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A POTENTIOMETRIC OXYGEN SENSOR USING LaF_3 SINGLE CRYSTAL OPERATIVE AT ROOM TEMPERATURE

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The electromotive force (EMF) of a solid-electrolyte cell using LaF_3 single crystal was found to respond to a change of oxygen partial pressure even at 25 °C, in accordance with the Nernst's law. The 90% response time of this sensor was as short as ca. 3 min at 25 °C.

Stabilized-zirconia oxygen sensors have been used in exhaust-gas control systems at temperatures higher than ca. 600 °C. Although various attempts have been made to lower the working temperature of the sensors, the lowest temperature ever achieved was ca. 300 °C mainly because the ionic conductivity of stabilized-zirconia becomes too small at low temperatures. On the other hand, a new type of potentiometric oxygen sensors using metal halides such as SrO-doped $SrCl_2$,[1] $PbSnF_4$,[2] and LaF_3[3] were recently proposed. These sensors can be operated at temperatures lower than ca. 250 °C, owing to higher ionic conductivities of these halides. For example, we have reported[3] that the EMF of the sensor using a LaF_3 pellet could detect a change of oxygen partial pressure at 50 °C. The response of the sensor, however, was rather slow at 50 °C; ca. 30 min for 90% response. Siebert et al. also reported[2] that the oxygen sensor using $PbSnF_4$ could work at 100 °C but needed as long as 340 min for 90% response. A solid-state oxygen sensor which exhibits both reproducible and fast responses at room temperature must have more wide applications. We report here an oxygen sensor using a LaF_3 single crystal in place of a LaF_3 pellet with a considerably fast response even at 25 °C.

The sensor element used is represented as follows:

$$\underset{(\text{reference electrode})}{Sn,SnF_2} \mid \underset{(\text{solid electrolyte})}{LaF_3 \text{ single crystal}} \mid \underset{(\text{sensing electrode})}{\text{Pt black, } O_2}.$$

Its schematic view is illustrated in Fig. 1. The LaF_3 single crystal containing 2% (mass fraction) Eu (10 mm × 10 mm × 3 mm) was purchased from Yamanaka Chemical Ind. Ltd. A satisfactory contact between the reference electrode and the solid electrolyte was obtained by melting SnF_2 powder on the surface

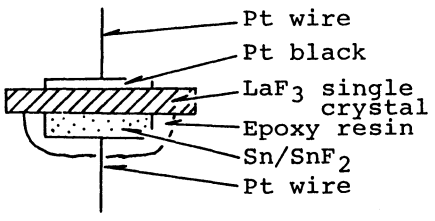

Fig. 1. Schematic view of the sensor.

of LaF_3 at ca. 220 °C in N_2. The reference electrode was covered with epoxy resin in order to avoid a contact with sample gas. As a sensing electrode a mixture of Pt black powder and a small amount of LaF_3 powder was applied onto the LaF_3 single crystal. Sample gases with various partial pressures of O_2 were prepared by mixing of O_2 and N_2 and passed over the cell at a rate of 100 cm^3/min. The EMF of the cell was measured by an electrometer (Takeda Riken Co. Ltd., TR-8651).

Figure 2 shows the dependence of the EMF of the sensor on the logarithm of oxygen partial pressure at temperature of 25 °C and 100 °C. The EMF increased linearly with increasing logarithm of oxygen partial pressure at each temperature, in accordance with the Nernst's law. As the potential of the Sn/SnF_2 reference electrode is independent of the changes in oxygen partial pressure at a constant temperature, the responses of EMF shown in Fig. 2 are caused by the change of the sensing electrode potential. The slopes of the straight lines at each temperature suggest the following 2-electron reaction of oxygen molecules.

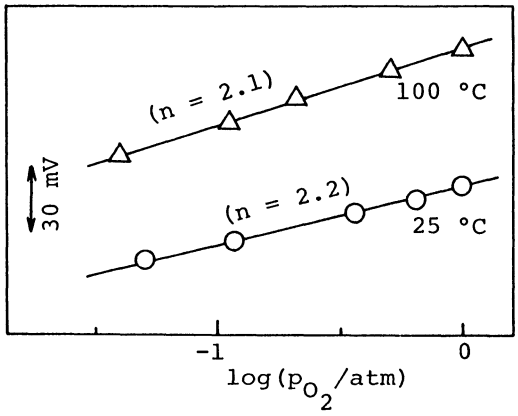

Fig. 2. Dependence of EMF of the sensor on oxygen partial pressure.

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

It is noteworthy that the present oxygen sensor works well even at 25 °C, where no response could be obtained with the pellet sensors. This can be attributed to the fact that the conductivity of LaF_3 single crystal is higher than that of the LaF_3 pellet: the resistances of present sensor element and the pellet type one are ca. 10^7 Ω and ca. 10^9 Ω, respectively, at 50 °C. As far as we know, there has been no solid-electrolyte oxygen sensor operative at a room temperature. Furthermore, the response of this sensor was fairly fast at 25 °C as shown in Fig. 3, i.e., the time for the 90% response was only ca. 3 min in the increasing direction of the oxygen partial pressure and ca. 5 min in the opposite direction. No clear explanation can be offered for such a remarkable response of this sensor at present. According to our experience the sensor response tends to become fast after exposure to water vapor. This suggests that surface hydroxyl groups of LaF_3 produced by hydrolysis may be contributing some positive effects on the quick response.

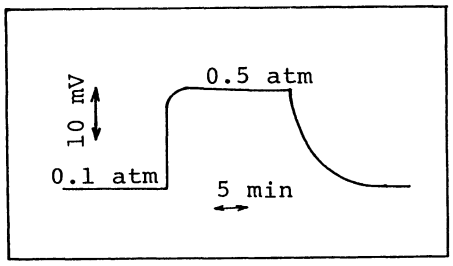

Fig. 3. Response curve of the sensor at 25 °C.

References

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2) E. Siebert, J. Fouletier, and S. Vilminot, Solid State Ionics, 9&10, 1291 (1983).

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