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Selective NO_2 detection using YSZ-based amperometric sensor attached with $NiFe_2O_4$(+ Fe_2O_3) sensing electrode

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ABSTRACT

A YSZ-based amperometric sensor using spinel oxide as a sensing electrode (SE) has been proposed here for detecting NO_2 sensitively and selectively. Among the examined spinel-oxide SEs, $NiFe_2O_4$-SE was found to give relatively sensitive and selective response to NO_2. Addition of 30 wt.% Fe_2O_3 into $NiFe_2O_4$-SE increased the NO_2 response, while the responses to other interfering gases were maintained small. The sensor using $NiFe_2O_4$(+30 wt.% Fe_2O_3)-SE could detect NO_2 as low as 5 ppm in humid air within 15 s (90% response time). The mechanism of NO_2 selective behavior given by the sensor using $NiFe_2O_4$(+30 wt.% Fe_2O_3)–SE was investigated.

1. Introduction

Combustion process in automotive engine, that emits various kinds of harmful gases, have challenged scientists in various levels including its environmental effects. Nitrogen oxides (NO and NO_2) are common pollutants from the combustion process and have been reported to be responsible for detrimental effects on human health and atmospheric environments. This compelled many countries to impose a stringent regulation regarding the emission of hazardous pollutants including NO_x. Therefore, a sensing device that can detect NO_x sensitively and selectively is highly important to monitor the emission of NO_x into environments.

For many years, the electrochemical sensor based on yttria-stabilized zirconia (YSZ) has been proposed as a high-performance gas sensor, owing to the mechanical, thermal and chemical stability of YSZ under harsh environments [1–5]. A practical zirconia-based amperometric sensor for NO_x detection had been developed by NGK group. This sensor employs two cells (pumping cell and sensing cell). The pumping cell is used to control the O_2 concentration down to a very low level and then NO_x can be detected in the sensing cell [6–9]. Usually, the sensing signal of an amperometric sensor is the change in current (I) upon the exposure toward sample gas and to base gas. Change in current can be observed, when electrochemical reaction of the sample gas diluted with base gas occurs at the interface between sensing electrode (SE) and YSZ. However, before reaching the interface, some amounts of the sample gas would be involved in the gas-phase reaction (oxidation or decomposition) in the porous SE layer (Eq. (1) in the case of NO_2) and it may reduce the amount of sample gas which can reach and react electrochemically at the SE/YSZ interface (Eq. (2)) [5].

$$NO_2(g) \rightleftarrows NO(g) + \frac{1}{2}O_2(g) \quad (1)$$

$$NO_2 + 2e^- \rightarrow NO + O^{2-} \quad (2)$$

As a result, the generated current (gas response) will be governed by the catalytic activity of the SE material toward gas-phase and electrochemical reactions. This makes the choice of SE material is important in developing a high-performance electrochemical YSZ-based gas sensor.

When it comes to prospective functional materials, spinel-type oxide has been reported to have attractive properties that can be

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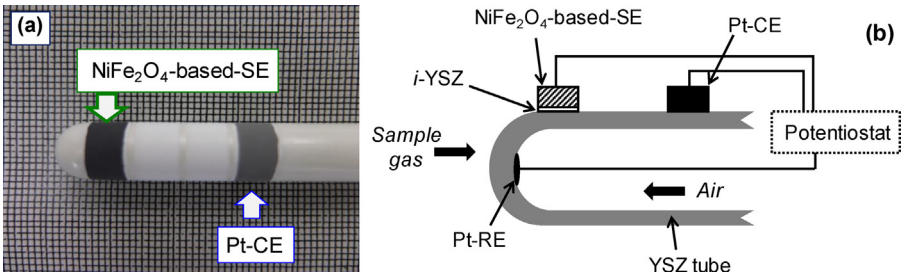

Fig. 1. Exterior view (a) and schematic illustration (b) of YSZ-based amperometric sensor using $NiFe_2O_4$-based-SE.

used for various applications, such as catalyst or electrode materials [10–14]. Spinel-type oxide has AB_2O_4 general formula that is built by a divalent cation occupying A site and a trivalent cation occupying B site. Spinel oxide has also been studied and reported to be applicable for NOx sensing materials for the YSZ-based potentiometric and impedancemetric sensors [15–19]. In this study, a highly selective and sensitive NO_2 sensor is proposed by the utilization of YSZ-based amperometric sensor by using $NiFe_2O_4$ spinel oxide and Fe_2O_3 additive as SE. The selective sensing performances as well as the sensing mechanism of the present sensor have been investigated here.

2. Experimental

2.1. Sensor fabrication

An open-end tubular YSZ (ZrO_2(+8 mol% Y_2O_3), Nikkato, Japan, with 300 mm in length, 5 mm inner diameter and 8 mm outer diameter), was used as a substrate to form electrodes. An intermediate layer of YSZ (*int*-YSZ) was prepared by applying the YSZ paste on the surface of YSZ tube. The YSZ paste was made by mixing YSZ powder (Tosoh, Japan) with α-terpineol. After drying at 100 °C overnight, the oxide SE layer was then fabricated by applying the oxide paste on the surface of *int*-YSZ layer. The oxide paste was made in similar fashion as the YSZ paste. The oxide powders used here were supplied by Kojundo Chemicals, Japan and Riken, Japan. Pt paste (Tanaka Kikinzoku, Japan) was also applied on the surface of YSZ layer to form counter electrode (CE) in parallel with SE. The reference electrode (RE) layer was made by applying the Pt paste on the inner surface of YSZ tube. After SE-, CE- and RE-paste were properly applied on YSZ, the whole YSZ tube was dried at 100 °C overnight and subsequently sintered at 1200 °C for 2 h. As the current collector, a Pt wire was coiled around the surface of each of SE, CE and RE. The RE was always open to atmospheric air to form Pt/air-RE. The final form of the fabricated sensor is depicted and illustrated in Fig. 1.

2.2. Sensing characteristic evaluation

The sensing signal was measured under amperometric mode with a 3-electrode system by using a potentiostat (HZ300, Hokuto Denko, Japan). The gas flow was alternated between the humidified base gas (air + 5 vol.% H_2O) and the humidified sample gas (CO, CH_4, C_3H_8, C_3H_6, H_2, NO, NO_2, NH_3 each + 5 vol.% H_2O) at a constant flow-rate of 100 cm^3/min. The sample gas concentration was always set at 100 ppm, except for the measurements of gas concentration dependence of current response. Gas response generated by an amperometric sensor is defined by the following Eq. (3):

$$\text{Gasresponse}(\Delta I) = I_{\text{samplegas}} - I_{\text{basegas}} \quad (3)$$

3. Results and discussion

3.1. Sensing characteristics of the sensor using $NiFe_2O_4$-based-SE

Nine different spinel oxides were selected as a prospective SE candidate for NO_2 detection. The sensing-characteristic measurements for the YSZ-based sensors using each of spinel SEs were carried out at operating temperature of 500 °C and with applied potential of −100 mV vs. Pt/air-RE. Among the examined SEs, $NiMn_2O_4$–SE gave not only the highest current value to 100 ppm NO_2 but also higher current value even in base gas, resulting in low NO_2 response ($\Delta I = 2.1$ μA) (Fig. 2). Compared with other examined spinel-oxide SEs, $NiFe_2O_4$-SE generated lower current value in base gas (close to 0 μA), while maintained higher response toward 100 ppm NO_2. This led to high NO_2 response. On the contrary, each of currents to other examined gases was found to be much lower than that to NO_2, resulting in high selectivity to NO_2 (Fig. 2). By considering the sensitivity as well as the selectivity to NO_2, $NiFe_2O_4$-SE was confirmed to be the most appropriate SE material for NO_2 detection.

To further improve the sensing characteristic to NO_2, Fe_2O_3 was incorporated into $NiFe_2O_4$-SE. Fe_2O_3 was selected as the additive owing to its low cost and the reported capability to detect NO_2 [20–23]. Since Fe is cheaper than Ni, incorporating Fe_2O_3 into $NiFe_2O_4$ is expected to reduce the fabrication cost of the SE material. Fe_2O_3 was then added into $NiFe_2O_4$ with incremental concentration and the sensing performances of the sensors using each of $NiFe_2O_4$(+Fe_2O_3)-SEs were examined at 500 °C under humid condition with the applied potential of −100 mV vs. Pt/air-RE. As can be seen from Fig. 3, the NO_2 response was found to increase with increasing Fe_2O_3 addition to $NiFe_2O_4$-SE up to 30 wt.%. The NO_2 response magnitude generated by the sensor using $NiFe_2O_4$(+ 30 wt.% Fe_2O_3)-SE was almost doubled, compared with that using $NiFe_2O_4$-SE. However, when Fe_2O_3 addition was higher than 30 wt.%, the response to NO_2 was decreased as the amount of Fe_2O_3 increased. On the other hand, the response to other gases were kept small, even when the amount of Fe_2O_3 addition was largely changed. Among the examined SE composition, $NiFe_2O_4$(+30 wt.% Fe_2O_3)-SE gave not only the highest response to NO_2 but also minor responses to other examined gases, resulting in high selectivity to NO_2.

The sensing performance of the sensor using $NiFe_2O_4$(+30 wt.% Fe_2O_3)-SE was then explored by varying the operating temperature from 450 °C to 600 °C, as shown in Fig. 4. At 450 °C, the sensor was insensitive to any tested gases. The gas response as well as the baseline value increased with increasing operating temperature. However, the most selective NO_2 response was observed when the operating temperature was set at 500 °C. Thus, 500 °C was selected hereafter as the optimum operating temperature for the sensor using $NiFe_2O_4$(+30 wt.% Fe_2O_3)-SE. The NO_2 sensing performance was also optimized by changing applied potential for the sensor. The sensing characteristic of the sensor using $NiFe_2O_4$(+30 wt.% Fe_2O_3)-SE was tested under three different applied potential; −100,