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AN IMPROVED TYPE OF PROTON CONDUCTOR SENSOR SENSITIVE TO H_2 AND CO AT ROOM TEMPERATURE

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The use of an Ag reference electrode inert to H_2 in air made it possible to fabricate a miniaturized proton conductor sensor element which did not necessitate separation of the sample gas from the reference gas (air). The sensor element was as small as 4 mm (diameter) × 8 mm (length) and showed both high sensitivity and fast response to small amounts of H_2 or CO in air, with satisfactory stability for a period of about one month.

In most solid-electrolyte gas sensors the sensor signal is the electromotive force (EMF) given by the Nernst equation.1) On the other hand, it has been reported2,3) that stabilized-zirconia sensors 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. Some compounds such as zirconium phosphate4) and antimonic acid5) have been reported to exhibit relatively high protonic conductivities at room temperature. We have recently found that these proton conductors are very useful for the potentiometric detection of small amounts of H_2 or CO in air even at room temperature.6,7) It was also verified that this sensor gives an anomalous EMF which is ascribable to a mixed potential at the sensing electrode (Pt).6) However, the electrode compartments of this sensor have to be separated by a solid electrolyte. Therefore, the structure of the sensor becomes rather complicated. Further experiments revealed that a silver electrode was inert to small amounts of H_2 in air. This means that silver can work as a reference electrode which requires no air reference. In this communication we describe the improvement of the construction of the sensor by the use of this Ag reference electrode and the performances of the improved sensor for H_2 or CO in air.

Figure 1 shows the structure of the proton conductor sensor with the Ag reference electrode. This structure is almost the same as that reported before.6) As the proton conductor we mainly used zirconium phosphate ($Zr(HPO_4)_2 \cdot nH_2O$) prepared from zirconium(IV) dichloride oxide and phosphoric acid according to Clearfield and Stynes.8) The sample powder was mixed with 60 wt% Teflon powder binder and then cold-pressed at 2500 kgf/cm^2 into a compact disc 20 mm in diameter and 3 mm in thickness. Platinum black powder and silver powder were applied on both ends of the disc as a sensing and a reference electrode, respectively. A platinum wire (0.3 mm diameter) wound around the disc was used as an external electrode. The disc with the attached electrodes was supported and sealed with O-rings between two glass tubes. Gold springs were used to ensure electrical contact between the electrodes and Cu tubes (electrical leads). A gas with identical composition (a mixture of H_2 or CO with air) was passed over each electrode at 90 cm^3/min. Commercial gases were used for all the experiments without purification, but they were moistened by passing them through water in order to avoid the drying of the proton conductor. Each electric potential of the sensing and the reference electrode was measured against the external electrode by means of two electrometers (Takeda Riken, TR 8651) at room temperature.

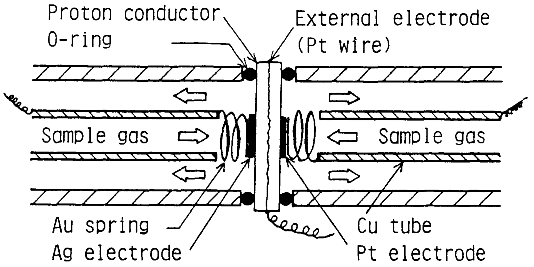

Fig. 1. Structure of the proton conductor sensor with Ag electrode.

First, the performances of the sensor with the Ag electrode were examined for the detection of H_2 contained in air. Figure 2 shows potential changes (responses) of the Pt sensing electrode and the Ag reference electrode to 2000 ppm (volume fraction) H_2 in air at room temperature. The responses were studied by changing the atmosphere of each electrode compartment simultaneously from air to the sample gas flows, and vice versa. It is noteworthy that the potential of the Pt electrode against the external electrode changed rapidly by converting the gas flows, while no change was observed in the potential of the Ag electrode. The 90% response time of the Pt electrode potential was as short as ca. 20 s.

In Fig. 3 the observed potentials of both electrodes are plotted against the volume fraction of H_2 in a range of 300 ppm - ca. 1%. The Pt electrode potential is an almost linear function of the logarithm of the H_2 volume fraction with a slope of ca. 145 mV/decade, which is in agreement with the value reported previ-

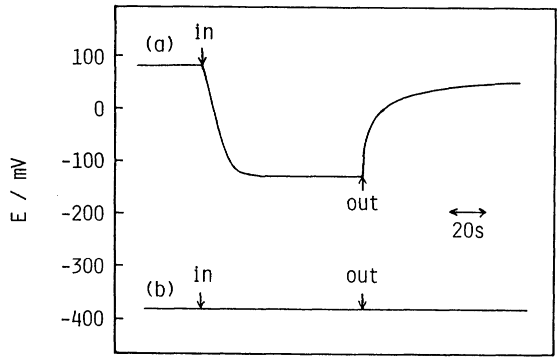

Fig. 2. Potential changes of electrodes (vs. external electrode) to 2000 ppm H_2 in air.
(a) Pt electrode, (b) Ag electrode.

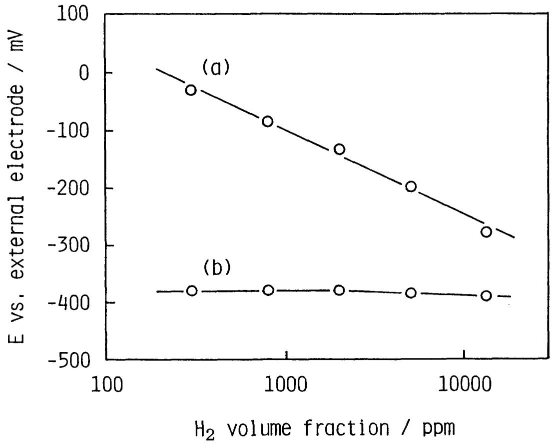

Fig. 3. Dependence of Pt- and Ag-electrode potentials on H_2 volume fraction in air.
(a) Pt electrode, (b) Ag electrode.

ously.[6)] This suggests that the sensing electrode is at a mixed potential determined by the electrochemical reactions (1) and (2).[6)]

$$\frac{1}{2}O_2 + 2H^+ + 2e \longrightarrow H_2O \qquad (1)$$

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

On the other hand, the Ag electrode potential was independent of the H_2 volume fraction up to ca. 1% as seen in Fig. 3. The potential is probably attributable to the electrode-electrolyte reaction (3).

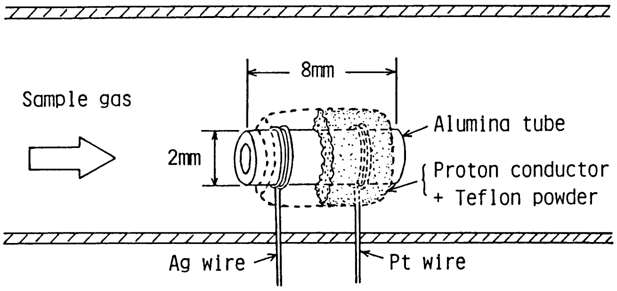

Fig. 4. Structure of the improved sensor with Ag reference electrode.

$$2Ag + H_2O = Ag_2O + 2H^+ + 2e \qquad (3)$$

This behavior of the Ag electrode shows that the electrode works as an air reference electrode even in H_2-containing air. This suggests that the use of the Ag electrode can eliminate the gas separating membrane from the sensor, thereby simplifying and miniaturizing the sensor structure.

An improved sensor was constructed, as depicted in Fig. 4. A platinum wire (sensing electrode) and an Ag wire (reference electrode) were wound around an alumina tube of 2 mm outer diameter x 8 mm length, the separation between the wires being about 4 mm. Proton conductors (such as zirconium phosphate) were mixed with about 50 wt% Teflon dispersion (dispersion medium : water) and the resulting paste was applied on the alumina tube in a thin coating layer of about 0.5 mm thickness. After drying at room temperature, the sensor was subjected to the performance test in a single gas flow apparatus as shown in this figure.

Figure 5 shows the sensitivity (EMF) and the 90% response time to H_2 in air. The EMF is seen to be linearly dependent on the logarithm of H_2 volume fraction ranging from 300 ppm to ca. 1%. The response time became longer as H_2 volume fraction decreased, but it was still as short as 70 s at 300 ppm H_2. Figure 6

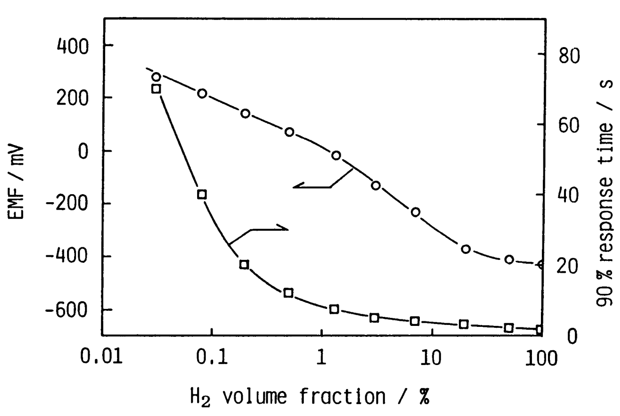

Fig. 5. Dependence of sensor response (EMF) and 90% response time on H_2 volume fraction in air.

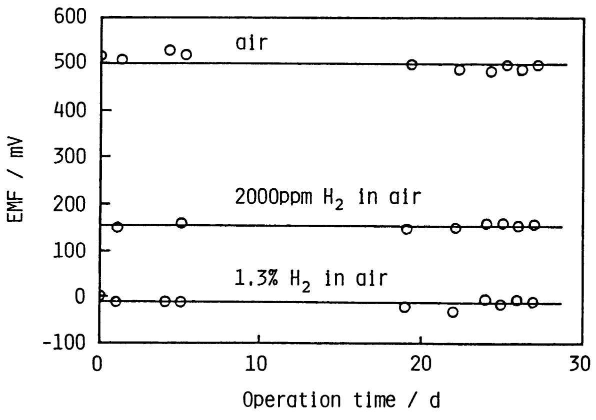

Fig. 6. Long-term stability of the improved sensor.

shows the results of a long-term stability test for the improved sensor at room temperature. The respective EMF values to air, 2000 ppm H_2, and 1.3% H_2 are stable and well reproducible for a period of about one month.

It was also found that this sensor was sensitive to small amounts of CO in air because the Ag reference electrode was inert to CO in air. Response curves to 1000 ppm and 120 ppm CO in air at room temperature are shown in Fig. 7. The sensitivity to CO was rather high, but the response was slower than in the case of H_2 detection. The mixed potential at the sensing electrode is probably determined by reactions (1) and (4). The sensor

$$CO + H_2O \longrightarrow CO_2 + 2H^+ + 2e \qquad (4)$$

was insensitive to methane (15000 ppm) and propane (7000 ppm) in air. This will enable the sensor to detect H_2 or CO selectively in the presence of these gases.

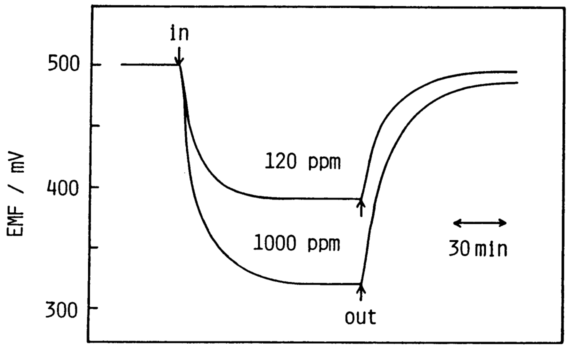

Fig. 7. Response curves of the improved sensor to CO in air.

References

1) M. Kleitz, A. Pelloux, and M. Gauthier, "Fast Ion Transport in Solids," Elsevier North Holland, Inc., (1979), p. 69.
2) F. Shimizu, N. Yamazoe, and T. Seiyama, Chem. Lett., 1978, 299.
3) H. Okamoto, H. Obayashi, and T. Kudo, Solid State Ionics, 1, 319 (1980).
4) P. Jerns and A. Clearfield, Solid State Ionics, 6, 79 (1982).
5) Y. Ozawa, N. Miura, N. Yamazoe, and T. Seiyama, Nippon Kagaku Kaishi, 1983, 488.
6) N. Miura, H. Kato, N. Yamazoe, and T. Seiyama, Denki Kagaku, 50, 858 (1982).
7) N. Miura, H. Kato, N. Yamazoe, and T. Seiyama, Proceedings of International Meeting on Chemical Sensors, Fukuoka, September 1983, in press.
8) A. Clearfield and J. A. Stynes, J. Inorg. Nucl. Chem., 26, 117 (1964).

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