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ScienceDirect

Procedia Engineering 87 (2014) 987 – 990

Procedia Engineering

www.elsevier.com/locate/procedia

EUROSENSORS 2014, the XXVIII edition of the conference series

Luminescent Optical Fiber Oxygen Sensor following Layer-by-Layer method

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Abstract

A sensor based on luminescence has been prepared depositing the luminescent complex platinum tetrakis pentrafluorophenyporphine (PtTFPP) onto a plastic-clad silica (PCS) optical fiber. The sensing film is constructed in terms of Layer-by-Layer method. A LED centered at 400 nm was used to interrogate the sensor in a reflection configuration, registering a luminescent signal from the sensing material located at 648 nm. The transduction principle is based on the quenching suffered by PtTFPP as the oxygen (O_2) concentration increases. The sensor was characterized for O_2 concentrations from 0% to 75%, showing a linear Stern–Volmer relationship ($R^2 = 0.9962$).

Peer-review under responsibility of the scientific committee of Eurosensors 2014

Keywords: Metalloporphyrine; Luminiscence; Optical Fiber Sensor; Gaseous Oxygen Sensing.

1. Introduction

Oxygen concentration is a key parameter for applications that belongs to different fields: food industry, biomedicine, or safety at work are just some of them. Oxygen is critical for aerobic biological activity: in some cases, as in food preservation, inert atmospheres are required, so the oxygen presence has to be continuously checked; for other applications, it is also required to determine in which areas there is any asphyxia risk. These representative examples define the background related with oxygen sensing: due to the extension of the field, several efforts have been focused on the developing of oxygen sensors. So far, most of them are based on electronic devices. However, there are some applications where this technology is not suitable: in the case of environments with a high inflammability risk, which is the case of chemical industry, where any electric signal could produce an explosion. For this specific case, optical fiber based sensors are a relevant alternative because they are passive devices: the interrogating signal is optical, so that there is no need of electrical feeding. Moreover, other relevant

Peer-review under responsibility of the scientific committee of Eurosensors 2014
doi:10.1016/j.proeng.2014.11.324

features such as their low dimensions and weight, as well as multiplexing capability have made many researchers to develop oxygen sensors based on this technology.

As optical fiber sensors are based on optical signal, sensing materials whose optical properties vary in the presence of oxygen are required. That is the case of PtTFPP, a metalloporphyrin whose luminesce decreased reversely in the presence of oxygen [1]. This compound shows a strong luminescence, as well as a high and large Stokes Shift and time stability, which make it and excellent compound for this kind of applications. One of the best ways to deposit it onto the optical fiber is by following the Layer-by-Layer technique (LbL), a wet based method that allows sensing films to be constructed at nanometer scale. One of most important advantages of LbL is that it does not depend on substrate geometry, which is very relevant when working with optical fiber [2]. Moreover, it is a cyclic procedure that ensures a high reproducibility and scalability. However, there are few works that deal with the fabrication of optical oxygen sensors fabricated by means of the LbL method. One of the reasons is that some of the best fluorescent oxygen indicators are insoluble in water, which is mandatory to prepare the precursor solutions in the LbL method. It is what happens with PtTFPP: there is no bibliographic reference about the incorporation of PtTFPP in LbL films. This work present an optical fiber sensor prepared with PtTFPP following LbL method, in a way that the hydrophobic nature of the sensing material has been successfully overcome.

2. Materials and Methods

2.1. Luminescence Compound

PtTFPP is a metalloporphyrin that has been successfully used to develop oxygen sensors. It shows an absorption peak at 389 nm, whereas the emission peak is centered at 648 nm (phosphoresce) [1]: therefore, the Stokes shift between the absorption and phosphoresce emission is 259 nm, which ensures no overlapping between the excitation and the response signal. It also exhibits good performing in terms of thermal and photo stability [1].

The luminescence is affected by molecular oxygen: it reacts with the excited state of the flurophore, limiting the luminescence emission, so that the higher gas concentration, the lower emission. This phenomenon is known as quenching, and it has been widely used to develop oxygen sensors. The material concentration in the sensor is another important parameter: if it is too high, self-quenching could reduce the intensity of the emission, shadowing the oxygen transduction; furthermore, a high concentration would induce self-quenching degradation.

2.2. Sensor construction

The fiber used to prepare the sensor is a Plastic Cladding Silica (PCS) one, with core and cladding diameters of 400 / 420 μm respectively. It was a UV/VIS fiber prepared to show low transmission losses in that spectral range: that is a very important fact as the exciting signal falls in the UV range. Once conectorized, the fiber was cleaved on its extreme [3].

The device was prepared in terms of LbL method. This procedure is based on the assembly of molecules with opposite electrical charges: therefore, one of the materials involved (considered as electrolytes) should show a positive charge, whereas the other material a negative one. Each electrolyte is dissolved in water, so that the substrate is alternatively dipped into each solution. In this work, the positive charged solution was prepared with PAH (poly allylamine hydrochloride) at a 10 mM concentration and its pH was adjusted at 10. As it was exposed before, the sensing material is not soluble in water, which is an important inconvenience. To overcome it, PtTFPP was firstly dissolved in acetone, and thereafter, mixed with a sodium dodecyl sulfate (SDS) 10 mM solution. The sensing material final concentration was 0.04 mg/mL to minimize any self-quenching or photo-bleaching. SDS molecules form negatively charged micelles with the PtTFPP ones [4]: on one way, it prevents the porphyrin molecules to join and eventually precipitate; on the other hand, the sensing molecules, which are initially apolar, show a negative charge, which allows the performing of the LbL method.

The cleaved end of the optical fiber was firstly cleat with ethanol and then immersed into NaOH for ten minutes in order to induce a negative superficial charge. Thereafter, it was alternatively dipped into the PAH solution and then into the emulsion (which is assumed as a construction cycle) for 10 times.

3. Experimental Set-up

The sensor was studied in a reflection configuration. The important component is a Y optical coupler with a 200 microns core: one of its branches was coupled into a LED centered at 400 nm and the other one to a USB2000-FLG spectrometer (both devices obtained from Ocean Optics). Finally, the sensor was connected to the remaining branch. The luminescence emission was registered at 649nm, and it was also referenced to the illuminating signal to avoid any artifact produced by undesired signal level fluctuations.

The different oxygen concentrations were prepared mixing this gas with molecular nitrogen by flow mass controllers: the flow of each gas was expressed in mL / min, so that the whole flow was kept constant and the contribution from each gas was varied. In this manner, O_2 concentration could be expressed in % of the total flow. The whole experimental set up is illustrated in the following image.

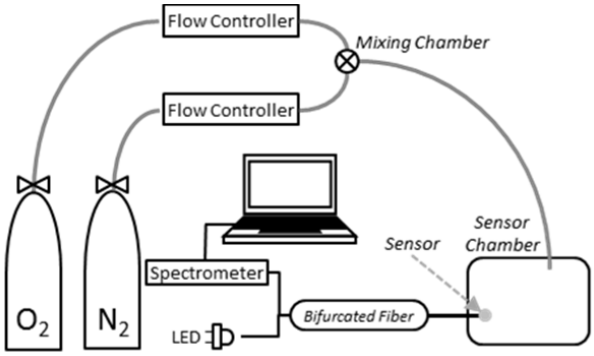

Fig. 1. Experimental set up used to study the sensor performance.

4. Results and Discussion

The sensor was initially exposed to different oxygen concentrations, from 0% up to 75% in increasing steps of 15%, following the procedure described in the previous section. Once the emission peak got stabilized, the respective spectrum was recorded, and thereafter, the O_2 concentration was increased. The results obtained are plotted in Fig. 2.a: it can be observed that the peak decreases as the concentration grows, what is expected due to the quenching effect.

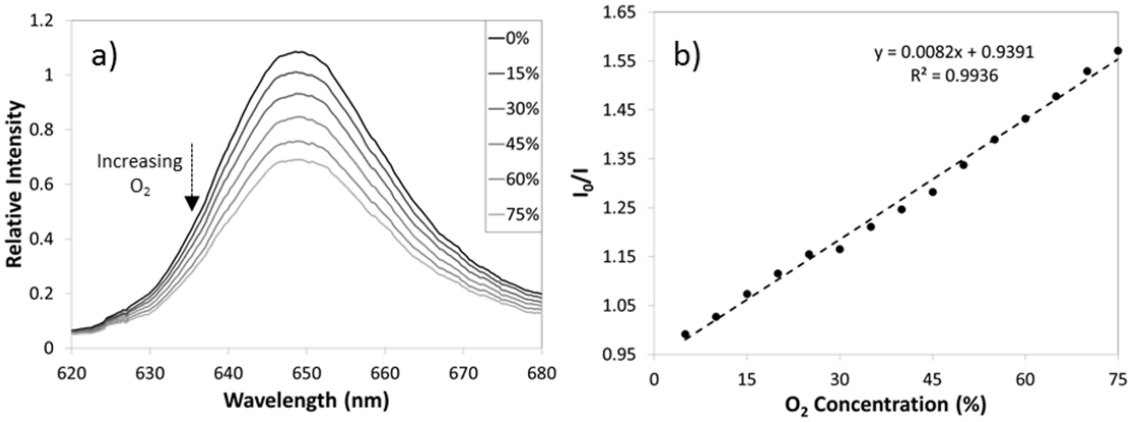

Fig. 2. Spectra of the phosphorescence emission peak (centered at 649 nm) for increasing O_2 concentrations.

In order to get a calibration for the sensor, the experiment was performed in a similar way, but with 5% steps. The emission peak was referenced to the amplitude registered with a 0% concentration (I_0) in order to follow the Stern – Volmer equation [5]. The linear approximation is very accurate because the R^2 factor is very close to 1: the signal variation is decreased around 65% from the value with 0% O_2 to the one registered with a 75% O_2.

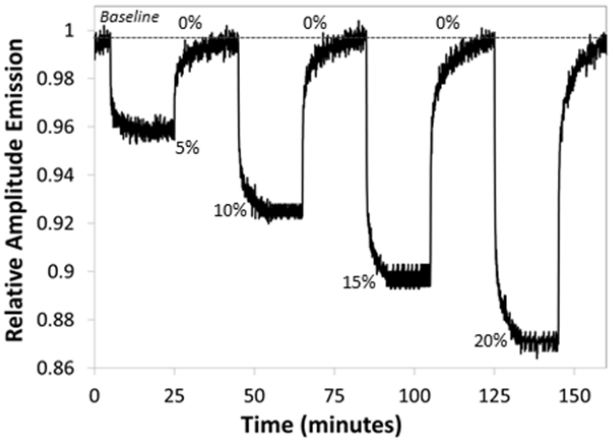

Fig. 3. Dynamic response of the sensor for increasing oxygen concentrations.

The response of the sensor was monitored on real time in order to study its dynamic performance. The tests were performed with the similar set up used to obtain de Stern – Volmer plot, but registering every 3 seconds the relative peak emission. The sensor was exposed to 5% increases in the relative oxygen concentration up to 20%. The results are plotted in Fig. 3. The baseline is preserved during the whole test, so that the sensor shows a reversible behavior.

5. Conclusions

In spite of the water insolubility of the sensing material and its complexity to be deposited by means of the LbL technique, an optical fiber sensor to detect gaseous oxygen has been prepared following the LbL method. The final device shows a linear response for different oxygen concentrations, as well as a reversible and repetitive response.

Acknowledgements

This work was supported by the Spanish Economy and Competitivity Ministry-FEDER TEC2010-17805. The authors thank Nadetech Inc. for the fabrication and fine tuning of the robot used for the deposition of the nanocoatings.

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