Advances in Electronic Ceramic Materials

A collection of papers presented at the 29th International Conference on Advanced Ceramics and Composites, January 23-28, 2005, Cocoa Beach, Florida

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Sheng Yao

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Preface

The Electronics Division of the American Ceramic Society sponsored two different electronic ceramics symposia at the 29th International Conference on Advanced Ceramics and Composites organized by the Engineering Division of the American Ceramic Society. This proceedings contains selected papers from the two symposia: (1) Emerging Sensor Technologies Based on Electroceramics and (2) Advanced Dielectric, Piezoelectric and Ferroelectric Materials.

The symposium on Emerging Sensor Technologies Based on Electroceramics proved to be a magnificent opportunity to discuss the latest breakthroughs in the field of sensor science and technology. With over 80% of the top scientists in the world in the ceramic sensor field gathered in one room on beautiful Cocoa Beach, it was truly a monumental event. Nowadays, sensor technology is widely used in many applications including critical care, industrial process control, emission monitoring, automotive and home security systems, and more recently, for homeland security. It has undoubtedly made a considerable impact on modern society and human life. The economic and social benefits of sensor technology are evident and multifaceted. In particular, because of the excellent thermal stability of ceramic materials, ceramic sensors have been shown to provide a promising gas detection methodology in harsh environments such as engine and fuel cell exhausts. These currently receive much attention for environmental protection and hence became one of the important topics in this symposium.

Sensor technology is largely dependent on the progress made in the field of material science. In this sensor symposium, for example, several reports discussed new catalysts to modify sensing electrodes of non-Nernstian type sensors and semiconducting ceramic sensors; big improvements in sensing performance have been achieved. Several new solid electrolyte materials have been developed and showed to be promising for constructing sensors. New nano-structured materials and SiC based high temperature ceramics showed unique properties for chemical sensing. Therefore, great progress in sensor technology has been made through developing and employing novel materials. In fact, sensors are becoming increasingly important in ceramic material applications. Constructive discussions and communications such as this symposium will advance unequivocally our understanding and perspective on sensor science.

The Advanced Dielectric, Piezoelectric and Ferroelectric Materials Symposium brought together researchers and engineers from Europe, Asia, North America and Australia to present and exchange ideas on the latest scientific and technical developments in the field of dielectric, ferroelectric and piezoelectric ceramics. Seventy-four papers and posters were presented. A particular strength of this meeting was the ample opportunity for informal, lively discussions of technical subjects among the meeting participants. Among the topics that attracted a great deal of interest were

the latest materials science discoveries for high dielectric constant copper calcium titanate materials, novel high temperature piezoelectrics, fundamental understanding of crystal structure and sub-nanometer distortions on microwave properties, and integration of Cu electrodes with BaTiO3 and PZT based thin films.

We gratefully acknowledged the efforts of the organizing committee for putting together a technical program that drew leading technical experts throughout the world as symposium speakers. We are also extremely grateful to all the speakers who contributed to this highly successful symposium, especially those from outside of North America.

Sheng Yao
Emerging Sensor Technologies Based on Electroceramics

Bruce Tuttle, Clive Randall and Dwight Viehland
Advanced Dielectric, Piezoelectric and Ferroelectric Materials

Emerging Sensor Technology Based on Electroceramics

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ZIRCONIA-BASED GAS SENSORS USING OXIDE SENSING ELECTRODE FOR MONITORING NOx IN CAR EXHAUST

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ABSTRACT

Solid-state electrochemical sensors using yttria-stabilized zirconia (YSZ) and oxide sensing electrode (SE) were fabricated and examined for NOx detection at high temperatures. Among various single-oxide SEs examined, NiO-SE for the mixed-potential-type NOx sensor was found to exhibit rather high sensitivity to NO_2 even in the high temperature range of 800-900°C. This sensor showed quicker response and recovery transients in the presence of water vapor, compared with that in the dry sample gas. The sensing mechanism of this type of sensor was discussed on the basis of the catalytic activities to the electrochemical and non-electrochemical reactions. It was also shown that the new-type complex-impedance-based (impedancemetric) NOx sensor attached with $ZnCr_2O_4$-SE exhibit good sensing characteristics to NOx at 700°C. Furthermore, the sensitivity to NO was almost equal to that to NO_2 in the concentration range from 0 to ca. 200 ppm at 700°C. A linear dependence was observed between the sensitivity of the impedancemetric sensor and the concentration of NOx even in the presence of 8 vol. % H_2O and 15 vol.% CO_2. The planar laminated-type structure for the impedancemeteric NOx sensor was proposed for protecting NOx sensitivity from the influences of the co-existing combustible gases as well as the change in oxygen concentration in exhaust gas.

INTRODUCTION

Recently, the demand for reliable, compact, low-cost solid-state sensors, which are capable of detecting nitrogen oxides (NOx) in different application, has been enhanced substantially. This demand has been driven by strong recent legislation in EU, USA and Japan. For example, in UK under Air Quality Regulations (1997) for NOx, standards of 150 *ppb* (hourly maximum) and 21 ppb (annual average) must be achieved by the end of 2005.[1] On the other hand, according to a new report by Fredonia Group, US demand for sensor products (including sensors, transducers and associated housing) is projected to increase 7.8% annually to $13.8 billion in 2008.[2] For monitoring in the automotive exhausts, the sensor should be able to detect NO_x concentration from 10 ppm up to 2000 ppm in very harsh environment where the temperature constantly fluctuates from 600°C up to 900°C, since the temperature of engine may occasionally reach up to 900°C, during vehicle acceleration. It is therefore vital to investigate thoroughly the SE materials of the NOx sensor in order to provide high NOx sensitivity and selectivity, long-term stability at high temperatures as well as fast response and recovery for a practical sensor.

Last decade, an ultra lean-burn (or direct-injection type) engine system has been developed to improve fuel efficiency as well as to reduce CO_2 and NOx emissions from engine. In this engine system, newly-developed NOx-storage catalyst should be used for compensating the low NOx-removal ability of the conventional three-way catalyst under the lean-burn (air rich) condition, as shown in Fig. 1.[3] It is important, therefore, to have high-performance NOx sensors installed at the point after (or both before and after) the NOx-storage catalyst for such a system. The mixed-potential-type NOx sensors based on YSZ and oxide SE have been receiving considerable attention among the others YSZ-based NOx sensors,[4] as potential candidates for practical sensor measuring car emissions. For example, last few years the most of the research groups have focused on the development of oxide SEs which are capable of working at high temperatures in car exhaust.[5-9] The use of oxide SE in this type of NOx sensor was found to be very effective for sensitive and selective NOx measurement at high temperature.[10] However, there are only a few designs of the NOx sensors reported to date[11-16] that can monitor total NOx ($NO + NO_2$) at high temperatures regardless of NO_2/NO ratio in real exhausts. One of these sensors is the complex-impedance-based NOx sensor originally designed and developed by our group.[15, 16] In addition, the most of results for oxide SEs published so far have revealed that the NOx sensors using the oxide SEs show relatively good sensing characteristics only in the temperature range of 450-700°C. The majority of these sensors have difficulty to operate at temperatures higher than 700°C. Such a higher limitation of operating temperature is caused by the substantial decrease in the NOx sensitivity with increasing temperature. Based on the above-mentioned facts and keeping it in mind that there are no commercial high-temperature NOx sensors available on the market at the moment, further search for oxide SE has been done. As a result, it was found quite recently that NiO is a very effective SE for measuring NOx concentrations at temperatures higher than 800°C.[17, 18] There were only limited number of publications reporting the properties and sensing characteristics of oxide SE that can measure NOx concentration at temperatures over 800°C.[17, 18] Furthermore, we have also discovered that the new complex-impedance-type NOx sensor using $ZnCr_2O_4$-SE shows rather good sensing characteristics for measurement of total NOx concentration at temperature as high as 700°C. Thus, we report here the sensing properties and sensing mechanism of the mixed-potential-type YSZ-based NOx sensor attached with NiO-SE at temperatures of 800-900°C as well as the main sensing performances of the new complex-impedance-type NOx sensor using $ZnCr_2O_4$-SE.

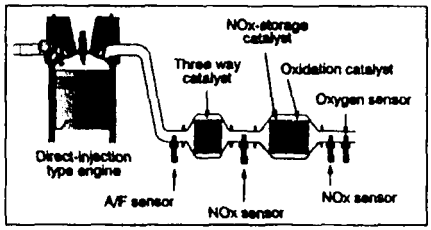

Fig. 1 Catalytic converter system equipped with NOx sensors for the exhaust gas emitted from a new-type car engine.

EXPERIMENTAL

A tubular NOx sensor was fabricated by using a commercial one-closed-end YSZ tube (8 wt.% Y_2O_3-doped, NKT). The tube is 300 mm in length and 5 and 8 mm in inner and outer diameters, respectively. NiO-powder paste was applied on the outer surface of the YSZ tube and sintered at 1400°C to form a sensing electrode (SE). A Pt lead wire was wound around the oxide layer to make a good electrical contact. Pt paste was painted onto the inside of the YSZ

tube and fired afterwards at 1000°C for 2 h to form a reference electrode (RE). Figure 2 shows the cross-sectional (schematic) view of the obtained tubular YSZ sensor attached with NiO-SE and Pt-RE.

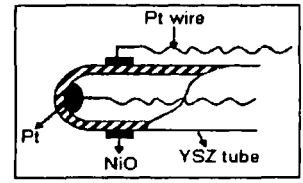

Fig. 2 Cross-sectional (schematic) view of the tubular YSZ sensor.

The fabrication of planar NOx sensor was done by the use of YSZ plates (8 wt. % Y_2O_3-doped, 10 x 10 mm; 0.2 mm thickness). Pt paste was printed on both sides of the YSZ plate and then was fired at 1000°C for 2 h in air. On the one side of the YSZ plate, two rectangular Pt-stripes were formed as Pt-RE of the sensor and, on the other side; six narrow Pt-stripes were formed as a base (current collector) for the NiO-SE film. NiO powder (Kojundo Chemical Lab. Co. Ltd., 99.97% purity) was thoroughly mixed with α-terpineol (20 wt.%) and the resulting paste was applied on the top side of the YSZ plate attached with narrow Pt-stripes by means of screen-printing technique to form SE. The planar sensors were sintered at 1100°C, 1200°C, 1300°C and 1400°C, respectively, for 2 h in air. Although the Pt-RE of the tubular YSZ-based NOx sensors has been always exposed to the atmospheric air during experiments,[19] the Pt-RE of the present planar sensor is always exposed to the measuring gas. Pt wires were spot-welded onto the Pt connecting-spots of both SE and one of REs to provide the good electrical contact with a measuring equipment.

The microstructure and surface topography of the NiO-SE films were examined by using an SEM (JEOL 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 CuKα radiation (λ=1.5406) and 0.5°/min angle step were used for the XRD measurement. The YSZ/NiO interface was observed by the use of a TEM (FEI Inc., Model TECNAI F20) at the Research Laboratory for High Voltage Electron Microscopy of Kyushu University. The accelerated voltage was 200 kV for all experiments. BET surface area was measured by using an automated gas-sorption system (Quantachrome Autosorb, version 1.20).

NOx-sensing experiments were carried out in a conventional gas-flow apparatus operating in the temperature range of 700-900°C, as shown in Fig. 3. The sample gas containing various concentrations of NO (or NO_2) was prepared by diluting with dry nitrogen and oxygen gases and was allowed to flow over the sensor at a constant flow rate of 100 cm^3 min^{-1}. The concentrations of NO and NO_2 were changed from 10 to 400 ppm. The difference in potential (emf) between NiO-SE and Pt-RE of the sensor was measured by a digital electrometer (Advantest, R8240). The base gas was 5 or 20.9 vol.% of dry O_2 diluted with dry N_2, and the sample gas was 10-400 ppm of NOx diluted with the base gas. In

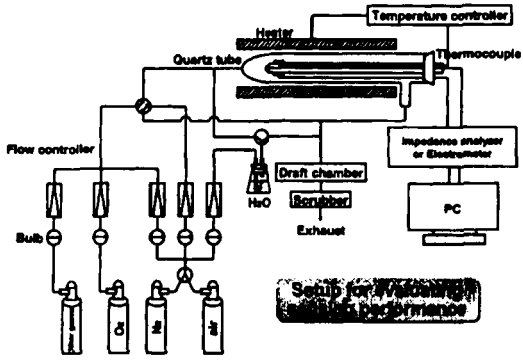

Fig. 3 Setup for evaluating sensing performances of NOx sensors.

order to humidify the base gas and the sample gas, 5 vol.% water vapor was mixed with them. For the impedance-based sensor, the complex impedance and the phase angle between SE and RE were measured with a complex impedance analyzer (Solarton, 1255 WB) in the frequency range of 0.01 Hz - 1 MHz to obtain complex-impedance (Nyquist) plots. As an output signal, the complex impedance value (|Z|) was used and was monitored at a fixed frequency of 1 Hz.

RESULTS AND DISCUSSION

Crystal Structure and Morphology of the Oxide SEs

One of the most important factors that affect the sensing characteristics of the mixed-potential-type NOx sensors is the composition or morphology of SE. XRD patterns for both NiO and $ZnCr_2O_4$ thick films sintered at 1400°C and 1200°C, respectively, contained only peaks of crystalline face-centered cubic NiO (JCPDS PDF#47-1049) phase or $ZnCr_2O_4$ (JCPDS PDF#22-1107) phase. It is seen that all peaks for the sintered NiO and $ZnCr_2O_4$ were narrow. This suggests the excellent thermal stability of NiO and $ZnCr_2O_4$.

Figure 4 shows SEM micrographs of the cross-section of the screen-printed NiO-SE films sintered at different temperatures on the YSZ substrate. The thickness of films was maintained at almost same value of about 7 μm even after sintering at different temperatures. With decreasing sintering temperature, the average pore size was found to increase from *ca.* 0.5 μm (for the 1100°C-sintered film) to ca. 2 μm (for the 1400°C-sintered film). This suggests that higher sintering temperature gives lower number of reaction site at a triple-phase-boundary (TPB) of gas/YSZ/NiO. These observations also show that the high sintering temperature provides relatively low surface-to-volume ratio on SE layer which consequently brings low catalytic activity to electrochemical reactions. The less surface area of the NiO film will also lead to lower heterogeneous catalysis (decomposition of NO_2 to NO). In the case of the $ZnCr_2O_4$–SE sintered at 1200°C, it was also relatively porous with an average grains size of about 0.2-0.8 μm.

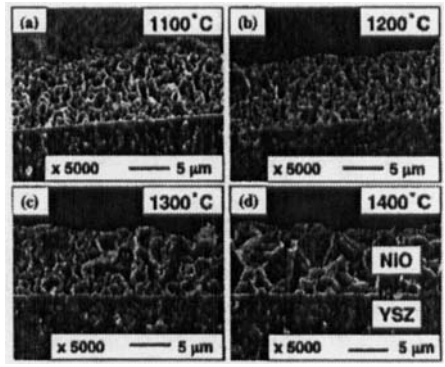

Fig. 4 SEM micrographs of the cross-section of the screen-printed NiO films (on YSZ substrate) sintered at various temperatures.

TEM image of the TPB (gas/YSZ/SE) for the NiO-SE sintered at 1400°C onto YSZ substrate is presented in Fig. 5. Analysis of this figure showed that the TPB, where all electrochemical reactions occur, is a small

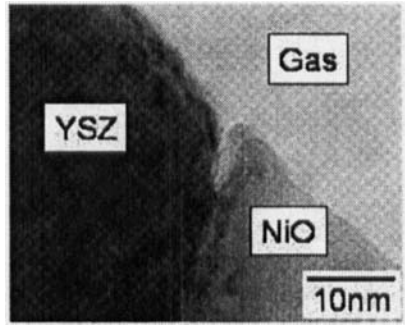

Fig. 5 TEM micrograph of the TPB at gas/YSZ/NiO for the NiO film sintered onto YSZ substrate at 1400°C.

curve which goes along with the YSZ/NiO interface. This nano-scale picture clearly shows that the YSZ/NiO interface is about 2 nm in thickness and goes along the boundary between the NiO and YSZ grains joined together. Thus, the TPB consists of the gas and the combination of the relatively small nano-scale curves along the YSZ/NiO interface as well as small islands when the YSZ and NiO grains connected to each other by one or a few single points.

Sensing Performances of the Mixed-potential-type NOx Sensor Using NiO-SE

Among the thirteen kinds of single-oxide SEs tested, the NiO-SE was found to give the highest NO_2 sensitivity at 850°C. The YSZ-based NOx sensor attached with NiO-SE showed a strong linear correlation between the gas sensitivity and the logarithm of NO_2 concentration from 50 ppm up to 450 ppm at temperatures of 800-900°C. Figure 6 shows the variation of the output emf values for the present sensor to 400 ppm NOx (NO or NO_2) when the operating temperature was changed from 800°C up to 900°C. The oxygen concentration was fixed at 20.9 vol.%. It is clear from this figure that the output emf of the NOx sensor decreases with increasing operating temperature. However, even at 900°C the sensor attached with NiO-SE gave the emf response of about 15 mV. Such a result is hard to see in the case of any other oxide-SEs tested here and reported to date. Figure 7 shows the response transients to 400 ppm NO_2 under dry and wet conditions for the tubular NOx sensor attached with NiO-SE at 850°C. The emf value was almost zero when the base gas was introduced to the sensor and changed quickly from the base level to the some emf value upon exposure to the sample gas containing NO_2. The 90% response time was about 40 s, however the recovery rate was very slow compared with the response rate. The emf value did not return to the base level and reached only the about 80% recovery level even after 20 min. Such a slow recovery can be explained by the fact that the catalytic activity for electrochemical reaction of oxygen ($\frac{1}{2}O_2 + 2e^- = O^{2-}$) is low for the 1400°C-sintered NiO-SE. Such a slow recovery of the present sensor was found to be improved by humidifying the sample gas. In this test, 5 vol.% of water vapor was incorporated into the dry sample gas. As shown in Fig. 7 (b), the recovery rate was greatly improved after the introduction of water vapor. Under the wet condition, the 90% response and 90% recovery times were about 20 s and about 3 min, respectively. The emf value returned completely to the original level within about 5 min. In addition, the sensitivity (75 mV to 400 ppm NO_2) under

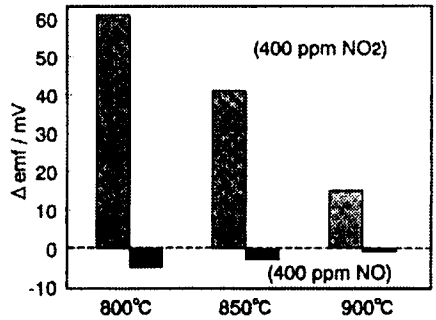

Fig. 6 Variation of the output emf for the NOx sensor using NiO-SE at operating temperatures of 800-900°C.

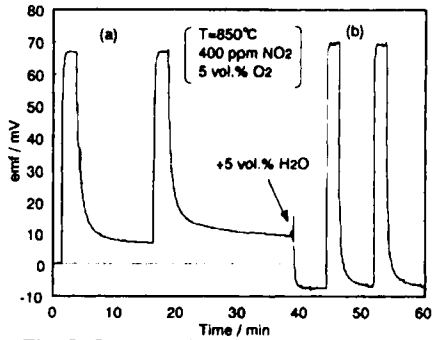

Fig. 7 Response/recovery transients to 400 ppm NO_2 in 5 vol.% O_2 (+N_2 balance) gas in the absence (a) and in the presence (b) of 5 vol.% water vapor at 850°C.

the wet condition was a bit higher than that (60 mV) under the dry condition. Moreover, the reproducibility of emf response to 400 ppm NO_2 was quite satisfactory. Thus, the presence of water vapor in car exhausts will give a positive effect to the performance of the present NOx sensor.

Figure 8 shows the comparison of the response transients to 200 ppm NO_2 at 800°C for the planar sensors attached with each of NiO-SEs sintered at various temperatures. It is seen that the steady-state emf value to 200 ppm NO_2 increased from 3 mV to 55 mV when the sintering temperature of SE was increased from 1100 to 1400°C. However, the response rate was lowered by increasing the sintering temperature. These results given in Fig. 8 clearly indicate that the NO_2 sensitivity of the present sensor can be enhanced by increasing the sintering temperature of SE.

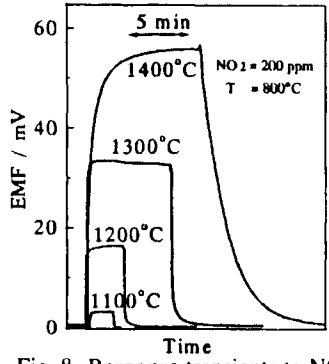

Fig. 8 Response transients to NO_2 at 800°C for the planar sensors using each of NiO-SEs sintered at different temperatures.

Elucidation of Sensing Mechanism for the Mixed-potential-type NO_2 Sensor

The NOx sensing mechanism for the YSZ-based sensors using metal-oxide SE is based on mixed-potential, as has been reported before.[8,17] For the NO_2 sensing, the following electrochemical reactions proceed simultaneously at the interface of YSZ/SE and consequently mixed potential appears on SE:

$$\text{(anodic)} \quad O^{2-} \longrightarrow \tfrac{1}{2} O_2 + 2e^- \qquad (1)$$

$$\text{(cathodic)} \quad NO_2 + 2e^- \longrightarrow NO + O^{2-} \qquad (2)$$

Based on the previously published results,[3,4,10] these reactions occur at different kinetic rates on the dissimilar electrodes. As a result, the emf response of the sensor is the difference in mixed potential on each electrode. Therefore, the catalytic activity to anodic reaction of O_2 (1) should be low and the catalytic activity to cathodic reaction of NO_2 (2) should be high. In order to verify this assumption, the complex impedance measurements were performed at the frequency range of 0.01 Hz ~ 1 MHz in the base gas (5 vol.% O_2 + N_2 balance) at 800°C for the planar sensors attached with each of the NiO-SEs sintered at different temperatures. It was seen that the resistance of electrode reaction in the base gas increased with increasing sintering temperature of SE. This implies that the higher sintering temperature of SE gives lower catalytic activity to anodic reaction of oxygen (1). The decrease in the catalytic activity to the anodic reaction in the case of higher sintering temperature of SE was also confirmed from the results of the polarization-curve measurements. At the same time, the low catalytic activity to the cathodic reaction of NO_2 (2) can be explained using the schematic view of the interface shown in Fig. 9. One can see that smaller NiO grains are present at TPB in the case of lower sintering temperature of SE. In contrast, larger grains are present at TPB in the case of higher sintering temperature. The larger grains may produce less number of reaction sites at TPB. Thus, we can speculate that, in the case of higher sintering temperature, the catalytic activity to

the cathodic reaction (2) is low compared to the case of lower sintering temperature, as observed for the anodic reaction.

Moreover, the oxide matrix also plays an important role in deciding the NO_2 sensitivity[17] when we consider the gas-phase reaction:

$$NO_2 \longrightarrow NO + \tfrac{1}{2}O_2 \qquad (3)$$

Based on our previous results,[3,5,19] low conversion of NO_2 in the gas-phase reaction would lead to high NO_2 sensitivity. In the present study, it was observed from the SEM images (see Fig. 4) that the large pores exist in the case of the 1400°C-sintered NiO-SE. As shown in Fig. 9, NO_2 gas makes less contacts with the surface of NiO grains when it diffuses through the large pores presenting in the 1400°C-sintered SE matrix, where its surface acts as a catalyst for gas-phase decomposition reaction of NO_2 (3). Thus, NO_2 can reach the YSZ/SE interface without serious decomposition to NO. In contrast, NO_2 makes a significant contacts with the surface of NiO grains when it diffuses through the small pores presenting in the 1100°C-sintered SE matrix where almost all NO_2 gas can be converted into NO before reaching the TPB. Thus, the low catalytic activity to anodic reaction of oxygen as well as less possible conversion of NO_2 to NO in the gas-phase reaction would lead to higher NO_2 sensitivity in the case of the 1400°C-sintered SE. Furthermore, the high catalytic activity for the anodic reaction of oxygen and the high conversion of NO_2 to NO lead to lower NO_2 sensitivity in the case of the 1100°C-sintered SE, in spite of the fact that the high catalytic activity to anodic reaction of oxygen can give faster recovery rate.

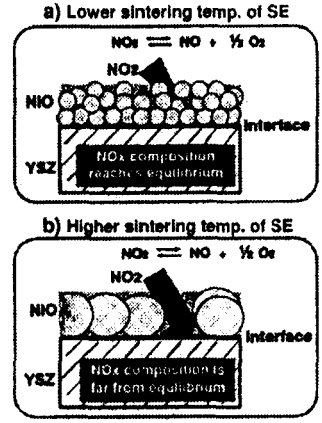

Fig. 9 Schematic views of the effect of both grain size and pore size of the SE matrix on catalytic activities to reactions (1) and (3).

All the above results presented here show that NiO-SE gives good sensing performances in the humid exhaust environment even at high temperatures of 800-900°C. Thus, we may conclude that this material is one of the potential candidates for SE of the mixed-potential-type NOx sensor which is capable of detecting NO_x on-board in car exhausts at high temperature.

Sensing Performances of the Complex Impedance-based NOx Sensor

In addition to the mixed-potential-type NOx sensors, our attention during last few years has been focusing on the development of principally new-type YSZ-based sensor for detecting NOx at high temperature.[3,16] In this type of NOx sensors, the change in the complex impedance of the device attached with oxide SE was measured as a sensing signal. Initially we investigated the complex-impedance plots for the devices using spinel-type oxides, such as $CrMn_2O_4$, $NiCr_2O_4$, $NiFe_2O_4$ and $ZnCr_2O_4$, as an SE in base air at 700°C. Both NO_2 and NO (200 ppm each, diluted with dry air) were used as the sample gas during experiments. The sensors attached with the first three oxides were found to provide large and flat semicircular arc in each Nyquist plots in the examined frequency range. The impedance values of these devices were not affected by the existence of NOx under the present condition. However, we found that in the case of the device attached with $ZnCr_2O_4$-SE, the impedance behavior was

entirely different from the above-mentioned results. Figure 10 shows how the resistance value (Z', the intercept) at the intersection of the large semi-arc with the real axis at low frequencies (around 0.1 Hz) varies with concentrations of both NO and NO_2. It is seen that the resistance value decreases with an increase in the concentration of both NO and NO_2. Such a behavior is completely different from that for the mixed-potential-type NOx sensor whose response direction to NO is opposite to that to NO_2 (see Fig. 6).

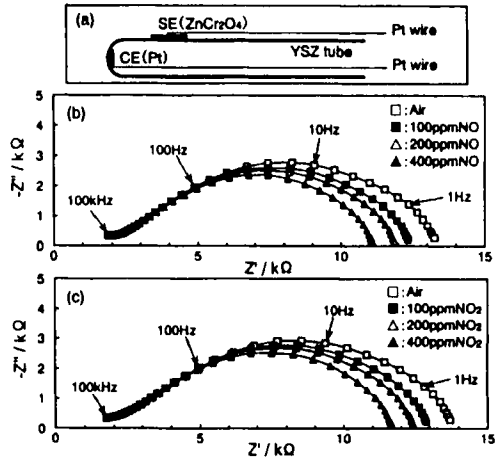

Fig. 10 (a) Cross-sectional view of the complex impedance-based NOx sensor using YSZ and $ZnCr_2O_4$-SE. (b), (c) Nyquist plots in the base air and the sample gas with each of various concentrations of NO and NO_2 at 700°C.

Meanwhile, the Z' value (the intercept, about 2000 Ohm) at the intersection of the large semi-arc at high frequencies (around 50 kHz) did not change even if the concentration of NOx was changed from 10 to 400 ppm. The difference between the impedance ($|Z|_{air}$) in the base air and the impedance ($|Z|_{gas}$) in the sample gas containing NOx at the fixed frequency of 1 Hz has been defined as 'gas sensitivity' of the device.[3, 15,16] We, therefore, investigated the sensitivity of sensor attached with $ZnCr_2O_4$-SE to both NO and NO_2 at high temperature and in the presence of high concentration of H_2O (3 to 8 vol.%) and CO_2 (10 to 15 vol.%), which are usually exist in car exhausts. All measurements were carried out at fixed temperature of 700°C for various NOx concentrations. This investigation revealed the existence of strong linear correlation between 'gas sensitivity' and the measuring NOx concentration from 0 to 200 ppm. Figure 11 shows that the sensitivity of the sensor at 1 Hz to both NO and NO_2 (200 ppm each) was almost constant in the presence of high H_2O and CO_2 concentrations. Moreover, the most interesting result taken into consideration from these tests is the fact that the sensitivity to NO is almost equal to that to NO_2 at 700°C. From the practical point of view, this means that the present device is capable of measuring total NOx (NO and NO_2) concentration in the gas mixture regardless of the NO/NO_2 ratio. This is very valuable point for the development of practical total NOx sensor for car exhausts.

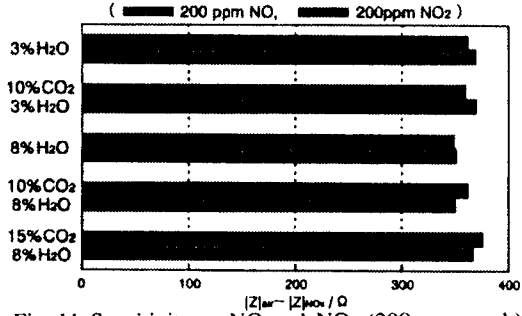

Fig. 11 Sensitivity to NO and NO_2 (200 ppm each) in the presence of rather high concentrations of H_2O (3-8 vol.%) and CO_2 (10-15 vol.%) at 700°C for the YSZ-based sensor using $ZnCr_2O_4$-SE.

Based on our previous experiences with the mixed-potential-type sensors, we can presume that it

is quite possible that the response of the present device is also intervened by the change in O_2 concentration in the sample gas.

In order to verify this assumption, O_2 concentration in the sample gas was changed from 5 vol.% to 80 vol.% at 700°C whilst 'gas sensitivity' of the device to 100 ppm of both NO and NO_2 was recorded. The results of these tests revealed that the value |Z| indeed varied linearly with the logarithm of O_2 concentration at 1 Hz. In the meantime, the 'gas sensitivities' to NO and to NO_2 were almost equal at any O_2 concentration examined. This suggests that the O_2 concentration in the sample gas existing at the space near the oxide-SE of the device should be controlled and should be kept constant during operation. For this purpose, both an O_2 sensor and an O_2-pump could be employed for monitoring and controlling O_2 concentration, respectively. These devices can be built into a new laminated-type YSZ-based device consisting of oxidation catalyst and NO_2 sensing electrode, as shown in Fig. 12. Combustible gases, therefore, can be oxidized by oxidation catalyst in this design of the sensor and the O_2 concentration can be kept constant. Consequently, the NOx sensitivity of the sensor will have no influence by the co-existence of combustible gases and by the O_2 concentration variation in the exhaust gas.

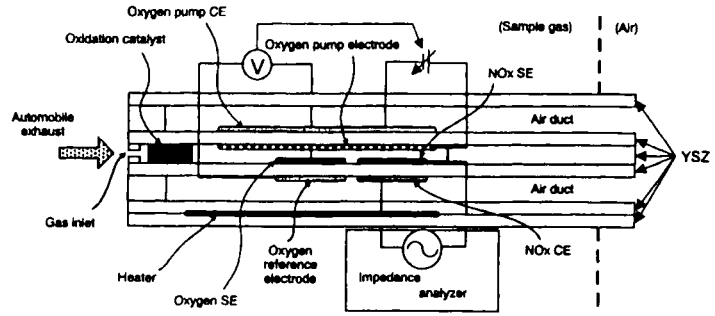

Fig. 12 A cross-sectional view of the proposed laminated-type complex impedance-based NOx sensor.

CONCLUSIONS

First, the tubular and planar YSZ-based sensors attached with each of the NiO-SEs sintered at various temperatures were fabricated for NOx detection at the different environments aiming for monitoring car exhausts. The sensing characteristics of these sensors were examined in the temperature range of 800-900°C. It was found that the NO_2 sensitivity of NiO-SEs was greatly influenced by changing the sintering temperature of SE. Rather high sensitivity to NO_2 was obtained even at 900°C for the sensor using the NiO-SE sintered at 1400°C. The NO_2 sensitivity observed at such a high temperature has never been reported before. The low catalytic activity to anodic reaction of oxygen (1) as well as the scanty conversion of NO_2 to NO on the gas-phase reaction (3) may lead to the high NO_2 sensitivity in the case of 1400°C-sintered SE having larger pores. In opposite, the high catalytic activity to anodic reaction and the high conversion of NO_2 to NO may lead to lower sensitivity in the case of 1100°C-sintered SE having smaller pores and smaller grains. The present investigation indicates that NiO is a promising candidate for the practical SE of on-board planar NOx