CHEMISTRY LETTERS, pp. 1197-1200, 1988.

A Solid-State Amperometric Oxygen Sensor Using NAFION Membrane Operative at Room Temperature

Shigeki KUWATA, Norio MIURA,† and Noboru YAMAZOE,*†
Department of Industrial Chemistry, Niihama National College of Technology, Niihama, Ehime 792
†Department of Materials Science and Technology, Graduate School of Engineering Sciences, Kyushu University, Kasuga, Fukuoka 816

New type amperometric oxygen sensors using a NAFION membrane were investigated for monitoring oxygen partial pressure at room temperature. The sensor element finally constructed had a structure in which an electrochemical cell was combined with a hydrogen-generation system and a gas-diffusion layer. Its sensing current under the short-circuit condition was found to vary linearly with the oxygen partial pressure. The 90% response time was about 3 min at 25 °C.

In recent years, several attempts have been made to develop solid-state oxygen sensors operative at ambient temperature, which are important especially in medical or bio-related applications. Solid-electrolyte oxygen sensors so far commercialized are classified into two types, i.e., potentiometric type in which electromotive force (e.m.f.) varies logarithmically with oxygen partial pressure, and amperometric type in which electrolytic current usually varies linearly with oxygen concentration. Both types have been commercialized typically by using stabilized zirconia such as ZrO_2-Y_2O_3, but these sensors must be operated at elevated temperature in order to ensure sufficiently large ionic conductivity. On the other hand, low-temperature ionic conductors such as fluolide ion conductors$^{1-3)}$ and proton conductors$^{4,5)}$ have recently been applied to potentiometric oxygen sensors workable at room temperature. For example, the sensors using LaF_3 (single crystal$^{6)}$ or sputtered film$^{7)}$) could respond to a change in oxygen partial pressure rather quickly at 25 °C. Although such potentiometric sensors can cover a broad range of oxygen concentration, they are inferior in principle to amperometric sensors in the accuracy of detection. This prompted us to investigate an amperometric oxygen sensor operative at room temperature. This paper deals with a new amperometric oxygen sensor using a NAFION membrane (proton conductor).

Three sensor types (Sensors A, B, and C) were used in this study, Sensors A and B are illustrated in Fig. 1. A NAFION membrane (H^+ type Nafion 117, 0.2 mm thick) treated in boiling water for 2 h was used as a solid electrolyte (proton conductor). The sensing and the counter Pt electrodes were attached onto the both sides of the NAFION membrane by means of chemical plating using chloroplatinic (V) acid. This membrane was then fixed to an end of pyrex glass tube by epoxy resin and a $H_2(2\%)-N_2$ mixture was allowed to flow over the counter electrode (Sensor A, prototype). In Sensor B (improved type), another NAFION membrane (Membrane II) with Pt electrodes was added beneath Sensor A (Membrane I) with a porous sheet of sponge being sandwiched in between. Humid air (70-80% relative humidity) was allowed to flow inside the tube, and DC voltage was applied between the cathode and the anode of Membrane II in order to electrolyze water vapor to supply hydrogen to the counter electrode of Membrane I. Sample gases with various oxygen partial pressures were prepared by mixing O_2 with N_2 and was moistened by passing through liquid water to prevent the NAFION membranes from drying. The gases were permitted to flow over the sensing Pt electrode at a rate of 100 cm^3/min. Response currents of both sensors were measured at 25 °C by means of an electrometer (Advantest Co. Ltd., TR-8641), with the Pt electrodes of Membrane I short-circuited.

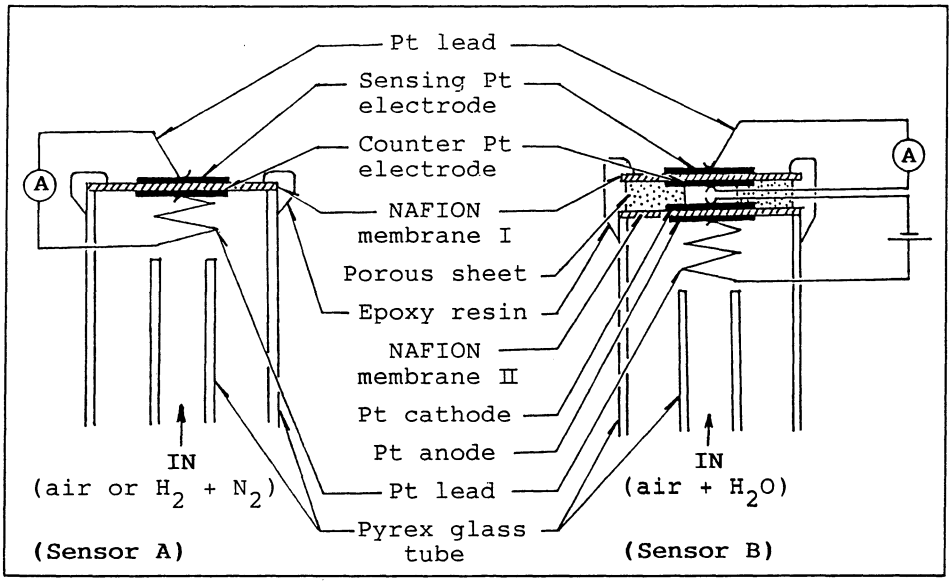

Fig. 1. Structures of the oxygen sensors using NAFION membrane.

Figure 2 shows the dependence of the short-circuit current of Sensor A on oxygen partial pressure in the sample gas at 25 °C. When moistened air was supplied to the counter electrode, the response current was very small (ca. 10^{-9} A) and almost independent of the oxygen partial pressure even when an external voltage of 1.0 V was applied. The supply of a H_2-N_2 mixture over the counter electrode drastically increased the current, which increased with an increase in oxygen partial pressure. This suggests that an

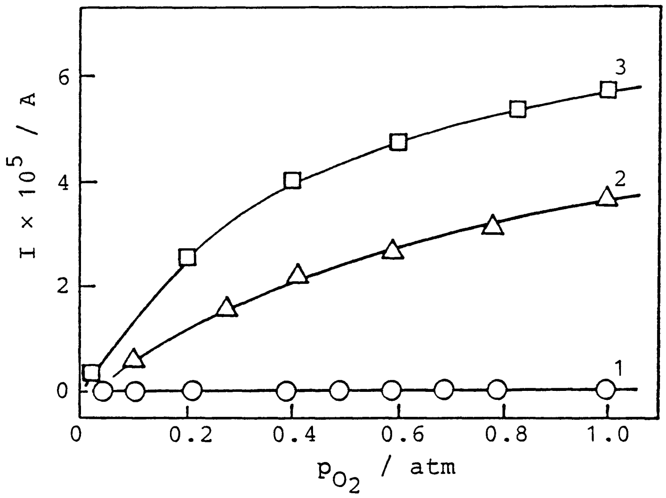

Fig. 2. Dependence of the current of the sensor on oxygen partial pressure in the sample gas at 25 °C.
Applied voltage: 1; 1.0 V(air),
2; 0 V(H_2-N_2),
3; 0.1 V(H_2-N_2)

electrochemical reaction involving oxygen takes place at the sensing electrode when H_2 is supplied to the counter electrode. It is noted that the responses to oxygen partial pressures can be obtained without applying an external voltage. The electrode reaction taking place on the counter electrode in the presence of H_2 can be represented as follows:

$$H_2 \longrightarrow 2\ H^+ + 2\ e^- \qquad (1)$$

The proton produced by Reaction (1) can migrate to the sensing electrode through the NAFION membrane. If oxygen exists in the atmosphere around the sensing electrode, the following electrochemical reduction (2) takes place on the sensing electrode.

$$O_2 + 4\ H^+ + 4\ e^- \longrightarrow 2\ H_2O \qquad (2)$$

Therefore, the sensor cell eventually consists of an H_2-O_2 fuel cell.

The above structure needs a supply of H_2 gas onto the counter electrode, which is disadvantageous for miniaturization and simplification of the sensor element. In order to overcome this demerit, Sensor B was investigated, which had a hydrogen self-generation system. In Sensor B, the electric current through Membrane I was defined as a sensing current. Figure 3 shows the oxygen sensitivity of Sensor B on oxygen partial pressure at 25 °C. The sensing current increased with an increase in oxygen partial pressure at applied voltages of 1.0 and 1.5 V, while the current at 0.7 V was considerably small and almost independent of oxygen partial pressure.

The non-linear dependence of the sensing current of Sensor B on oxygen partial pressure seemed to suggest that the rate was determined by electrode reactions, not gas-diffusion step. Then Sensor B was covered with a porous sheet (0.2 mm thick) made with a mixture of Teflon (20 wt%) and antimonic acid as shown in Fig. 4 (a). With this construction (Sensor C), an almost linear dependence of the short-circuit current on oxygen partial pressure was obtained as given in Fig 4 (b), although the current values was far smaller than those of sensor B. This means that the porous sheet functions as a gas-diffusion layer. Figure 5 depicts response transients of Sensor C to a change in oxygen partial pressure from 0.2 to 0.6 atm and vice versa at 25 °C. The 90% response times were ca. 3 min and ca. 5 min for increasing and decreasing oxygen partial pressure, respectively. These values are fairly small compared with those

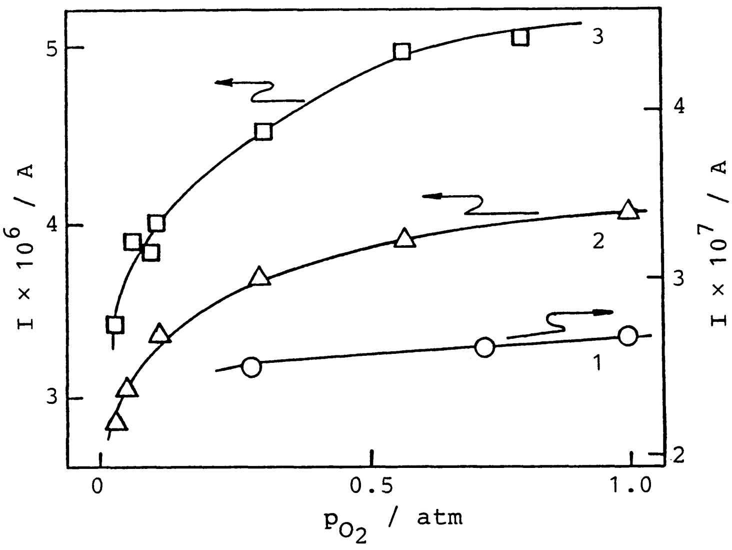

Fig. 3. Dependence of the short-circuit current of Sensor B on oxygen partial pressure at 25 °C. Applied voltage: 1;0.7 V, 2;1.0 V, 3;1.5 V

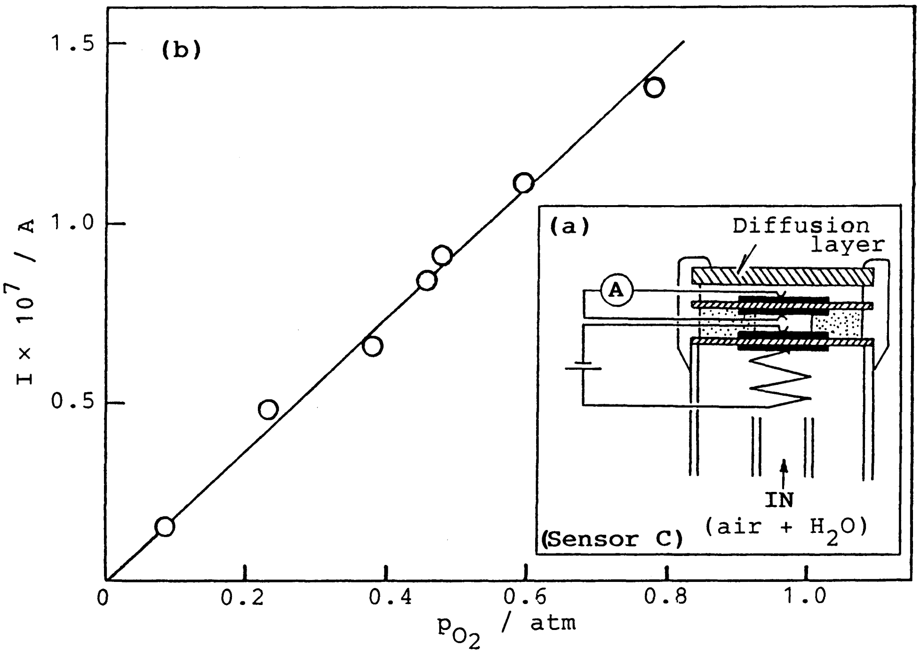

Fig. 4. (a) Structure of Sensor C with the gas-diffusion layer, (b) Dependence of the short-circuit current of Sensor C on oxygen partial pressure at 25 °C. Applied voltage:1.0 V

of the potentiometric oxygen sensor using proton conductors reported before.$^{4)}$ These results suggest that a practical sensor may be constructed based on this principle, though more details are required to be examined.

This work was partially supported by Grant-in-Aids for Scientific Research from the Ministry of Education, Science and Culture of Japan.

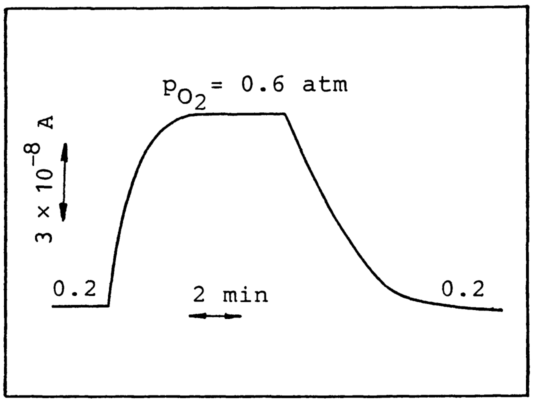

Fig. 5. Response cureve of Sensor C to change in oxygen partial pressure at 25 °C.

References

1) A. Yamaguchi and T. Matsuo, Proc. 1st Sensor Symp., Tsukuba, (1981), p.99.
2) G. Couturier, Y. Danto, R. Gibaud, and J. Salardenne, Solid State Ionics, 5, 621 (1981).
3) E. Siebert, J. Fouletier, and S. Vilminot, Solid State Ionics, 9&10, 1291 (1983).
4) N. Miura, H. Kato, N. Yamazoe, and T. Seiyama, Denki Kagaku, 52, 376 (1984).
5) S. Kuwata, N. Miura, and N. Yamazoe, Nippon Kagaku Kaishi, 1987, 1518.
6) N. Yamazoe, J. Hisamoto, N. Miura, and S. Kuwata, Sensors and Actuators, 12, 415 (1987).
7) N. Miura, J. Hisamoto, S. Kuwata, and N. Yamazoe, Chem. Lett., 1987, 1477.

(Received April 6, 1988)