Composite material for optical oxygen sensor

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Abstract. A new composite material for use in optical molecular oxygen sensors is proposed. The absence of pores on the surface of the material avoids microbiological fouling and concomitant deterioration of the characteristics with time, and the presence of the mesoporous phase results in a linear calibration and acceptable response times, even for layers that are significant in thickness.

1. Introduction

A very urgent task for aquaculture and other production processes associated with the saturation of solutions with molecular oxygen, for example microbiological processes in wastewater treatment, is the creation of dissolved oxygen (DO) analyzers and biosensors based on them, which are resistant to poisoning and microbiological fouling. The introduction of such operational monitoring devices will allow the creation of self-regulating systems with significantly increased energy efficiency.

At present the optical method of DO measurement is considered to be the best for these purposes in comparison with the traditional Winkler titration and amperometric Clark electrode [1]. However optical sensor poses a number of requirements for the matrix material in which the sensing dye is distributed. First of all, it must be resistant to singlet oxygen, an unavoidable by-product in the optical measurement. It is also extremely desirable to linearize the calibration curve, as this facilitates the operation of the sensor. Exploitation in a medium with a high content of biomass requires protection of the surface of the sensing element from biological fouling.

Mesoporous structures obtained by the sol-gel process [2, 3] satisfy most of the requirements. They are widely used including biosensors [4], but their exploitation in environments with a high content of biomass is associated with the inevitable contamination of voids. As a result, the performance of the sensor deteriorates.

Perfluorinated polymers are the alternative materials with good oxygen permeability [5] and almost omniphobic surface that prevents the adhesion of the biomaterial. Their drawbacks include the nonlinearity of calibration curve, which sometimes is very significant [6], possible aggregation of dye molecules due to poor solubility in the polymer, as well as poor adhesion to the substrate material.

Another approach is the chemical immobilization of the dye molecule on the substrate. It allows one to obtain linear calibration and makes the sensor resistant to many solvents, but worsens the photostability of the indicator [7].

In this paper we propose the composite material combining good oxygen permeability of fluorinated polymers with a uniform distribution of the photostable dye on a large surface and linear calibration, which are the case for mesoporous structures.
2. Experimental

2.1. Sensor fabrication

The schematic structure of the composite material is shown in the Figure 1. It consists of two phases with different functionalities. The gas-permeable layer (2) is made of amorphous fluorinated polymer. In present work we used fluoroelastomer 42V (similar to Kynar 7200), because it is highly stable, has good adhesion to the substrate and is soluble in a wide range of solvents. Another phase is presented by microparticles of nanostructured SiO2 (3), which are used as centers for the distribution of the sensing dye. Pt(II) complex of meso-tetra(pentafluorophenyl)porphyrin (Pt-TFPP) was chosen as an indicator due to excellent photostability, good quantum yields [8] and commercial availability. Microparticles of SiO2 were synthesized according to a known procedure [2, 3]. The average particle size was 30 µm.

![Figure 1. The schematic structure of the composite material.](image-url)

The particles with adsorbed dye were added to the polymer solution in a suitable solvent, and then the mixture was knife-coated on the circular sand blasted glass substrate (4). The tablet then was dried at 60 °C for 1 h. After that the additional white reflecting layer (1) based on the same polymer as in the case of layer (2) was deposited on the outer surface to increase the signal intensity. Finally the prepared tablet was dried at 60 °C for 24 h. Protective coating (1) from oxygen-transmitting fluoropolymer can be applied with thickness of 0.5…3 µm using vacuum technologies [9–11].

2.2. Instrumentation

The characteristics of the SiO2 microparticles were determined using Micromeritics Gemini VII 2390t surface area analyzer.

The phosphorescence lifetime was measured by means of analyzer Expert-009 (Econix-Expert, Russia). The design of the analyzer and the principle of operation are described in detail earlier [12]. The measurement is based on determination of the phase shift of the LED sine wave modulation. This value can then be converted into a phosphorescence lifetime τ (assuming mono-exponential behavior of the decay curve) with the Equation:

\[
τ = \frac{\tan(ϕ/2\pi)}{f}
\]

in which \(ϕ\) is the phase of the modulation signal, \(f\) is the modulation frequency.

The experimental setup used to characterize the composite matrix sensor is shown in Figure 2. The optical sensor (1) with sensor layer to be examined is fixed in the sealed chamber (2) by means of a special fixing element (3). The assembled unit is placed in a liquid thermostat (4) with accuracy of temperature maintenence ±0.1 °C, controlled by the reference thermometer (5). The readouts are displayed on the display analyser (6) and transmitted to the PC. The chamber (2) is connected by a gas line with a certified vacuum gauge (7) (accuracy class 0.25) and a three-way valve (8) with a buffer volume (9) and vacuum pump (10). This experimental setup allows to set the internal chamber pressure in the range from atmospheric \((P_{\text{atm}})\) to vacuum 1 at, i.e. up to \(P = P_{\text{atm}} - 98,0665 \text{ kPa}\) with an error of no more than 0.250 kPa. The partial pressure of oxygen was determined, taking into account
its percentage in air (20.9476 % by volume). Measurements at the residual pressure of the vacuum pump (passport value $2 \times 10^{-3}$ kPa), were taken as sensor readings in an oxygen-free environment.

![Experimental setup for the sensor calibration.](image)

**Figure 2.** Experimental setup for the sensor calibration.

### 3. Results and discussions

#### 3.1. SiO$_2$ microparticles properties

The particles were examined before and after adsorption of the dye. According to IUPAC, the pores are divided into three types: micro ($< 2$ nm), meso ($2 \ldots 50$ nm) and macro ($> 50$ nm). It was found that the surface area of the micropores is $382 \pm 2 \text{ m}^2/\text{g}$ (micropore volume $0.20 \text{ cm}^3/\text{g}$) and does not change with the adsorption of the dye. This behavior is expected, since Pt-TFPP molecule is too large to pass into the micropores.

The surface of mesopores decreased up to 20 % in comparison with the initial particles (from 374 to 299 m$^2$/g). Further increase in dye content led to self-quenching, that is, the limiting distribution of the dye monolayer was reached for this material.

#### 3.2. Oxygen sensing properties

The Stern-Volmer calibration plots of the sensor are shown in Figure 3. In contrast to earlier created sensor based on poly(hexafluoropropylene) (PHFP) [6], the composite structure has a nearly linear dependence in the whole temperature range studied. This allows us to use for calculation the simple form of the Stern-Volmer Equation:

$$[\text{O}_2] = (\tau_0/\tau - 1)/k_q \tau_0,$$

where $\tau_0$ is the excited state phosphorescence lifetime in the absence of oxygen, $k_q$ is the bimolecular rate constant. Two-point calibration is sufficient to calibrate such a sensor.

The response time of the sensor (establishing stable readings with accuracy not worse than 5 %) was about 40 s in a gaseous medium and not more than 2 minutes in an aqueous medium. The increase in the response time in the latter case can be explained by the lower diffusion rate in solution as compared with the gas phase. These sensor characteristics are slightly worse than those obtained earlier for a sensor based on PHFP [6].
Swelling of the polymer matrix can lead to dye leaching, which causes the change in the calibration dependence or the failure of the sensor. To test the stability of the sensor material against the effects of organic solvents, the sensor was immersed in chloroform, toluene, and cyclohexane. Even after two weeks of continuous contact, migration of the dye to the solution was not observed.

![Figure 3. Temperature dependence of the Stern–Volmer calibration for the composite matrix based sensor. The series temperatures in degrees Celsius are as follows: (1) 0.1; (2) 14.0; (3) 19.9; (4) 24.8; (5) 29.6; (6) 34.6 °C.](image)

Photostability of the sensor is similar to that observed for other sensors based on Pt-TFPP [3], because physical adsorption with properly selected dye concentration does not lead to properties degradation, unlike the covalent coupling [7].

4. Conclusion

The created composite material with the use of structured SiO₂ is a suitable matrix for manufacturing the sensing element of an optical oxygen sensor, which greatly simplifies the operation of the analyzer in comparison with polymer matrix sensor [6]. It is resistant to the action of a number of organic solvents and their vapors, which allows us to quickly determine the oxygen content even in nonaqueous media. The absence of pores on the surface of the material avoids microbiological fouling and dye leaching, preventing degradation in time.

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