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CO and H_2 Sensing Properties of Proton-Conductor Sensor Using Pt-Loaded Oxide Electrodes

Norio MIURA, Kuniaki KANAMARU, Youichi SHIMIZU, and Noboru YAMAZOE*
Department of Materials Science and Technology, Graduate School of Engineering Sciences, Kyushu University, Kasuga, Fukuoka 816

An amperometric proton-conductor sensor was newly developed for the selective detection of CO at room temperature by using a couple of Pt-loaded oxide (SnO_2 and WO_3) electrodes. The CO sensitivity of the sensor element was about 7 times higher than the H_2 sensitivity and the 90% response time was about 3 min. The selective detection of H_2 was possible when a Pt-black electrode was combined with a Pt-loaded WO_3 electrode.

Sensitive and selective detection of CO is important for preventing fatal gas accidents caused by incomplete combustion of gases in houses and factories. Many solid-state CO sensors using semiconductors or solid electrolytes have been reported, i.e., ThO_2-doped SnO_2 sensor,1) diode-type sensor,2) SnO_2 sensor with a heat cleaning function,3) stabilized ZrO_2 sensor with an SnO_2 catalyst as a gas filter,4) and so on. However, these sensors must be operated at elevated temperatures such as about 100-300 °C to achieve stable and quick responses. We recently reported that potentiometric-,5) amperometric-,6) and four probe-7) sensors using proton conductors could detect H_2 and CO in air stably even at room temperature. Such low-temperature operation is advantageous for both decrease in power consumption and simplification in sensor system. The proton-conductor sensors reported so far used Pt electrodes, and their sensitivity to CO was rather low compared with that to H_2. To overcome this situation, attempts were made to replace the Pt electrodes by oxide electrodes based on WO_3 and SnO_2. Tungsten oxide is famous for its electrochromic reaction, $WO_3 + xH^+ + xe^- \rightarrow H_xWO_3$. It is also known that WO_3 reacts with molecular hydrogen, $WO_3 + (x/2)H_2 \rightarrow H_xWO_3$, in the presence of Pt catalyst.8) Tin oxide has also been well studied as a semiconductor electrode. When these oxides, loaded with a small amount of Pt, were utilized as the electrodes, sensing properties were found to be changed greatly. It was found that a CO-sensitive element of an amperometric-type could be fabricated eventually by using a couple of oxide electrodes. This paper describes the properties of the oxide electrodes as introduced to the proton-conductor sensors as well as the sensing performances of the new-type CO sensor.

The sensor elements fabricated here were composed of a proton-conductor disc and two electrodes, as shown schematically in Fig. 1. The electrode materials chosen were Pt-loaded WO_3, Pt-loaded SnO_2 and Pt black. The loading of fine Pt particles (0.1-0.5wt%) on WO_3 (or SnO_2) powder was carried out by a conventional impregnation method. To prepare the proton-conductor disc, Antimonic acid powder ($Sb_2O_5 \cdot 2H_2O$; donated by Toagosei Chem. Ind.) was mixed with 20 wt% Teflon powder (Lubron L-2 ; Daikin Ind.) and cold-pressed into a disc at 10 MPa. The disc was sandwiched between the layers of powder electrode materials and cold-pressed once again into a sensor element (disc), 10 mm in diameter and 5 mm thick, at 15 MPa. Electrical contacts between each electrode and Cu leads were secured by carbon paste. A sample gas prepared by mixing a small amount of flammable gas (H_2, CO, etc.) with air was passed over the sensor element at 50 cm^3/min. The gas flow was always humidified by passing through liquid water to prevent the proton conductor from drying. As a signal output, short-circuit current was measured by means of an ammeter (Zero Shunt Ammeter, HM-104; Hokuto Denko) at room temperature.

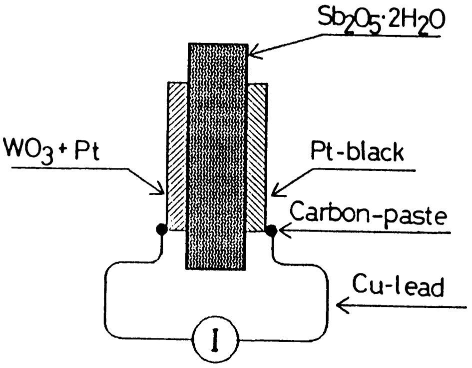

Fig. 1. Structure of the proton-conductor sensor (Element I).

In order to know the properties of the oxide electrodes, the first sensor element tested had a WO_3(+0.1 wt% Pt) electrode and a Pt-black electrode (Element I): WO_3(+0.1 wt% Pt) | AAD | Pt-black, (AAD:Antimonic Acid Disc). Figure 2 shows the response of this element to H_2 in air. In the sample gas, the short-circuit current was found to flow from the oxide electrode to the Pt electrode through the proton conductor disc. The short-circuit current increased in proportion to the H_2 concentration up to 1.3%. The 90% response time to 1.0% H_2 in air was as short as about 60 s at room temperature. These sensing characteristics were similar to those of the previously reported element which had a pair of Pt-black electrodes with a gas diffusion layer covering one electrode.[6] Combination of an oxide electrode with a Pt electrode was thus found to give an element which was almost the same in sensing characteristics but simpler in structure. The element showed a modest sensitivity to CO but no sensitivities to other reducing gases at room temperature, as shown in Table 1. It should be remarked that the loading of Pt on WO_3 was essential, because pure WO_3 gave no significant electrode activities to any gases at room temperature. As is well known, the loaded Pt is considered to act as an activator for gases.

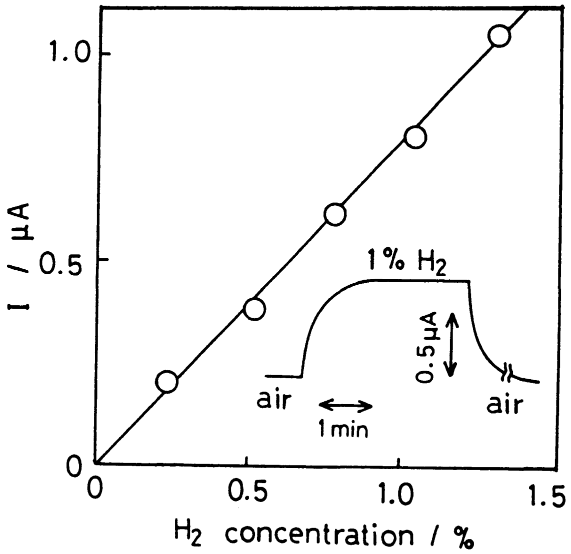

Fig. 2. Dependence of the short-circuit current of Element I on H_2 concentration in air at room temperature and response curve to 1% H_2.
Element I : WO_3+0.1wt%Pt | AAD | Pt.

The gas sensing mechanism of the above sensor element appears to be essentially similar to that of the previously reported element discussed elsewhere.[9] In the sample gas flow (H_2 + air), the electrochemical oxidation of H_2 (1) and the electrochemical reduction of O_2 (2) will proceed at the same time on each electrode. Under the open-circuit conditions, the rates of these reactions eventually become

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

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

equal to give steady concentrations of electrons (a mixed potential) and protons at the electrode-proton conductor interface. Under the short-circuit conditions, however, the two reactions can not be balanced off on each electrode, causing a flow of H^+ from one electrode to another. In the case of Element I, the flow of H^+ took place in a direction from the oxide electrode to the Pt electrode. This indicates that Reactions (1) and (2) dominate on the oxide electrode and the Pt electrode, respectively. As reported previously, Reaction (1) is a diffusion-limited process on each electrode because of low concentrations of H_2 in the sample gas, so that the flux of H^+ flow should also be proportional to the H_2 concentration, as was observed experimentally.

Table 1. Sensitivity of Sensor Elements I and II to various gases

Gas	Conc. (ppm)	Current (μA)	
		Element I	Element II
H_2	1300	0.10	0.17
CO	1000	0.02	1.18
CH_4	14000	0	0
C_3H_8	7000	0	0
i-C_4H_{10}	1000	0	0.06
C_2H_5OH	1000	0	0.09

In order to increase the CO sensitivity of the above type element, examinations were extended to include various semiconductive oxides other than WO_3. As a result, a Pt-loaded SnO_2 electrode was found to endow the element with a higher CO sensitivity. Moreover, the sensitivity ratio of CO to H_2 could be changed drastically by controlling the amount of Pt dispersed on SnO_2. For example, a SnO_2(+0.5 wt% Pt) electrode gave a CO sensitivity about twice as high as an H_2 sensitivity. These results allowed us to conceive a new way for improving the selectivity to CO, i.e., combination of a SnO_2-based electrode and a WO_3-based electrode. By this way, we found that the CO selectivity could be enhanced fairly well by controlling the amounts of Pt dispersed in both oxide electrodes. For example, a very high CO sensitivity was marked by the following element (Element II): WO_3(+0.1 wt% Pt) | AAD | SnO_2(+0.5 wt% Pt). Figure 3 shows the responses of Element II to 1000 ppm CO and 1300 ppm H_2 in air at room temperature. It is rather surprising that the sensitivity to CO, about 7 times as high as that to H_2, was obtained with the 90% response of about 3 min. The current (H^+

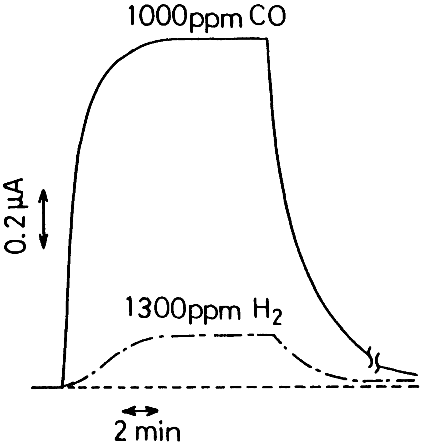

Fig. 3. Response curves of Element II to 1000 ppm CO and 1300 ppm H_2 in air. Element II: WO_3+0.1wt%Pt | AAD | SnO_2+0.5wt%Pt.

flow) was conducted from the SnO_2-based electrode to the WO_3-based electrode for both CO and H_2. The dependence of the short-circuit current on the CO concentration was not linear for this element as shown in Fig. 4, and the accuracy of CO detection tended to increase relatively in a lower concentration range below 200 ppm. The sensitivities of Element II to various gases are summarized in Table 1. Unlike Element I, this element showed sensitivities to i-C_4H_{10} and C_2H_5OH. Nevertheless the sensitivity to CO was conspicuously high compared with those to other reducing gases. This seems to assure that the new type element with a couple of oxide electrodes is promising for the sensitive detection of CO in air at room temperature.

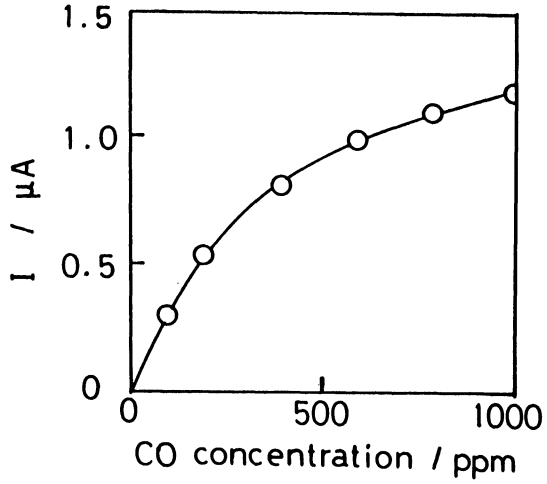

Fig. 4. Dependence of short-circuit current on CO concentration in air. Element II: WO_3+0.1wt%Pt | AAD | SnO_2+0.5wt%Pt.

It is considered that CO is oxidized electrochemically as follows.

$$CO + H_2O \rightarrow CO_2 + 2H^+ + 2e^- \quad (3)$$

Therefore Reactions (2) and (3) take place simultaneously on each electrode in the presence of CO. A large current flow from the SnO_2-based electrode to the WO_3-based electrode suggests that the former electrode is much more active for Reaction (3) than the latter. On the other hand, a low sensitivity to H_2 suggests that the two electrodes are not different so much in activities for Reaction (1). Thus the virtue of Element II appears to come from its structure which allows a large imbalance in the CO oxidation activity between the coupled electrodes while keeping a fair balance in the H_2 oxidation activity. It is expected that more elaborate control of the Pt dispersion would lead to a better balance in the H_2 oxidation activity, and this seems to give an element more selective to CO over H_2.

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