Biplanar Visualization of Oxygen Pressure by Sensory Coatings of Luminescent Pt–Porpholactone and –Porphyrin Polymers

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Luminescent oxygen sensory polymer coatings composed of platinum tetrakis(pentafluorophenyl)porpholactone and -porphyrin with poly(trimethylsilylpropyne) were prepared. Two luminescence peaks at 750 and 650 nm from the coating ascribed to the porpholactone and the porphyrin, respectively, were efficiently quenched with oxygen and were separately monitored to allow the simultaneous measurement of oxygen partial pressure distribution upon two planar surfaces.

Measurement of oxygen partial pressure or concentration is significant in various fields of science and engineering such as aerodynamics, medical studies, and environmental analyses.[1] Optical sensors for oxygen partial pressure (concentration) have been widely investigated. Luminescence from organic dye dispersed in a polymer coating under irradiation is often quenched by oxygen, and the quenching behavior obeys the Stern–Volmer equation.[2] Monitoring of the luminescence intensity leads to determination the oxygen partial pressure or concentration upon the polymer-coated surface. The optical sensor coating could visualize distribution of the oxygen partial pressure (air pressure) with a high spatial resolution upon a target body and a channel surface.[3] We coated an airplane model and the air flow channel of a polymer electrolyte fuel cell (PEFC) with poly(1-trimethylsilyl-1-propyne) (PMSP) containing platinum–tetrakis(pentafluorophenyl)porphyrine (PtPP) and successfully visualized oxygen pressure distribution on the surface of the airplane model in a cryogenic wind tunnel[4] and inside of the air flow channel of PEFC.[5]

Simultaneous measurement of oxygen pressure distribution on two parallel planes will be of importance for some applications such as the upper and lower surfaces of the inside of air flow channels. Sensing or visualizing oxygen partial pressure or concentration on two surfaces simultaneously could be effective in designing a high efficient fluid channel, e.g., internal structures of micro-electromechanical systems (MEMS) and PEFC. However, to the best of our knowledge, there has been no report of optical sensor coatings for the biplanar visualization of oxygen pressure.

In this paper, we report for the first time a simultaneous biplanar oxygen sensory system by using two luminescent dye polymer coatings. The coatings were excited under the same wavelength-UV irradiation and emitted two strong luminescence peaks separated from each other by ca. 100 nm, both of which were quenched efficiently with oxygen. We used, based on our previous paper, high gas-permeative PMSP[6] as the polymer matrix of coating and PtPP as the oxygen sensitive dye molecule. Platinum tetrakis(pentafluorophenyl)porpholactone (PtPL)[7] was chosen as the second oxygen-sensitive dye molecule, because its luminescent peak was apart from the luminescence of PtPP and its oxygen sensitivity was high in the oxygen partial pressure range of 0–21 kPa. This paper also reports one successful example of simultaneously visualizing the biplanar oxygen pressure distributions two parallel coatings.

A 10 mL portion of a toluene solution of PtPL or PtPP (2.5 mg) and PMSP (weight average molecular weight $M_w = 5.2 \times 10^4$ and $M_w/M_n = 1.4$, 60 mg) was spray-coated onto a nonluminescent glass plate with an air brush for a coating thickness of ca. 2 μm. The coatings were tough, smooth, transparent, and magenta-colored for the PtPL coating and red-colored for the PtPP coating.

Steady-state luminescence and excitation spectra of the PtPL/PMSP and PtPP/PMSP coatings on the nonluminescent glass plates were measured. The polymer-coated plate was mounted at a 45° angle in a fully partitioned quartz cell (Chart 1). Oxygen streams (in the oxygen partial pressure range of 0–21 kPa) were prepared by controlling the flow rates of the oxygen and nitrogen gases and by passing them through a gas mixing chamber. The total gas pressure was maintained at 100 kPa. It required less than a few seconds to achieve equilibrium in the luminescence for both coatings. All the experiments under a series of oxygen partial pressures were performed at 25 °C controlled by a thermocontroller.

Soret bands of absorption spectra of PtPL and PtPP were at the same peak 395 nm. However, Q-band for PtPL was at 575 nm and for PtPP were at 506 and 538 nm, which did not overlap their absorptions. Luminescence spectra of the PtPL/PMSP and the PtPP/PMSP coatings set as in Chart 1, under irradiation (395 nm) are shown in the inset of Figure 1 and are not overlapping with observed luminescent peaks of two dyes. The luminescent peaks at 750 and 650 nm were ascribed to PtPL and PtPP, respectively, similar to the individual toluene solutions. We used the individual PtPL/PMSP coating and PtPP/PMSP coating in the following experiments.

The luminescence intensities from the PtPL/PMSP and PtPP/PMSP coatings decreased with oxygen partial pressure from 0 to 21 kPa (Figure 1 inset), representing quenching of the luminescences with oxygen. The two luminescence peaks were separated enough (ca. 100 nm) to monitor the luminescence intensity changes with oxygen partial pressure without any influence of other luminescence changes.

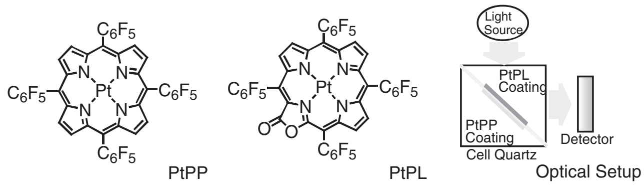

Chart 1.

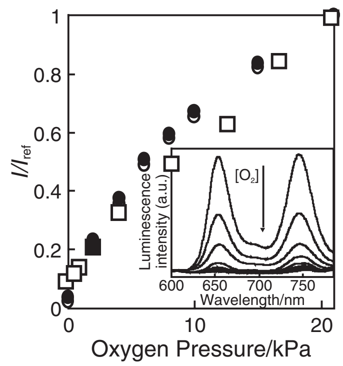

Figure 1. Normalized luminescence intensity (I/I_{ref}) vs. oxygen partial pressure, the Stern–Volmer plots for the PtPL/PMSP coating (○) and the PtPP/PMSP coating (●) monitored with a spectrofluorophotometer at 750 and 650 nm, respectively, and for the PtPP/PMSP coating monitored with a CCD camera (□). Inset: Luminescence spectra of the PtPL/PMSP and PtPP/PMSP coatings under oxygen partial pressure of 0–21 kPa, $\lambda_{ex} = 395$ nm, at 25 °C.

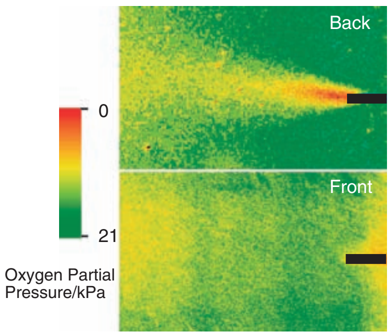

Figure 2. Biplanar visualization image of oxygen partial pressure for the rectangle tube composed of the PtPL/PMSP- and the PtPP/PMSP-coated plates under ambient condition with nitrogen flowing from a needle. The PtPP/PMSP-coated back plate and the PtPL/PMSP-coated front plate with the nitrogen gas blowing of the pressure (10 kPa).

Figure 1 shows the relationship between the luminescence intensity (I and I_{ref} at oxygen partial pressure of 21 kPa) and oxygen partial pressure and the Stern–Volmer plots for the PtPL/PMSP and PtPP/PMSP coatings. The Stern–Volmer plots showed a good functional correlation in the oxygen partial pressure range 0–21 kPa, which could be applicable to oxygen partial pressure visualization with reasonable sensitivity. The Stern–Volmer plots were not influenced by overlapping of the two coatings, by using both a spectrofluorophotometer and a CCD camera, suggesting a simultaneous visualization of oxygen distribution upon surfaces of the two coatings.

Figure 2 displays an example of biplanar visualization images of oxygen partial pressure obtained from a test using the PtPL/PMSP- and PtPP/PMSP-coated rectangle tube[8] under blowing nitrogen gas from a needle, using a CCD camera under UV irradiation at 405 nm and different emission filters (viewed through a 650 ± 50 nm bandpass filter for the back PtPP/PMSP plate and through 700 nm longpass filter for the front PtPL/PMSP plate). During nitrogen flow through the needle, the luminescence from the PtPP/PMSP coating at the point of nitrogen impact became strongly brighter in response to the local decrease of oxygen partial pressure, tracing an image of the nitrogen impact area (Figure 2). The nitrogen flow was detected to the PtPL/PMSP-coated front plate, and the luminescence from the PtPL coating became brighter widely at the end of tube, visualizing planar distribution of the oxygen pressure decrease or the nitrogen gas spread. Figure 2 would be effective data to analyze the gas flow distribution.

Biplanar visualization of oxygen partial pressure using the PtPP/PMSP and PtPL/PMSP coatings could be a tool for aerodynamic studies.

This work was partially supported by the HiPer-FC Project from NEDO, Japan, and the Global COE Program at Waseda University from MEXT, Japan. The authors thank Prof. J. Inukai of University of Yamanashi and Dr. T. Suga of Waseda University for their discussions of this work.

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8 Supporting Information is available electronically on the CSJ-Journal Web site, http://www.csj.jp/journals/chem-lett/index.html.