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Development of oxygen and temperature sensitive membranes using molecular probes as ratiometric sensor

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ABSTRACT

In this work we show that, the combination of (i) high mechanical stability (provided by a PS matrix), (ii) high sensitivity and selectivity (provided by a two-dye system of Tris (1,10-phenanthroline)ruthenium(II) chloride hydrate ($Ru(phen)_3$) and 7-Methoxy-4-methylcoumarin) and (iii) high reproducibility in the output signal/response, results in a membrane able for monitoring O_2 and temperature in membrane processes at laboratory and industrial scales.

Due to the matched sensitivity of the developed ratiometric probe to oxygen and temperature a simple correction algorithm was implemented, which allows at overcoming the vulnerability of the ratiometric signal to the temperature, leading to a robust evaluation of the oxygen concentration.

The impact of introducing this photochemical activity in membranes opens a new perspective for non-invasive monitoring of membrane processes (e.g. measurement of temperature in membrane distillation processes, oxygen measurement for monitoring of biofilm onset and development in reverse osmosis).

1. Introduction

Membrane processes are governed by physical-chemical interactions between the boundary layer of the solutions in contact with the membranes and the membrane surfaces [1]. Efforts in membrane science have been devoted to the development of innovative materials and optimization of operating conditions in order to maximize the selective permeant-membrane interactions, increasing the performance of the process in terms of productivity, selectivity and stability [2]. Moreover, it is notorious that these interactions dynamically change at the membrane surface due to variations of the operating conditions and membrane properties related to phenomena such as the concentration and/or thermal polarization, fouling, swelling and membrane deterioration [2–6].

Nowadays, common analytic technologies are used for the monitoring of the global performance of the process, estimating the permeability and the selectivity of the membrane and evaluating the long-term stability of the separation process. Oxygen (O_2) and temperature (T) are two fundamental parameters affecting every chemical and biological process, including membrane processes and electrochemical sensors, such as thermocouple for temperature monitoring and Clark electrode for detection of oxygen levels (yO_2), are used as accurate and inexpensive technologies with a rapid response time [12–13]. However, the miniaturization of the sensors is critical for some applications in innovative research fields [14–18] and industrial processes [19–22].

Even with miniaturized approaches, there is still a gap in providing real-time information at the micron and submicron scale about the phenomena occurring in the permeant-membrane interface with impact in the global process, i.e., in-situ real-time monitoring of membrane processes, operating at a molecular scale [7].

The immobilization of luminescent molecular probes in/onto polymeric matrices, is an attractive technology for non-invasive monitoring, allowing to obtain functional materials with a continuous response to temperature changes and/or oxygen content [8] at micrometric and sub-micrometric scale [9,10] with a short response time [11].

The performance of the functional material to be used as an optical sensing device will strongly depend on the fundamental properties of the polymer (e.g. oxygen permeability, transparency, mechanical stability) [23] and the fluorescent probe (e.g. quenching efficiency by oxygen and/or temperature, long term stability) but also on the operating conditions (changes on the geometry of the optical setup, fluctuations of the excitation source, inhomogeneous probe concentration distribution).

In general, polymers with high oxygen permeability, such as poly(dimethylsiloxane) (PDMS), are employed in oxygen sensing, however, a rigid support is often required [24] due the lack of mechanical stability. Furthermore, poor solubility of luminescent

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probes in silicone resins can lead to inhomogeneous dispersion of the molecules and self-quenching effects [13]. On the other hand, glassy polymers such as polystyrene (PS), present a reasonable oxygen permeability and good mechanical properties which allow the preparation of self-consistent films, with improved versatility [24,25].

Several works in the literature are devoted to the development of luminescent probes with high sensitivity to oxygen and long term stability [26–29]. Luminescent transition metal polypyridyl complexes and metalloporphyrins have been widely employed [29]. In particular, Ru(II) polypyridyl complexes present unmatched photostability despite they suffer from pronounced cross talk between oxygen and temperature sensing, since their triplet states are subjected to severe thermal quenching. Strategies like the immobilization of the molecular probes in polymers with low oxygen permeability such as polyacrylonitrile [30] were employed to produce temperature sensing materials insensitive to oxygen. It is thus a common limitation of optical sensors based on fluorescence (or phosphorescence) quenching by oxygen, that both the emission intensity and the excited state life time, are affected by temperature [31,32].

A strategy to overcome these drawbacks is the simultaneous use of two luminescent probes dispersed in the same polymeric matrix, which allow the combination of their emission intensities in a ratiometric signal, for the correction of errors produced by the fluctuations of the operative conditions [33–35].

In the present work Tris(1,10-phenanthroline)ruthenium(II) ($Ru(phen)_3$), a luminescent transition metal polypyridyl complex, was used as oxygen sensitive probe. The performance of polystyrene (PS) and poly(β-hydroxybutyrate-β-hydroxyvalerate) (PHBV) membranes as the solid matrices for the fluorescence sensor was evaluated. The ratiometric response was achieved through the co-dispersion of a second fluorophore insensitive to oxygen: 7-Methoxy-4-methylcoumarin, Dansyl Chloride and Quinine Sulfate were evaluated.

Finally, a correction model was implemented to compensate temperature drifts along the operation of monitoring O_2 concentration. This strategy yields a response to oxygen concentration which is independent from temperature, optical setup, fluctuations in the excitation light intensity and changes in transmission properties of the membrane, providing a way to accurately monitor O_2 levels at laboratory and real case situations.

The impact of introducing this photochemical activity to membranes opens a new perspective for non-invasive monitoring of membrane processes (e.g. mapping of the temperature on membrane surfaces during membrane distillation processes, oxygen measurement for monitoring of biofilm onset and development in reverse osmosis).

2. Materials and methods

2.1. Materials

Polystyrene (PS, M_w=192,000) was purchased from Sigma Aldrich Chemistry (Spain), whereas Poly(3-hydroxybutyrate-*co*-3-hydroxyvalerate) (PHBV, M_w=300,000) containing 3 mol% of 3-hydroxyvalerate units was obtained from Tianan Biologic Material Co. Ltd. (China). Tris(1,10-phenanthroline)ruthenium(II) ($Ru(phen)_3$) was synthesized according to the procedure reported in the literature [36]. The other molecular probes 7-methoxy-4-methylcoumarin (Coumarin), Dansyl Chloride and Quinine hemisulfate salt monohydrate (Quinine Sulfate) and the solvent (Chloroform) were purchased from Sigma Aldrich Chemistry (Spain).

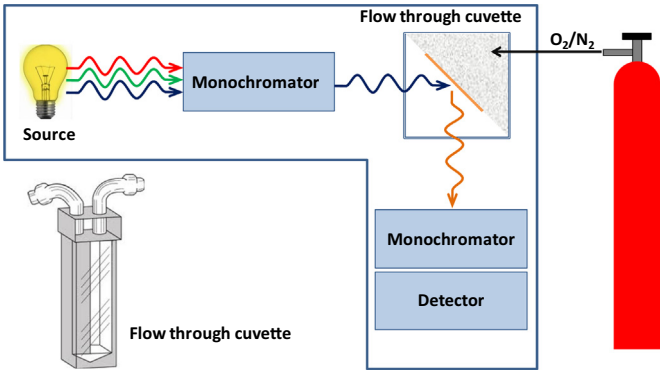

Fig. 1. Scheme of the spectrofluorometer and cuvette used for preliminary experiments.

2.2. Methods

2.2.1. Fluorescence measurements

Fluorescence measurements were performed with a Horiba-Jobin-Yvon SPEX Fluorolog 3.22 spectrofluorimeter equipped with a 450 W Xe lamp. All spectra were collected with a 5 nm slit bandwidth for excitation and emission and corrected.

Preliminary tests for the selection of the materials and evaluation of the response of the membranes to the oxygen level were performed using a flow through cell (10 mm optical path) with inlet/outlet tubes which allow a constant flow of gas. The optical sensing membrane was placed on the surface of a triangular prism made of porous glass in order to establish an angle of 45° between excitation and emission light while allowing for non-hindered gas transport trough the membrane (Fig. 1).

The two-dye ratiometric sensing membranes response to oxygen concentration and temperature was characterized with the setup depicted in Fig. 2. The sensing membrane was mounted in a steel cell with a quartz window. A bifurcated optical fiber bundle, in contact with the quartz window, transports the excitation light and collects the emission of the membrane, while the emission spectrum is registered by a spectrofluorimeter. Mixtures of oxygen/nitrogen with different oxygen concentrations (0%, 10%, 21%, 50% and 100% v/v) purchased from Praxair (Spain) were fed to the cell that was subsequently sealed using two valves (Fig. 2). The pressure of the cell during the experiments was kept at 1 atm. The area of the optical sensing membrane was 1 cm^2. The distance between the optical fiber and the membrane was 1.5 cm. The chamber was kept at constant temperature, which was varied from 25 °C to 50 °C to study the effect of temperature.

2.2.2. Membrane preparation

The membranes were prepared by dry-casting a dope solution of polystyrene (PS) solubilized in 10 ml of chloroform (25 w/v%).

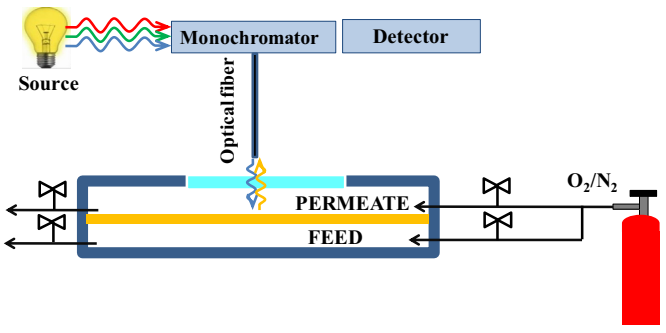

Fig. 2. Scheme of experimental set-up used for evaluation of probe sensitivity to oxygen and temperature.