12

Amperometric Proton-Conductor Sensor for Detecting Hydrogen and Carbon Monoxide at Room Temperature

Norio Miura, Hiroshi Kato, Noboru Yamazoe, and Tetsuro Seiyama

Department of Materials Science and Technology, Graduate School of Engineering Sciences, Kyushu University, Kasuga-shi, Fukuoka 816, Japan

A new type of amperometric gas sensor using a proton conductor (antimonic acid) and its sensing mechanism are proposed for detecting small amounts of H_2 (or CO) in air at room temperature. The sensing element is composed of the following electrochemical cell : (counter electrode) air, Pt | proton conductor | Pt, sample gas (sensing electrode). The short circuit current of the cell is found to be in direct proportion to the concentration of H_2 (or CO). It is also shown that the sensor can be modified into a simpler construction which eliminates the reference gas (air). This modified sensor is found to exhibit performances as good as that of the original one, with satisfactory stability for about two months.

In recent years, gas sensors operating at room temperature are becoming increasingly more important in many fields. These sensors can be used as so called "cordless sensors", because they need no external electric sources to heat the 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, etc. at room temperature (1-3), they often have time-related problems such as leakage and corrosion. The problems are minimized if solid electrolytes are used in place of liquid electrolytes.

It has been reported (4,5) that solid electrolyte sensors using stabilized zirconia can detect reducible gases in ambient atmosphere by making use of an anomalous EMF which is unusually larger than is expected from the Nernst equation. However, these sensors should be operated in a temperature range above ca. 300°C mainly because the ionic conductivity of stabilized zirconia is too small at lower temperatures. On the other hand, solid state proton conductors such as antimonic acid (6,7), zirconium phosphate (8), and dodecamolybdophosphoric acid (9) are known to exhibit relatively high protonic conductivities at room temperature. We recently found that the electrochemical cell using these proton conductors could detect

0097-6156/86/0309-0203$06.00/0

small amounts of H_2 or CO contained in air (10-12). This solid-state sensor can be operated even at room temperature and belongs to a potentiometric class which utilizes electromotive force (EMF) as a sensor signal.

The sensing performances of the potentiometric proton conductor sensor are shown in Figure 1. It is seen that the 90 % response time to 2000 ppm H_2 in air at room temerature is about 10 seconds and the EMF value of the sensor cell changes almost in proportion to a logarithm of H_2 concentration. It has been shown that the sensing electrode is at a potential determined by electrochemical oxidation of H_2 (or CO) and electrochemical reduction of O_2 (11). Although such a potentiometric sensor is convenient for detecting a broad range of gas concentration, the accuracy of gas detection is inferior to an amperometric sensor in which the sensor signal is in direct proportion to the sample gas concentration. Thus we tried to develop an amperometric sensor using proton conductors and found that the short circuit current of the proton conductor sensor is proportional to the H_2 (or CO) concentration in air (13). We describe here the fabrication, performances, and the sensing mechanism of the new type of amperometric proton conductor gas sensor.

Experimental

The first sensor element examined is represented as follows:

Ammeter

air, Pt black | proton conductor disc | Pt black, sample gas
(counter electrode) (solid electrolyte) (sensing electrode)

Figure 2 shows the structure of this sensor which is similar to that of the potentiometric sensor reported earlier (10). The only difference is that in this sensor a short circuit current between the sensing electrode and the counter electrode is measured with an ammeter. The proton conductor, antimonic acid ($Sb_2O_5 \cdot 2H_2O$), was prepared from antimony trioxide and hydrogen peroxide according to a method described elsewhere (7,14). The sample powder was mixed with 20 wt% Teflon powder binder (Lubron L-2, Daikin Ind. Co. Ltd.) and then cold-pressed at 4200 kgf/cm^2 into a compact disc 10 mm in diameter and 1 mm in thickness. Platinum black powder was applied on both ends of the thin disc to form a sensing- and a counter-electrode with a geometric area of ca. 0.4 cm^2. The disc was then fixed to an end of a glass tube by means of Epoxy resin. Electrical contacts between each electrode and Pt leads were 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, while only air was fed to the counter electrode at the same gas flow rate. Commercial gases without purification were used for all the experiments. The gases were humidified by passing them through water. This is necessary to prevent the proton conductor from drying. The sensor signal, a short circuit current of the cell, was measured at room temperature by means of an ammeter (Hokuto Denko Co, Ltd., Zero Shunt Ammeter HM-101).

Results and Discussion

Sensing performance for H_2. Sensing performance of the amperometric sensor was examined for the detection of H_2 in air. Figure 3 shows the response curve for 2000 ppm H_2 in air at room temperature. The response was studied by changing the atmosphere of the sensing electrode from an air flow to the sample gas flow. With air the short circuit current between two electrodes was zero. On contact with the sample gas flow, the current increased rapidly. The 90% response time was about 10 seconds and the stationary current value was 10 μA. When the air flow was resumed, the current returned to zero within about 20 seconds.

Figure 4 shows how the short circuit current depends on the concentration of H_2 which is diluted with air or N_2. It is noteworthy that for H_2 in air the short circuit current is approximately in direct proportion to the H_2 concentration. As mentioned before, this fact suggests that for practical purpose the amperometric sensor is more accurate than a potentiometric sensor. When H_2 was diluted with N_2, the sensor exhibited a very different behavior with far greater current values and a nonlinear dependence on H_2 concentration. In this case, the cell is actually an H_2-O_2 fuel cell which accounts for the greater current values.

Sensing mechanism. As shown previously (11), when the circuit of the cell is open, the potential of the sensing electrode is determined by the following reactions (1) and (2).

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

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

In an atmosphere of H_2 and air, these reactions proceed simultaneously to form a local cell on the sensing electrode. In this situation the potential of the sensing electrode is a mixed potential (E_M) where the anodic current $i_{(1)}$ is equal to the cathodic one $i_{(2)}$. The mixed potential is determined as an intersection of both anodic and cathodic polarization curves as shown in Figure 5. It is important that the anodic polarization curve have a limiting current region as mentioned before (11). On the counter electrode where air is passed over, only reaction (2) takes place endowing the counter electrode with a potential near E_C. Thus, the potentiometric sensor observes the potential difference between the sensing electrode and the counter electrode E_M-E_C. On the other hand, when the two electrodes are electrically connected with a lead (short circuit), both the sensing and the counter electrodes are forced to be at the same potential (E_{SC}) as shown in the same figure. This means that the potential of the sensing electrode shifts to the direction where reaction (2) is unfavorable, while that of the counter electrode shifts favorably for reaction (2).

In order to confirm such potential shift we observed the actual behavior of the sensing and counter electrode potential under both open and short circuit conditions. Each potential was measured against a silver reference electrode which was attached to the sensor element as shown in Figure 6. Figure 7 depicts the response curves against 500 ppm H_2 in air under both conditions. When the circuit is open, the change in potential occurs only at the sensing

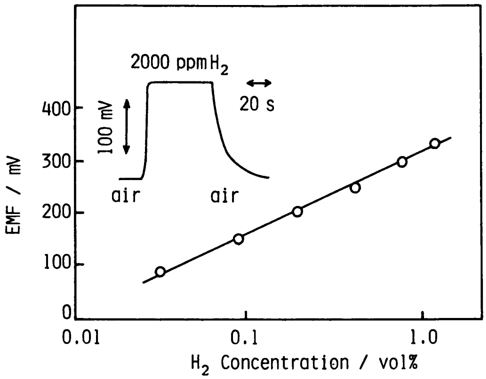

Figure 1. Response curve of the potentiometric sensor to 2000 ppm H_2 and dependence of EMF of the sensor on H_2 concentration in air.

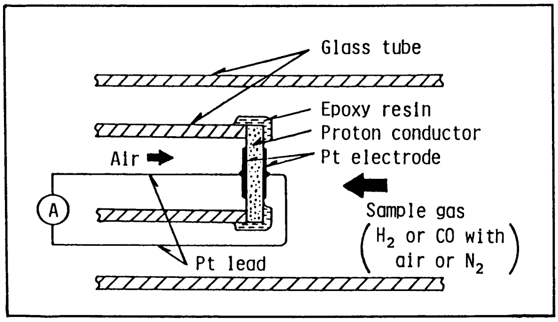

Figure 2. Structure of the amperometric sensor. "Reproduced with permission from Ref. 13. Copyright 1984, 'The Chemical Society of Japan'."

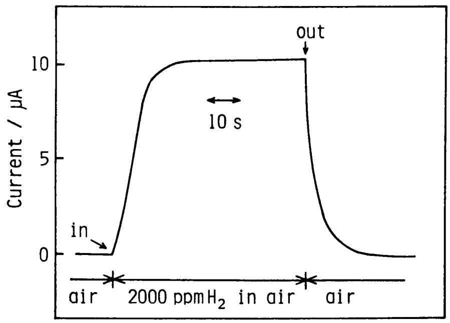

Figure 3. Response curve of the amperometric sensor to 2000 ppm H_2 in air at room temperature.

Schuetzle and Hammerle; Fundamentals and Applications of Chemical Sensors
ACS Symposium Series; American Chemical Society: Washington, DC, 1986.

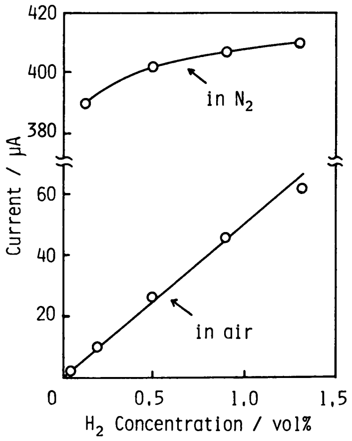

Figure 4. Short circuit current of the amperometric sensor vs. H_2 concentration in air or N_2.
"Reproduced with permission from Ref. 13. Copyright 1984, 'The Chemical Society of Japan'."

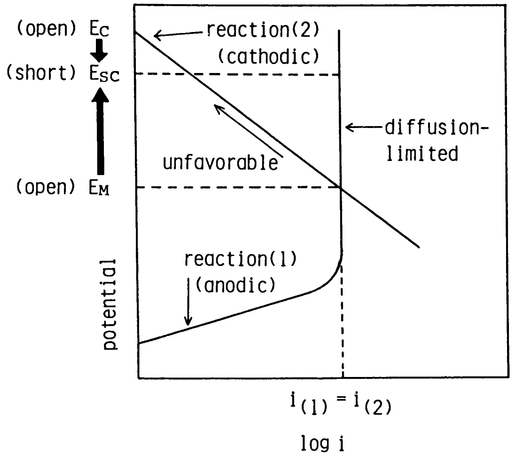

Figure 5. Schematic polarization curves for reactions (1) and (2).
"Reproduced with permission from Ref. 13. Copyright 1984, 'The Chemical Society of Japan'."

electrode. Under the short circuit condition the sensing and the counter electrode are forced to shift to a potential in between as mentioned above. Moreover, it is noticed that the potential shift is larger for the sensing electrode.

Thus, we illustrate schematically the sensing mechanism of the amperometric sensor in Figure 8. When the circuit is open, reactions (1) and (2) are balanced at the sensing electrode; the proton produced by the electrochemical oxidation of H_2 will be consumed at the sensing electrode by the electrochemical reduction (2). It is important that the anodic reaction has been shown to be a diffusion-limited process. Under the short circuit condition, these two reactions are not balanced at the sensing electrode. The cathodic reaction at the sensing electrode becomes unfavorable, so that the consumption of H^+ by reaction (2) at the sensing electrode is suppressed. The excess H^+ thus produced on the sensing electrodes migrates toward the counter electrode through the proton conductor membrane to be consumed by the reaction (2). This process is accompanied by a flow of equivalent electrons as an external current. The anodic oxidation reaction of H_2 remains as a diffusion-limited process under the short circuit conditions, so that the amount of H^+ produced by the anodic reaction is proportional to the H_2 concentration. This eventually gives rise to an external current roughly proportional to the H_2 concentration in the gas phase.

Modification of the sensor structure. The above amperometric sensor has a rather complicated construction, because the sample gas (H_2 + air) is separated from the reference air. So, we tried to simplify the sensor structure as shown in Figure 9. As proton conductor we used a thin antimonic acid membrane (mixed with Teflon powder) of 0.2 mm thickness. This membrane is thin and porous enough to allow a part of the sample gas to permeate. On the other hand, the counter Pt electrode was covered with Teflon and Epoxy resin in order to avoid a direct contact with the sample gas.

The modified sensor was found to exhibit the excellent response to small amounts of H_2 in air as shown in Figure 10. The 90 % response time for 2000 ppm H_2 was about 10 seconds and the short circuit current depends linearly on the H_2 concentration in the same manner as observed in the original sensor.

Sensing mechanism of the modified sensor. The sensing mechanism in this modified sensor should be essentially the same as that of the unmodified one. It is noteworthy that a stationary short circuit current was obtained in spite of such sensor construction that the counter electrode was covered with Epoxy resin. Since the sensing electrode is placed in the same situation as the unmodified sensor, this fact indicates that the cathodic reaction is allowed to take place stationarily at the counter electrode. The proton conductor membrane is as thin as 0.2 mm, so that the reactant O_2 and the produced H_2O will permeate the membrane as shown in Figure 11. 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.

Furthermore, the rate of H_2 supply to the counter electrode through the membrane is rather small as compared with that to the

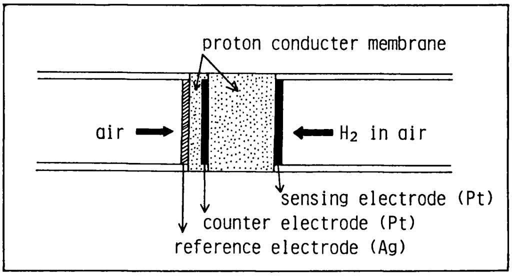

Figure 6. Configuration of the sensor attached with reference Ag electrode.

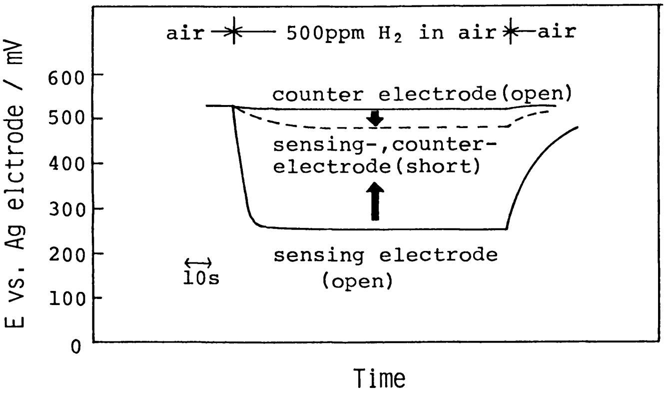

Figure 7. Behaviors of respective electrode potential under open circuit and short circuit conditions.

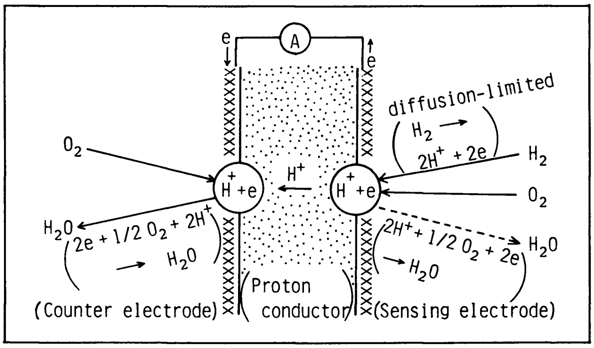

Figure 8. Sensing mechanism of the amperometric sensor. "Reproduced with permission from Ref. 13. Copyright 1984, 'The Chemical Society of Japan'."

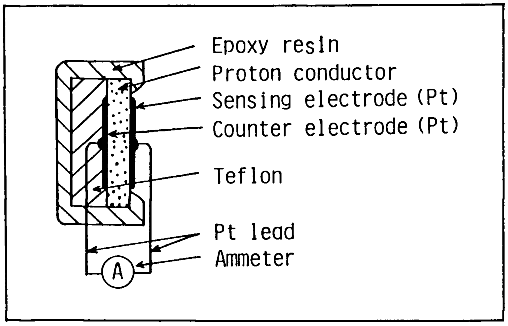

Figure 9. Structure of the modified amperometric sensor. "Reproduced with permission from Ref. 13. Copyright 1984, 'The Chemical Society of Japan'."

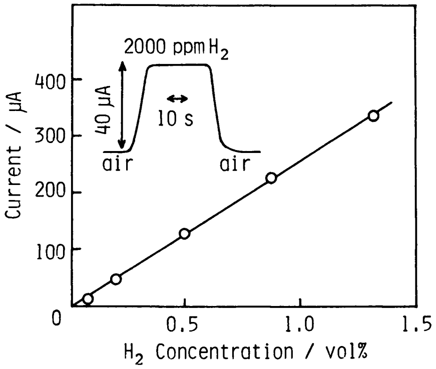

Figure 10. Response curve of the modified amperometric sensor to 2000 ppm H_2 and dependence of short circuit current of the sensor on H_2 concentration in air.
"Reproduced with permission from Ref. 13. Copyright 1984, 'The Chemical Society of Japan'."

sensing electrode from the gaseous bulk. Therefore, 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 can account for the stationary flow of short circuit current.

Performances for CO. This modified sensor was found to be also sensitive to small amounts of CO in air. Figure 12 shows response curves to CO in air at room temperature. Although the value of short circuit current is rather small as compared with that for H_2 detection, the response is still rapid enough. It is noteworthy that the current value is also in direct proportion to CO concentration as shown in Figure 13. The sensing mechanism is considered to be almost the same as in the case of H_2 detection. The anodic reaction for CO can be expressed by the following reaction.

$$CO + H_2O \longrightarrow CO_2 + 2H^+ + 2e \qquad (3)$$

It was confirmed that this sensor was insensitive to methane (15000 ppm) and propane (7000 ppm) in air.

Long-term stability. As for a practical use, the long-term stability is one of the important factors. Figure 14 shows the results of a long-term stability test for the modified sensor at room temperature. Except for the beginning of the test period, the short circuit current to 1.3 vol% H_2 in air was stable for about two months. The anomalously large current at the beginning has not been understood well yet.

Conclusions

The results of our work may be summarized as follows:

1) A new type of amperometric sensor using a proton conductor could detect small amounts of H_2 or CO in air at room temperature.
2) The short circuit current of the sensor cell was in direct proportion to the sample gas concentration.
3) The possible sensing mechanism of this sensor was proposed.
4) The sensor could be modified into a simpler construction where the reference gas (air) was no longer necessary.
5) The modified sensor was stable for about two months.

Acknowledgments

This work was partially supported by the Grant-in-Aid for Developmental Scientific Research (No. 60850151) from the Ministry of Education, Science and Culture, Japan.

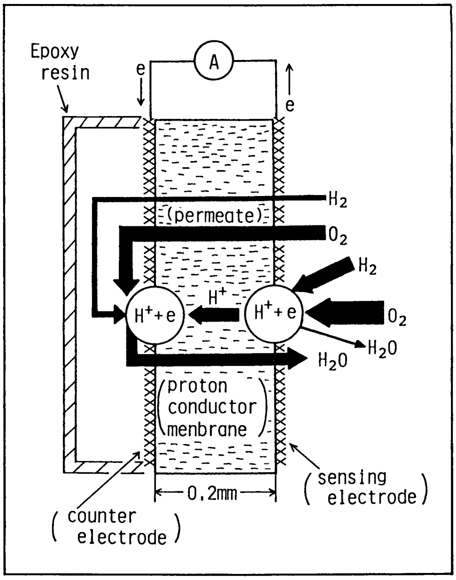

Figure 11. Sensing mechanism of the modified amperometric sensor.

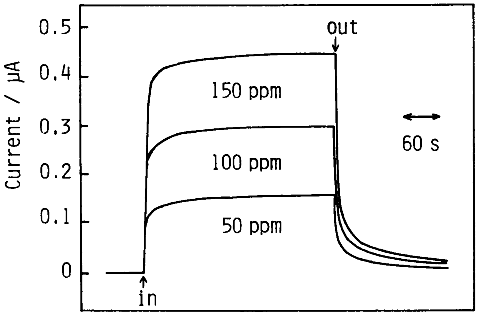

Figure 12. Response curves of the modified amperometric sensor to CO.

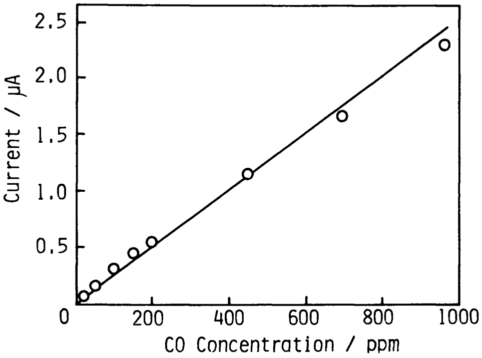

Figure 13. Short circuit current of the modified amperometric sensor vs. CO concentration in air.

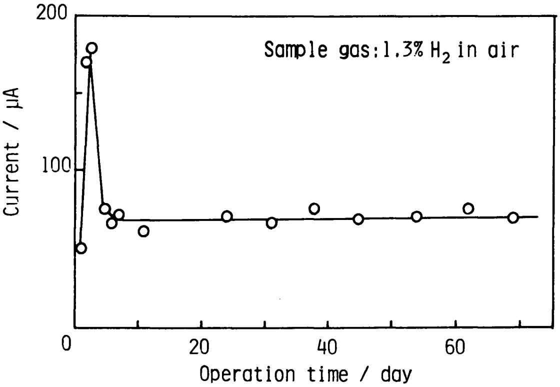

Figure 14. Long-term stability of the modified amperometric sensor at room temperature.

Literature Cited

1. Dietz, H. ; Haecker, W. ; Jahnke, H. "Advances in Electrochemistry and Electrochemical Engineering " Gerischer H. ; Tobias, C., Ed. ; John Wiley & Sons: New York, 1977, Vol. X, p.1.
2. Belanger, G. Anal. Chem. 1974, 46, 1576.
3. Isobe, M. Keisoku Gijustu 1976, 4, 43.
4. Shimizu, F. ; Yamazoe, N. ; Seiyama, T. Chem. Lett. 1978, 229.
5. Okamoto, H. ; Obayashi, H. ; Kudo, T. Solid State Ionics 1980, 1, 319.
6. England, W. A. ; Cross, M. G. ; Hammett, A. ; Wiseman, P. J. ; Goodenough, J. B. Solid State Ionics 1980, 1, 231.
7. Ozawa, Y. ; Miura, N. ; Yamazoe, N. ; Seiyama, T. Nippon Kagaku Kaishi 1983, 488.
8. Jerus, P. ; Clearfield, A. Solid State Ionics 1982, 6, 79.
9. Nakamura, O. ; Kodama, T. ; Ogino, I. ; Miyake, Y. Chem. Lett. 1979, 17.
10. Miura, N. ; Kato, H. ; Yamazoe, N. ; Seiyama, T. Denki Kagaku 1982, 50, 858.
11. Miura, N. ; Kato, H. ; Yamazoe, N. ; Seiyama, T. " Proc. of the Int. Meeting on Chemcal Sensors " Seiyama, T. ; Fueki, K.; Shiokawa, J. ; Suzuki, S., Ed.; Kodansha/Elsevier, Tokyo, 1983; p.233.
12. Miura, N. ; Kato, H. ; Yamazoe, N. ; Seiyama, T. Chem. Lett. 1983, 1573.
13. Miura, N. ; Kato, H. ; Ozawa, Y. ; Yamazoe, N. ; Seiyama, T. Chem. Lett. 1984, 1905.
14. Miura, N. ; Tokunaga, K. ; Harada, T. ; Yamazoe, N. ; Seiyama, T. Denki Kagaku 1978, 46, 113.

RECEIVED October 31, 1985