Influence of Annealing Temperatures of NiO Sensing - Electrode on Sensing Characteristics of YSZ-based Mixed-potential-type NO_x Sensor

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1. INTRODUCTION

There is an expanding interest on the development of NOx sensors with improved sensing characteristics for operation at temperatures higher than 600°C. Despite a number of mixed-potential-type NOx sensors based on yttria stabilized zirconia (YSZ) and oxide sensing electrode (SE) being reported to date[1, 2], most of them show poor sensitivity at temperatures above 700°C. Hence, there is a strong need for the NOx sensors with improved sensing characteristics at higher temperatures. The morphology, materials and type of solid electrolyte have been found to influence the sensing characteristics of the solid-electrolyte based mixed-potential-type NOx sensor [3]. However, there is no report on the effect of sintering temperature of SE on sensing characteristics which is also an important factor of the sensor. Here, we demonstrated the effect of sintering temperature on sensing characteristics of an YSZ-based-planar type NOx sensor using NiO-SE by potentiometric and imepdancemetric studies in the higher temperature range of 700-900°C.

2. EXPERIMENTAL

A Pt paste was printed on both sides of commercially available YSZ (8 wt.%) plates (10 x 10 mm, 3 mm thickness) and dried at 1000°C for 2 h in air. NiO powder was thoroughly mixed with α-terpineol (20 wt.%) and the resulting paste was printed on one side of YSZ (thickness: ca. 7 µm) by means of screen printing. The obtained oxide-printed YSZ plates attached with Pt leads were annealed at 1100°C, 1200°C, 1300°C and 1400°C for 2 h in air. The sensor was assembled in a quartz tube (350 mm x 24 mm). The crystal structures were examined by means of X-ray diffraction analysis (with Cu Kα radiation, RIGAKU, RINT 2100 VLR/PC) and the surface morphology was observed by using FE-SEM (JEOL JSM-6340 F).

Gas sensing characteristics were performed in a conventional gas flow apparatus. The total flow rate of the sample gas (or the base gas, 5 vol.% $O_2 + N_2$ balance) was fixed at 100 cm^3/min and flood over the electrode surface. The NO_2 concentration was varied from 50 to 400 ppm. The EMF output was measured with a digital electrometer (Advantest R8240). The impedance measurements were performed by means of an impedance analyzer (Solarton, 1255 WB) in the frequency range of 1 MHz to 0.001 Hz.

3. RESULTS AND DISCUSSION

XRD studies revealed that the NiO-SE retained its crystallographic phase even sintering at 1400°C. The SEM observations confirmed that all the SEs have relatively uniform thickness of about 7 µm throughout the matrix. It was also seen that the grain size and the pore size were increased as the annealing temperature was increased.

The EMF responses to various NO_2 concentrations were studied in the temperature range of 700-900°C. It was observed that, the EMF was changed rapidly from the base value upon switching the base gas to the sample gas with different NO_2 concentrations. As seen in Fig. 1a the EMF values varied linearly to the NO_2 concentrations in logarithmic scale, which is typical for mixed-potential-type sensors. It is observed that, as the annealing temperature increased, the EMF output was also increased to each of NO_2 concentrations. This result clearly indicates that the sensitivity can be improved by increasing the sintering temperature of SE. However, the response rate (Fig. 1b) was lowered with increasing annealing temperature. The NO_2 gas makes less contact on the surface of NiO grains when it diffuses through the large pores presenting in the 1400°C-annealed sensor matrix where the surface acts as a catalyst for gas-phase decomposition of NO_2. Thus, NO_2 can reach the YSZ/oxide interface as such without major converting into NO. Due to which, the composition of NO_2 and NO is far from the equilibrium at the interface. In contrast, NO_2 makes a significant contact on the surface of NiO grains when it diffuses through the small pores presenting in the 1100°C-annealed sensor matrix where almost NO_2 gas can be converted into NO before reaching the interface. Moreover, as seen from the impedance data (Fig. 2), the diameter of semicircle which reflects the resistance of electrode reaction, increased with increasing annealing temperature. This implies that the catalytic activity to anodic reaction of oxygen at the interface is low in the case of the 1400°C-annealed SE. Such a low catalytic activity leads slow recovery. Based on the mixed-potential theory[1], the low catalytic activity to anodic reaction of oxygen also leads to high sensitivity and in addition, the low conversion of NO_2 to NO in gas-phase reaction is another reason for high sensitivity of the 1400°C-annealed SE. In contrast, due to the high catalytic activities to both the anodic reaction of oxygen and the gas-phase reaction, the low sensitivity is obtained for the 1100°C-annealed SE, while the high catalytic activity to anodic reaction of oxygen leads fast recovery.

REFERENCES

[1] N. Miura, et al., *Electrochem. Solid-State Let.* **4,** H19 (2001).

[2] N. Miura, et al, *Sens. Actuators B* **83,** 222 (2002).

[3] F. H. Garzon, et al., *Solid State Ionics* **136-137,** 633 (2000).

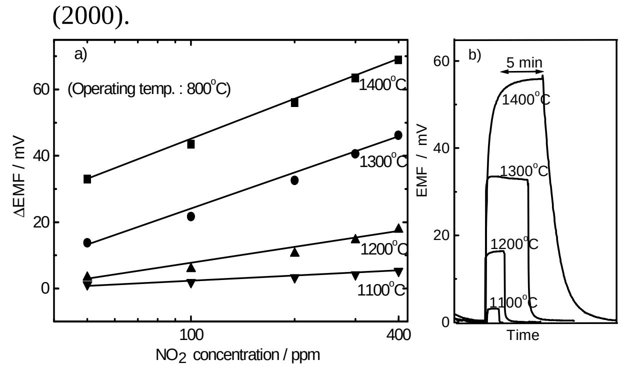

Fig. 1 Variation of EMF to various NO_2 concentrations (a) and response transients to 200 ppm NO_2 (b) at 800°C for the planar sensors using each of NiO-SEs annealed at various temperatures.

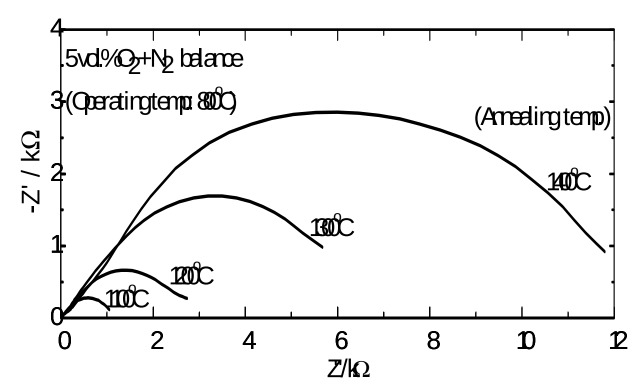

Fig. 2 Complex impedance plots of the planar sensors attached with each of NiO-SEs annealed at various temperatures.