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A Solid-State Proton Conductor Sensor with an Ammonia Sensitivity at Room Temperature

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A new type of solid-state gas sensor using proton conductor (antimonic acid) is proposed for detecting small amounts of NH_3 in air at room temperature. The sensor element has a four-probes type structure with outer two Pt electrodes and inner two Ag probes. The sensor response was found to vary with the NH_3 concentration (from 50 ppm to 5030 ppm) in air.

Ammonia concentration has been determined by methods such as acidimetry and spectrophotometry. These conventional methods, however, are not suitable for continuously monitoring NH_3 concentration in chemical processes, such as in the production of NH_3 or in environmental protection applications. Furthermore, the facilitation of NH_3 concentration determination is gaining importance in medical, biochemical, and food technologies. Consequently, the development of a simple, small, sensitive gas sensor to continuously monitor NH_3 concentration at ordinary temperature is presently receiving much interest.

Three types of solid-state NH_3 gas sensors, i.e., the polypyrrole polymer type,1) the oxynitride type,2) and the metal-oxide-semiconductor (MOS) type,3) have been reported to detect small amounts of NH_3 in air without using liquid electrolytes. However, these solid-state type sensors have poor performance at room temperature such as a slow response, a poor NH_3 sensitivity, and a poor reproducibility. We have recently developed the following three types of gas sensors which can detect small amounts of H_2 in air at room temperature: a potentiometric type,4-6) an amperometric type,7-9) and a four-probes type sensor.10) These new types of sensors utilize basically the mixed potential, which is determined by the electrochemical oxidation of H_2 (1) and the electrochemical reduction of O_2 (2), at the sensing electrode. If the electrochemical oxidation of NH_3 could

$$H_2 \longrightarrow 2H^+ + 2e^- \tag{1}$$

$$(1/2)O_2 + 2H^+ + 2e^- \longrightarrow H_2O \tag{2}$$

occur at the sensing electrode, the proton conductor sensor could also detect NH_3 gas in air even at room temperature.

In this paper, the performances of the four-probes type proton conductor sensor for detecting NH_3 gas at room temperature are described.

The basic sensor element is composed of the following electrochemical cell, its construction being illustrated schematically in Fig. 1.

sample gas, Pt_1 | AAM, Ag_1, AAD, Ag_2, AAM | Pt_2, AAM, sample gas

The antimonic acid disk, AAD, (10 mm in diameter, 2 mm in thickness) was cold-pressed (420 MPa) from a mixture of 80 wt% antimonic acid ($Sb_2O_5 \cdot 4H_2O$, donated by Toa Gosei Co. Ltd.) and 20 wt% Teflon powder binder (Lubron L-2, Daikin Ind. Co. Ltd.). The silver wire probe and antimonic acid membrane, AAM, (0.1 mm in thickness, 20 wt% Teflon) were successively placed on each end of the AAD, and then the entire element was cold-pressed at 450 MPa. Platinum black electrodes were then applied to each end of the sensor element (onto the AAMs) to form the sensing electrode and the reference (or counter) electrode with a geometric area of about 0.4 cm^2. One of these Pt electrodes was subsequently covered with another AAM to eliminate a reference air gas in order to simplify the sensor structure as in the improved type amperometric sensor.[9] The circumferential edge of the disk was covered with an Epoxy resin.

The sample gas was prepared by mixing the NH_3 gas (in air) with air, using mass flow controllers (FC260, TYLAN), to produce a total flow rate of 300 cm^3/min over the sensor element. The NH_3 concentration in air was varied from 50 ppm to 5030 ppm. The sensor signal, the potential difference between Ag probes, was measured with an electrometer (610C, Keithly Instruments) at room temperature, while the two Pt electrodes were either short-circuited or open-circuited.

In order to observe the behavior of the Pt electrodes in NH_3 gas, ΔE_{Pt} (the potential of electrode Pt_1 relative to the potential of electrode Pt_2) was measured first, while the two Ag electrodes were open-circuited. As shown in Fig. 2 (curve A), ΔE_{Pt} was almost zero in the air flow. When the sample gas (150 ppm NH_3 in air) was flowed over the sensor, ΔE_{Pt} increased slowly in the negative direction. The fact that a potential difference is observed between two electrodes using the same Pt black is due to the AAM covering one of the Pt electrodes. The Pt electrode covered with the AAM could be working as a stable reference electrode even in the sample gas flow. The 90% response time was about 10 min, and the almost steady value of ΔE_{Pt} was as negative as -310 mV. When the air flow was resumed, ΔE_{Pt} returned to the initial value. However, the returning response was quite slow, since ΔE_{Pt} was still as negative as -200 mV even 30 min after the air flow was resumed. These results indicate that the sensitivity of the Pt electrode to NH_3 in air is rather high. This sensitivity is seems to be due to a mixed potential similar to that proposed in the H_2 gas sensor.[4] In the case of the NH_3 detection, the mixed potential is determined by both the electrochemical oxidation of NH_3 probably given by reaction (3) and the

$$(2/3)NH_3 \longrightarrow (1/3)N_2 + 2H^+ + 2e^- \qquad (3)$$

electrochemical reduction of O_2 (2). The slow returning response can be attributed to the irreversible absorption of NH_3 in the interface between the proton conductor and the Pt electrode or to the chemical reaction of NH_3 with protons near the surface of the antimonic acid. On the other hand, the response of the potential difference between the two Ag electrodes (ΔE_{Ag}), with the Pt electrodes short-circuited, was different from that of ΔE_{Pt}. Although ΔE_{Ag} was

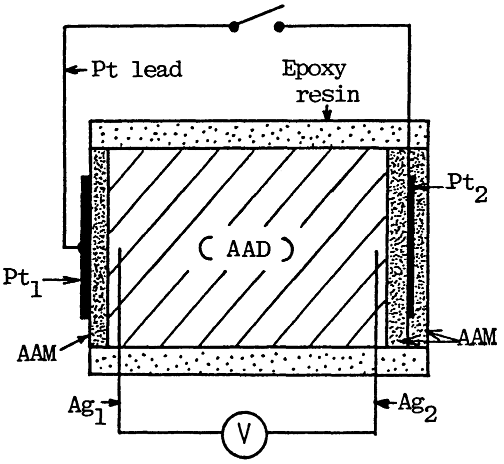


Fig. 1. Structure of the four-probes type NH_3 sensor using proton conductor.
AAD : Antimonic acid disc.
AAM : Antimonic acid membrane.

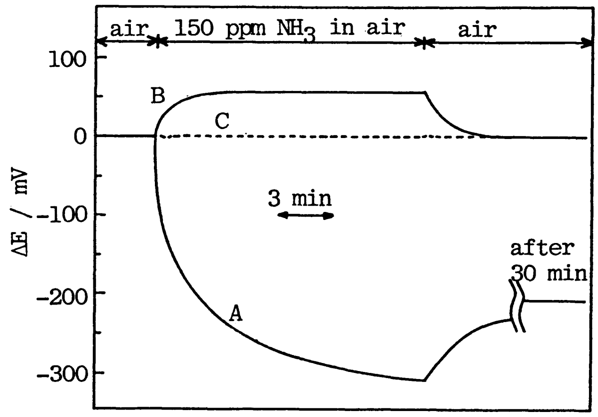
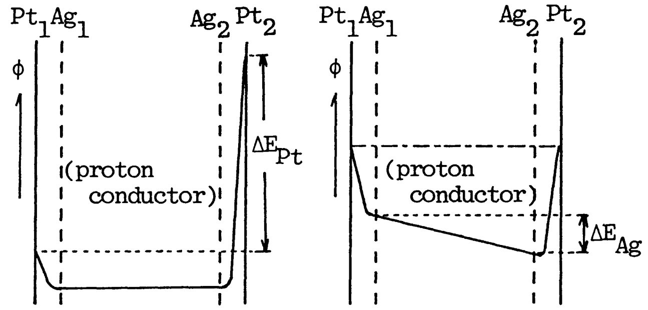


Fig. 2. Response curves of ΔE_{Pt} and ΔE_{Ag} to 150 ppm NH_3 in air at room temperature.
A : ΔE_{Pt}, with the Ag probes open-circuited,
B : ΔE_{Ag}, with the Pt electrodes short-circuited, C : ΔE_{Ag}, with the Pt electrodes open-circuited.

almost zero in air, the value of $\Delta E_{Ag}(E_{Ag1} - E_{Ag2})$ increased in the positive direction and reached a steady value of 53 mV in 150 ppm NH_3 (in air) as shown in Fig. 2 (curve B). The 90% response time to the flow of sample gas was about 2 min and ΔE_{Ag} returned to zero within about 6 min after the air flow was resumed. In this case, since the Pt electrodes are short-circuited, the protons will move from the Pt_1 side of the sensor to the Pt_2 side. The driving force for this movement is considered to be a difference in the chemical potential of proton in the proton conductor. Since the proton movement will continue for a while after the atmosphere is changed back from NH_3 to air, the NH_3 molecules remaining near the Pt electrodes will be consumed rather quickly by this proton movement. Consequently, ΔE_{Ag} will return relatively rapidly to its original value. Figure 2 (curve C) also shows the behavior of ΔE_{Ag} while the Pt electrodes are open-circuited. It is interesting to note that ΔE_{Ag} showed little response under the open-circuit condition, whereas ΔE_{Ag} responded to the sample gas flow under the short-circuit condition. This indicate that there is no potential difference (or no difference in the chemical potential of proton) in the bulk of the proton conductor under the open-circuit condition. Therefore, the large potential change seems to occur in the proton conductor near the Pt electrode as shown in Fig. 3(a). Under the short-circuit condition, on the contrary, there is no potential difference between the two Pt electrodes and the relatively large potential difference is observed between the two Ag probes. Therefore, the potential profile in the proton conductor under the short-circuit condition seems to be drawn schematically as shown in Fig. 3(b).

Figure 4 shows the dependence of ΔE_{Ag}, under the short-circuit condition, on the NH_3 concentration in air at room temperature. ΔE_{Ag} varied logarithmically



(a) (b)

Fig. 3. Schematic potential profiles in the proton conductor of the four-probes type sensor in the NH_3 (+ air) gas flow.
(a) : Under the open-circuit condition.
(b) : Under the short-circuit condition.

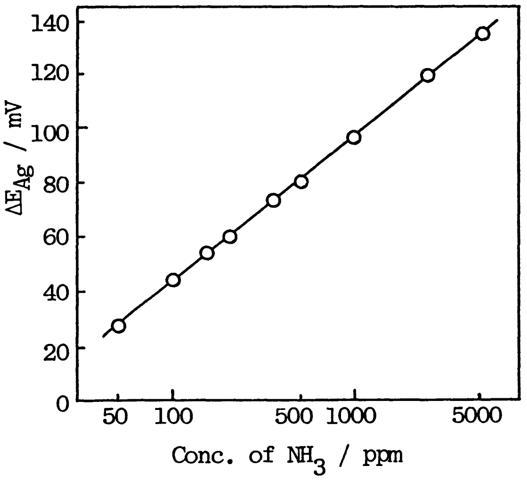


Fig. 4. Dependence of ΔE_{Ag} on the NH_3 concentration in air at room temperature.

with the NH_3 concentration, showing the slope of about 50 mV/decade. It is noteworthy that this logarithmic relation extended over three orders of magnitude of the NH_3 concentration. In the case of H_2 detection using the four-probes type sensor, ΔE_{Ag} varied linearly with H_2 concentration.[10] The explanation of this difference is not yet clarified. The reproducibility of the response of this sensor was fairly good in the short term (a couple of days). However, further studies on the long-term stability, the gas selectivity, and the exact sensing mechanism of this sensor will be necessary for an actual application.

References

1) C. Nylander, M. Armgarth, and I. Lundstrom, Proc. Int. Meet. Chemical Sensors, Fukuoka (1983), p. 203.
2) G. Rosse et al., Proc. 2nd Int. Meet. Chem. Sensors, Bordeaux (1986), p. 134.
3) F. Winquist, A. Spetz, and I. Lundstrom, Anal. Chim. Acta, 164, 127 (1984).
4) N. Miura, H. Kato, N. Yamazoe, and T. Seiyama, Proc. Int, Meet. Chem. Sensors, Fukuoka (1983), p. 233.
5) N. Miura, H. Kato, N. Yamazoe, and T. Seiyama, Chem. Lett., 1983, 1573.
6) N. Yamazoe, N. Miura, H. Arai, and T. Seiyama, Proc. Int. Conf. Solid-State Sensors & Actuators, Philadelphia (1985), p. 340.
7) N. Miura, H. Kato, Y. Ozawa, N. Yamazoe, and T. Seiyama, Chem. Lett., 1984, 1905.
8) N. Miura, H. Kato, H. Kaneko, and N. Yamazoe, Nippon Kagaku Kaishi, 1986, 435.
9) N. Miura, H. Kato, N. Yamazoe, and T. Seiyama, "Fundamentals and Applications of Chemical Sensors," ed by D. Schuetzle and R. Hammerle, ACS, Washington, DC (1986), p. 203.
10) N. Yamazoe, H. Kaneko, and N. Miura, Proc. 6th Sensor Symposium, Tsukuba (1986), in press.

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