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Tapered polymer optical fiber oxygen sensor based on fluorescence-quenching of an embedded fluorophore

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ABSTRACT

We have developed a new method of processing fiber optic oxygen gas sensors based on fluorescent quenching by directly and locally incorporating the fluorophore into the optical fiber that is going to serve as waveguide. This procedure circumvents the preparation steps of the sensing polymer matrix and the later coating of the optical fiber. The sensor combines a side illumination technique with the localized tapering of the fiber, where the fluorophore is placed, to increase the signal to noise ratio. We have fully characterized it and our sensor performance is comparable in sensitivity and response time to those based on polymer matrix fluorophore embedding. We also have studied the addition of a second fluorophore unresponsive to oxygen to serve as a reference for the stability of the excitation source.

1. Introduction

Oxygen is an ubiquitous reactant which also plays an essential role as product in many chemical and biochemical processes [1]. Therefore, quantification of oxygen gas concentration has been an issue in many application fields such as the environment quality measurements, transportation, medicine and agriculture [2–4]. Thus developing efficient sensors capable of accurately measuring the concentration of oxygen is of considerable importance and significant effort has been devoted to this task. Given the breadth of applicability of such sensors, a wide variety of embodiments have been proposed such as solid electrolyte based potentiometric, amperometric and metal oxide based semiconducting resistive type sensors for measuring at high temperature, as well as sensors based on Clark electrodes for oxygen in solution [5]. Common drawbacks of these kinds of sensors are the relatively long response time, oxygen consumption and sensor surface poisoning by organic compounds [3,6,7]. These problems can be circumvented with the use of optical-based sensors [6], which are mainly based on fluorescence measurements of luminophores whose optical emission depends on the surrounding oxygen concentration [8]. The use of fluorescence techniques came into the field because they provide non-invasive, highly sensitive, fast and reversible measurements plus low toxicity [9,10]. This kind of sensing does not consume oxygen which generates a more reliable measurement and also it is impervious to electrical interference.

A further advantage of the fluorescence-based oxygen sensors is their ability to be integrated with fiber optic schemes. Indeed, the use of optical fibers as light carrier provides an excellent interface to follow the changes in fluorescence intensity, as well as smaller and lighter devices, immunity to electromagnetic interferences, multiplexing capabilities and operability in harsh environments at long distances. Furthermore, optical fiber sensors offer the possibility of being implemented in distributed and quasi-distributed sensor networks.

Therefore, a number of fiber optic oxygen gas sensors based on fluorescence quenching have been developed in the last years [10–14]. It is possible to find in the literature two main basic arrangements for measuring fluorescence with optical fibers. The first one uses a fluorophore attached to the fiber tip. Thus, the excitation light travels down to the fiber tip where interacts with the fluorophore. There, the fluorescence is back emitted and guided to the detection system. These schemes present the drawback of the weak fluorescence signal which is also superimposed to the excitation one. Then, bifurcated fibers and optical filters have to be used to separate both signals. The final result is a fluorescence signal with a poor signal-to-noise-ratio (SNR) which needs from complex and expensive measurement setups [15]. The second option is the use of evanescent wave interaction between the guided light by the fiber and a fluorophore side deposited on the fiber surface. In this case, a complete transmissive setup can be used, which avoids the use of bifurcating fibers, although does not eliminate the needed of optical filters. Still, the fluorescence signal is too weak, mainly due

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both to the small penetration depth of the evanescent wave into the fluorescent medium and the low energy carried on by this evanescent field [16,17], although this field extent can be improved with the use of special light sources [18]. Even it is possible to find in literature a combination of both systems, where evanescent wave interaction plus back emitted fluorescence are present [19,20].

A further issue for fluorescence-based optical fiber sensing is the immobilization of the fluorophore either at the fiber tip or on top of the fiber surface [6]. Different materials have been used to this aim. Zeolites [21], polymers like polystyrene or silicon rubber [22,23], sol–gels [6,8,12] and xerogel [24] among others have been studied as matrices. And since the matrix interacts with the fluorophore, it contributes to the sensing performance [25]. Furthermore, after the matrix has been chosen, a series of additional, time-consuming steps need to be followed. First the matrix has to be prepared and the fluorophore has to be embedded in it. Then a suitable optic probe needs to be manufactured in which the matrix, with the fluorophore already embedded in it, is kept in contact with the optical fiber. This configuration also presents some disadvantages as the matrix creates a new interface with different not optimized optical properties which can further reduce the fluorescence intensity gathered by the optical fiber.

To get higher SNR in fluorescence-based fiber optic sensors, side-illumination schemes have also been proposed recently [26–29]. In this case, the excitation light impinges directly on the fluorescent area and the emitted light is gathered by the optical fiber to be guided to the detection device. A higher SNR is obtained if the fiber is locally tapered, which can be done by following either a thermo-mechanical [29,30] or chemical process [28,31].

In this work, we present the use of an optical fiber transducer for oxygen gas measurements. It is based on a locally tapered polymer optical fiber made of poly methyl methacrylate (PMMA), with a cationic ruthenium complex directly incorporated into it. The device is side illuminated with a light emitting diode (LED). Several test have been performed to get both intensity-based and fluorescence lifetime-based measurements. The obtained results show a highly linear response with a sensitivity and accuracy comparable to some other sensors already reported in literature. The versatility and simplicity of the employed setup make the system easy to be implemented. It also provides the possibility of fabricating inexpensive disposable devices for real field applications.

2. Operational principle and transducers fabrication

Luminescence is a well-known analytic method widely used for the specific detection of molecular compounds [32]. In short, it is a process in which a luminophore absorbs light to raise an electron from a ground-state level to a excited-state one, followed by a spontaneous relaxation in which the electron returns back to the ground state. In this later transition, a photon with the energy equivalent to the difference between both excited and ground states is emitted [33]. Two different luminescent processes can be found in nature, and the only difference is the time involved in the whole process. When the process is fast enough (time in the range of ns up to around 0.1 μs), the process is called *fluorescence*. In the case of larger time process (up to ms), we speak about *phosphorescence*.

The operational principle of fluorescence-based oxygen gas sensors is the quenching of such fluorescence. In this process, the fluorescence of a dye is reduced due to the interaction with the oxygen molecules. In order to get a feasible measurement, it is important to use long lifetime fluorophores. In this sense, among the dyes and compounds that present oxygen fluorescence quenching and that have been employed as oxygen sensors we can find transition-metal complexes of palladium, platinum and ruthenium [10,24,34], with ruthenium complexes being the most commonly used. These fluorophores present long lifetimes, a reasonable quantum yield and a large shift between the excitation and fluorescence peaks.

Although fluorophore quenching depends on several factors, this effect can be described in the simplest scenario of a fluorophore in a homogeneous environment through the Stern–Volmer [35,36] equation

$$\frac{I_o}{I} = 1 + K_{SV}[O_2] = 1 + k_q \tau_o [O_2], \quad (1)$$

where I_o is the intensity in the absence of the quencher and I is the intensity in the presence of a quencher, K_{SV} is the Stern–Volmer quenching constant and $[O_2]$ is the oxygen concentration. τ_o is the fluorescence lifetime of the fluorophore and k_q is the bimolecular quenching rate constant or quencher rate coefficient. Thus in the ideal case, a plot of I_o/I versus concentration is linear with a slope that corresponds to K_{SV} and an intercept of 1, allowing the application of a simple single-point sensor calibration scheme.

In our case, the selected fluorophore is a Ru(II) polypyridyl complex [37]. This complex, tris(2,2′-bipyridyl) dichlororuthenium(II) hexahydrate, ($[Ru(bpy)_3]^{2+}Cl_2 \cdot 6H_2O$), presents a long excitation lifetime (around 5 μs), a high quantum yield (above 70%) and a high Stokes shift between excitation wavelength (<460 nm) and the maximum emission one around 591 nm. As stated in the previous section, this dye must be immobilized on the sensor surface.

The substrate for the developed transducer is a polymer step-index optical fiber Super Eska SK-40 (Mitsubishi Rayon Co.), with a 1 mm diameter (980 μm core diameter made of PMMA) and a numerical aperture of 0.5. This choice comes from the dependence of the fluorescence-based sensors with the sensing area. Indeed, the sensitivity increases with increasing surface area per unit mass [4]. Then, a large diameter fiber could improve the sensor performance without an increase in the transducer length. Although the use of PMMA presents a drawback due to its lower oxygen diffusion coefficient in comparison to other materials already employed as polymer matrix [23], its polarity makes it a better solvent for ionic and polar molecules such as the ruthenium complex used. It also provides better mechanical properties, compatibility with human tissues (medical grades), chemical stability, and in our case optimized light transmission properties.

The increase of SNR in the recorded signal has also been pointed out, and it is based in a local tapering of an optical fiber. The method employed to get tapered polymer optical fibers has been depicted elsewhere [29,30] and its reproducibility is ensured by its controlling parameters such as fiber pulling speed and heater oscillation amplitude and speed. It is based in a traveling-heater scheme where a single coil made of a nickel–chromium alloy wire (NiCrom) which moves in an oscillating way while the fiber is gently pulled from both extremes. For our application, the heather coil is fed at 2 A by a constant current source. With this system, we have fabricated biconical shaped tapers with a waist in the range of 400–600 μm and 11–12 mm total length. Although the effective surface area is reduced with this procedure, light coupling to the fiber is improved on the tapered section, as it has been shown elsewhere [28]. Hence the fluorescence signal that is produced on the surface of the taper also benefits from this increase in coupling efficiency. Anyway, a trade-off must be adopted between the light-gathering ability and the mechanical stability and robustness of the sensor.

After tapering the fiber, the fluorophore is introduced in the tapered section. Tapering and the afterwards introduction of the fluorophore on the small dimension taper provides a confined localized sensor. To fixate the ruthenium compound to the fiber, the complex was dissolved in a 30% solution of acetone in water. The fiber was afterwards introduced in the solution for 3 min. At this stage the control of only two parameters provides the reproducibility of the process, the parameters being the concentration of the