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High-temperature operating characteristics of mixed-potential-type NO_2 sensor based on stabilized-zirconia tube and NiO sensing electrode

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Abstract

This paper focuses on the gas sensing properties of the mixed-potential-type yttria stabilized zirconia (YSZ)-based NO_2 sensor aiming at monitoring high-temperature car emission. The sensor device was fabricated by using an YSZ tube and a NiO sensing electrode (SE), and then its NO_2 sensing properties were investigated in the operating temperature range of 800–900 °C. The X-ray diffraction (XRD) patterns confirmed that the SE film containing the face-centered cubic NiO phase was thermally stable after the 1400 °C sintering. The scanning electron microscope (SEM) observations showed that the SE film sintered at 1400 °C was smooth and uniform with 3–5 μm sized NiO grains. The thickness of the SE film was about 33 μm. The *emf* output of the sensor increased linearly with an increase in NO_2 concentration on a logarithmic scale at each temperature examined. Among the various single-oxide SEs tested here and reported to date, NiO provided the highest sensitivity to NO_2 even at 850 °C. The present NO_2 sensor using NiO-SE showed faster recovery rate in the wet sample gas containing 5 vol.% water vapor than that in a dry sample gas. The Δemf value to 400 ppm NO_2 under the wet condition was as high as 75 mV at 850 °C, while the value under dry condition was 60 mV. The improvement effect of water vapor on the sensing performances was examined by means of impedance and polarization techniques.

Keywords: NO_x sensors; Mixed potential; Solid electrolytes; NiO; Stabilized zirconia

1. Introduction

Last decade, the demand for reliable solid-state gas sensors capable of detecting nitrogen oxides (NO_x) in different application has been substantially enhanced. Specifically, the EU emission limits for passenger cars and heavy-duty diesel vehicles will be soon reconsidered and will be finalized. In UK, for example, local authorities are obliged to conduct periodic review and assessment of current and future air qualities in their areas and to take action where objectives are at risk of being breached. Under Air Quality Regulations (1997) for NO_x, standards of 150 ppb (hourly maximum) and 21 ppb (annual average) must be achieved by 2005 [1]. On the other hand, it is said that US demand for sensor products (including sensors, transducers and associated housing) is projected to increase 7.8% annually. The growth is being fueled recently by new applications, such as on-board gas sensors, particularly in the large motor-vehicle market. Therefore, both λ-sensors and NO_x sensors based on advanced technologies will lead the growth. Furthermore, the economic recovery will support gains in many of the more mature applications, such as process control and conventional automotive sensors. For the automotive exhaust monitoring, NO_x sensors should be able to detect NO_x concentration from 10 up to 2000 ppm in very harsh environment where the temperature fluctuates from about 500 °C up to 900 °C. The engine temperature may occasionally reach up to 900 °C during vehicle acceleration and may keep it for a while thereafter. It is therefore inevitable that for a practical implementation of the reliable NO_x sensor, the SE must be investigated for high sensitivity as well as high selectivity to NO_x, long-term sta-

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bility at high temperatures, fast response and recovery rates. An ideal *on-board* NO_x sensor should attain stability over a long period of operating time (more than 10 years) and sensitivity to low concentrations of NO_x. In actual case, the optimum sensor performance is not achieved well due to insufficient understandings of the SE–gas interactions as well as the sensing mechanism. For instance, deposition techniques and processing parameters can affect the chemical composition, the microstructure and the morphology of metal oxide films, consequently influencing the gas sensing properties. Thus, it is important to study the microstructure of the SE film for fabrication of practical NO_x sensors as well as for understanding of the sensing mechanism.

Ceramic NO_x sensors based on YSZ solid electrolyte appear to be more convenient as an active device for a practical sensing system, providing their thermal and chemical stability, especially in combustion exhaust environment [2–4]. The mixed-potential-type NO_x sensors based on YSZ and oxide-SE have been receiving considerable attention among other YSZ-based NO_x sensors especially last decade. For instance, last few years, substantial efforts have been made by different research groups towards the development of the reliable oxide-SE capable to work at high temperatures since our first reports in 1996 [5,6]. It has been revealed that the use of the oxide-SE in this type of NO_x sensor is very effective for sensitive NO_x measurement at high temperature. A lot of published papers have reported the use of various oxide-SE materials for YSZ-based NO_x sensors [7–29]. However, despite a progress in the development of reliable oxide-SEs, there are only a few designs of the NO_x sensors reported to date capable to measure total NO_x ($NO + NO_2$) at high temperature [30–36]. In addition, most of the results for oxide-SEs published so far revealed that the NO_x sensors employed these SEs showed relatively good sensing characteristics only in the temperature range of 450–700 °C. Unfortunately, it is rather hard to operate these sensors at temperatures in excess of 700 °C. Such a limitation in operation is based on a drastic decrease in the NO_x sensitivity with increasing temperature. It has been found that the NO_x sensitivity is greatly dependent on the kind of metal oxides used as a SE material.

Based on the fact that there are no commercially available high-temperature on-board NO_2 sensors, further search for the oxide-SE has been made. Consequently, it has been found quite recently that NiO-SE is very effective to measure NO_2 concentrations at 850 °C [37]. There were only a limited number of publications reporting properties and sensing characteristics of oxide-SEs capable of measuring NO_2 concentration at temperatures above 800 °C [37,38]. It quickly became evident that a study of detailed sensing performances of the mixed-potential-type NO_2 sensor attached with NiO-SE at such a high temperature was required. In this paper, we attempt to examine the NO_2 sensing properties of the sensor attached with NiO-SE, especially the effect of water vapor on its NO_2 sensing performances, at temperatures of 800–900 °C. We believe that the results presented in this paper will be of interest to the researchers engaged in practical applications of gas sensors, especially, automotive exhaust sensors.

2. Experimental

The sensor consisted of a commercially available one-closed-end YSZ tube (8 wt.% Y_2O_3-doped, NKT), a NiO-SE and a reference Pt electrode (Pt-RE). A Pt wire (0.2 mm diameter) was wound around the NiO layer by one circle as a current collector. The Pt-RE was formed by using Pt paste, which was painted onto the inside of the closed end of the YSZ tube and then was fired at 1000 °C for 2 h in air. The Pt-RE was always exposed to the atmospheric air during experiments. Another Pt electrode was also formed on the outer surface of the YSZ tube as a counter electrode (CE). The YSZ tube was 300 mm long and had an outer diameter of 8 mm with a wall thickness of 1.5 mm. Electrical contact with the inner Pt-RE was made by inserting a small alumina four-bore tube containing a Pt wire to make contact with Pt-RE mechanically, a pathway for diffusing reference air as well as a K-type thermocouple for temperature measurement. For fabrication of NiO-SE, commercial NiO powder (Kishida Chemicals Co. Ltd.) was mixed with a mixture of polyethylene glycol (PEG) 6000 and α-terpineol organic solvent (added with 5 wt.% cellulose) in a weight ratio of 4:1:4 (NiO:PEG:α-terpineol) in an agate mortar to make uniform paste. The obtained paste was applied on the outer surface of the YSZ tube and kept in air for 12 h and subsequently sintered at 1400 °C for 2 h to form SE. The thickness of the NiO-SE obtained was about 33 μm. Fig. 1 shows a schematic cross-sectional view of the tubular sensor.

The microstructure and surface topography of the NiO-SE films were examined by using an SEM (JEOL field emission type electron microscope, JSM-340F) operating at 15 kV. The crystal structure of the films was studied by means of a wide-angle XRD (RIGAKU X-ray diffractometer, RINT 2100VLR/PC). The Cu Kα radiation ($\lambda = 1.5406$ Å) and 0.5°/min angle step were used for the XRD measurement.

NO_2-sensing experiments were carried out in a conventional gas-flow apparatus equipped with a furnace operating in the temperature range of 800–900 °C. The sample gas containing various concentrations of NO_2 was prepared by diluting a commercially available standard NO_2 with nitrogen and oxygen, and was allowed to flow over the sensor at a constant flow rate of 100 cm^3 min^{-1}. The concentration of NO_2 was changed from 10 to 400 ppm. The ppm refers to the volume concentration of NO_2

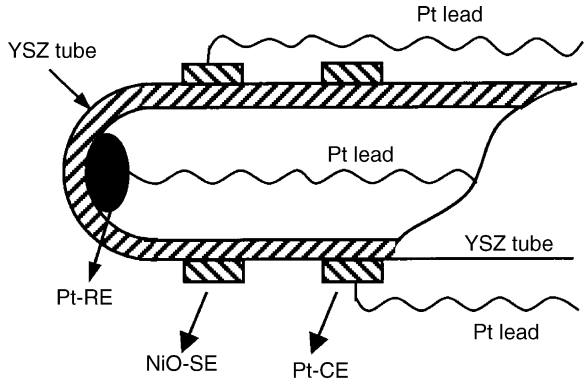

Fig. 1. Schematic cross-sectional view of NO_2 sensor using YSZ tube and NiO-SE.