Mixed-potential-type Zirconia-based Sensor Using In_2O_3 Sensing-Electrode for Selective Detection of Methane at High Temperature

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We have fabricated a mixed-potential-type yttria-stabilized zirconia (YSZ)-based sensor and examined its sensing characteristics to methane (CH_4) at high operating temperatures. Among various oxide sensing electrodes (SEs) tested, In_2O_3 was found to give the highest sensitivity as well as good selectivity to CH_4 at 790 °C, although the response was very slow. To improve the response rate, sintering temperature of In_2O_3-SE was changed in the range of 1200–1400 °C. As a result, the sensor attached with the 1300 °C-sintered In_2O_3-SE showed quicker response which was about fifteen times higher than that for the 1400 °C-sintered In_2O_3-SE.

There has been a strong concern on environmental pollution due to emissions from automobiles and various industrial furnaces. In fact, some of the hydrocarbons (HCs) have strong photochemical reactivity which leads to urban ozone and greenhouse effect. Thus, there is a strong demand for in situ detection and monitoring of HCs. So far, there have been many reports on HCs sensors using YSZ as a solid electrolyte.[1–12] At the moment, there are few reports on selective CH_4 sensor for automobile exhausts,[13] because CH_4 has not been regulated as an air pollutant. However, it is highly possible to be regulated in future owing to it's high contribution to greenhouse effect. Thus, we have focused here on selective detection of CH_4 by means of the mixed-potential-type YSZ-based sensor using oxide-SE. The CH_4 sensing characteristics of the sensor were examined at high temperatures, especially in excess of 700 °C. The sintering temperature of SE and the operating temperature of sensor were modulated to obtain higher selectivity and quicker response.

A commercially available one-end-opened YSZ tube (8 mol % Y_2O_3-doped, NKT, Japan) was used for fabrication of a sensor device. The length of the YSZ tube was 300 mm, and its inner and outer diameters were 5 and 8 mm, respectively. Each of commercial oxide (ZnO, SnO_2, TiO_2, Cr_2O_3, Fe_2O_3, In_2O_3, 99.9% each, Kishida Chemical, Japan) powder samples was thoroughly mixed with an organic solvent (α-terpineol) in the weight ratio of 1:1, and the resulting paste was applied as SE on the outer surface of the YSZ tube. In addition, the pure Pt paste (Tanaka Kikinzoku, TR-7601, Japan) was applied on the top of the inner surface of the tube to form a Pt/air reference electrode (RE). Finally, the YSZ tube attached with SE and RE layers was sintered at temperatures of 1200–1400 °C for 2 h in air.

The fabricated sensor was assembled in a quartz tube, and its sensing characteristics were measured by using a conventional gas-flow apparatus equipped with a furnace operating in the temperature range of 700–850 °C. The total flow rate of the base gas (dry synthetic air) or the sample gas was kept constant at $100\,cm^3/min$. The water vapor (5 vol % H_2O) was introduced into the sensor along with the base gas or the sample gas by means of a home-made water-vapor generator. The sample gas containing each of various gases (CH_4, CO, NO, NO_2, C_3H_6, and C_3H_8) was prepared by diluting the respective parent gases with dry synthetic air. The difference in potential (emf) between SE and RE of the tubular sensor was measured with a digital electrometer (Advantest, R8240) as a sensing signal.

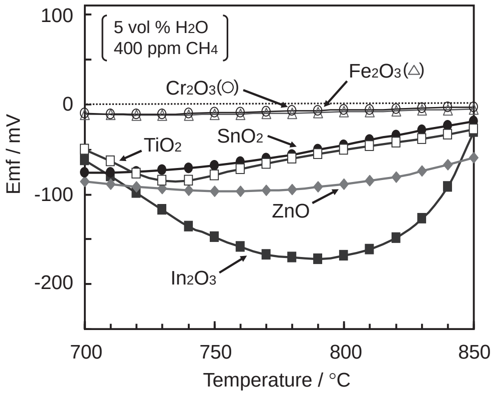

Figure 1. Temperature dependence of emf value to 400 ppm CH_4 for the sensors using each of various oxide-SEs under the wet condition.

To choose the best oxide-SE and operating temperature for the selective detection of CH_4, various metal oxides sintered at 1400 °C (ZnO and SnO_2: 1200 °C) were examined as SE, and the emf responses to 400 ppm CH_4 were measured in the temperature range of 700–850 °C in the presence of 5 vol % H_2O (Figure 1). The operating temperature was increased from 700 °C with 10 °C step in every 10 min, and the steady-state emf value was measured at each temperature. It is seen that among the various oxide-SEs examined, In_2O_3-SE gives the highest emf value to 400 ppm CH_4 at around 790 °C. Therefore, emf response transients to various gases (400 ppm each) for the sensor attached with In_2O_3-SE were examined in the temperature range of 770–840 °C under the wet condition, the results of which are shown in Figure 2. It is noted that the emf values to the examined gases, except for CH_4, are changed from negative to positive at around 790 °C. In fact, at this temperature, the emf value to each of these gases (CO, NO, C_3H_6, and C_3H_8) is almost 0 mV, whereas emf to CH_4 is significantly low. Thus, there is a high possibility for the selective detection of CH_4. Hereafter, the detailed sensing characteristics were examined for the sensor using In_2O_3-SE operating at 790 °C.

Figure 3a shows the response transients to various gases for the present sensor. The sensor shows high emf response of about −90 mV after 10 min flowing of 400 ppm CH_4, while insignificant cross sensitivities to CO, NO, C_3H_6, and C_3H_8 were ob-

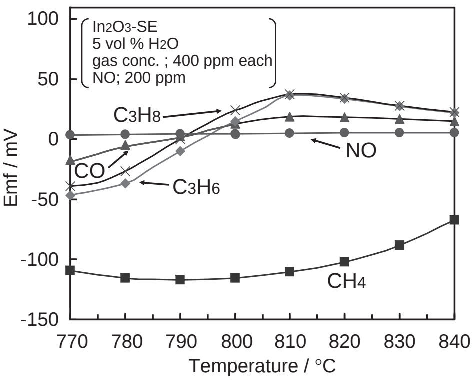

Figure 2. Temperature dependence of emf value to various gases for the sensor attached with In_2O_3-SE under the wet condition.

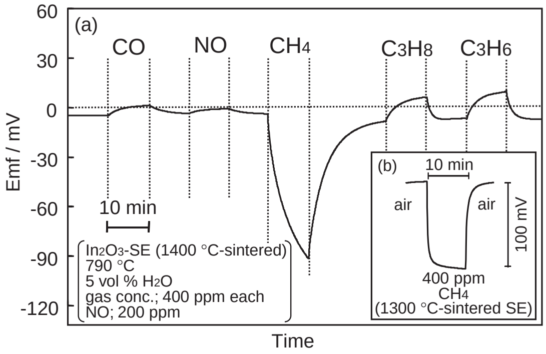

Figure 3. (a) Response transients to various gases at 790 °C for the tubular sensor using the 1400 °C-sintered In_2O_3-SE under the wet condition. (b) Response transient to 400 ppm CH_4 for the sensor using the 1300 °C-sintered In_2O_3-SE.

served. However, the response/recovery to CH_4 was very slow. It took about an hour to reach the steady-state emf value. In fact, the 90% response time was as long as about 40 min. Such a slow response is not acceptable to the actual application.

By the way, we have already reported that the grain size and the pore size of oxide-SE in the case of mixed-potential-type NO_2 sensor can affect the response/recovery rate owing to the change in the number of reaction sites at YSZ/SE interface.[14,15] It has been observed that smaller grains and pores lead to quicker response/recovery. Thus, to increase the number of reaction sites at YSZ/SE interface and to improve response/recovery rate of the present sensor, the sintering temperature of In_2O_3-SE was decreased from 1400 °C down to 1200 °C. Then, the emf responses to 400 ppm CH_4 for the sensors attached with each of In_2O_3-SEs sintered at 1200, 1300, and 1400 °C were examined at 790 °C under the wet condition. As a result, it was found that the decrease in sintering temperature of SE improved response rate significantly, as expected. Actually, the mean grain sizes observed by SEM were ca. 2, 0.8, and 0.4 µm for In_2O_3-SE sintered at 1400, 1300, and 1200 °C, respectively. However, the sensitivity of the sensors was also decreased a bit with decreasing the sintering temperature, probably owing to the decrease of porosity (smaller pore size and higher surface area). Such a high surface area can promote the conversion rate of the gas-phase oxidation of CH_4 during the diffusion through the In_2O_3-layer. Thus, by considering the response/recovery rate as well as the CH_4 sensitivity, the optimum sintering temperature of In_2O_3-SE was determined to be 1300 °C.

Figure 3b shows the response transient to 400 ppm CH_4 for the sensor attached with the 1300 °C-sintered In_2O_3-SE. It is clear that response/recovery rate is significantly improved and the 90% response is as short as 150 s. In this case, the response is about 15 times faster, compared with the sensor using the 1400 °C-sintered SE under the same operating condition. In addition, it was found that the sensitivity ($\Delta\text{emf} = \text{emf}_{\text{sample}} - \text{emf}_{\text{air}}$) varied almost linearly with the CH_4 concentration on a logarithmic scale for the sensor attached with each of the 1300 °C- and 1400 °C-sintered In_2O_3-SEs, as has been reported previously for the mixed-potential-type NO_2 sensor.[16,17] It is noteworthy that the CH_4 sensitivity as well as the CH_4 selectivity are not changed even if the sintering temperature is decreased from 1400 to 1300 °C. The improvement in response rate observed for the sensor attached with the 1300 °C-sintered In_2O_3-SE can be attributable to the increased number of reaction site at YSZ/SE interface. However, further investigation on the detailed sensing characteristics as well as the sensing mechanism is needed for actual application of the present sensor.

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