High Temperature NOx Sensor Based on Stabilized Zirconia and $ZnFe_2O_4$ Electrode

Serge Zhuiykov*, Midori Muta*, Takashi Ono**, Akira Kunimoto**, Noboru Yamazoe*** and Norio Miura*

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

**R&D Division, Riken Corporation, Kumagaya-shi, Saitama 360-8522, Japan

***Interdisciplinary Graduate School of Engineering Sciences, Kyushu University, Kasuga-shi, Fukuoka 816-8580, Japan

SUMMARY

Electrochemical sensors using tubular yttria-stabilized zirconia (YSZ) and the spinel-type oxide sensing-electrode (SE) were fabricated and examined for NOx detection at high temperatures. The $ZnFe_2O_4$-attached device gave a linear correlation between EMF and the logarithm of NO_2 (NO) concentration from 50 ppm to 436 ppm in the temperature range 550-700℃. This sensor was found to give the highest sensitivity to NO_2 in air among the spinel-type oxides tested and reported to date. The sensing mechanism of the sensor was discussed on the basis of the catalytic activity and the TPD data for the oxides examined.

Keywords: *NOx sensor, mixed potential, oxide electrode*

Introduction

In order to solve the NOx (NO_2 and NO) related pollution problems, it is necessary to develop compact sensors capable to monitor NOx in the combustion exhausts and in environments. Many solid-state NOx sensors based on the yttria-stabilized zirconia (YSZ) and metal-oxide-SE have been developed and reported to date. Some of them are based on a sensing mechanism involving mixed potential. These sensors using the oxide SE, such as $CdMn_2O_4$ [1], $CdCr_2O_4$ [2,3] and $NiCr_2O_4$ [4], are capable to detect NO or NO_2 in oxygen containing atmospheres in the temperature range 500-650℃. However, their sensitivities to NOx are still low at temperatures over 600℃. Therefore the search for new oxide-SE is definitely important to obtain excellent sensing performance.

It has been also found that the careful selection of an oxide material for the SE brings about significant improvement in both sensitivity and selectivity of the sensor [4]. Based on this fact, we have examined the NOx sensitivity of sensors using each of spinel-type oxides in the temperature range 550-700 ℃. Consequently, we have found that the $ZnFe_2O_4$-SE is stable and gives the highest sensitivity to NOx at temperatures examined. Furthermore this material is easy to synthesize and is environmentally friendly. This report deals with the main sensing properties of the potentiometric NOx sensor based on YSZ and the $ZnFe_2O_4$-SE. In addition, the factors causing the high NOx sensitivity at higher temperature are also discussed.

Experimental

A commercial half-opened YSZ tube (8 mol.% Y_2O_3 doped, NKT) was used for fabrication of the device. It is 30 cm in length and 5 and 8 mm in inner and outer diameter, respectively. The oxide SE was applied on the outer surface of the YSZ tube and then sintered at 1200℃ for 2 h. The adhesion between the oxide layer obtained and the zirconia surface was reasonably good. The sintered oxide layer was about 30 μm thick. Pt paste was applied on the inner surface of the YSZ tube and then calcined at 1000℃ for 2 h to form a reference electrode (RE). The RE was always exposed to atmospheric air.

Gas sensing experiments were carried out in a conventional gas-flow apparatus equipped with a furnace in the temperature range 550-700℃. The sample gases containing various concentrations of NO_2 (or NO) were prepared by diluting parent dry gases with synthetic air (or $N_2 + O_2$). The total flow rate of the sample gas or the base air was fixed at 100 cm^3/min. The difference in potential (EMF) between SE and RE was monitored as a sensing signal with a digital electrometer. Both NO and NO_2 concentrations were changed from 50 ppm to 436 ppm.

The adsorption-desorption behavior of NO_2 and oxygen were examined by using a temperature-programmed-desorption (TPD) apparatus (Bell Japan Inc. TPD-1-AT). The oxide powder (0.3g) was set in the quartz-tube cell of the TPD apparatus. The sample was heated up to 800°C in He gas stream and was exposed to pure O_2 at this temperature, followed by cooling down to 50°C in the O_2 stream. Then, the sample was treated with 1000 ppm NO_2 diluted with He at 50°C for 5 min for the NO_2 adsorption. The desorbed NO_x and O_2 from the sample were detected with a chemiluminescence NOx analyzer (Yanako, ECL-88A) and a QP-mass spectrometer, respectively, when the sample was heated up to 800°C at heating rate of 10°C/min in a He stream. The catalytic activity of each oxide (0.01g) for the gas-phase decomposition of NO_2 was evaluated by using the TPD apparatus and the NOx analyzer in the temperature range 200-700°C. Space velocity (W/F) was set to 0.006 $g \cdot s \cdot cm^{-3}$ for the all experiments.

Results and Discussion

Several spinel-type oxides were examined for the SE properties as attached to the tubular sensor. The EMF characteristics of the YSZ devices using each of the $ZnFe_2O_4$- and $NiCr_2O_4$-SE are shown in Fig. 1. The EMF of the both sensors was almost linear to the logarithm of NO or NO_2 concentration at each temperature examined. Characteristically the direction of the EMF response was positive and negative to NO_2

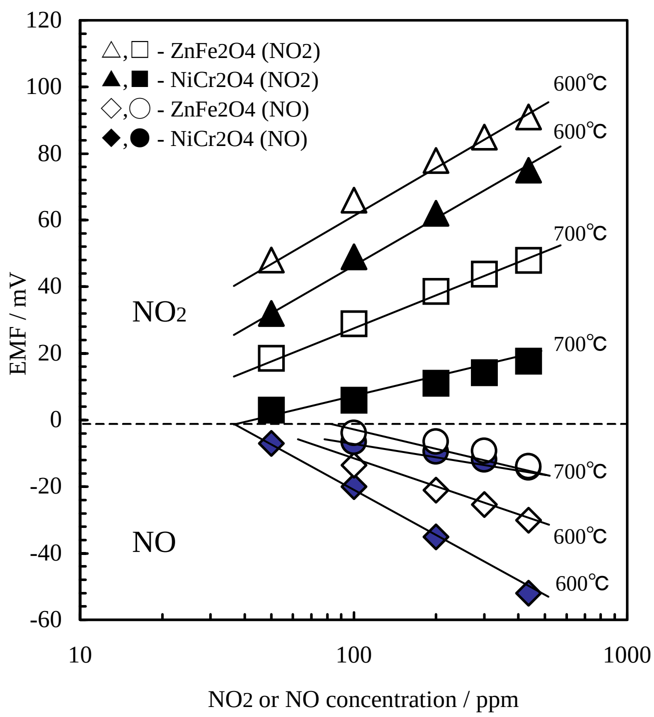

Fig. 1 *Dependence of EMF on the logarithm of NO or NO_2 concentration for the YSZ sensors using each of $ZnFe_2O_4$- and $NiCr_2O_4$-SE.*

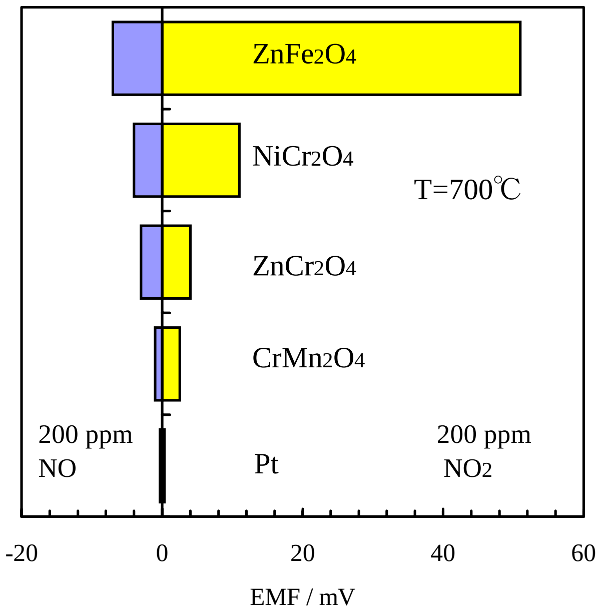

Fig. 2 *Comparison of the EMF responses at 700°C for the sensing devices attached with each of various spinel-type electrodes.*

and NO, respectively, as seen in the previous papers [1-4]. The reproducibility of the measured EMF was reasonably good (±1 mV). This sensor is capable of detecting NO or NO_2 from 50 ppm to 436 ppm. The slopes of the output EMF to NO and to NO_2 are larger at 600°C than at 700°C. The responses to NO_2 in air for the sensor were repeatable over the certain number of tests at 700°C.

Fig. 2 compares the EMF responses obtained to both of 200 ppm NO and 200 ppm NO_2 in air at 700°C. In the carrier gas (dry synthetic air), the EMF value was close to zero. Thus, the measured EMF values were regarded to the sensitivities to NO and NO_2. As clearly shown in this figure, pure Pt gave no sensitivity to both NO_2 and NO at this temperature. The EMF values measured here are based on mixed potential [3] on the SE. Among the examined and previously published spinel-type oxides, $ZnFe_2O_4$ gave the highest sensitivity to NO_2 in the temperatures range 600-700°C. Therefore the main attention was paid on the YSZ sensor using the $ZnFe_2O_4$-attached SE in the following tests. The evaluation of the sensing performances of the NOx sensors using different spinel-type oxide electrodes revealed that the NOx sensitivities for the $ZnFe_2O_4$-SE were rather stable even at 700°C. In some cases of other spinel-type oxides, the visible degradation was seen in sensitivity to both NO and NO_2 after one month operation at 700°C. The EMF values to 100 ppm NO_2 as well as the base EMF (in dry synthetic air) at 700°C for the sensor using the $ZnFe_2O_4$-SE were almost constant after 20 days up to 120 days operation examined in dry synthetic air.

Fig. 3 shows TPD profiles of NO_2 for the various spinel-type oxides examined here. As clearly shown in this figure, the amount of NO_2 desorption from $ZnFe_2O_4$ is larger than those from other oxides ($NiCr_2O_4$, $CrMn_2O_4$ and $ZnCr_2O_4$) and the desorption peak for $ZnFe_2O_4$ is seen at the highest temperature. Any desorption of NO_2 were not observed in the temperature range 500-800℃ for all oxides tested. 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℃ (Fig. 2). The higher the amount and the peak temperature of NO_2 desorption, the higher the NO_2 sensitivity. Therefore $ZnFe_2O_4$ can give the highest NO_2 sensitivity compared with the other oxides. It should be noted here that the condition of the TPD measurement differs significantly from the sensor-operation condition. Although the NO_2 gas was swept from the oxide sample by He gas at the TPD measurement, the oxide SE of the sensor is always exposed to NO_2 gas during the sensor operation even at high temperature.

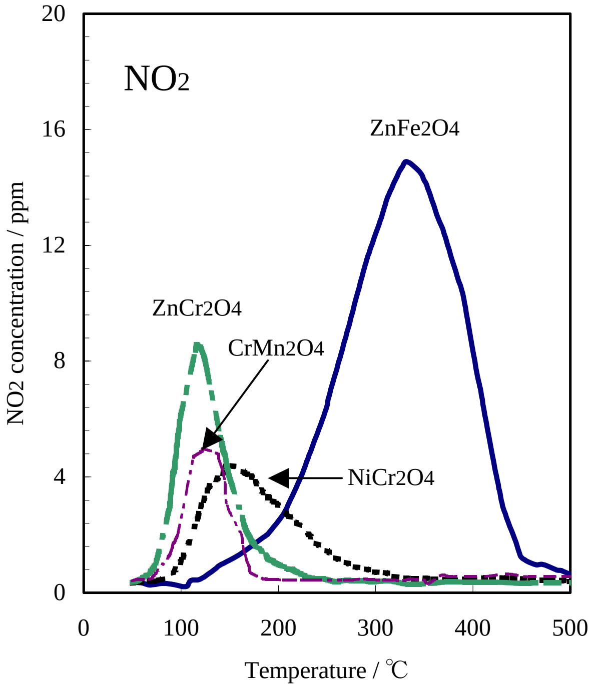

Fig. 3 *TPD profiles of NO_2 for various spinel-type oxides examined.*

In addition, the investigation on O_2 desorption revealed that the oxygen adsorbed on the oxide SE also plays a significant role in the sensing mechanism. Fig. 4 shows that the O_2 desorption behavior is also related to the NO_2 sensitivity for the oxides tested.

The amount of O_2 desorbed from $ZnFe_2O_4$ at around 700℃ is much larger than those from other oxides. The temperature of O_2 desorption peak is also high in the case of $ZnFe_2O_4$. It means that the oxygen can be

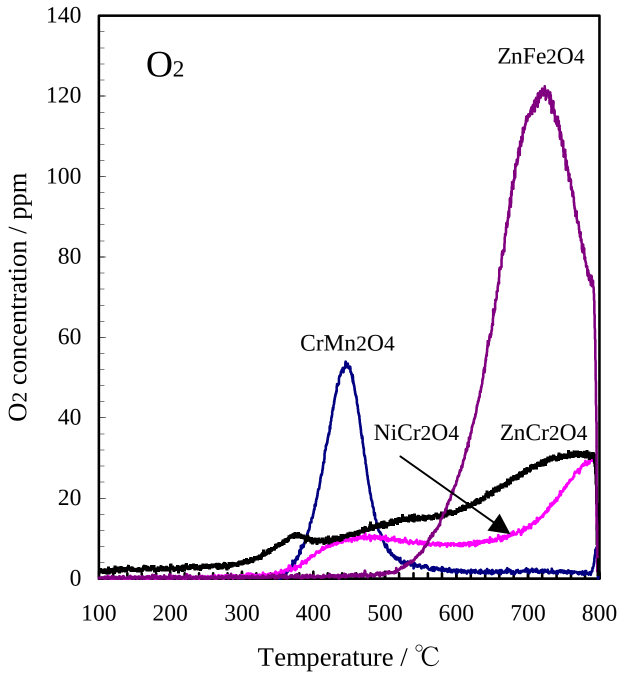

Fig. 4 *TPD profiles of O_2 for various spinel-type oxides examined.*

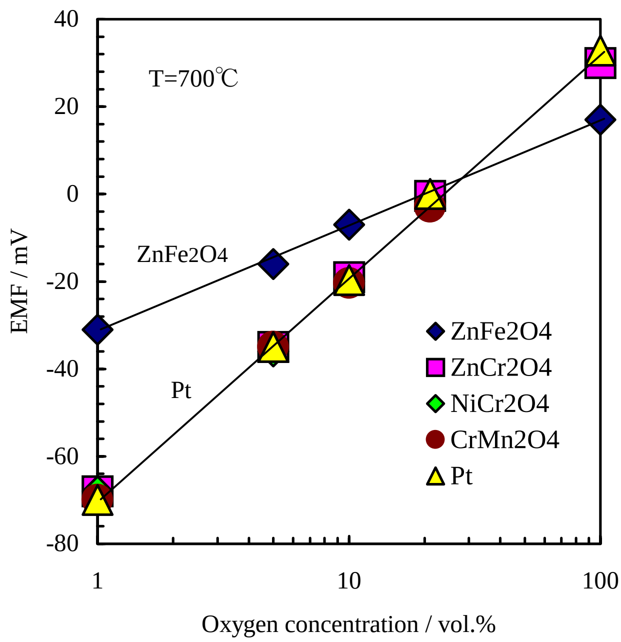

Fig. 5 *Dependence of EMF on the logarithm of O_2 concentration for the YSZ sensor using spinel-type oxide SE.*

adsorbed rather strongly on the surface of the oxide. Consequently, the oxygen adsorption-desorption process may not be completely reversible on the $ZnFe_2O_4$-SE even at 700℃.

In order to confirm this assumption, we investigated the oxygen sensing properties for all oxides. Fig. 5 shows the Nernstian plots at 700℃ for the devices using each of the oxides tested. The data for the sensor using Pt were also indicated as comparison. All oxides except for $ZnFe_2O_4$ gave the theoretical Nernstian plots (electron number: n=4.0) as the Pt electrode did. The slope (24 mV/decade) of the plots for $ZnFe_2O_4$ was smaller than the theoretical one (48mV/decade) at 700 ℃. Furthermore, the response time for $ZnFe_2O_4$ was very slow compared with the other oxides. For example, the 90% of the response time from 100% O_2 to air for $ZnFe_2O_4$ was about 10 min, while 20 ~ 60 s for the other oxides. From these results we may say that $ZnFe_2O_4$ is working as an irreversible O_2 electrode. This means that the catalytic activity of $ZnFe_2O_4$ for the electrochemical reaction of O_2 is low. Therefore, according to the sensing mechanism based on mixed potential, lower electrochemical catalytic activity for anodic reaction of O_2 can lead to higher NO_2 sensitivity.

Fig. 6 shows the NO_2 conversion due to the non-electrochemical gas-phase reaction ($NO_2 \rightarrow NO + 1/2O_2$) in the sample gas mixture of 100 ppm NO_2, 21% O_2 and He balance. Since NO dominates in the equilibrium gas mixture at temperatures above 500℃, the conversion of NO_2 to NO is usually high when the catalysts are used. If the catalytic activity of SE is high, NO_2 easily converts to NO through the oxide layer. Thus, the actual NO_x composition of the sample gas reaches to the equilibrium near the interface of YSZ/SE/gas. This leads to the low NO_2 sensitivity. However, if the catalytic activity of SE is not high, NO_2 can diffuse to the interface and, therefore, the NO_2 sensitivity will be high for the device using such SE. Fig. 6 shows, in the temperature range 500-600℃, the NO_2 conversion on $ZnFe_2O_4$ is low compared with those on the other oxides. These results can also explain the reason why $ZnFe_2O_4$ gives the highest NO_2 sensitivity among the oxides tested here.

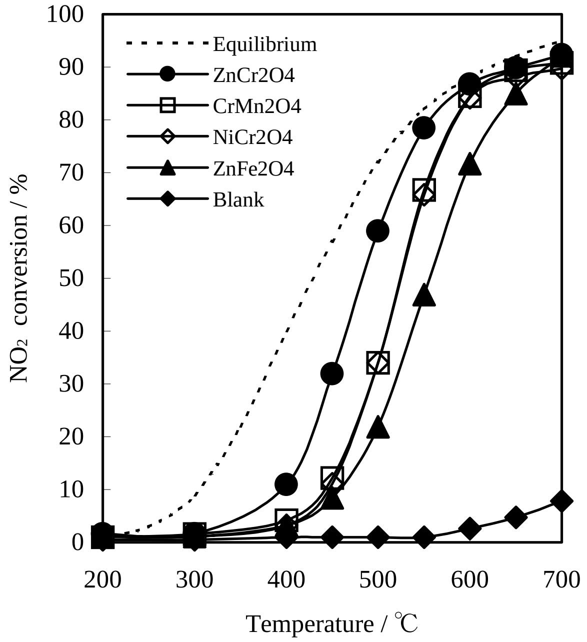

Fig. 6 *Temperature dependence of NO_2 conversion to NO on the various oxides tested.*

Conclusions

The mixed-potential type NO_x sensors using different oxide SE were fabricated and examined for the sensing properties in the temperature range 550-700℃. As a result, the device using the $ZnFe_2O_4$-SE was found to give the highest sensitivity to both NO and NO_2 at 700℃ among the spinel-type oxides examined here and reported to date. The sensor is rather stable even at high temperatures. It seems that the NO_2 sensitivity could be indirectly determined by the several factors such as the adsorption-desorption behavior of NO_2 and O_2, the electrochemical catalytic activities of SE, and the non-electrochemical catalytic activity of SE for NO_2 decomposition. Consequently, the results obtained suggest that $ZnFe_2O_4$ is one of excellent candidate for SE of the high-temperature NO_x sensor.

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