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RESPONSE OF A SOLID-STATE POTENTIOMETRIC SENSOR USING LaF_3 TO A SMALL AMOUNT OF H_2 OR CO IN AIR AT LOWER TEMPERATURES

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A solid electrolyte cell using LaF_3 was found to be able to detect a small amount of H_2 or CO in air at lower temperatures. The 90% response of the electromotive force (EMF) of the sensor to 1.3% H_2 in air was as fast as 3 min at 20 °C. The sensing mechanism is attributed to a mixed electrode potential on the sensing electrode.

Recently we have found that the proton conductors such as $Zr(HPO_4)_2 \cdot H_2O$ and $Sb_2O_5 \cdot nH_2O$ are very useful for the potentiometric detection of small amounts of H_2 or CO in air even at room temperature.[1,2] The excellent performance of the sensors at room temperature is attributed to the high ionic conductivities of the proton conductors. It has been also found that the EMF of the solid electrolyte cell using the fluoride ion conductors such as LaF_3[3,4] and $PbSnF_4$[5] could respond to a change of oxygen partial pressure at temperature lower than 100 °C. These fluorides are known to have relatively high ionic conductivities at lower temperatures. We report here that the solid electrolyte cell using LaF_3 can also detect small amounts of H_2 or CO in air at lower temperatures.

The sensor element used is expressed as the following cell;

$$Sn,SnF_2\binom{\text{reference}}{\text{electrode}} \mid LaF_3 \text{ pellet}\binom{\text{solid}}{\text{electrolyte}} \mid \text{Pt black}\binom{\text{sensing}}{\text{electrode}}.$$

The structure of the sensor is almost the same as that reported before.[3] The powder of LaF_3 was pressed at 6×10^4 N/cm^2 into a compact pellet 10 mm in diameter and 0.5 mm in thickness. Platinum black powder was applied on the end of the pellet as a sensing electrode. The mixture of Sn and SnF_2 was applied on the other end of the pellet as a reference electrode. This reference electrode was covered with epoxy resin in order to avoid a contact with a sample gas. Sample gases were prepared by mixing of air and small amounts of H_2 (or CO). The EMF of the cell was measured by an electrometer (Takeda Riken Co. Ltd., TR-8651) in a sample gas flow (100 cm^3/min).

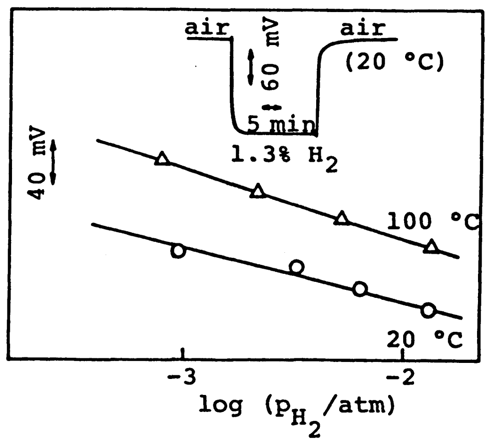

Fig. 1. Response curve and dependence of EMF on H_2 partial pressure in air.

The response curve of the sensor to 1.3% H_2 in air at 20 °C is shown in Fig. 1. The 90% response was as fast as 3 min. Birot et al.[6] reported that a cell using $PbSnF_4$ had a sensitivity to H_2 at 20 °C but needed as long as about 5 h for 90% response. Figure 1 also shows the dependence of the EMF of the present sensor on p_{H_2} in air at 20 and 100 °C. The EMF decreased linearly with an increase in the logarithm of p_{H_2} at each temperature in a similar manner as the case of the proton conductor sensors,[1] in which the response to H_2 in air has been shown to be attributed to a change in mixed potential.[2] The EMF behavior of this cell shown in Fig. 1 seems to be due to the mixed potential on the sensing electrode. In air the reaction (1) was suggested to be equilibrated on the sensing electrode of the similar type of cell.[4] The generation of EMF of the cell in the oxygen

$$O_2 + 2e = 2O^- \qquad (1)$$

atmosphere has been discussed elsewhere.[3,4] If a small amount of H_2 exists in the atmosphere around the sensing electrode, the reaction (2) also takes place on the electrode to consume O^- ion. Thus the sensing electrode of this sensor is at

$$H_2 + O^- = H_2O + e \qquad (2)$$

a mixed potential determined by these reactions (1) and (2). It is added that the sensor showed no proper response in a gaseous mixture of H_2 and N_2.

Futhermore, this cell was found to respond to a small amount of CO in air as shown in Fig. 2. The response, however, was rather slow compared with that to H_2, needing ca. 10 min for 90% response at 100 °C. It is also seen from this figure that the EMF of the cell decreased linearly with increasing p_{CO} at 100 °C, while the EMF was independent of the p_{CO} at 50 °C. This fact suggests that reaction (3) takes place on the sensing electrode at 100 °C simultaneously with reaction (1). Therefore,

$$CO + O^- = CO_2 + e \qquad (3)$$

the response to CO is considered to be attributed to the mixed potential determined by both reactions (1) and (3). The poor response of the sensor to CO at 50 °C seems to be ascribable to that reaction (3) cannot proceed smoothly at lower temperatures. As for the sensing mechanism of the sensor, further investigation is under way.

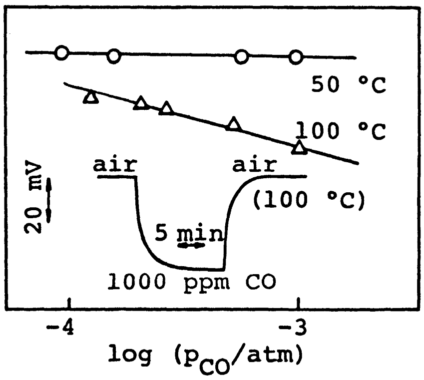

Fig. 2. Response curve and dependence of EMF on CO partial pressure in air.

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