Development of an Oxygen Sensor Based on Visual Observation of Luminescence Color Change

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With oxygen sensors based on luminescence quenching, the intensity or lifetime of the luminescence has to be measured precisely with a photodetector coupled with an electronic circuit. Thus, practical application of such sensors is limited by the photodetection systems. We propose here a new type of oxygen sensor based on visual observation of luminescence color change. In our sensor, red luminescence was observed under oxygen-free conditions, and the color changed to blue at 5% oxygen content.

The luminescence of many organic molecules is efficiently quenched by oxygen through energy-transfer processes. The possibility of using this quenching process for oxygen sensing was proposed more than 50 years ago.[1,2] Since then, luminescence oxygen sensors of various designs have been proposed,[3] and some of them are available as commercial products. This sensing technique has a fast response, and no oxygen is consumed. Thus, the technique has been used in a large variety of applications, such as combustion, pressure-sensitive paints, and blood gas analysis.[3]

To improve the performance of these sensors, researchers have extensively explored materials for supporting the sensing molecules. In many proposed sensor designs, the sensing molecules are doped in polymer matrices having rather high oxygen permeability. Oxygen molecules reach the sensing molecules by diffusing into the films. Although this type of sensor is easy to prepare and is rather stable, it has some disadvantages, such as slow response time and low sensitivity, because the diffusion of oxygen molecules in the films is slow.[3,4] Proposals for supporting the sensing molecules in sol–gel matrices[5] and zeolites[6] have also been reported. Recently, nanostructured porous alumina has been used as a supporting material,[7–9] and fast response and high sensitivities have been demonstrated.

In luminescence oxygen sensors, luminescence quenching by oxygen is detected by the observation of a decrease in the intensity or a shortening of the lifetime of the luminescence. After calibration curves using standard gases are prepared, the concentration of oxygen can be determined. However, precise measurement of luminescence intensity requires a highly sensitive photodetector, such as a photomultiplier, in addition to an excitation light source. To measure luminescence lifetime precisely, a high-speed electronic circuit is needed. In both cases, the practicality of such sensors is limited by the complexity and cost of the photodetection systems. In this report, we propose new type of luminescence oxygen sensor based on visual observation of luminescence color change without the need for elaborate equipments; except for a small LED used as an excitation light source.

A luminescent sensor plate was prepared based on a methods described in previous reports.[7–9] Briefly, a porous alumina film is prepared on an aluminum plate by an electrochemical oxidation process under acidic conditions. After the oxidation, the plate is immersed in an aqueous dye solution for a few minutes and washed with water several times to remove physically adsorbed dyes. Then, dye molecules are tightly adsorbed on the surface through chemical bonding. In the present study, a commercial porphyrin derivative (5,10,15,20-tetraphenyl-21*H*,23*H*-porphinetetrasulfonic acid, Dojindo) was used as a sensing molecule. Luminescence color could easily be detected visually under illumination with a small LED at 360 nm. Luminescence spectra were measured with a multichannel monochromator (Ocean Photonics, USB2000) with excitation by 380-nm light from an LED (Ocean Photonics, LS-450). The sensor plate was placed in a stainless vessel equipped with a quartz window in which the oxygen content was controlled by means of a flowing mixture of dried oxygen and nitrogen. All measurements were carried out at room temperature.

In Figure 1 are presented photographs of the luminescence colors of the sensor plate at various oxygen concentrations. The bright spots in the centers of the photographs correspond to the areas illuminated by the LED excitation light. Luminescence intensity is high enough for visual detection of the color change. The luminescence color clearly changes from red to blue at 5% oxygen concentration. Accordingly, the oxygen concentration could easily be determined from the luminescence color change. The oxygen concentration at which the color change occurred could be controlled by changing the immersion time of the plate in the dye solution. Long-time immersion leads to high density

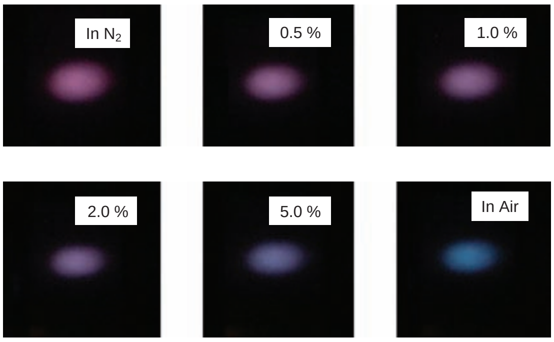

Figure 1. Luminescence color of the sensor plate at various oxygen concentrations.

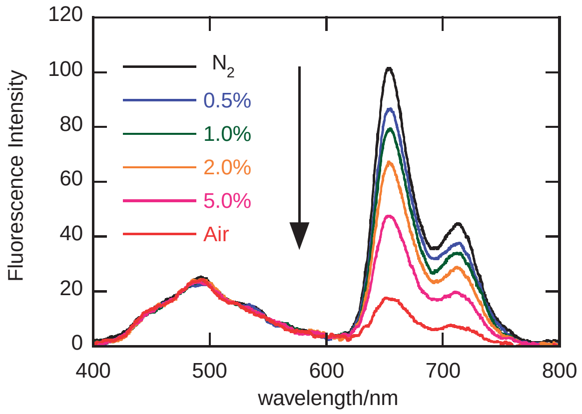

Figure 2. Luminescence spectra of the sensor plate at various oxygen concentrations.

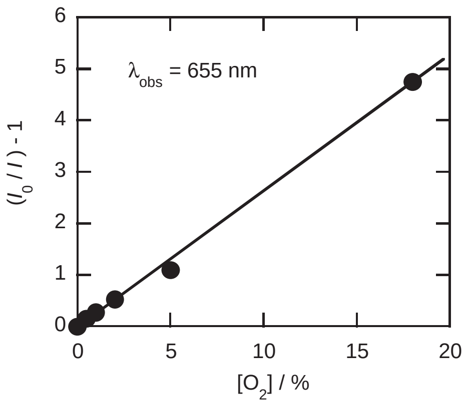

Figure 3. Stern–Volmer plot of the luminescence of the dye on the sensor plate recorded at 665 nm.

of dye on the surface and, therefore, the detectable oxygen concentration increases. The response time of the luminescence change was very fast: the blue fluorescence color observed in ambient air changed to red immediately when the plate was flushed with nitrogen gas. The color change was reversible.

Luminescence spectra of the sensor plate were measured to determine the origin of the luminescence color change. Figure 2 shows the spectra of the sensor plate at various oxygen concentrations. The blue luminescence (at 490 nm) was not quenched by oxygen. In contrast, the red luminescence (at 650 nm) was efficiently quenched by oxygen. This result clearly indicates that the color change due to oxygen originated from the presence of both sensitive and insensitive parts of the sensor plate. We assigned the blue luminescence to the alumina plate itself, on the basis of the similarity of the blue luminescence to the luminescence observed previously.[10,11] Although the oxygen-sensitivity of the luminescence of an alumina plate has not yet been studied, the blue luminescence can be expected to be insensitive to oxygen because oxygen cannot easily penetrate into the dense alumina films. We assigned the red fluorescence to the dye adsorbed on the alumina surface, on the basis of the similarity of the red luminescence to the luminescence of the dye molecules in solution. Because the dye molecules are adsorbed chemically on the surface of the alumina films, they are easily attacked by an oxygen molecule before the excited state relaxes.

Fluorescence quenching processes can be described by the Stern–Volmer equation: $I_0/I = 1 + K_{SV}[O_2]$, where I and I_0 are the luminescence intensities with and without oxygen, respectively, K_{SV} is the Stern–Volmer constant, and $[O_2]$ is the oxygen concentration. When the luminescence intensity ratio (I_0/I) is plotted against $[O_2]$, the slope of the plot gives K_{SV}. For luminescence oxygen sensors, deviation from this simple linear relationship is often observed, and the origin of this deviation has been discussed in detail.[12] Figure 3 shows the Stern–Volmer plot of the present oxygen sensor plate. The K_{SV} value was smaller than those obtained previously for pyrene-doped polymer films[4] and for a pyrene derivative anchored on nanoporous alumina films.[7–9] This fact is due to the difference in the lifetimes of the excited states of the dyes. We have estimated the lifetime of the excited state of the dye used in this experiment in the sensor plate to be 8 ns in nitrogen and 2 ns in air. For pyrene and its derivatives, the lifetime of the luminescence under oxygen-free conditions is known to be sufficiently long (>100 ns), and, therefore, oxygen quenching occurs efficiently before the excited state relaxes.

In conclusion, we have developed a novel luminescence oxygen sensor based on visual observation of a luminescence color change. Red luminescence was observed under oxygen-free conditions, and the color changed to blue at 5% oxygen content. The fact that no optical detection system is required makes this new sensor versatile for various applications.

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