in this case. We fixed the PtOEP film and optical fiber together to eliminate the influence resulted from the relative position changing, and put them in the

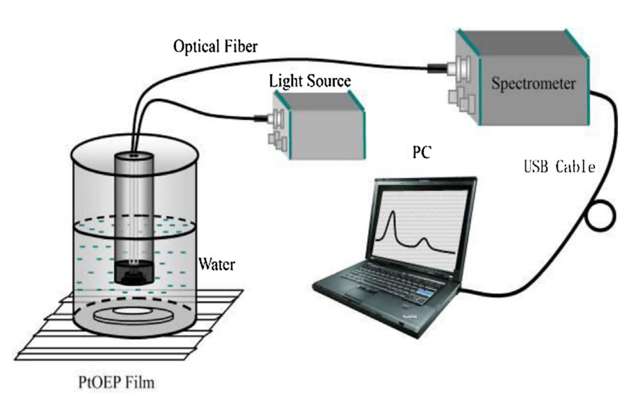

Fig. 2. A measuring system of fluorescence intensity after quenching by dissolved oxygen.