CHEMISTRY LETTERS, pp. 1905 - 1908, 1984.

AMPEROMETRIC GAS SENSOR USING SOLID STATE PROTON CONDUCTOR SENSITIVE TO HYDROGEN IN AIR AT ROOM TEMPERATURE

Norio MIURA, Hiroshi KATO, Yoshihiro OZAWA, Noboru YAMAZOE,* and Tetsuro SEIYAMA
Department of Materials Science and Technology, Graduate School of
Engineering Sciences, Kyushu University, Kasuga, Fukuoka 816

A new type of amperometric gas sensor using a proton conductor (antimonic acid) and its working mechanisms are proposed for detecting small amounts of H_2 in air at room temperature. The short circuit current of the sensor cell was found to be proportional to the concentration of H_2. It is also shown that the sensor could be modified into a simpler construction where the reference gas (air) is no longer necessary.

In recent years, gas sensors operative at room temperature are becoming increasingly important in many fields. These sensors can be used as so called "cordless sensors", because they need no external electric sources to heat sensor elements. Although electrochemical gas sensors which utilize liquid electrolytes are available to detect inorganic gases, e.g., O_2, CO, Cl_2, H_2S, and so on, at room temperature,[1)] they often have time-related problems such as leakage and corrosion. The problems seem to be solved if solid electrolytes are used in place of liquid electrolytes.

Solid state proton conductors such as antimonic acid[2,3)] and zirconium phosphate[4)] are known to exhibit relatively high protonic conductivities at room temperature. We recently found that the electrochemical cell using these proton conductors could detect small amounts of H_2 contained in air even at room temperature.[5,6)] It was also reported that the sensor response (EMF of the cell) was almost proportional to a logarithm of the H_2 concentration and the sensing mechanism was attributed to a mixed potential at the sensing electrode.[7)] Further investigations, however, have revealed that the short circuit current of the cell is proportional to the H_2 concentration. We describe here the performances of this new type of amperometric sensor, its working mechanism, and a modification of the sensor construction.

The sensor element examined first is represented as follows:

$$\underset{\left(\begin{array}{l}\text{counter}\\ \text{electrode}\end{array}\right)}{\text{air, Pt black}} \;\Big|\; \underset{\text{(solid electrolyte)}}{\text{proton conductor membrane}} \;\Big|\; \underset{\left(\begin{array}{l}\text{sensing}\\ \text{electrode}\end{array}\right)}{\text{Pt black, sample gas.}}$$

Figure 1 shows the structure of this sensor which is similar to that of the potentiometric sensor reported before.[6)] Antimonic acid powder was mixed with 20 wt% Teflon powder and then pressed at 4200 kgf/cm^2 into a proton conductor membrane 10 mm in diameter and 1 mm in thickness. Platinum black powder was applied on both

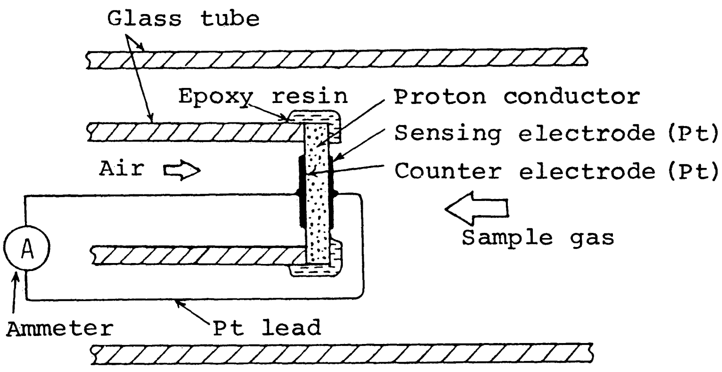

Fig.1. Structure of the amperometric sensor.

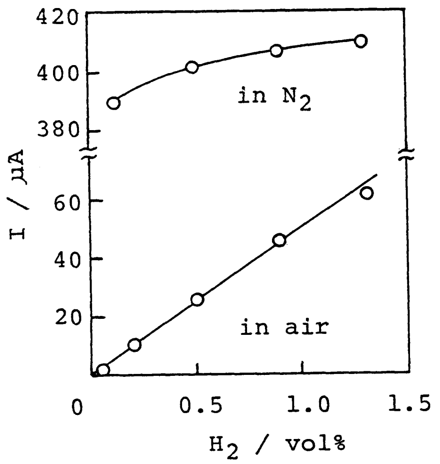

Fig.2. Short circuit current of the amperometric sensor vs. H_2 concentration in air or N_2.

sides of the membrane as a sensing- and a counter-electrode with a geometric area of ca. 0.4 cm^2. The membrane was then fixed to an end of a glass tube by means of Epoxy resin. An electrical contact between the electrode and the Pt lead was made by carbon paste. The sample gas prepared by mixing small amounts of H_2 with air (or N_2 in some cases) was passed over the sensing electrode at 90 cm^3/min. Only air was fed to the counter electrode at the same gas flow rate. All gases were moistened by passing them through water to prevent the proton conductor from drying. As a sensor signal a short circuit current of the cell was measured by means of an ammeter (Hokuto Denko Co, Ltd., Zero Shunt Ammeter HM-101) at 20 °C.

Figure 2 shows how the short circuit current depends on the concentration of H_2 diluted with air or N_2. It is noteworthy that for H_2 diluted with air the short circuit current is approximately proportional to the H_2 concentration. As the response of the previous potentiometric sensor was proportional to the logarithm of the H_2 concentration, this fact suggests that for practical purpose the amperometric sensor is more accurate than the potentiometric one. When H_2 was diluted with N_2, this sensor exhibited quite different behavior with far greater current values and a nonlinear dependence on H_2 concentration.

As shown previously,7) reactions (1) and (2) proceed simultaneously to form a local cell at the sensing electrode in the atomosphere of H_2 + air, while only reaction (1) takes place at the sensing electrode in $H_2 + N_2$. When the circuit of the cell is open in H_2 + air, the sensing electrode is at a mixed potential

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

$$2H^+ + 1/2O_2 + 2e \longrightarrow H_2O \qquad (2)$$

(E_M). E_M is determined as the intersection of both anodic and cathodic polarization curves as shown in Fig. 3 where the anodic current $i_{(1)}$ is equal to the cathodic one $i_{(2)}$. The electrode reaction at the counter electrode is the same as reaction (2). The potentiometric sensor observes the potential difference between the sensing electrode and the counter electrode under this condition. When the two electrodes are electrically connected with a lead (closed circuit), both

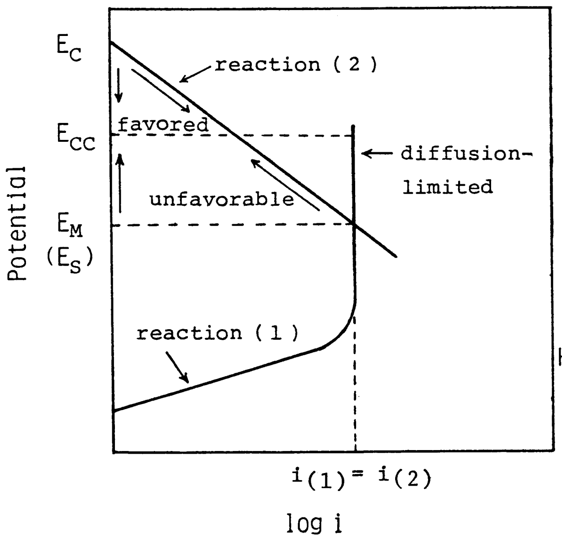

Fig.3. Schematic polarization curves for reactions (1) and (2).

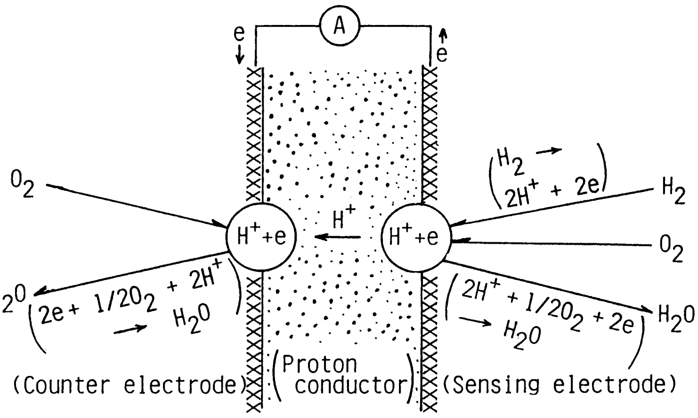

Fig.4. Sensing mechanism of the amperometric sensor.

sensing- and counter-electrode are forced to be at the same potential (E_{CC}) as shown in Fig. 3. This means that the potential of the sensing electrode shifts to the direction where reaction (2) is unfavorable, while that of counter electrode shifts favorably for reaction (2). Under this condition, reactions (1) and (2) are not balanced at the sensing electrode, and the excess H^+ produced tends to migrate toward the counter electrode to be consumed there by reaction (2). This process is accompanied by a flow of equivalent electrons as an external current. These processes are schematically shown in Fig. 4. Under the open circuit conditions, reaction (1) has been shown to be a diffusion-limited process as shown in Fig. 3 and this gives rise to a theoretical basis for the almost linear dependence of the EMF on the logarithm of the H_2 concentration.[7)] Under the closed circuit conditions, reaction (1) should remain as a diffusion-limited process. This means that the concentration of H_2 at the sensing electrode is essentially zero and the amount of H^+ produced by reaction (1) is proportional to the H_2 concentration in air. If it is assumed that the consumption of H^+ at the sensing electrode by reaction (2) is very limited, the excess H^+ to be transported toward the counter electrode will be roughly proportional to the H_2 concentration in the gas phase. At present, we presume that such a situation can explain the almost linear dependence of the short circuit current on the H_2 concentration.

The above amperometric sensor has a rather complicated construction so as to separate the sample gas (H_2 + air) from the reference gas (air). We tried to simplify the sensor structure as shown in Fig. 5 where a thin antimonic acid membrane (mixed with Teflon powder) of 0.2 mm thickness was used as solid electrolyte and the counter electrode (Pt) was covered with Teflon and Epoxy resin. The modified sensor was found to exhibit the excellent response to small amounts of H_2 in air as shown in Fig. 6 : the 90% response time for 2000 ppm H_2 was as short as ca. 10 s and the short circuit current depended linearly on the H_2 concentration.

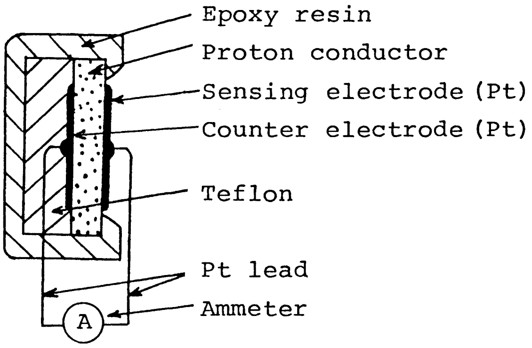

Fig.5. Structure of the modified amperometric sensor.

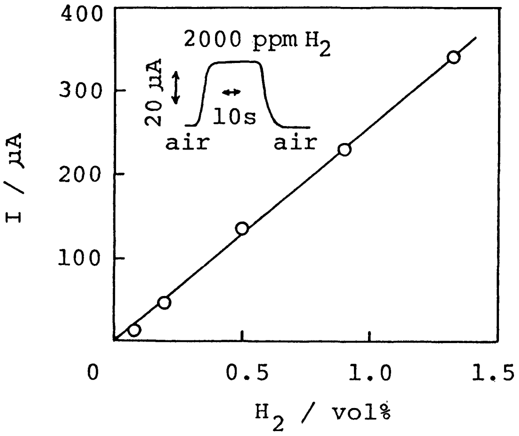

Fig.6. Response curve of the modified sensor to 2000 ppm H_2 and dependence of short circuit current of the sensor on H_2 concentration in air.

The working mechanism of this modified sensor should be essentially the same as the unmodified one. It is noteworthy that a stationary short circuit current was obtained in spite of the sensor construction where the counter electrode was covered with the polymers. Since the sensing electrode is placed in the same situation as the unmodified sensor, this fact indicates that reaction (2) is allowed to take place stationarily at the counter electrode even under this condition. A plausible sensing mechanism of this sensor is as follows. It is suggested that the membrane is thin enough to allow the necessary permeation of reactant O_2 (and the produced H_2O). A part of H_2 will naturally also permeate through the membrane, but the transfered H_2 will be consumed by the reaction with O_2 electrochemically or catalytically at the counter electrode (Pt) as in the case at the sensing electrode. The rate of H_2 supply to the counter electrode through the membrane would be rather small as compared with that to the sensing electrode from the gaseous bulk, so that the H_2 concentration around the counter electrode is considered to be lower than that around the sensing electrode. This difference in H_2 pressure between the two electrodes may be responsible for the sensor response.

Investigations on sensing mechanism, gas selectivity, and stability of the new amperometric sensors are in progress.

We thank Toa Gosei Chemical Industry Co. Ltd. for donation of the thin antimonic acid membrane.

References

1) H. Dietz, W. Haecker, and H. Jahnke, " Advances in Electrochemistry and Electrochemical Engineering, " Vol.10, ed by H. Gerischer and C. Tobias, John Willy & Sons, New York(1977), p.1.
2) W. A. England, M. G. Cross, A. Hammett, P. J. Wiseman, and J. B. Goodenough, Solid State Ionics, 1, 231 (1980).
3) Y. Ozawa, N. Miura, N. Yamazoe, and T. Seiyama, Nippon Kagaku Kaishi, 1983, 488.
4) P. Jerus and A. Clearfield, Solid State Ionics, 6, 79 (1982).
5) N. Miura, H. Kato, N. Yamazoe, and T. Seiyama, Denki Kagaku, 50, 858 (1982).
6) N. Miura, H. Kato, N. Yamazoe, and T. Seiyama, Chem. Lett., 1983, 1573.
7) N. Miura, H. Kato, N. Yamazoe, and T. Seiyama, " Proc. of the Int. Meeting on Chemical Sensors, " ed by T. Seiyama, K. Fueki, J. Shiokawa, and S. Suzuki, Kodansha/Elsevier, Tokyo(1983), p.233.

(Received August 9, 1984)