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OXYGEN DETECTION VIA OPTICAL FIBERS USING BIS(HISTIDINATO)COBALT(II) AS INDICATOR

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Abstract A new kind of oxygen sensitive transducer was realized. It is based on the reflectance change of *bis*(Histidinato)Cobalt(II), $Co(His)_2$, solution immobilized on a Thin Layer Chromatographic plate (TLC plate). The treated TLC plate was coated with a 2-component silicone layer in order to ensure a wet microenvironment and to guarantee a mechanical protection for the sensitive layer. Experimental characterization of such a probe has been carried out in order to determine the response time as a function of the pH of the solution.

INTRODUCTION

Oxygen detection is of extreme importance in industrial, environmental and biomedical fields[1]; some examples may be: quality control in industrial field, estimate of free waters pollution in environmental studies, diagnosis of pulmonary diseases in biomedical field. Moreover, most of enzymatic reactions are oxygen-consuming so that many important physiological parameters, such as glucose[2], lactate[3], cholesterol[4], can be evaluated in an indirect way through oxygen analysis.

In recent years, the application of optical fibers to sensor technology has made possible the realization of new and actractive sensors since they have the traditional advantages of optical fibers, such as easy handling, absence of electrical contacts and of electromagnetic interference, high grade of miniaturization and possibility of remote monitoring.

So far, to detect oxygen via optical fiber its well-known behavior as fluorescence quencher has been exploited[5-10]. This method is highly sensitive, but nevertheless has some drawbacks: other substances may compete with oxygen in the quenching process and this might alter the measurement; the optoelectronic system may be rather expensive and not easy to industrialize. On the contrary, since an absorption spectrum variation is often related to a chemical reaction, a sensor working on an absorption basis is intrinsically more selective. Furthermore, the chromophore may be chosen so that the working wavelength is in the visible region and the source can be a LED. Therefore our research focused on the realization of an absorption optical-fiber oxygen-sensor

Such a sensor could be realized using as transducer an oxygen carrier, i.e. a metallo-organic molecule capable to bind in a reversible manner molecular oxygen[11].

A previous work[12] has shown that, among these compounds, *bis*(Histidinato)cobalt(II), $Co(His)_2$, is the most suitable one in order to realize an absorption sensor. On the basis of this study an early prototype, with the probe consisting of a polymeric hollow-fiber membrane filled with a solution of the compound was realized[13]. However such a probe did not appear completely satisfactory, owing to its time-consuming preparation and to the possibility of leakage of the solution, which may alter the measurement.

This work concerns with the immobilization of $Co(His)_2$ on a solid support and with the characterization of the sensitive material.

EXPERIMENTAL

Materials.

The 2-component silicone (PE1055) was obtained from Petrarch Systems. The thin layer chromatographic plates (TLC plates), silica gel, L-histidine (L-His), cobalt sulphate hexahydrate ($CoSO_4 \cdot 6H_2O$) were obtained from Merck. Phosphate buffers were obtained from Carlo Erba (Milan). Thin film membranes were realized by using a special device which allows to control the thickness.

Experimental characterization of the sensitive layers were carried out with a Perkin Elmer spectrophotometer (mod. 552) equipped with an external integrating sphere connected with the spectrophotometer by means of optical fibers.

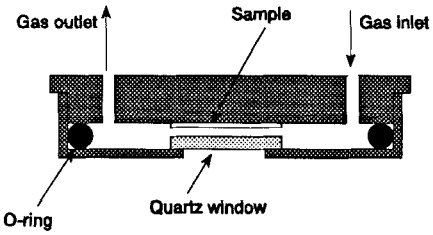

FIGURE 1 Sketch of the flow cell used in order to define the TLC plates.

In order to carry out the measurements a proper flow cell, shown in figure 1, was realized. The body of the cell is made with two aluminum rods, which were painted black to avoid parasitic reflections. On the bottom there is a quartz window (diameter 1 cm) to allow the spectrophotometric investigation of the sample; the airproof assembly is guaranteed by an O-ring which also assures an appropriate distance between the sample and the observation window. On the top there are two openings for the inlet and outlet of gases. This device was realized in order to perform investigation with an integrating sphere but it is apparent that, by changing the window with a proper fiber connector, the cell may be used successfully as an optrode for an optical fiber oxygen sensor.

Co(His)$_2$ synthesis

In an inert atmosphere, operating with de-oxygenated solvents, 10 mmoles of L-His were added to a solution of 5 mmoles of $CoSO_4 \cdot 6H_2O$ in 20 ml of water. To this solution 10 ml of NaOH 1M and 75 ml of ethanol were added. The obtained Na_2SO_4 precipitate was filtered out. Concentrating the resulting solution under reduced pressure, a pink precipitate of Co(His)$_2$ was obtained (1.8g, yield 98%). The precipitate was filtered, washed with a mixture of ethyl ether and ethanol and carefully dried in an inert atmosphere. The compound obtained is very soluble in water and methanol, but insoluble in other organic solvents (acetone, benzene, toluene, dimethylformamide, tetrahydrofuran). Moreover, it resulted stable in the solid state when exposed to dry air while, on the contrary, it is highly sensitive to oxygen in the presence of water.

Immobilization procedure

TLC plates (thickness of the layer 0.2 mm) were used as solid supports. The compound was allowed to be adsorbed on a TLC plate and the plate, still wet, was coated with a silicone rubber layer (thickness 225 μm) and placed in a wet environment until the polymerization process was completed. The silicon layer is necessary in order both to keep a wet microenvironment and to guarantee mechanical protection for the sensitive layer. When the TLC plate, treated as above described, was exposed to nitrogen the color markedly changed and then was reversively recovered in the presence of oxygen.

RESULTS AND DISCUSSION

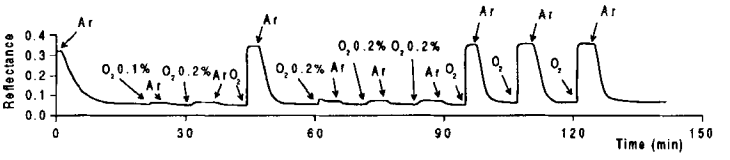

FIGURE 2 Reflectance as a function of time for a TLC plate sensitized with a 10 mM Co(His)$_2$ solution at pH≈7.8, λ=408nm.

Figure 2 shows the reflectance behavior as a function of time for a TLC plate sensitized with a 10 mM Co(His)$_2$ solution in phosphate buffer at pH≈7.8 following its exposure to different oxygen concentrations. The reflectance change was monitored at λ=408 nm where Co(His)$_2$ has an absorption peak related to the binding with molecular oxygen.

It is apparent that the binding of oxygen is perfectly reversible. It can also be noted that even a small oxygen concentration of 0.1% (in volume) in an argon stream can be detected without any doubt.

A different behavior of the sensitized TLC plates at different pH values is to be expected due to the acid-base dissociation of L-his.

Table 1 summarize the results found for the rate constants for a 10 mM concentration of the sample. Four facts should be noted: *i)* the absence of response at pH 4, *ii)* the constant value of the rate constant for pH less than 12.5, *iii)* the near-linear

pH	τ_o(1/e) (sec)	τ_d(1/e) (sec)	τ_o(10%→90%) (sec)	τ_d(10%→90%) (sec)	ΔR	Hysteresis
4.0	-	-	-	-	-	-
7.8	12	65	6	180	0.275	No
9.0	12	100	18	162	0.287	Small
10.1	12	198	24	522	0.295	Strong
12.5	30	264	42	696	0.164	Strong

- No response observed.

TABLE I Oxygenation and de-oxygenation times (τ_o,τ_d), reflectance variation between the steady states (ΔR)at different pH values. 10 mM $Co(His)_2$ solutions

increasing of the oxygenation time when defined as the lapse of time needed to the signal to increase from 10% to 90% of the final level when the pH value of the solution increases, *iv)* the increasing of a hysteresis effect at high pH values.

Although further studies are necessary, these facts can be attributed to the effect of the pH on the $Co(His)_2$-buffer solution system. As reported in the literature[14], L-His has three different values of dissociation constant: pK_1=1.78, pK_2=6.02 and pK_3=9.08. Accordingly we have three acid-base equilibria involving L-His, each one related to the loss of one H^+ ion Moreover, the lack of response at low pH values and the constant value of the rate constant at pH near the neutrality indicates that the only oxygen-sensitive species is $Co(H_2R^-)_2$. In fact the system dynamics can be described by the following equations in which H_xR represents the L-His:

$$Co^{2+} + 2HR^- \xrightarrow{K_c} Co(HR^-)_2; \qquad O_2 + 2Co(HR^-)_2 \xrightarrow{K_o} [Co(HR^-)_2]_2O_2;$$

$$H_3R^+ \overset{K_1}{\rightleftharpoons} H_2R + H^+; \qquad H_2R \overset{K_2}{\rightleftharpoons} HR^- + H^+; \qquad HR^- \overset{K_3}{\rightleftharpoons} HR^{2-} + H^+.$$

A preliminary numerical solution of these equations, in equilibrium conditions and in de-oxygenated solvents at different pH values, has shown that at low pH values the $Co(His)_2$ concentration is low. Increasing the pH, at first the $Co(His)_2$ concentration increases, reaching a maximum when the pH is between 7.2 and 7.9, and then it decreases slowly. The changes in the oxygenation and de-oxygenation times are to be blamed on the changing of the initial conditions. The increasing of hysteresis is to probably due to a progressive decomposition of the compound at high pH values.

CONCLUSIONS

This study demonstrates the possibility of using $Co(His)_2$ immobilized on a TLC plate as an oxygen sensitive transducer for an optical fiber sensor. An important point is the control of the pH of the $Co(His)_2$ solution which should be near 7.5 both to minimize

the hysteresis effect and to obtain a short response time. When these conditions were fulfilled it is possible to detect a concentration of 0.1% (in volume) of oxygen in an argon stream with a rate constant of 12 s and 65 s for the oxygenation and de-oxygenation processes respectively.

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