ELSEVIER

Ceramics International 30 (2004) 1135–1139

CERAMICS INTERNATIONAL

www.elsevier.com/locate/ceramint

Development of NO_x sensing devices based on YSZ and oxide electrode aiming for monitoring car exhausts

N. Miura*, M. Nakatou, S. Zhuiykov

Art, Science and Technology Center for Cooperative Research, Kyushu University, Kasuga-shi, Fukuoka 816-8580, Japan

Received 27 November 2003; accepted 18 December 2003

Available online 30 April 2004

Abstract

Recent progress in the development of zirconia-based sensing devices using zinc-family oxide electrodes for both mixed-potential and complex impedance-based types has been focused on the detection of NO_x in the temperature range of 600–700 °C. The sensing characteristics of these sensors were investigated in different gaseous environments. The mixed-potential-type NO_x sensor using $ZnFe_2O_4$ sensing electrode (SE) have shown the highest sensitivity to NO_x among other spinel-type oxides tested as SEs in the temperature range of 600–700 °C. It was also shown that the complex-impedance-based NO_x sensor attached with $ZnCr_2O_4$-SE gave rather good sensing characteristics to NO_x at 700 °C. Furthermore, it was discovered that the sensitivity to NO is almost equal to the sensitivity to NO_2 from 0 to 200 ppm for this sensor at 700 °C. The observed NO_x sensitivity and the measured NO_x concentration had almost linear correlation even in the presence of 8 vol.% H_2O and 15 vol.% CO_2. Based on the results obtained, we proposed laminated-type sensor structure that is the best for the present complex impedance-based NO_x sensor.

Keywords: Ceramic NO_x sensors; Solid electrolytes; $ZnCr_2O_4$; $ZnFe_2O_4$; Stabilized zirconia; Mixed potential; Complex impedance

1. Introduction

Strong demand for reliable solid-state gas sensors capable of detecting different gaseous pollutants have been enhanced last few years substantially due to recent legislation in EU, USA and Japan. Specifically, the EU emission limits for passenger cars and heavy-duty diesel vehicles soon will be reconsidered again and will be finalized for 2005. The 2005 (Euro IV) emission standards set limit values for carbon monoxide (CO)—1.5 g/kWh, hydrocarbons (C_xH_y)—0.46 g/kWh and nitrogen oxides (NO_x)—3.5 g/kWh [1]. Moreover, in 2008 (Euro V proposal), the NO_x limit of 2.0 h/kWh is inseparably connected to the need for efficient techniques and sensors based on these techniques, to monitor CO, C_xH_y and NO_x both in combustion exhausts and in atmospheric environments [2]. The most reliable sensors capable to work "in situ" at high temperatures above 600 °C in very harsh environment of car exhausts are yttria-stabilized zirconia (YSZ)-based oxygen sensors. Their attractive features, such as fast response, compactness and low cost create a possibility to control emissions on-line. It is said that the world-wide production of the YSZ oxygen sensors for automobiles is about 100,000,000 pieces per year.

Lately, 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 NO_x emissions from engine. In this new engine system, recently developed NO_x-storage catalyst should be used in order to compensate the low NO_x-removal ability of the conventional three-way catalyst under the lean-burn (air rich) condition, as shown in Fig. 1a [3]. It is vital to have high-performance NO_x sensors installed at the point after (or both before and after) the NO_x-storage catalyst for such a system. Temperature range of 650–700 °C is critical to optimize the catalyst performance and, therefore, "in situ" NO_x sensor should be able to work reliably in the exhaust gas at the above-mentioned temperatures. The NO_x concentration in the gas flow from the NO_x-storage catalyst increases gradually with time based on the saturation of NO_x-storage capacity of the catalyst as shown in Fig. 1b. Fuel-rich gas containing high concentrations of hydrocarbons is allowed to flow through the catalyst to regenerate the storage ability. As a result, NO_x concentra-

* Corresponding author. Fax: +81-92-583-8976.
E-mail address: miura@astec.kyushu-u.ac.jp (N. Miura).

0272-8842/$30.00
doi:10.1016/j.ceramint.2003.12.014

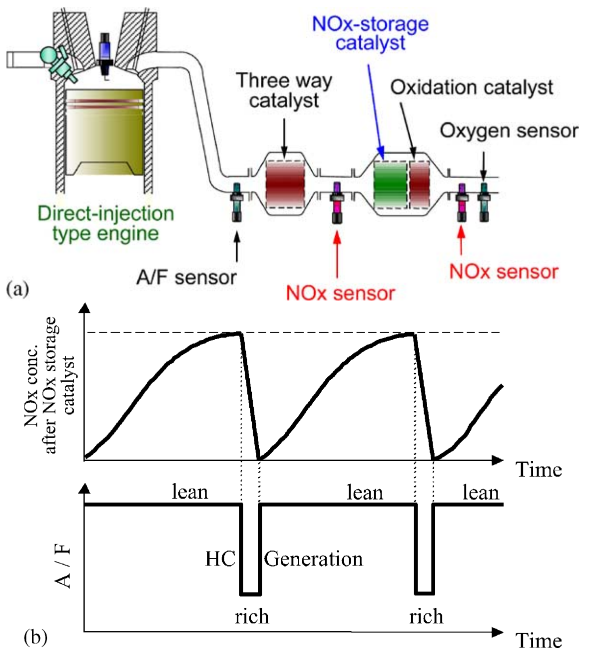

Fig. 1. (a) Catalytic converter system equipped with NO_x sensors for the exhaust gas emitted from a new-type car engine; (b) regeneration pattern of NO_x-storage catalyst.

tion in the gas emitted from this new catalyst drops rapidly down to zero level and then gradually increases again. Consequently, one of the major requirements to *on-board* NO_x sensor is determination the NO_x concentration in the gas flow from the new catalyst and monitoring timing for regenerating the catalyst.

Solid-state gas sensors could be classified into three main categories according to the detection principles, i.e. equilibrium potential, electrochemical pumping-current and mixed potential. Among them, the last one, based on mixed-potential gas sensing principle, has been paid special attention due to its high sensing performance to air pollutants in oxygen containing atmospheres at high temperatures. For instance, we have extensively investigated several oxides as SEs for NO_x sensor, such as $CdMn_2O_4$ [4]; $CdCr_2O_4$ [5]; WO_3 [6]; $NiCr_2O_4$ [7]; $ZnFe_2O_4$ [8,9] and $ZnCr_2O_4$ [10], since our first report in 1996 [4,11] revealed that the use of oxide SE in this type of NO_x sensor is quite effective for sensitive and selective detection NO_x at high temperatures. Furthermore, recently, we found that the new complex impedance-based type NO_x sensor using $ZnCr_2O_4$-SE has shown rather good sensing characteristics towards “in situ” NO_x measurement at temperature as high as 700 °C [12]. Therefore, the purpose of this paper is to report the sensing performances of zirconia-based NO_x sensors employing zinc-family oxide SEs.

2. Experimental

A closed-one-end of YSZ tubes (8 mol% Y_2O_3 doped, NKT Co., Ltd.) were used for fabrication of NO_x sensors. The $ZnCr_2O_4$ and $ZnFe_2O_4$ powders were prepared by a conventional solid-state reaction method on the outer surface of YSZ tube to form SE. The Pt paste was applied on the inner surface of the YSZ tube and then also sintered at 1200 °C for 2 h to form the counter electrode (CE). The sensing performances of both mixed-potential-type and complex-impedance-based YSZ sensors were evaluated in conventional gas-flow apparatus in the temperature range of 600–700 °C from 50 up to 450 ppm of NO_x concentration in the presence (or absence) of 8 vol.% H_2O and 15 vol.% CO_2. The potential difference between SE and CE was measured by means of a digital electrometer (Advantest, R8240) as a sensing signal of the mixed-potential-type sensor when SE was exposed to the base air or to the sample gas with different NO_x concentrations. The CE was always exposed to the atmospheric air during experiments. For the impedance-based sensor, the complex impedance and the phase angle between SE and CE were measured by a complex-impedance analyzer (Solarton, 1255WB). The frequency was changed from 0.1 Hz to 100 kHz to obtain complex-impedance (Nyquist) plots. As an output sensor signal, the complex impedance value ($|Z|$) was used and was monitored at fixed frequency of 1 Hz.

3. Results and discussion

3.1. Sensing performance of the mixed-potential-type NO_x sensor

Fig. 2 compares the EMF responses obtained to both NO and NO_2 concentrations in air for the tubular YSZ-based sensors using each of two zinc-family oxide SEs tested at 600 and 700 °C, respectively. In the carrier gas (dry synthetic air), the EMF value was close to zero. Thus, the

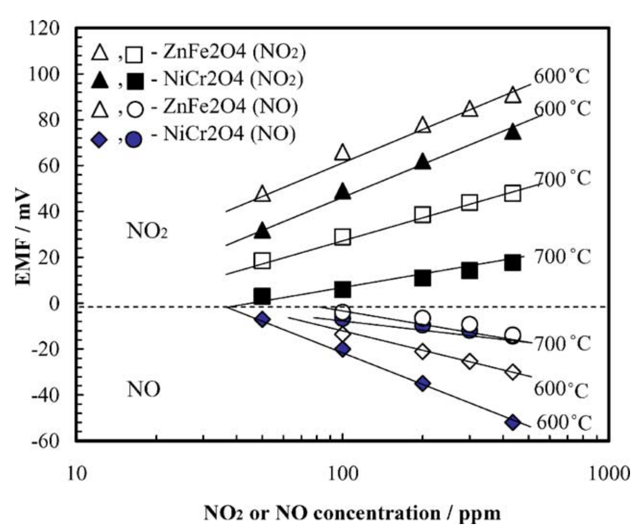

Fig. 2. EMF of the mixed-potential type YSZ-based sensor with $ZnFe_2O_4$-SE and $ZnCr_2O_4$-SE as a function of NO_x concentration at different temperatures.

measured EMF values were regarded to the sensitivities to NO and NO_2. The gas sensitivity was almost linear to NO_x concentration from 50 to 450 ppm at tested temperatures for both sensors. Moreover, as clearly shown in this figure, the mixed-potential sensor using $ZnFe_2O_4$-SE provided higher sensitivity to NO_x, compared to the same sensor using $NiCr_2O_4$-SE in the measured temperature range of 600–700 °C. Indeed, among the examined and previously published spinel-type oxides, $ZnFe_2O_4$ gave the highest sensitivity to NO_2 in the above-mentioned temperature range. The evaluation of sensing performances of the NO_x sensors using each of different zinc-family oxide SEs revealed that the NO_x sensitivities, especially for the $ZnFe_2O_4$-SE, were relatively stable at 700 °C up to 8 months examined and the EMF of air base was almost stable during the test period.

We have also examined the correlations between the NO_2 sensitivity and the various properties of different spinel-type oxides tested, such as gas adsorption–desorption behavior, oxygen sensing characteristics and the catalytic activity for the gas-phase reaction of NO_2 in order to clarify the reason why the $ZnFe_2O_4$-SE provides the highest NO_2 sensitivity in the temperature range of 600–700 °C. The examination of the temperature-programmed-desorption profiles of NO_2 for various spinel-type oxides showed that the amount of NO_2 desorption from $ZnFe_2O_4$ is larger than those from other spinel-type oxides ($NiCr_2O_4$; $ZnCr_2O_4$ and $CrMn_2O_4$) and the desorption peak for $ZnFe_2O_4$ was observed at the highest temperature (about 350 °C). Interestingly, the amount of NO_2 desorbed as well as the temperature of NO_2 desorption peak are roughly correlating to the NO_2 sensitivity at 700 °C, the higher the amount and the peak temperature of NO_2 desorption, the higher the NO_2 sensitivity. This fact suggests that the NO_2 gas adsorbed at the YSZ/SE interface may promote the rate of the following cathodic reaction (1) of NO_2 at high temperatures:

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

Fig. 3 shows the NO_2 conversion due to the following non-electrochemical gas-phase reaction in the sample gas mixture of 100 ppm NO_2, 21 vol.% O_2 and He balance:

$$NO_2 \rightarrow NO + \tfrac{1}{2}O_2 \quad (2)$$

The NO_2 conversion on $ZnFe_2O_4$-SE is relatively low in the temperature range of 500–600 °C, compared with those on the other oxides. In fact, the catalytic activity at 550 °C for the oxides is roughly correlating to the NO_2 sensitivity obtained at 700 °C; the lower the catalytic activity of oxide, the higher the NO_2 sensitivity of the sensor. Since NO, thermodynamically, dominates in the equilibrated NO_x gas mixture at temperatures above 500 °C [4], the conversion of NO_2 to NO is usually high when the catalysts are used. If the catalytic activity of SE is reasonably high at high temperatures, most of NO_2 can be easily converted to NO accordingly to the gas-phase reaction (2) on the surface or in the bulk of oxide SE layer and thus it is rather hard to NO_2 to reach to the YSZ/SE interface. As a result, the NO_2 sensitivity is low for the device using such SE. In opposite, if the catalytic activity of SE is relatively low at high temperatures, the porosity of such SE is high and SE itself is thin enough, NO_2 can diffuse through the SE layer without decomposition to NO and then reach to the YSZ/SE interface, resulting high NO_2 sensitivity.

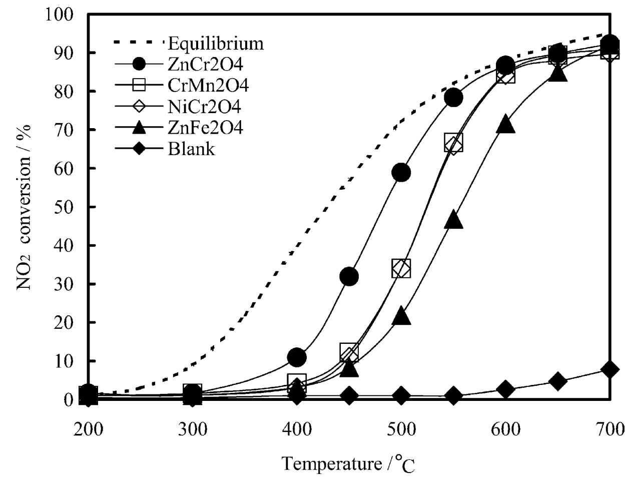

Fig. 3. Comparison of the NO_2 conversion at different temperatures for the devices attached with each of various spinel-type oxide SEs.

Thus, during our investigation of mixed-potential-type NO_x sensors, the device using $ZnFe_2O_4$-SE was found to give the highest sensitivity to both NO and NO_2 at the temperature range of 650–700 °C among the several spinel-type-oxide SEs examined and reported to date. In addition, this SE was relatively stable even at 700 °C, as mentioned above. Consequently, the results obtained here suggest that, although the response rate for the sensor using $ZnFe_2O_4$ needs to be improved [9], this material is one of the promising candidate for SE of the high-temperature NO_x sensor.

3.2. Sensing performance of the complex impedance-based NO_x sensor

In addition to the mixed-potential type NO_x sensors, our attention in last couple of years has been focusing on the development of principally new-type YSZ-based sensor for detecting NO_x at high temperature [3,10]. The changing in the complex impedance of the device attached with oxide SE was measured as a sensing signal in this type of NO_x sensors. During our initial investigation of complex-impedance plots for the devices employed spinel-type oxides ($CrMn_2O_4$, $NiCr_2O_4$, $NiFe_2O_4$ and $ZnCr_2O_4$) as SE, in base air, 200 ppm NO_2, and 200 ppm NO, at 700 °C, we found that in the first three cases, a large and flat semicircular arc was observed in each Nyquist plots in the examined frequency range and the shape of semi-arc for each device was almost similar in each gas. This indicated that the impedance values of these devices are not

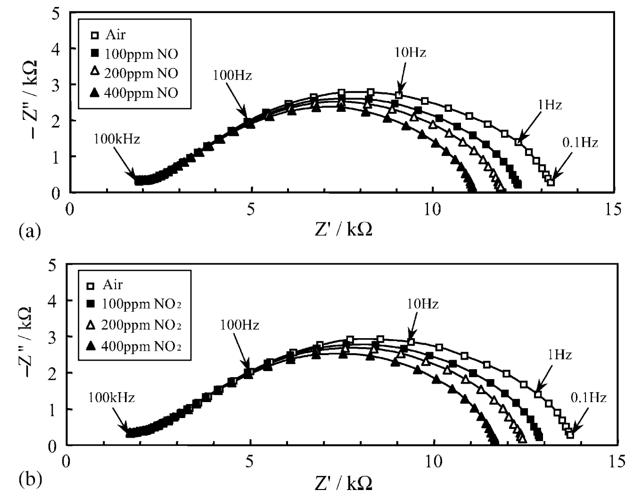

Fig. 4. Complex impedance plots in base air and the sample gas with each of various concentration of NO (a) and NO_2 (b) at 700 °C for the YSZ-based NO_x device attached with $ZnCr_2O_4$-SE.

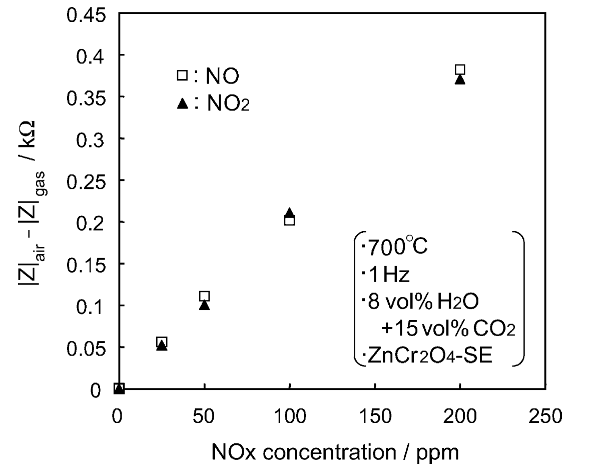

Fig. 5. Dependence of 'gas sensitivity' of the complex impedance-based sensor using $ZnCr_2O_4$-SE on measuring NO_x concentration in the presence of 8 vol.% H_2O and 15 vol.% CO_2 at 700 °C.

affected by the co-existence of NO_x in the sample gas under the present condition and then these SE are insensitive to NO_x gas at high temperature. However, we found that for the device attached with $ZnCr_2O_4$-SE, the impedance behavior was found to be entirely different from the above-mentioned results. As shown in Fig. 4, 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) varied with the concentration of both NO and NO_2 in the sample gas. In addition, the resistance value decreased with an increase in the concentration of both NO and NO_2. Such a trend is completely different from that for the mixed-potential type NO_x sensors whose response direction to NO is opposite to that to NO_2 (see Fig. 2). Meanwhile, the Z' value (the intercept, about 2000 Ω) at the intersection of the large semi-arc at high frequencies (around 50 kHz) did not change even if the concentration of NO_x was changed from 0 to 400 ppm.

The difference between the impedance ($|Z|_{air}$) in the base air and the impedance ($|Z|_{gas}$) in the sample gas containing NO_x concentration at the fixed frequency of 1 Hz has been defined as 'gas sensitivity' of the device [3]. It was, therefore, interesting to investigate the gas sensitivity of sensor using $ZnCr_2O_4$-SE to both NO and NO_2 at high temperature and in the presence of high concentration of humidity (H_2O; 8 vol.%) and CO_2 (15 vol.%), which are usually exist in car exhausts. The measurements were made for various NO_x concentrations at fixed temperature of 700 °C. Fig. 5 shows the dependence of 'gas sensitivity' on the concentration of NO and NO_2 for the complex impedance-based NO_x device. Strong linear correlation between 'gas sensitivity' and the measuring concentration of both NO and NO_2 was found from 0 ppm to 200 ppm at 700 °C. Moreover, the most interesting result taken into consideration from these tests was based on the fact that the sensitivity to NO was almost equal to the sensitivity to NO_2 at 700 °C. This means, from

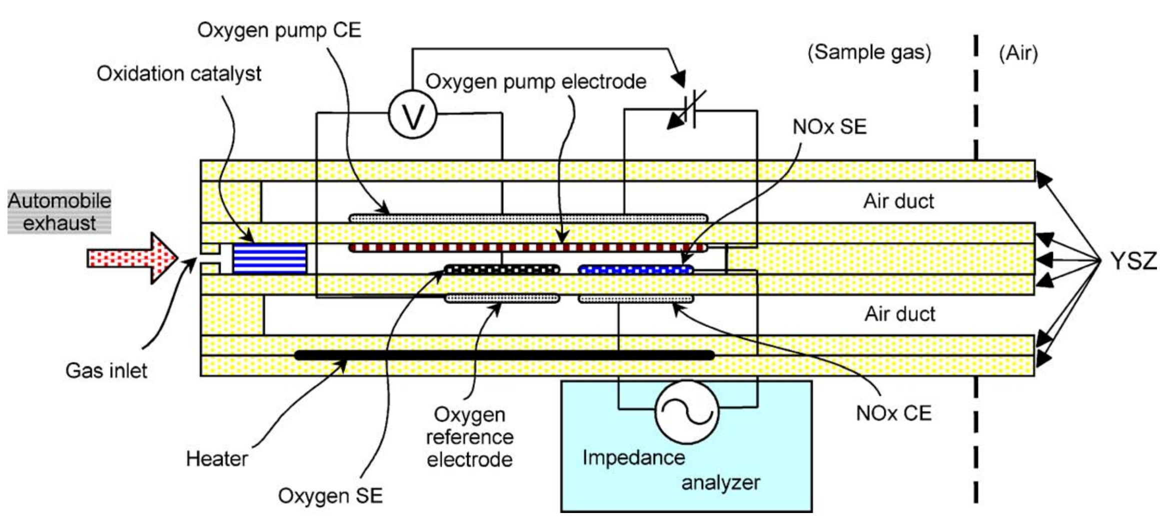

Fig. 6. A cross-sectional view of the proposed laminated-type complex impedance-based NO_x sensor.

the practical point of view, that the present device is capable of measuring total NO_x (NO and NO_2) concentration in the gas mixture regardless of the NO/NO_2 ratio at 700 °C. This is very valuable point for the development of practical NO_x sensor for car exhausts.

Based on our previous experience with the mixed-potential-type sensors employing spinel-type oxides as SE, we presumed that it is quite possible that the response of the present device is also intervened by the change in oxygen concentration in the sample gas. In order to check this point, O_2 concentration in the sample gas was changed from 5 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 showed strong linear correlation to 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 result indicates 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 at all times. For this purpose, both O_2 sensor and YSZ-based O_2-pump could be used for monitoring and controlling O_2 concentration, respectively. These functioning devices can be combined into new laminated-type YSZ-based device comprising oxidation catalyst, O_2 sensor, O_2 pump and NO_x SE, as shown in Fig. 6. In this design, combustible gases can be oxidized by oxidation catalyst and the O_2 concentration can be kept constant at all times. Consequently, the NO_x sensitivity of the sensor will not be affected by the co-existence of combustible gases and by the variation in O_2 concentration in the exhaust gas.

4. Conclusions

(1) $ZnFe_2O_4$-SE has shown the highest sensitivity to NO_x at the temperature range of 600–700 °C among other spinel-type oxide SEs tested and reported to date for the mixed-potential type NO_x sensor.
(2) $ZnCr_2O_4$-SE has shown rather good NO_x sensing performance at 700 °C for the complex impedance-based YSZ sensor.
(3) The sensitivity to NO was almost equal to the sensitivity to NO_2 from 0 ppm to 200 ppm for the impedance-based NO_x sensor employing $ZnCr_2O_4$-SE at 700 °C.
(4) The observed NO_x sensitivity and the measured NO_x concentration had strong linear correlation even in the presence of 8 vol.% H_2O and 15 vol.% CO_2 at 700 °C.
(5) New laminated-type structure for the complex impedance-based NO_x sensor has been designed. The main advantage of this design is that NO_x sensitivity of the sensor protected from the influence of the co-existing combustible gases and from the deviation of oxygen concentration in exhaust gas.

Acknowledgements

The work was partially supported by a Grant from the Ministry of Education, Science, Sports and Culture of Japan.

References

[1] Official Journal of the European Communities, L 350, vol. 41 European Directive 2000/25/EC, 22 May 2000.
[2] M. Khai, J. Lemare, S. Fischer, Achieving heavy-duty diesel NO_x/PM levels below the EPA 2002 standards—an integrated solution, SAE 2000-01-0187.
[3] N. Miura, M. Nakatou, S. Zhuiykov, Impedancemetric gas sensor based on zirconia solid electrolyte and oxide sensing electrode for detecting total NO_x at high temperature, Sens. Actuators B 93 (2003) 221–228.
[4] N. Miura, H. Kurosawa, M. Hasei, G. Lu, N. Yamazoe, Stabilized zirconia-based sensor using oxide electrode for detection of NO_x in high-temperature combustion-exhausts, Solid State Ionics 86–88 (1996) 1069–1073.
[5] N. Miura, G. Lu, N. Yamazoe, High-temperature potentiometric/amperometric NO_x sensors combining stabilized zirconia with mixed-metal oxide electrode, Sens. Actuators B 52 (1998) 169–178.
[6] G. Lu, N. Miura, N. Yamazoe, Stabilized zirconia-based sensors using WO_3 electrode for detection of NO and NO_2, Sens. Actuators B 65 (2000) 125–127.
[7] S. Zhuiykov, T. Nakano, A. Kunimoto, N. Miura, N. Yamazoe, Potentiometric NO_x sensor based on stabilized zirconia and $NiCr_2O_4$ sensing electrode operating at high temperatures, Electrochem. Commun. 3 (2001) 97–101.
[8] S. Zhuiykov, M. Muta, T. Ono, A. Kunimoto, N. Yamazoe, N. Miura, Stabilized zirconia-based NO_x sensor using $ZnFe_2O_4$ sensing electrode, Eletrochem. Solid State Lett. 4 (2001) H19–H21.
[9] N. Miura, S. Zhuiykov, T. Ono, M. Hasei, N. Yamazoe, Mixed potential type sensor using stabilized zirconia and $ZnFe_2O_4$ sensing electrode for NO_x detection at high temperature, Sens. Actuators B 83 (2002) 222–229.
[10] S. Zhuiykov, T. Ono, N. Yamazoe, N. Miura, High-temperature NO_x sensors using zirconia solid electrolyte and zinc-family oxide sensing electrode, Solid State Ionics 152–153 (2002) 801–807.
[11] N. Miura, G. Lu, N. Yamazoe, Mixed potential type NO_x sensor based on stabilized zirconia and oxide electrode, J. Electrochem. Soc. 143 (1996) L33–L35.
[12] N. Miura, M. Nakatou, S. Zhuiykov, Impedance-based total-NO_x sensor using stabilized zirconia and $ZnCr_2O_4$ sensing electrode operating at high temperature, Electrochem. Commun. 4 (2002) 284–287.