Bull. Chem. Soc. Jpn., 75, 2697–2698 (2002)

Controlling the Oxygen-Sensitivity of 1-Pyrenedecanoic Acid Chemisorption Layer onto Anodic Oxidized Aluminium Plate

Yuki Fujiwara and Yutaka Amao*

Department of Applied Chemistry, Oita University,
Dannoharu 700, Oita 870-1192

(Received June 25, 2002)

Controlling the oxygen-sensitivity of optical sensor using layers of 1-pyrenedecanoic acid and myristic acid co-chemisorbed onto anodic oxidized aluminium plate was attempted. The oxygen-sensitivity was controlled by varying the molar ratio of myristic acid to 1-pyrenedecanoic acid.

Oxygen sensing techniques are applied to various fields, which include chemical, clinical analysis and environmental monitoring.[1–3] Several methods for oxygen measurement, including methods based on titration,[4] amperometry,[5] chemiluminescence,[6] and thermoluminescence,[7] have been reported. Among these methods, the most popular method has been the amperometric method using an oxygen electrode.[5] Recently, a variety of devices and sensors based on luminescence quenching of organic dyes, polycyclic aromatic hydrocarbons immobilized in an oxygen permeable polymer (e.g., silicone polymer and polystyrene) were developed to measure oxygen concentration.[8–10] As organic dyes directly interact with polymer molecules, the properties of sensing films depend strongly on the properties of polymer matrices. Chemisorption layers are formed using spontaneous binding between a mercapto group and a metal surface (e.g., Au, Ag, or Pt)[11] or between a carboxyl group and a metal oxide surface (e.g., Al_2O_3, Fe_2O_3, or TiO_2).[12] As the sensing dyes are arranged on the solid surface directly by using this technique, a highly sensitive device for oxygen sensing will be obtained by using chemisorption layers. On the other hand, among polycyclic aromatic hydrocarbons, pyrene derivatives display strong fluorescence with high quantum yield and long lifetime.[13] Among pyrene derivatives, pyrene with a carboxyl group is suitable for optical oxygen sensing devices using chemisorption layer because of the formation of a stable layer onto anodic oxidized aluminium and carboxyl group of 1-pyrenedecanoic acid. We previously reported an optical oxygen sensor using 1-pyrenedecanoic acid chemisorption layer onto anodic oxidized aluminium plate.[15] However, the control of the oxygen-sensitivity of this sensor has not been attained yet.

In this work we describe controlling the oxygen-sensitivity of optical sensor using layers of 1-pyrenedecanoic acid and myristic acid co-chemisorbed onto anodic oxidized aluminium plates.

Experimental

1-Pyrenedecanoic acid and myristic acid were obtained from Wako Chemical Ltd (Osaka, Japan). All the other reagents were the highest grade available. Anodic oxidized aluminium plate was electrically prepared by anodic oxidation of the surface of aluminium plates (1.2 × 4.0 cm) in dilute sulfuric acid. The co-chemisorbed layer of 1-pyrenedecanoic acid and myristic acid onto anodic oxidized aluminium plate was prepared as follows. An anodic oxidized aluminium plate was immersed in methanol solution with different molar composition ratios of 1-pyrenedecanoic acid to myristic acid at room temperature for 10 min.

1-Pyrenedecanoic acid and myristic acid layer co-chemisorbed onto the anodic oxidized aluminium plate showed fluorescence at 376 and 396 nm, when excited at 340 nm. The fluorescence spectra shape of 1-pyrenedecanoic acid and myristic acid layer co-chemisorbed was almost the same as the 1-pyrenedecanoic acid layer chemisorbed. The fluorescence intensities of the 1-pyrenedecanoic acid and myristic acid co-chemisorbed layer depended on the oxygen concentration. This result indicates that the fluorescence of 1-pyrenedecanoic acid onto anodic oxidized aluminium plate was quenched by oxygen. The ratio I_0/I_{100}, where I_0 and I_{100} represent the detected fluorescence intensities from a substrate exposed to 100% argon and 100% oxygen, respectively, is used as an indicator of the sensitivity of the sensing film. In general, a sensor with I_0/I_{100} of more than 3.0 was a suitable oxygen-sensing device.[15] The I_0/I_{100} value of 1-pyrenedecanoic acid chemisorbed layer is estimated to be 34.2. The I_0/I_{100} values of chemisorption layers with different molar composition ratios of 1-pyrenedecanoic acid to myristic acid are summarized in Table 1. At a composition ratio of one 1-pyrenedecanoic acid to ten myristic acids, the I_0/I_{100} attained its maximum value and then the ratio decreased with increase in the molar ratio of myristic acid to 1-pyrenedecanoic acid. The reason why the I_0/I_{100} value was maximum at composition ratio of one 1-pyrenedecanoic acid to ten myristic acid is as follows. For the optical oxygen sensor using pyrene, the interaction between photoexcited pyrene molecules is strong and the energy transfer between photoexcited pyrene molecules reduces the oxygen quenching efficiency of pyrene. At the composition ratio of one 1-pyrenedecanoic acid to ten myristic acids, the energy transfer between photoexcited 1-pyrenedecanoic acid molecules may be suppressed by myristic acid molecules and so the oxygen quenching efficiency of photoexcited 1-pyrenedecanoic acid may be improved. These results indicate that the oxygen-sensitivity of the 1-pyrenedecanoic acid layer is controlled by the co-chemisorption of myristic acid.

Figure 1 shows Stern–Volmer plots of 1-pyrenedecanoic acid and myristic acid co-chemisorbed layer. Demas et al. reported a

Table 1. The I_0/I_{100}, K_{SV} and f Values Chemisorption Layers with Different Molar Composition Ratios of Myristic Acid to 1-Pyrenedecanoic Acid

Ratio of myristic acid to 1-pyrenedecanoic acid	I_0/I_{100}	$K_{SV}/\%^{-1}$	f
0	34.2	0.97	0.98
10	47.4	1.20	0.99
50	20.8	0.59	0.97
100	20.0	0.53	0.97
200	5.32	0.34	0.79

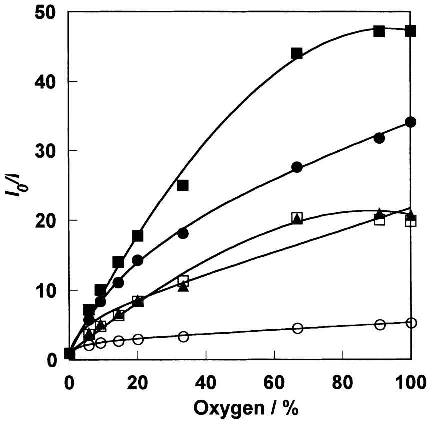

Fig. 1. Stern–Volmer plots for the co-chemisorbed layer of 1-pyrenedecanoic acid and myristic acid onto anodic oxidized aluminium plate. The ratios of myristic acid to 1-pyrenedecanoic acid: 0 (●), 10 (■), 50 (▲), 100 (□), and 200 (○).

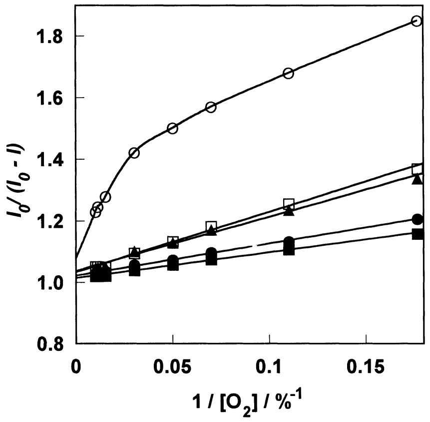

Fig. 2. Modified Stern–Volmer plots for the co-chemisorbed layer of 1-pyrenedecanoic acid and myristic acid onto anodic oxidized aluminium plate using Eq. 2. The ratios of myristic acid to 1-pyrenedecanoic acid: 0 (●), 10 (■), 50 (▲), 100 (□), and 200 (○).

two-site model in which the oxygen sensing film has different oxygen-accessible sites.[16] There are two oxygen accessible sites in the sensing film; one is an oxygen easily accessible site and the other is an oxygen difficult accessible site. According to this model, each site has its own individual characteristic quenching constant. Since the observed fluorescence intensity is the sum of emission from different oxygen-accessible sites with their own characteristic quenching constants, the Stern–Volmer relationship is given by

$$I_0/I = [\Sigma(f_n/(1 + K_{\mathrm{SV}n}[\mathrm{O_2}]))]^{-1} \quad (1)$$

where n is an integer. f_n is the fractional contribution to each oxygen accessible site, and $K_{\mathrm{SV}n}$ is the quenching constant for each site. Assuming that there are k accessible (and n-k non-accessible) molecules with the same K_{SV}, one can then express Eq. 1 as

$$I_0/(I_0 - I) = 1/(f K_{\mathrm{SV}} [\mathrm{O_2}]) + 1/f \quad (2)$$

where $f = \Sigma f_i$. This is the maximum mole fraction of dye molecules that are accessible to oxygen.[17] If only a single class of dye molecules with the same accessibility to oxygen is present, $1/f$ in Eq. 2 should be 1. Figure 2 shows the modified Stern–Volmer plot for 1-pyrenedecanoic acid and myristic acid co-chemisorbed layer plotted using Eq. 2. The plot of $I_0/(I_0 - I)$ against $1/[\mathrm{O_2}]$ showed good linearity, which enhanced compared with the plot of I_0/I against $[\mathrm{O_2}]$, exclusive of the composition ratio of one 1-pyrenedecanoic acid to two hundred myristic acids. In order to obtain the f value, the regression line is extrapolated to $1/[\mathrm{O_2}] = 0$. The value of f indicates the oxygen quenching mole fraction of the 1-pyrenedecanoic acid molecule and $f = 1$ means that all excited 1-pyrenedecanoic acid molecules are quenched equally by oxygen. For 1-pyrenedecanoic acid chemisorbed layer, the f and K_{SV} values were 0.98 and 0.97 $\%^{-1}$, respectively. The K_{SV} and f values of chemisorption layers with different molar composition ratios of 1-pyrenedecanoic acid and myristic acid are summarized in Table 1. At composition ratio of one 1-pyrenedecanoic acid to ten myristic acids, the K_{SV} attained a maximum value and this then decreased with increase the molar ratio of myristic acid to 1-pyrenedecanoic acid. As the myristic acid chemisorbed layer controlled the oxygen-diffusion onto anodic oxidized aluminium surface, the K_{SV} value of the 1-pyrenedecanoic acid layer is controlled by the co-chemisorption of myristic acid.

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

References

1 C. Prininger, I. Klimant, and O.S. Wolfbeis, *Anal. Chem.*, **66**, 1841 (1994).

2 R. C. Martin, S. F. Malin, D. J. Bartnil, A. M. Schilling, and S. C. Furlong, *Proc. SPIE.*, **2131**, 426 (1994).

3 M. J. Atkinson, F. I. M. Thomas, N. Larson, E. Terrill, K. Morita, and C. C. Lium, *Deep-Sea Res. I.*, **42**, 761 (1995).

4 D. A. Skoog, D. M. West, and F. J. Holler, “Fundamentals of Analytical Chemistry,” Saunders, Philadelphia (1988), p. 344.

5 L. C. Clark, *Trans. Am. Artif. Intern. Organs.*, **2**, 41 (1956).

6 T. M. Freeman and W. R. Seitz, *Anal. Chem.*, **53**, 98 (1981).

7 H. D. Hendricks, US Patent., 3 709 663 (1973).

8 T. Ishiji and M. Kaneko, *Analyst*, **120**, 1633 (1995).

9 A. Sharma and O. S. Wolfbeis, *Appl. Spectrosc.*, **42**, 1009 (1988).

10 E. D. Lee, T. C. Werner, and R. Seitz, *Anal. Chem.*, **59**, 279 (1987).

11 A. Ulman, “An Introduction to Ultrathin Organic Films From Langmuir–Blodgett to Self-Assembly,” Academic Press, San Diego, CA, USA (1990).

12 K. D. Dobson and A. J. McQuillan, *Spectrochim. Acta, Part A*, **55**, 1395 (1999).

13 E. Mohyi, J. Abu-Zeid, R. Lopez, P. Martinez, J. C. Acevedo, and R. Groff, *Chem. Phys. Lett.*, **46**, 558 (1977).

14 Y. Fujiwara and Y. Amao, *Sens Actuator B*, **85**, 175 (2002).

15 B. D. MacCraith, C. M. McDonagh, G. O’Keeffe, E. T. Keyes, J. G. Vos, B. O’Kelly, and J. F. McGilp, *Analyst*, **118**, 385 (1993).

16 J. N. Demas, B. A. DeGraff, and W. Xu, *Anal. Chem.*, **67**, 1377 (1995).

17 S.-K. Lee, Y.-B. Shin, H.-B. Pyo, and S.-H. Park, *Chem. Lett.*, **2001**, 310.