Photoluminescent Oxygen Sensing on a Specific Surface Area Using Phosphorescence Quenching of Pt-Porphyrin

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A highly reliable optical sensor for oxygen-pressure measurements was developed. It was based on the phosphorescence quenching of platinum octaethylporphyrin incorporated in polymer films by oxygen. In this work, in order to overcome the shortcomings when the traditional spectrophotometer is used for oxygen sensing, the sensor behaviors were studied using a CCD-camera scanning technique. The Stern-Volmer plots of oxygen sensors showed improved linearity, compared with those of the traditional luminometer. The sensor was proved to have a good operational stability and <10% of the photobleaching was observed after storage for more than 1 year in the absence of light at room temperature.

Keywords Optical sensor, phosphorescence quenching, platinum octaethylporphyrin, Stern-Volmer plot, photobleaching

Optical sensors using photoluminescent molecules for oxygen-concentration measurements have received considerable attention in recent years because of their superior properties compared to a Clark electrode;¹ they are free from electromagnetic interference, inexpensive and capable of remote sensing and invasive detection for *in vivo* measurements, and do not require oxygen consumption. Several types of oxygen sensors have been developed based on thermoluminescence², chemiluminescence³ or photoluminescence quenching.⁴⁻⁶ Optical sensors based on photoluminescence quenching usually need to measure the luminescence intensity^{7,8} or lifetime⁹ of an organic dye immobilized in a polymer film that is changed by the concentration of the analyte. However, in the development of an optical oxygen sensor, the detection method and the film-preparation method are crucial factors as well as the choice of dye and matrix material.¹⁰

In the case of the conventional luminescence intensity measurement, there are severe problems concerning calibration procedures and long-term reliability. The fluorescent intensity may vary due to the excitation intensity, light losses in fibers and photobleaching of the probe, as well as changes in light-scattering or -absorption characteristics of the sample. Thus, while fluorescent-intensity methods may yield almost perfect results in an optically clean environment, their use in most sensing applications, like blood or microbial cultures, is severely limited. Especially, in order to apply a pressure-sensitive coating (PSC) to aerodynamic fields, such as wind-off and wind-on tests and in-flight environment, the luminescence value must be measured for every point on the model, because illumination varies

over the different surfaces of the model and changes with the model movement. These nonintrusive global pressure measurements cannot be easily accomplished using the laser-induced intensity technique, which scans only at one point or line. Recently, a charge-coupled device (CCD) camera scanning technique has been developed in order to detect and image oxygen pressure and/or oxygen pressure distribution on the surface of interest.¹¹⁻¹³ Such a pressure-mapping technique using photoluminescent quenching offers a potential saving in time and expense for wind-tunnel test over conventional transducer.

In the present work, an intensity measurement using the CCD camera technique (video capturing method) was applied to measure the oxygen pressure on a specific surface area. This promising method of oxygen detection involves optical measurements of phosphorescence quenching of platinum octaethylporphyrin (PtOEP), a strongly phosphorescent dye, by oxygen. This method proved to be suitable for the entire range of aerodynamic and environmental oxygen pressure.

The objectives in this study were to develop PSC materials and their applications to luminescent pressure measurements with high reliability for aerodynamic facilities.

Theory

Oxygen-pressure measurements using PSC samples are based on a quenching phenomenon by oxygen, an active quencher of phosphorescence. In contrast to fluorescence, phosphorescence is a delayed emission, typically with a longer lifetime (from 10⁻³ s to some seconds). From the standpoint of the optical-sensing application, the most interesting fact is that the excited

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Fig. 1 Cross section of a PSC sample consisting of a polymer matrix where PtOEP molecules are immobilized, and glass or steel is used as a substrate.

singlet and triplet states can be deactivated by quenching processes. The luminescence quenching of the PSC is represented by the Stern-Volmer equation¹⁴,

$$\frac{I_0}{I} = 1 + K_{SV} \cdot p_{O_2}, \quad (1)$$

where p_{O_2} is the oxygen pressure. I_0 and I are the luminescence intensities in the absence and presence of oxygen, respectively, and K_{SV} is the Stern-Volmer constant. At constant oxygen pressure, the luminescence intensity is proportional to the excitation-light intensity, I_{ex} . However, since it is difficult to measure I_{ex} precisely, the relative intensity, $I(\text{ref})$, at a known oxygen pressure, $p_{O_2}(\text{ref})$, is usually adopted. Another reason for using a reference pressure is that zero-oxygen conditions are difficult to achieve. Assuming that the temperature is constant,

$$\frac{I(\text{ref})}{I} = A + B \left[\frac{p_{O_2}}{p_{O_2}(\text{ref})} \right], \quad (2)$$

where constant A and B are

$$A = \frac{1}{1 + K_{SV} \cdot p_{O_2}(\text{ref})}, \quad B = \frac{K_{SV} \cdot p_{O_2}(\text{ref})}{1 + K_{SV} \cdot p_{O_2}(\text{ref})}$$

and $A + B = 1$.

For determining the oxygen pressure by PSC (2) is a fundamental equation.

Experimental

Chemicals

PtOEP was purchased from Porphyrin Products (Logan, UT, USA) and was used as received. A silicone polymer (GP-197) was obtained from Genesee Polymer Co. Poly(vinyl chloride) (PVC) and polystyrene (PS,

average M.W. 280000, GPC grade) were purchased from Wako Chemical Co. and Aldrich, respectively. All of the solvents used were of analytical grade, and were distilled and dried over a type-4 Å molecular sieve before use. The preparation of PtOEP-containing PSC films has already been reported elsewhere.¹⁵

Sensor construction

Figure 1 shows the oxygen-sensing element. It consists of a sensing layer with immobilized PtOEP molecules tightly coated on a steel or glass substrate. The oxygen-sensing films ($1.2 \times 2.6 \text{ cm}^2$) were pink-colored and optically transparent. When a sensing film was excited using visible light, luminescence can be emitted from a film. Based on the luminescence intensity of the surface of interest detected by a CCD camera, the oxygen pressure can be obtained.

Apparatus and procedure

The absorption spectra of films were measured using a Hitachi Model U-2000 spectrometer. A Hitachi Model F-4010 fluorescence spectrometer using visible excitation (150 W xenon lamp) was used for room-temperature phosphorescence (RTP) spectra measurements and photostability tests.

The experimental set-up used to characterize PSCs in the present work was provided by NAL (National Aerospace Laboratory, Chofu, Japan).^{15b} A PSC sample was placed inside a vacuum chamber with an optical access window. The pressure inside the chamber could be controlled and measured by a pressure transducer. The temperature on the coating sample was adjusted by a temperature controller and monitored by a thermometer. A highly stable xenon lamp (300 W, Hamamatsu

Fig. 2 Block diagrams of the assembly for an oxygen-pressure measurement. A, personal computer; B, excitation light source; C, excitation-light band pass filter; D, CCD camera; E, emission-light band pass filter; F, pressure chamber; G, manometer; H, temperature and pressure controllers; I, vacuum system.

Photonics) was used as an excitation source and an optical-fiber bundle was used in order to produce a spatially uniform irradiation beam. Visible light filtered by a 380 ± 50 nm bandpass filter passed into the chamber and excited the luminescent sample. The luminescence emission was collected with a lens, filtered by a 650 ± 20 nm bandpass filter, focused onto a photodetector and imaged onto a cooled CCD camera (C4880, Hamamatsu Photonics). The luminescence signal was sampled by a PC computer while the pressure was varied. The shooting condition was a camera iris with F16 and the exposure time was 150 ms. The number of total pixels was 512×512 . A brief block diagram of the instrument is shown in Fig. 2. Unless otherwise stated, all measurements were conducted at room temperature (293.2 K).

Results and Discussion

Spectral properties

As a typical instance for the oxygen-sensing films, the absorption and phosphorescence spectra of PS-based PSC are illustrated in Fig. 3. As can be seen in Fig. 3(a), the absorption spectrum has three peaks: the Soret band (382 nm) and two Q bands (502 and 535 nm), absorption peaks characteristic of metalloporphyrins. When excited at 535 nm, a intensive RTP peak was observed at 646 nm (Fig. 3(b)). The luminescence intensity at 646 nm under argon was largely quenched in air, and further quenched by oxygen, indicating that the present PSC samples are applicable to oxygen-pressure determination. Furthermore, a large Stoke's shift (>100 nm) of PtOEP immobilized in PSC completely excluded secondary scattered light from overlapping with the emission peak, and did not interfere with the RTP measurement. The absorption and RTP spectra of PSCs were the same as that of PtOEP in a solvent, and were not affected by the type of polymer binder. These results imply that there is no, or little, interaction between PtOEP molecules and the polymer binder.

Effect of a polymer matrix on Stern-Volmer plots

A polymer matrix may significantly affect the photophysical properties of the oxygen sensor through a complicated interaction between the oxygen-sensitive dye and the macromolecules of the matrix. Since the detailed role of the polymer matrix in controlling the

Fig. 3 Absorption and luminescence spectra of PS-based sensing film: (a) absorption spectrum and (b) luminescence spectra under different atmospheric conditions: a, argon; b, air; c, oxygen. Excitation wavelength was 535 nm.

photophysical processes is not well understood, in order to obtain a preferable oxygen sensor, it is basically a trial-and-error process to find the optimal choice and combination of a luminophore and a polymer. A robust, easily applicable and oxygen-permeable polymer can be a preferable matrix for an oxygen sensor. In this context, PVC, PS and polydimethyl siloxane (PDMS) GP-197 polymers were used as sensor matrices. Table 1 lists the material composition and physical properties of the sensing films.

To demonstrate the precision and linearity of the response of the oxygen sensor, it was compared with a traditional fluorescence spectrometer using the same film. In a previous study^{15c}, several oxygen-sensing

Table 1 Material composition and physical properties of PtOEP/polymer systems

Material composition			Mechanical property	Transparency property	Average thickness/ μm
Polymer	Substrate	Solvent			
PVC	steel	MEK	moderate	a little turbid	90
GP-197	glass	toluene	brittle	transparent	90
PS	steel	toluene	good	transparent	100

Fig. 4 Stern-Volmer plots for PSC sensor systems: ■, PVC; ●, PS; ▲, GP-197. Unless otherwise stated, $I(\text{ref})$ represents an RTP intensity at 100 kPa $p_{\text{O}_2}(\text{ref})$. Each point was obtained under steady response.

polymer films were prepared, and their sensing properties were studied using the traditional luminometer. When the traditional spectrophotometer was used for oxygen sensing of a film, the difference in the luminescence intensity at different points to be detected on the same sample was observed. In order to characterize the sensing film, therefore, it is preferable to average the intensities from many points on the sample. Stern-Volmer plots using a CCD camera-scanning technique showed improved linearity, compared with those of the traditional spectrophotometer.^{15c}

Stern-Volmer quenching plots of different polymer-type PSCs are shown in Fig. 4. A PDMS GP-197 matrix showed the highest oxygen quenching efficiency and the best sensitivity among the matrices in this study. For the GP-197 sample, A and B in Eq. (3) were 0.335 and 0.679, respectively, the correlation factor (R^2) was >0.997 and the sum of A and B was nearly 1. Table 2 summarizes the analytical features of PSC samples. On the other hand, for PS and PVC films, a lower oxygen quenching degree and nonlinearity in Stern-Volmer plots were observed. Usually, this nonlinearity is explained in term of a two-site model. Demas and co-workers¹⁶ have proposed a two-site model, the existence of two sites with different quenching constants occupied by dye molecules in the same oxygen-sensing film. One is accessible by oxygen, and the other is not. The latter is thought to be distributed in the same sensing film where it is little affected by oxygen. The enhanced linearity can be accomplished if mole fractions of two sites and their contribution to quenching of the sensing layer can be calculated. This result is being studied and will be reported later.

Effect of a polymer matrix on the response time

The GP-197 sample showed fast response times (t_{90} : 90% of total intensity change to occur): 10 s on going

Table 2 Analytical features of PtOEP/polymer systems as oxygen sensors

Pressure-sensitive coating	A	B	R^2
PVC-based coating	0.66	0.323	0.962
GP-197-based coating	0.335	0.679	0.998
PS-based coating	0.434	0.603	0.978

A and B are constants in Eq. (3) (see text), and R^2 , the correlation factor.

In this study, $I(\text{ref})$ in Eq. (3) means the room-temperature phosphorescence intensity at reference pressure, 100 kPa.

from fully oxygenated to fully de-oxygenated atmospheres and 50 s on going from oxygenated to de-oxygenated conditions. On the other hand, PS and PVC with a lower oxygen permeability showed rather inferior results concerning the response time, sensitivity and linearity. The response times (t_{90}) of PS and PVC films were 35–40 s on going from nitrogen to oxygen and 100 s on going from oxygen to nitrogen, respectively. These results were interpreted in terms of gas permeability. PDMS has a higher oxygen permeability than do other organic polymers, including PS and PVC (permeability coefficient for PDMS, PS and PVC are 367, 1.9–2.0 and 0.034×10^{13} [cm^3 (273.15 K; 1.013×10^5 Pa) cm]/[cm^2 s Pa]).¹⁷

Effect of the coating thickness

It is well known that the sensing properties of PSC, such as the response time and quenching efficiency, are strongly affected by the thickness of the polymer film. In theory, a thinner film needs less time for the oxygen inside of the film to reach equilibrium with the outside environment. However, thin films would produce a lower luminescence intensity. In a preliminary investigation, three GP-197 coatings with 9.7, 6.9 and 2.5 μm thickness were applied, and a thicker film showed a higher RTP intensity. However, the quenching efficiency of PSC seems to be little affected by differences in the coating thickness. These observations suggest that the O_2 quenching efficiencies are almost the same for 9.7, 6.9 and 2.5 μm thick GP-197 coatings. This thickness effect is being studied in detail.

Effect of temperature

Figure 5 shows the effect of temperature on the RTP intensity of the PS-based PSC. The temperature dependence of the PSCs was investigated from 253 to 333 K. As shown in Fig. 5, the intensity decreased approximately 1–2% per K over this range. Usually, the decrease in the intensity with increasing temperature is well known. An internal conversion deactivation of the excited triplet state via vibrational deactivation and collisions as well as triplet-triplet annihilation is a normal reason for a loss of phosphorescence intensity. In practice, the intensity became very small at higher temperatures, and constants A and B in Eq. (3) fluctuated

Fig. 5 Effect of the temperature on the intensity of a PS-based sensor system.

at higher temperatures. It is thought that a calibration of temperature effect is inevitable in determining the oxygen pressure of a specific area with a large temperature change due to air flow on the surface of the sample.

Photostability

Photostability tests were carried out by illuminating freshly prepared PSC samples continuously for 1 h. The fluorescence spectrometer with a 150-W xenon lamp was used for photostability tests. The results are shown in Fig. 6. Freshly prepared PSCs illuminated (excitation wavelength=535 nm) at room temperature showed >30% of photobleaching compared with that of nonilluminated samples (the photobleaching degrees were 45, 36 and 30% for PVC, PS and GP-197 films, respectively). Photobleaching tests were also carried out under different atmospheric conditions. As shown in Fig. 6, curves d and e, under air and Ar conditions, the GP-197 sample showed 11 and 17% photobleaching. In the case of after this period (for about 100–150 min from initial illumination), however, only minor decreases in the luminescence intensities were observed. Although the mechanism of the photobleaching or photodegradation of organic dye is currently not well understood, several attempts have been made to increase the photostability of the dye immobilized in PSC by matrix modification¹⁸ and the modification of the existing dyes.¹⁹ The sensing properties of PSC, such as the oxygen-quenching efficiency, were also affected by the length of the storage time, because PtOEP was gradually photobleached. After storage for more than one year, PSCs showed approximately a 10% decrease in luminescence intensity, compared with those of the original values. These results imply that a calibration should be carried out at least after 1 year of use.

Repeatability and reproducibility

Each pressure sensitivity test in this work was con-

Fig. 6 Effect of continuous illumination on the intensity of a PSC sensor systems: a, b and c, PVC, PS and GP-197 at room-temperature, respectively; d and e, GP-197 under Ar and air conditions, respectively. Photostability tests of sensor systems were taken under continuous illumination for 100 min; the data were normalized for an easy comparison.

Fig. 7 Effect of repeatability tests on the intensity reproducibility of a PS-based sensor system. The open squares and filled circles represent the first and second tests, respectively.

ducted two times, continuously. The first test was on going from low to high O_2 pressure; the second test was in the reverse direction for first test. The repeatability test result of PS-based sample is shown in Fig. 7. The positions at each pressure point in both intensities and Stern-Volmer plots showed little change for all PSC samples, indicating that the tests were very reproducible.

Long-term stability and repeatability tests were conducted after storage at room temperature for more than 1 year. The intensity decreased by <10%, compared with the original value. These observations probably result from a deterioration and bleaching of the sample.

In conclusion, a pressure-sensitive coating for optical measurements of oxygen have been prepared by incorporating a room-temperature phosphorescent dye, platinum octaethylporphyrin into several commercial polymer matrices. The oxygen-sensing properties of these materials were characterized by using a CCD-camera scanning technique. Modified Stern-Volmer plots of the pressure-sensitive coatings showed good linearity and operational repeatability. From a critical viewpoint, however, several problems remained unsolved. These include the lack of photostability, which is significant for long-term light illumination. Also, the effect of the temperature must be considered in calibrating the pressure-sensitivity data of PSC. Further studies involving the preparation and characterization of improved stable PSCs are in progress in our laboratory.

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