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Impedancemetric NOx Sensor Using YSZ-Based Solid Electrolyte Attached with Oxide Receptor

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Abstract
New type simple solid-electrolyte NOx (NOx; NO, NO_2) sensor devices were fabricated using an yttria-stabilized zirconia (YSZ) as an impedance transducer and metal oxides (Fe_2O_3, Co_3O_4, NiO, CuO and ZnO) as receptors. The sensor signal could be simply detected as the impedance change of the only YSZ plate. The sensing performance of the impedancemetric NOx sensor for the detection of NOx in the range 10 ~ 150 ppm at 300 ~ 500˚C was investigated using AC impedance analyzer. The NiO/YSZ-based compact impedancemetric sensor device showed good sensing properties for NO and NO_2 at 400˚C on 100 kHz.

Key words: Impedance, Nitrogen oxide, Gas sensor, Nickel oxide, YSZ

Introduction

Nitrogen oxides (NOx; NO, NO_2) emissions in exhaust gases coming from automobiles have been becoming the cause of atmospheric pollutants such as an acid rain and photochemical smog.[1] Therefore, monitoring of the exact amount of NOx and development of compact sensors applicable to automobiles are becoming important for the protection of global environments. So far, various types of NOx gas sensors, including semiconductor type,[2] solid electrolyte-based potentiometric type,[3,4] amperometric type[5] and impedancemetric type[1] sensors, have been investigated. Yttria-stabilized zirconia (YSZ)-based gas sensors are considered to be one of candidates for reliable sensor material.[6] Also, the solid electrolyte type is of particular interest from the viewpoints of sensitivity, selectivity, and stability at high temperatures.[7,8] Therefore, we have proposed and investigated a new concept of a solid-state NOx sensor combined with an YSZ plate as an impedance transducer and metal oxides (Fe_2O_3, Co_3O_4, NiO, CuO, ZnO) as a receptor.[4,7,8] The new type of impedancemetric sensor has an advantage in its simple sensor structure, in which there is no need for reference and/or counter electrodes at the opposite side of the senor device. An impedancemetric solid-state sensor using a zirconia solid electrolyte transducer attached to an oxide layer as a gas-sensing receptor showed relatively good NOx sensing properties; however, the impedance changes as the response intensity were as low as several percent for practical applications.[4,7] In this study, we used yttria-stabilized zirconia as a solid electrolyte transducer and metal oxides as a receptor for a new type of simple solid-state impedancemetric NOx sensor. We report the NOx sensing performance and the effect of the receptor materials on the impedancemetric solid electrolyte NOx sensor.

Experimental

The sensor device was fabricated using an 8 mol%-YSZ plate (Nikkato Corp., Japan) as a transducer and reagent-grade metal oxide (Fe_2O_3, Co_3O_4, NiO, CuO, ZnO) as receptors. The sensor consisted of an YSZ plate (10×10×1t mm), a receptor layer, and two Au electrodes at the opposite surface of the YSZ plate as shown in Fig. 1. The Au electrodes were tightly coated with an inorganic adhesive (ARON CERAMIC, TOAGOSEI, Japan). A receptor paste prepared with the appropriate amount of oxide and α-terpineol was painted onto the surface of the YSZ plate, and then the plate was dried and sintered at 500˚C for 2h. NOx sensing experiments were carried out in a conventional flow apparatus equipped with a heating facility at 300 ~ 500˚C.

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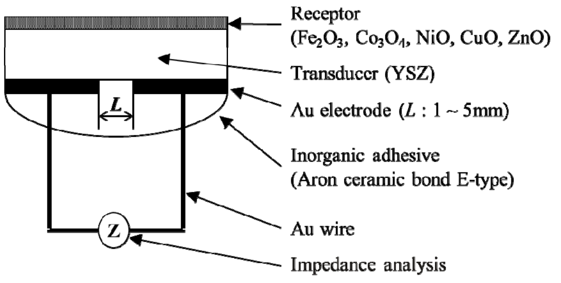

Fig. 1. Schematic diagram of the impedancemetric sensor device.

Nyquist's plots of this sensor were measured between 50 Hz and 5 MHz, and the sensor responses (resistance and capacitance) were measured at various concentrations of each NOx gas with an impedance analyzer (LCR 3532-50, HIOKI, Japan). Sample gases containing NO or NO_2 were prepared from each parent gas at a fixed O_2 pressure of 21 vol% and NO diluted with nitrogen or NO_2 diluted with a dry synthetic air (79vol%N_2 + 21vol%O_2 gas mixture), by mixing it with N_2 (99.999 vol%) or air at a total flow rate of 100 ml/min.

Results and Discussion

Nyquist's plots between Au electrodes at the YSZ layer of the oxide/YSZ sensor showed that impedance change at various concentrations of NOx was caused at the interface impedance area.[1] We investigated the response property of the sensor at the fixed frequency of 100 kHz as a sensing signal, because response change was observed from 100 kHz as shown in Fig. 2.

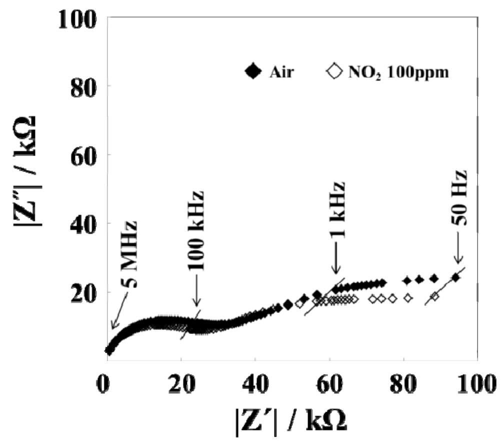

Fig. 2. Nyquist's plots of the NiO/YSZ sensor in air and NO_2 at 400˚C.

Responses of the NOx sensors could be obtained and they could be divided into resistance and capacitance components. Figure 3 shows response curves of each resistance component (R) and capacitance component (C) of the NiO/YSZ sensor for various concentrations of NO and NO_2 at 400˚C, 100 kHz.

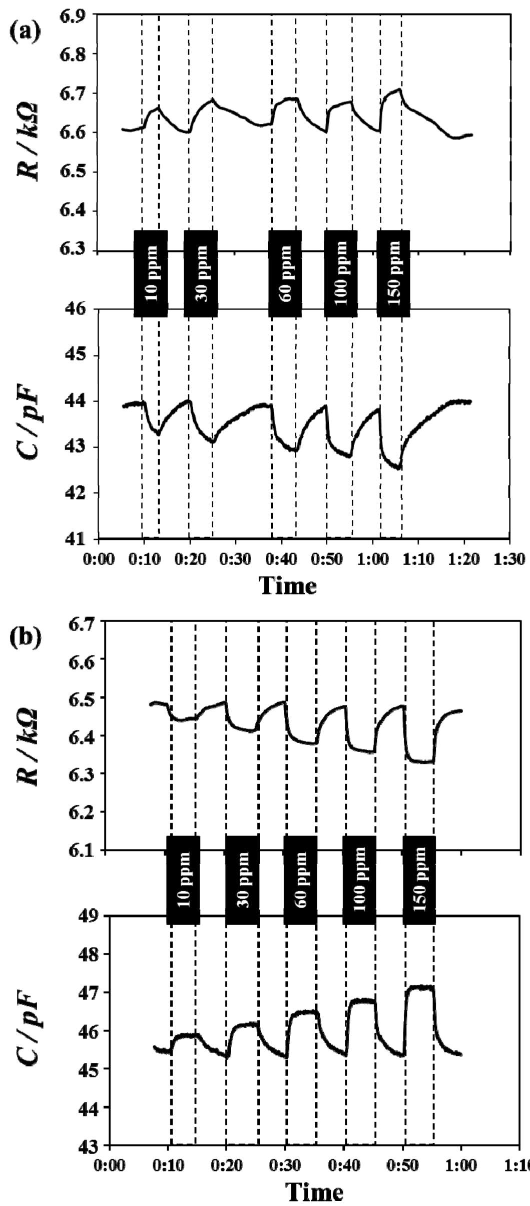

Fig. 3. Sensing response curves of the NiO/YSZ sensor for various concentrations of NO (a) and NO_2 (b) at 400˚C, 100 kHz.

In the case of NO, the response curve of the resistance component (R) tended to increase with increasing NO concentration, while the capacitance component (C) decreased. Also, the response curve of NO_2 showed good response sensitivity and stability as both the resistance component (R) and capacitance component (C); the resistance decreased and capacitance increased with increase in NO_2 concentration. Moreover, this showed be applicable to selective sensing by sensing performance of negative response for NO or positive response for NO_2 on resistance component (R). The NiO/YSZ sensor showed excellent NO_2 sensing response and good dependence for each NO_2 concentration. In the same way, the other metal oxide receptors were examined. The sensitivities of each of the

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sensors for various receptor materials are summarized in Fig. 4. The response property of excellent resistance or capacitance change was observed in the case of NiO and/or CuO. The value of the relative sensitivity (S_R or S_C) was defined as $S_R = (R_{gas} - R_{air}) / R_{air} \times 100$ (%) or $S_C = (C_{gas} - C_{air}) / C_{air} \times 100$ (%), in which R_{gas} (C_{gas}) and R_{air} (C_{air}) is resistance (capacitance) in gas and that in air, respectively. The sensitivities of these sensors were affected by the ability of the receptor materials used to detect the gas at different NOx concentrations, and the NiO receptor showed the highest sensitivity among the sensors.

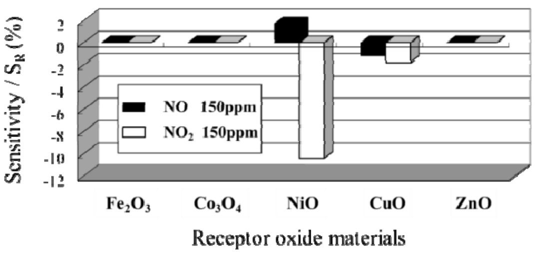

Fig. 4. Sensitivities of the impedancemetric sensor device for various receptor materials at 400 ˚C, 100 kHz.

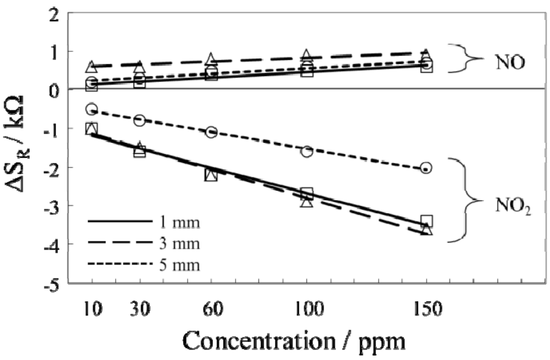

Fig. 5. Effect of Au electrode distance on the NiO/YSZ sensor for various concentrations of NO and NO_2 at 400 ˚C, 100 kHz.

We also investigated the effect of distance between Au electrodes, and the results are presented in Fig. 5. The results showed that the sensing property of the NiO/YSZ sensor was weakened by increase in electrode distance from 1 mm to 5 mm.

Tab. 1: Table caption Sensing response property of NiO/YSZ sensor for various working temperatures.

Temp. (°C)	Sensitivity (%)				Stability
	NO 100 ppm		NO_2 100ppm		
	S_R	S_C	S_R	S_C	
300	0	0	-2.40	0.73	Poor
400	1.30	-0.60	-4.70	1.10	Good
500	0.28	-0.83	-0.54	0.74	Fair

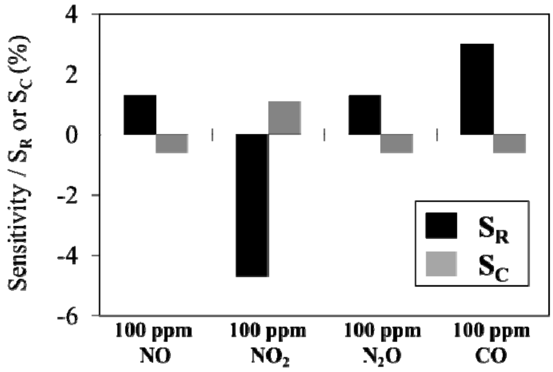

Fig. 6. Sensitivities of the NiO/YSZ sensor for various gases at 400˚C, 100 kHz

Therefore, we fixed the receptor material and electrode distance as NiO and 1 mm. In this condition, the effect of working temperature was examined from 300 to 500 ˚C. The sensitivity and stability of the NiO/YSZ sensor at various working temperatures are summarized in Table 1. The response properties of the NiO/YSZ sensor could be obtained good properties for NO_2, at 400˚C. Moreover, the response properties showed good selective and stable performance for NO_2. This results showed be applicable to selective sensing by NO_2. The NiO/YSZ sensor showed good sensitivity for NO_2 but not for the other gases as shown Fig. 6. The sensing mechanism of the NiO/YSZ sensor is shown schematically in Fig. 7. First, the NiO/YSZ sensor is exposed to clean air, and then oxygen ions (O^-) would form at the surface of NiO in a sequence of physisorption and

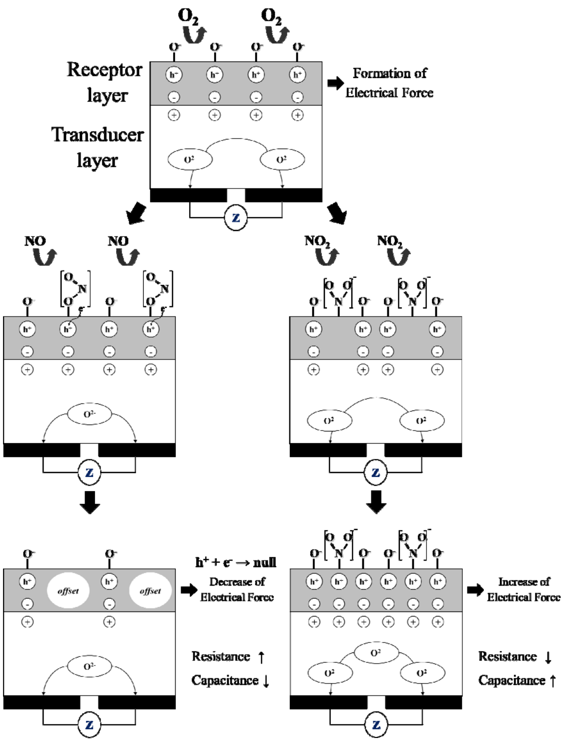

Fig. 7. Sensing mechanism of the NiO/YSZ sensor for response of NOx.

charge exchange reactions with the bulk of NiO grains, as described by Eq. (1). The adsorption of oxygen ions would result in the generation of electrical force by polarization in the receptor layer. After the NiO/YSZ sensor has been exposed to NO, the NO gas would react with $O^{-}_{(ads)}$, as Eq. (2), and cause reduction of holes in the receptor layer, resulting in a decrease in the electrical force. For this reason, the resistance component of the NiO/YSZ sensor decreases.

$$O_2 \rightarrow 2O^{-}_{(ads)} + h^{+} \quad (1)$$
$$NO + O^{-}_{(ads)} \rightarrow NO_2 + e^{-} \quad (2)$$

On the other hand, when the NiO/YSZ sensor is exposed to NO_2, NO_2 would react with the receptor layer, as Eq. (3), and cause an increase in holes by adsorption of NO_2^{-}, resulting in a decrease in the resistance component.

$$NO_2 \rightarrow NO_2^{-}{}_{(ads)} + h^{+} \quad (3)$$

Thus, it is thought that the sensing response occurs at the receptor layer due to adsorption of O_2 and/or NOx on the surface of the receptor.

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