Transactions of the Materials Research Society of Japan 29 [3] 923-926 (2004)

The Response Characteristic of Optical Carbon Dioxide Sensor Using pH Indicator Immobilized in Ethyl Cellulose Film

Naoki Nakamura* and Yutaka Amao
Department of Applied Chemistry, Oita University, Dannoharu 700, Oita 870-1192, Japan
Fax: 81-97-554-7972, e-mail: nankin55@cc.oita-u.ac.jp

A new optical CO_2 sensor based on the overlay of the CO_2 induced absorbance change of pH indicator α-naphtholphthalein with fluorescence of tetraphenylporphine (TPP) was developed and its CO_2 sensing characteristics were studied. The observed fluorescence intensity from TPP at 655 nm increased with increasing CO_2 concentration. The I_{100}/I_0 value that shows the sensitivity of sensor containing 13.4 mmol dm^{-3} α-naphtholphthalein concentration is estimated to be 168, where I_0 and I_{100} represent observed fluorescence intensities from a film exposed to argon and CO_2 saturated condition, respectively. The response time of the sensing film containing 13.4 mmol dm^{-3} α-naphtholphthalein concentration was 3.8 s for switching from argon to CO_2 and the recovery time of the sensing film also was 6.8 s for switching from CO_2 to argon.

Key words: optical CO_2 sensor, α-naphtholphthalein, tetraphenylporphine

1. INTRODUCTION

CO_2 measurement techniques are used in various fields, such as chemical monitoring, clinical breath monitoring, and environmental monitoring. In recent years, optical CO_2 sensors based on the colorimetric or fluorometric changes of pH indicators or CO_2 sensitive dyes have been developed [1-12].

Optical CO_2 sensors are classified into two types. One is the sensor based on the colorimetric change of a pH indicator, such as thymolsulfonphthalein (thymol blue), phenolsulfonphthalein (phenol red), cresol red, and so on [1-4]. The other sensor is based on the CO_2-induced fluorescence change of a fluorescent dye such as 1-hydroxypyrene trisulfonate and ruthenium (II) complexes [5-9]. The CO_2 sensor based on the fluorescence intensity changes of a dye is a simple and convenient method. For the fluorescent phenol-based CO_2 sensor, the fluorescence intensity change with the shift of fluorescent dye from its fluorescent form into the non-fluorescent form is used. However, the number of compounds for which fluorescence intensity is changed by CO_2 is extremely limited. To solve this problem, an optical CO_2 sensor with a combination of a colorimetric change of pH indicator and fluorescent dye (internal reference dye) is developed [10-12]. The fluorescence of the internal reference dye is unchanged by CO_2. In principle, this type of CO_2 sensor will be developed by the wavelength overlap between the fluorescence band of the internal reference dye and the absorption band, which is changed by CO_2, of the pH indicator.

We described the development of CO_2 sensor based on the overlay of the CO_2 induced absorbance change of α-naphtholphthalein with the fluorescence of tetraphenylporphine (TPP) and the response characteristic of CO_2 sensor. As TPP shows the red fluorescence with ultra-visible light, the conventional optical CO_2 sensor using cheap black light will be developed.

2. MATERIALS AND METHODS

Ethyl cellulose (ethoxyl 48%), tributyl phosphate, and α-naphtholphthalein were obtained from Wako Pure Chemical Co. Ltd. Tetraphenylporphine (TPP) and tetraoctylammonium hydroxide was obtained from Tokyo Chemical Industry Co. Ltd. Non-fluorescence glass slides were obtained from Mitsubishi Chemical Co. Ltd. The other reagents were of the highest grade available. To improve the response and recovery times, and sensitivity of the sensor based on the pH indicator immobilized polymer film, tributyl phosphate was used as a plasticizer [1-3].

The CO_2 sensing film was the composition CO_2 indicator dye / phase-transfer agent / polymer / plasticizer / solid support / reference fluorescence dye / polymer, i.e. α-naphtholphthalein / tetraoctylammonium hydroxide / ethyl cellulose / tributyl phosphate / non-fluorescent glass slide / TPP / polystyrene. At first, a mixture of 1.10 mmol dm^{-3} α-naphtholphthalein, 0.7 mol dm^{-3} tetraoctylammonium hydroxide, 0.25 g ethyl cellulose and 82 mmol dm^{-3} tributyl phosphate in 2.25 ml toluene-methanol solution was casted on the one side of the glass slide (1.4 x 5.0 cm). Thickness of the film was ca. 5.0 μm by use of a micron-sensitive caliper. The film was dried at room temperature and then a mixture of 0.25 g polystyrene and 1.42 mmol dm^{-3} TPP in 4 ml toluene solution was casted on the opposite side of the glass slide. The thickness of TPP immobilized in polystyrene film was ca. 10 μm. α-Naphtholphthalein and TPP immobilized film defined as CO_2 sensing film.

Fluorescence spectra of the CO_2 sensing film were measured using a Shimadzu RF5300-PC fluorescence spectrometer with a 150 W xenon lamp as an excitation light source. Excitation and emission bandpasses were 3.0 nm. The sample substrate was mounted at 45° angle in the quartz cell to minimize light scattering from the sample and substrate. Different CO_2 standards (in the range 0-100%) in a gas stream were produced by controlling the flow rates of CO_2 and argon gases entering a mixing chamber. The total pressure was maintained at 760 Torr (1 Torr = 133.322 Pa). All the experiments were carried out at room temperature.

3. RESULTS AND DISCUSSION

The CO_2-induced fluorescence spectrum change of the CO_2 sensing film using α-naphtholphthalein when excited at 350 nm under various CO_2 concentrations is shown in Fig.1. Fluorescence intensity of CO_2 sensing film increased with increasing CO_2 concentration. On the other hand, the fluorescence change of TPP immobilized in polystyrene film was not caused by CO_2 gas. These results indicated that the fluorescence of TPP was not affected by the CO_2. Thus, an optical CO_2 sensor based on the fluorescence intensity change of TPP resulting from the absorption changes of α-naphtholphthalein with CO_2 was developed.

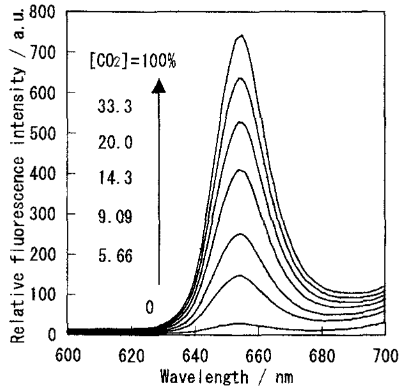

Fig. 1. Fluorescence spectrum change of CO_2 sensing film containing 13.4 mmol dm^{-3} α-naphtholphthalein concentration under various CO_2 concentrations. The excitation wavelength was 350 nm.

The I_{100}/I_0 values represented the sensitivity of the sensing film when α-naphtholphthalein concentration changed in ethyl cellulose film are shown in Table I, where I_0 and I_{100} represent the observed fluorescence intensities from a sensing film expose to argon and CO_2 saturated condition, respectively. In general, the sensor is a suitable sensing device when the I_{100}/I_0 value is more than 3.0. This result indicates that the sensor film with 13.4 mmol dm^{-3} α-naphtholphthalein in ethyl cellulose has highly sensitivity compared with the other sensor films. The sensitivity of sensing film depends on the number of α-naphtholphthalein molecules in the ethyl cellulose film. Since CO_2 is excess to α-naphtholphthalein molecules, the observed signal change is saturated under lower CO_2 concentration. The I_0/I_{100} value of sensing film containing lower concentration of α-naphtholphthalein is small. Since α-naphtholphthalein molecules are excess to CO_2, on the other hand, the observed signal change also is saturated under higher CO_2 concentration. The I_0/I_{100} value of sensing film containing higher concentrations of α-naphtholphthalein also is small. Thus, the I_0/I_{100} value of sensing film has maximum point at 13.4 mmol dm^{-3} of α-naphtholphthalein.

Table I. I_{100}/I_0 values of CO_2 sensing films.

[α-Naphtholphthalein] /mmol dm^{-3}	I_{100}/I_0
3.41	3.43
5.16	7.01
13.4	168
34.9	107
58.0	51.2

[α-Naphtholphthalein] is the concentration in ethyl cellulose film. I_0 and I_{100} are fluorescence intensities of sensing film exposed to argon and CO_2 saturated condition, respectively. The excitation and emission wavelengths are 350 and 655 nm, respectively.

The reaction process between α-naphtholphthalein and CO_2 is described as shown in Eq. (1);

$$\{Q^+T^- \cdot xH_2O\} + CO_2 \underset{}{\overset{K}{\rightleftharpoons}} \{Q^+HCO_3^- \cdot (x\text{-}1)H_2O \cdot HT\} \quad (1)$$

where $\{Q^+T^- \cdot xH_2O\}$ is the ion pair formed between the tetraoctylammonium cation Q^+ and the deprotonated form of α-naphtholphthalein T^-. K is equilibrium constant. The ratio of the concentrations of the α-naphtholphthalein in its protonated and deprotonated forms is proportional to the concentration of CO_2. In contrast, the observed fluorescence intensity at 655 nm increased in proportion to the transmittance (T) of the deprotonated form of α-naphtholphthalein (T^-). The T of the deprotonated form of α-naphtholphthalein is expressed as follows:

$$T = 10^{-\varepsilon d[\{Q^+T^- \cdot xH_2O\}]} \quad (2)$$

where ε and d are molar extinction coefficient and thickness of sensor film, respectively. Thus, $-\varepsilon d$ is constant and can be replaced by A. The relationship between fluorescence intensity I and T is expressed as follows:

$$I = BT = B10^{A[\{Q^+T^- \cdot xH_2O\}]} \quad (3)$$

where B is a constant. The concentration of $\{Q^+T^- \cdot xH_2O\}$ was expressed as Eq. (4):

$$[\{Q^+T^- \cdot xH_2O\}] = -KA[\{Q^+T^- \cdot xH_2O\}]_0/(K + [CO_2]) \quad (4)$$

Here, $KA[\{Q^+T^- \cdot xH_2O\}]_0$ is replaced by a constant C. Then Eq.3 is re-written to Eq. (5).

$$I = B10^{(-C/(K+[CO_2]))} \quad (5)$$

The observed fluorescence intensity change by CO_2 was expressed to be I/I_0. Thus, the relationship between observed fluorescence intensity at 655 nm and CO_2 concentration was following the Eq. (6).

$$I/I_0 = 10^{(-C(1/(K+[CO2])-(1/K))} \qquad (6)$$

Figure 2 shows the plot of I/I_0 versus CO_2 concentration. The CO_2 sensing films contain various α-naphtholphthalein concentrations. In Fig. 2, the solid line is the best-fit using Eq. (6). The correlation factor of the plots, r^2, is estimated to be 0.995 by the least squares method. This result indicates that CO_2 sensor film is calibrated by Eq. (6).

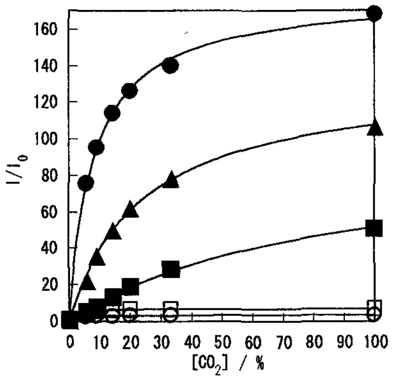

Fig. 2. The I/I_0 value of CO_2 sensing films under various CO_2 concentrations. The excitation and emission wavelengths were 350 and 655 nm, respectively. The solid line is the best-fit using Eq. (6).
[α-Naphtholphthalein]: ○ ;3.41, □ ;5.16, ●;13.4, ▲;34.9, and ■;58.0 mmol dm^{-3}.

The C and K values calculated by fitting using Eq. (6). The C and K values increased with increasing α-naphtholphthalein concentration in ethyl cellulose film are summarized in Table II. Both the C and K values represented response of sensing film. When the C and K values are higher, the response time of sensing film is rapid. When the C and K values are lower, in contrast, the recovery time of sensing film is rapid.

Table II. The C and K values of CO_2 sensing films

[α-Naphtholphthalein]/ mmol dm^{-3}	C	K
3.41	0.612	1.12
5.16	11.4	1.61
13.4	1430	8.02
34.9	3150	23.7
58.0	7370	79.5

[α-Naphtholphthalein] is the concentration in ethyl cellulose film. C and K are $KA[\{Q^+T^- \cdot xH_2O\}]_0$ and equilibrium constant.

An operational stability test was conducted by reading the fluorescence intensity signal of CO_2 sensing film containing 13.4 mmol dm^{-3} α-naphtholphthalein concentration while CO_2 and argon saturated conditions were alternated for 400 s as shown in Fig. 3 as an example. The response and recovery times for optical CO_2 sensor are defined the 90% response and recovery times exhibited by the sensors when they are exposed to an alternating atmosphere of CO_2 and argon, respectively. The response time of the sensing film was 3.8 s for switching from argon to CO_2 and the recovery time of the sensing film was 6.8 s for switching from CO_2 to argon. The signal changes were fully reversible and hysterisis was not observed during the measurements.

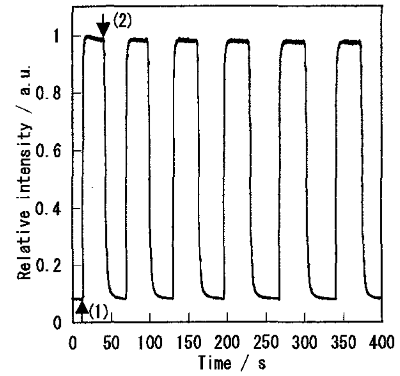

Fig. 3. Response time and relative intensity change for CO_2 sensor containing 13.4 mmol dm^{-3} α-naphtholphthalein concentration from on switching between CO_2 (1) and argon saturated condition (2). The excitation and emission wavelengths were 350 and 655 nm, respectively.

The response and recovery times of CO_2 sensing films are summarized in Table III. From Table III, the sensing film with 3.41 mmol dm^{-3} α-naphtholphthalein in ethyl cellulose has fast response time compared with those of the other sensing films. The sensing film with 58.0 mmol dm^{-3} α-naphtholphthalein in ethyl cellulose has rapid recovery time compared with those of the other sensing films. These results also indicate the same tendency as the C and K values obtained by curve fitting using Eq. (6).

Table III. The response and recovery times of CO_2 sensing films

[α-Naphtholphthalein]/ mmol dm^{-3}	$[Ar]100\% \rightarrow [CO_2]100\%/s$	$[CO_2]100\% \rightarrow [Ar]100\%/s$
3.41	3.2	6.4
5.16	3.9	5.7
13.4	3.8	6.8
34.9	9.9	5.5
58.0	23.9	4.7

[α-Naphtholphthalein] is the concentration in ethyl cellulose film. The time for switching from CO_2 to argon defined as response time. The time for switching from argon to CO_2 defined as recovery time.

The previously reported values for the response and recovery times of optical CO_2 sensors using pH indicator in polymer film were over 1 min [1,2,8]. These results indicate that CO_2 sensing film using α-naphtholphthalein and TPP has fast response and recovery times.

4. CONCLUSION

In this work, the optical CO_2 sensor based on the combination of α-naphtholphthalein and TPP developed and its CO_2 sensing characteristics were studied. The observed fluorescence intensity of sensing film at 655 nm increased with the increasing CO_2 concentration. The I_{100}/I_0 value of sensing film with 13.4 mmol dm^{-3} α-naphtholphthalein concentration is estimated to be 168. The response and recovery times of the sensing film with 13.4 mmol dm^{-3} α-naphtholphthalein concentration were 3.8 s for switching from argon to CO_2 and 6.8 s for switching from CO_2 to argon, respectively.

ACKNOWLEDGMENT

This work is partially supported by "Molecular Sensors for Aero-Thermodynamic Research (MOSAIC) ", the Special Coordination Funds from the Ministry of Education, Culture, Sports, Science and Technology Agency.

References

[1] A. Mills and L. Monaf, *Analyst.*, 121, 1-6 (1986).
[2] A. Mills, Q. Chang and H. M. McMurray, *Anal. Chem.*, 64, 1383-89 (1992).
[3] A. Mills, A. Lepre and L. Wild, *Sens. Actuators, B.*, 38-39, 419-25 (1997).
[4] Y. Kawabata, T. Kamichika, T. Imasaka and N. Ishibashi, *Anal. Chim. Acta.*, 219, 223-29 (1989).
[5] M. D. Marazuela, M. C. Moleno-Bondi and G. Orellana, *Sens. Actuators, B.*, 29, 126-31 (1995).
[6] Z. Zhujun and R. Seitz, *Anal. Chim. Acta.*, 160, 305-09 (1984).
[7] O. S. Wolfbeis, L. J. Weis, M. J. P. Leiner and W. E. Ziegler, *Anal. Chem.*, 60, 2028-30 (1988).
[8] A. Mills and Q. Chang, *Analyst*, 118, 839-43 (1993).
[9] C. Munkholm, D. R. Walt, and F. P. Milanovich, *Talanta.*, 35, 109-12 (1988).
[10] N. Nakamura and Y. Amao, *Anal Bioanal Chem.*, 376, 642-46 (2003)
[11] N. Nakamura and Y. Amao, *Bull. Chem. Soc. Jpn.*, 76, 1459-62 (2003)
[12] N. Nakamura and Y. Amao, Sensors and *Actuators B.*, 92, 98-101 (2003)

(Received October 10, 2003; Accepted January 31, 2004)