

# Improving NO<sub>2</sub> Sensitivity by Adding WO<sub>3</sub> during Processing of NiO Sensing-Electrode of Mixed-Potential-Type Zirconia-Based Sensor

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A planar NO<sub>2</sub> sensor was fabricated by using an yttria-stabilized zirconia plate and NiO-based sensing electrode (SE). The improvement in sensing characteristic of mixed-potential-type planar NO<sub>2</sub> sensor was examined by the addition of various metal oxides to NiO-SE. Among the metal-oxide additives tested, WO<sub>3</sub> was found to give a significant enhancement in NO<sub>2</sub> sensitivity. In addition, this enhancement was maximum when the initial WO<sub>3</sub> content in the NiO-based paste before sintering was 10 wt %. The sensitivity ( $\Delta$  electromotive force) to 50 ppm NO<sub>2</sub> was as high as about 70 mV for the sensor using the 10 wt % WO<sub>3</sub>-added NiO-SE at 800°C under the wet condition (containing 5 vol % H<sub>2</sub>O). The sensitivity of this sensor was still 8 mV even down to 1 ppm NO<sub>2</sub> at 800°C. The NO<sub>2</sub> sensitivity was found to be invariant to different concentrations of H<sub>2</sub>O and CO<sub>2</sub> in the examined range of 5–15 and 5–20 vol %, respectively. It is speculated that the modification of morphology of the NiO-SE layer by the addition of WO<sub>3</sub> is the main contributing factor for the improved NO<sub>2</sub> sensitivity of the sensor. © 2007 The Electrochemical Society. [DOI: 10.1149/1.2747532] All rights reserved.

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In order to reduce exhaust emissions and to improve fuel efficiency, the automotive industries have recently introduced ultraleanburn gasoline vehicles into the market.<sup>1,2</sup> However, in the newly introduced ultralean-burn gasoline vehicles, it is necessary to use additionally a new NO<sub>x</sub>-storage catalyst. This is because NO<sub>x</sub> emitted from these vehicles cannot be decomposed sufficiently into nitrogen under lean-burn (air-rich) conditions by a conventional threeway catalyst. Moreover, because the NO<sub>x</sub> storage ability of the new catalyst reaches saturation quickly, the catalyst has to be regenerated by flowing fuel-rich gas periodically to decompose the absorbed NO<sub>r</sub>. In this regard, in order to detect regenerating timing and to monitor the catalyst performance, it is highly required to develop high-performance  $NO_x$  sensor. Such a high-performance solid-state NO<sub>x</sub> sensor can also be used for an advanced on-board diagnosis system which can inform a driver directly about the state of emission of his/her car, in the future.

So far, lots of potentiometric, amperometric, and impedancemetric NO<sub>x</sub> sensors based on solid electrolyte have been examined and reported.<sup>3</sup> Among these NO<sub>x</sub> sensors, the mixed-potential-type NO<sub>x</sub> sensors based on yttria-stabilized zirconia (YSZ) have been examined intensively, aiming at detection and monitoring of automotive exhausts.<sup>4-41</sup> The operating temperature of mixed-potential-type sensors was usually lower than 700°C. This is because operation in excess of 700°C usually results in poor NO<sub>x</sub> sensitivity.

Furthermore, because the temperature of exhausts from a gasoline engine occasionally rises to 900°C during accelerating or cruising at high speed, it is important that the NO<sub>x</sub> sensor should work efficiently even at such a high temperature. We have first reported that NiO could be used as a sensing electrode (SE) even at temperatures of 800–900°C under wet conditions.<sup>36-39</sup> However, the sensitivity of the sensor needs to be further improved for actual application.

Quite recently, we have found that the addition of Rh to NiO–SE can bring about remarkable improvement in NO<sub>2</sub> sensitivity.<sup>40</sup> However, the use of Rh seems to not be preferable for actual application because of its high cost. Thus, it is necessary to find a cheaper alternative additive instead of Rh. Among the examined various oxide additives not including precious metals, WO<sub>3</sub> was found to give the largest improvement effect in NO<sub>2</sub> sensitivity. Thus, we report

here the selection process of the oxide additive and the sensing characteristics of mixed-potential-type zirconia-based  $NO_2$  sensor using the WO<sub>3</sub>-added NiO-SE.

# Experimental

Fabrication of sensor device.-- YSZ plates (8 wt %  $Y_2O_3$ -doped,  $10 \times 10$  mm, 0.2 mm thickness) were used for the fabrication of the planar sensor. Commercial NiO powder (Kojundo Chemical Lab. Co., Ltd., 99.97% purity) was thoroughly mixed with an appropriate amount of each of various oxide additives in ethanol by means of ultrasonication. After evaporating ethanol, the remaining solid was mixed with  $\alpha$ -terpineol (40 wt %) to obtain a paste. The resulting paste was applied on the front side of the YSZ plate attached with narrow Pt stripes (served as a current collector) by means of the screen printing technique to make a sensing electrode. A commercial Pt paste (Tanaka Kikinzoku Co., Ltd., TR 7907) was printed on the back side of YSZ plate as a reference electrode (RE). To make a good electrical contact with a measuring equipment, Pt wires (0.1 mm in diameter) were fixed by using a Pt paste onto Pt connecting spots of both SE and RE. The planar sensor thus obtained was kept at 130°C for 2 h in atmospheric air and was subsequently sintered at 1400°C for 2 h in air. Figure 1 shows the sche-



Figure 1. Schematic view of front and back sides of the planar  $NO_2$  sensor used.

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matic view of the planar sensor used in the present investigation.

Characterization of sensing materials.— The crystal structures of pure NiO and WO<sub>3</sub>-added NiO samples were examined with an X-ray diffractometer (Rigaku, RINT 2100VLR/PC). The Cu K $\alpha$  radiation ( $\lambda = 1.5406$  Å) and 0.5°/min angle step were used for all measurements. The morphology of SE was observed by the use of a scanning electron microscopy (SEM, Hitachi, S–3000N, operating at 20 kV) and the composition of SE was analyzed using an energy dispersive X-ray analyzer (EDX, Horiba, EX-220SE).

Evaluation of sensing performances and electrochemical properties.— The measurements of NO<sub>x</sub>-sensing characteristics were performed using a conventional gas-flow apparatus equipped with a furnace operating at 800°C. The sample gas containing various concentrations of NO<sub>2</sub> ranging from 5 to 100 ppm was prepared by diluting a parent gas (500 ppm  $NO_2$  in dry  $N_2$ ) with dry  $N_2$  and  $O_2$ . The ppm refers to the volume concentration of  $NO_2$  in the gaseous mixture. The base gas was composed of 5 vol %  $O_2$  (+ $N_2$  balance). Both the sample gas and the base gas were humidified with 5 vol %(50,000 ppm) H<sub>2</sub>O vapor by means of a homemade water-vapor generator. Both the base gas and the sample gas were allowed to flow over the sensor at a constant flow rate of 100 cm<sup>3</sup>/min. SE and RE were exposed simultaneously to the sample gas or the base gas. The difference in potential (emf) between SE and RE of the planar sensor was measured at 800°C with a digital electrometer (Advantest, R8240) as a sensing signal. The potential of the SE was always positive with respect to RE.

The current-voltage (polarization) curves were measured by means of an automatic polarization system (Hokuto Denko, HZ-3000) based on potential-sweep method at a scan rate of 2 mV/min for a two-electrode configuration at 800°C in the base gas (5 vol %  $O_2 + N_2$  balance) and in the sample gas containing 50 ppm NO<sub>2</sub> (+ the base gas). The current axis of the anodic polarization curve was subtracted from that of the cathodic polarization curve at each potential so as to obtain the modified polarization curve in which the current axis was expressed in an absolute scale. The compleximpedance measurements of the sensor were performed by means of a complex-impedance analyzer (Solarton, 1255 WB) in the frequency range from 0.01 Hz to 1 MHz at 800°C.

*Measurements of NO*<sub>2</sub> *conversion to NO*.— The catalytic activity of the gas-phase decomposition of NO<sub>2</sub> (100 ppm NO<sub>2</sub> + 5 vol % O<sub>2</sub> + N<sub>2</sub> balance) to NO was evaluated for pure NiO, 10 wt % WO<sub>3</sub>-added NiO, and 50 wt % WO<sub>3</sub>-added NiO (ca. 0.2 g each) sintered at 1400°C using a conventional flow cell as well as a NO<sub>x</sub> analyzer (Yanaco, ECL-88A) in the temperature range of 200–900°C.

#### **Results and Discussion**

Selection of the best metal-oxide additive .-- In order to select the best oxide additive, each of various metal oxides, such as WO<sub>3</sub>, ZnO, Ta<sub>2</sub>O<sub>5</sub>, SnO<sub>2</sub>, In<sub>2</sub>O<sub>3</sub>, Cr<sub>2</sub>O<sub>3</sub>, Fe<sub>2</sub>O<sub>3</sub>, CuO, Nb<sub>2</sub>O<sub>5</sub>, and CeO<sub>2</sub>, was added (10 wt % each) to NiO-SE. Then, the sensitivity ( $\Delta$ emf) to 50 ppm NO<sub>2</sub> for the sensor attached with each of these SEs was measured at 800°C in the presence of 5 vol %  $O_2$  and 5 vol % water vapor. Here, the sensitivity is defined as the difference between the emf value in the sample gas and that in the base gas  $(\Delta \text{emf} = \text{emf}_{\text{sample}} - \text{emf}_{\text{base}})$ . It is seen from Fig. 2 that, among the various metal-oxide additives examined, WO<sub>3</sub>, ZnO, Ta<sub>2</sub>O<sub>5</sub>, SnO<sub>2</sub>, In<sub>2</sub>O<sub>3</sub>, and Cr<sub>2</sub>O<sub>3</sub> can give some sort of improvement in NO<sub>2</sub> sensitivity, while the addition of other metal oxides, such as Fe<sub>2</sub>O<sub>3</sub>, CuO, Nb<sub>2</sub>O<sub>5</sub>, and CeO<sub>2</sub>, shows decrement in NO<sub>2</sub> sensitivity. Interestingly, WO<sub>3</sub> showed the highest improvement in NO<sub>2</sub> sensitivity. Figure 3 shows the variation of  $\Delta$ emf to 50 ppm NO<sub>2</sub> at 800°C for the sensor using NiO-SE sintered after the addition of various amounts of WO<sub>3</sub>. The initial content of WO<sub>3</sub> in the NiO-based oxide paste before sintering was changed from 5 to 50 wt %. It is seen that the NO<sub>2</sub> sensitivity is improved when the initial content of



**Figure 2.** (Color online) Comparison of sensitivity ( $\Delta$ emf) to 50 ppm NO<sub>2</sub> at 800°C for the sensors using NiO-SE added with various metal-oxide additives. (Base gas 5 vol % O<sub>2</sub> + 5 vol % H<sub>2</sub>O + N<sub>2</sub> balance.)

WO<sub>3</sub> is in the range of 5–15 wt %, while the sensitivity is degraded when the content is more than 20 wt %. The maximum NO<sub>2</sub> sensitivity was observed at the initial content of 10 wt %. Thus, the detailed sensing characteristics were examined for the sensor attached with NiO-SE sintered after the addition of 10 wt % WO<sub>3</sub>. Hereafter, we call such a NiO-based SE sintered after the WO<sub>3</sub> addition WO<sub>3</sub>-added NiO-SE.

Characterization of sensing-electrode materials.— In order to examine the thermal stability of NiO and WO<sub>3</sub>-added NiO, X-ray diffraction (XRD) patterns (not shown here) were recorded for each of the oxide powders sintered at 1400°C for 2 h in air. It was observed that, in all cases, NiO retains its crystallographic phase (facecentered cubic) corresponding to JCPDS PDF (no. 44-1159). Due to the sintering effect, all the peaks assigned to NiO were very narrow. However, in the case of WO<sub>3</sub>-added NiO powders, there were no Bragg reflections corresponding to WO<sub>3</sub> and only the peaks for NiO were observed. It was also confirmed from this XRD study that there was no formation of solid solution between WO<sub>3</sub> and NiO after sintering at 1400°C. This indicates that, in the case of WO<sub>3</sub>-added NiO-SE, most of the WO<sub>3</sub> seemed to be evaporated from the NiO matrix during the sintering process because of its ease evaporation at



Figure 3. Variation of  $\Delta$ emf to 50 ppm NO<sub>2</sub> at 800°C for the sensor using NiO-SE added with different WO<sub>3</sub> contents. (Base gas 5 vol % O<sub>2</sub> + 5 vol % H<sub>2</sub>O + N<sub>2</sub> balance.)



Figure 4. SEM images of the surface of (a) NiO, (b) 10 wt % WO<sub>3</sub>-added NiO, (c) 50 wt % WO<sub>3</sub>-added NiO, and (d) 10 wt % Nb<sub>2</sub>O<sub>5</sub>-added NiO SEs.

such a high temperature. It is noted that the evaporation temperature of WO<sub>3</sub> in air is reported to be 1400°C and the minimum detection limit of minor constituent in XRD measurement is usually about 5%.

Because WO<sub>3</sub> seemed to be evaporated from the NiO matrix, there should be a weight change in the sample after sintering at 1400°C. Thus, to verify this, the weight of 10 wt % WO<sub>3</sub>-added NiO was measured before and after sintering. As a result, it was confirmed that there was a clear change in the weight of the sample and the weight loss observed after sintering was exactly corresponding to the weight of WO<sub>3</sub> added.

Figure 4 shows the SEM images of (a) NiO, (b) 10 wt % WO<sub>3</sub>-added NiO, and (c) 50 wt % WO<sub>3</sub>-added NiO samples on an YSZ plate sintered at 1400°C for 2 h in air, along with (d) a 10 wt % Nb<sub>2</sub>O<sub>5</sub>-added NiO sample for comparison. It is seen that the grain sizes of NiO range from 1 to 2  $\mu m$  in pure NiO and 10 wt % WO<sub>3</sub>-added NiO. In 10 wt % WO<sub>3</sub>-added NiO matrix, there appears to be increased porosity (larger pores) throughout the matrix, compared with the pure NiO matrix. The increased porosity may lead to lower gas-phase NO<sub>2</sub> conversion to NO and then to increased NO<sub>2</sub> sensitivity. The formation of such pores could be due to the evaporation of WO3 from the NiO matrix during sintering at a high temperature of 1400 °C. The surface of 50 wt % WO\_3-added NiO consists of bald surfaces with less large NiO grains (size:  $>2 \ \mu$ m) on YSZ, as seen in Fig. 4c. This implies that the 50 wt % WO<sub>3</sub> addition to NiO results in the formation of very porous NiO matrix. In fact, the underlying YSZ can be clearly seen in this case. Such large pores would decrease the number of reaction sites at the interface between 50 wt % WO3-added NiO-SE and YSZ. Consequently, the sensor using 50 wt % WO3-added NiO-SE is expected to show diminished NO<sub>2</sub> sensitivity. The addition of 10 wt %Nb<sub>2</sub>O<sub>5</sub> to NiO leads to a very dense matrix, as seen in Fig. 4d. Such a dense matrix would retard the gas diffusion through itself, and hence 10 wt % Nb<sub>2</sub>O<sub>5</sub>-added NiO-SE would show much lower NO<sub>2</sub> sensitivity as given in Fig. 2. Thus, it can be said that WO<sub>3</sub> can act as a kind of pore-creating agent and Nb<sub>2</sub>O<sub>5</sub> is working as an effective sintering agent. There is a possibility for the formation of solid solution between Nb<sub>2</sub>O<sub>5</sub> and NiO at such a high temperature of sintering. However, the details in this regard are not considered in this paper.

The evaporation of WO<sub>3</sub> from the NiO matrix at 1400°C was also verified on the basis of the results obtained from EDX analysis. Figure 5 shows the SEM image of the cross-sectional view and EDX spectrum of 10 wt % WO<sub>3</sub>-added NiO and 50 wt % WO<sub>3</sub>-added

NiO after sintering at 1400°C. There are no peaks corresponding to W element in the NiO matrix in both cases. This implies that there is no indication of the presence of WO<sub>3</sub> in NiO matrix. This confirms that almost all WO3 is evaporated from the NiO matrix, as speculated above. Such a complete evaporation of WO<sub>3</sub> lead to many pores and bald surfaces in the case of 50 wt % WO<sub>3</sub>-added NiO-SE. EDX analysis was also performed on 10 wt % WO3-added NiO and 50 wt % WO<sub>3</sub>-added NiO samples before sintering (the results were not shown here). In both cases, the peaks corresponding to W element were evidently present. The composition obtained from the observed W peak intensity matched well with the nominal WO<sub>3</sub> content before sintering. Based on the results obtained from XRD, weight change measurement, SEM, and EDX analysis, it can be concluded that the addition of WO3 to NiO can create many pores on the NiO matrix and the amount of pores formed (after sintering) seems to depend strongly on the initial content of WO<sub>3</sub> added before sintering. Such a difference in porosity of NiO matrix leads to the difference in NO<sub>2</sub> sensitivity.

Sensing performances of the NO<sub>2</sub> sensor using WO<sub>3</sub>-added NiO-SE.— The response transients to various concentrations of NO2 were examined at 800°C for the planar sensor attached with pure NiO-SE, 10 wt % WO<sub>3</sub>-added NiO-SE, and 50 wt % WO<sub>3</sub>-added NiO-SE. The obtained results are shown in Fig. 6. It is seen that all sensors respond well to NO2 and the steady-state emf values are attained at each NO2 concentration rather quickly. The sensor attached with 10 wt % WO<sub>3</sub>-NiO-SE shows the highest sensitivity among the sensors tested in the examined range of 10-100 ppm. This indicates that the NO<sub>2</sub> sensitivity is significantly improved by the addition of 10 wt % WO3 to NiO. However, the response and recovery rates were found to be almost equal in all cases. The typical 70% response and recovery times for the sensor using 10 wt % WO<sub>3</sub>-NiO and NiO-SEs are about 28 and 29 s, respectively. Figure 7 depicts the dependence of  $\Delta$ emf on NO<sub>2</sub> concentration at 800°C for the sensors attached with NiO-SE, 10 wt % WO3-added NiO-SE, and 50 wt % WO<sub>3</sub>-added NiO-SE. In all cases, almost a linear relationship between the  $\Delta$ emf and the logarithm of NO<sub>2</sub> concentration is observed. The  $\Delta$ emf values for 10 wt % WO<sub>3</sub>-NiO-SE are always much higher than those for NiO-SE and 50 wt % WO3-added NiO-SE under the present condition. For instance, the  $\Delta$ emf value to 50 ppm NO<sub>2</sub> at 800°C for the sensor using 10 wt % WO3-NiO-SE and NiO-SE is about 70 and 42 mV, respectively. The  $\Delta$ emf to NO<sub>2</sub> in the range of 1–20 ppm was also measured at 800°C and the obtained results are shown in Fig. 8. It is surprising that the sensor using 10 wt % WO3-added NiO-SE can detect even 1 ppm NO<sub>2</sub> with acceptable sensitivity ( $\Delta$ emf:8 mV). In this case,  $\Delta$ emf varies linearly with NO<sub>2</sub> concentration in the range of 1-20 ppm. The reason for the occurrence of such a linear dependance of NO<sub>2</sub> sensitivity in the low concentration range is under investigation.

It is well known that the amounts of water vapor and  $CO_2$  in real exhausts from cars vary from 5 to 13 and 5 to 20 vol %, respectively. Thus, it is important to examine the effects of water vapor and  $CO_2$  on the NO<sub>2</sub> sensitivity over the wide concentration range. Figure 9 shows the dependence of emf to 50 ppm NO<sub>2</sub> at 800°C on the concentrations of water vapor and  $CO_2$  in the sample gas for the sensor using 10 wt % WO<sub>3</sub>-added NiO-SE. It is seen that the emf value of the sensor to 50 ppm NO<sub>2</sub> is hardly affected by the concentrations of water vapor and  $CO_2$  in such a wide range. This suggests that the present sensor can work well under actual exhaust conditions.

We have previously reported that the addition of a small amount of Rh to NiO also gives improvement in NO<sub>2</sub> sensitivity.<sup>40</sup> The improvement degree of NO<sub>2</sub> sensitivity of the present sensor using 10 wt % WO<sub>3</sub>-added NiO-SE is almost the same as that of the sensor using Rh-added NiO-SE. Thus, the merit of the present sensor is that the price of WO<sub>3</sub> is much cheaper than that of Rh.



**Figure 5.** SEM images of cross-sectional view and EDX spectrum of 1400°C-sintered (a) 10 wt % WO<sub>3</sub>-added NiO and (b) 50 wt % WO<sub>3</sub>-added NiO SEs.

*Explanation of WO*<sub>3</sub>*-addition effect.*— In order to rationalize the effect of WO<sub>3</sub> addition on NO<sub>2</sub> sensitivity of the sensor, the current-voltage (polarization) curves of the sensor using each of the NiO-based SEs were measured at 800°C in the base gas (5 vol % O<sub>2</sub> + N<sub>2</sub> balance) and in the sample gas containing 50 ppm NO<sub>2</sub> (+ the base gas). The obtained results are shown in Fig. 10, in which the current axis is expressed in an absolute scale. It is seen that the polarization curve for the anodic reaction of O<sub>2</sub> is almost same in each sensor irrespective of the initial content of WO<sub>3</sub>. This implies



**Figure 6.** (Color online) Response transients to NO<sub>2</sub> for the sensors attached with pure NiO-SE, 10 wt % WO<sub>3</sub>-added NiO, and 50 wt % WO<sub>3</sub>-added NiO-SE at 800°C. (Base gas 5 vol % O<sub>2</sub> + 5 vol % H<sub>2</sub>O + N<sub>2</sub> balance.)



that the catalytic activity to the anodic reaction of O<sub>2</sub> is not changed

even after 50 wt % addition of WO3. Such an unaltered rate of

oxygen reaction may be due to the presence of the minimally re-

**Figure 7.** (Color online) Variation of  $\Delta$ emf to different NO<sub>2</sub> concentrations in the range of 10-100 ppm at 800°C for the sensors attached with NiO-SE, 10 wt % WO<sub>3</sub>-added NiO, and 50 wt % WO<sub>3</sub>-added NiO-SE. (Base gas 5 vol % O<sub>2</sub> + 5 vol % H<sub>2</sub>O + N<sub>2</sub> balance.)



Figure 8. (Color online) Variation of  $\Delta$ emf to different NO<sub>2</sub> concentrations in the range of 1-20 ppm at 800°C for the sensors attached with NiO-SE and 10 wt % WO<sub>3</sub>-added NiO-SE. (Base gas 5 vol % O<sub>2</sub> + 5 vol % H<sub>2</sub>O + N<sub>2</sub> balance.)

quired reaction sites in all cases irrespective of different morphology. Thus, the sensor exhibited almost equal response/recovery rates. The polarization curve for the cathodic reaction of NO<sub>2</sub> shifts upward when the SE of the sensor is changed from pure NiO to 10 wt % WO<sub>3</sub>-added NiO, while the polarization curve shifts downward when the SE is changed to 50 wt % WO3-added NiO. This suggests that the catalytic activity to the cathodic reaction of NO<sub>2</sub> is strongly dependent on the initial content of WO<sub>3</sub> added to NiO and is highest when the WO3 content is 10 wt %. We have previously reported that, even though the rate of anodic reaction of oxygen is unaltered, the sensitivity can be changed due to the change in the rate of cathodic reaction of NO2 for a mixed-potential-type sensor.40 As a result, the intersection (estimated emf value) between the anodic polarization curve and the cathodic polarization curve increases largely from 41 to 69 mV when the SE of the sensors is changed from pure NiO to 10 wt % WO3-added NiO and decreases to 19 mV when the SE is changed to 50 wt % WO3-added NiO. Each intersection value is in good agreement with the actual  $\Delta$ emf value of each NO<sub>2</sub> sensor. Such a close coincidence of the estimated and



Figure 9. (Color online) Dependence of  $\Delta$ emf to 50 ppm NO<sub>2</sub> on different concentrations of H<sub>2</sub>O and CO<sub>2</sub> for the sensor using 10 wt % WO<sub>3</sub>-added NiO-SE at 800°C.



Figure 10. (Color online) Modified polarization curves obtained in 5 vol %  $O_2$  and in 50 ppm NO<sub>2</sub> at 800°C for the planar sensors attached with pure NiO-SE, 10 wt % WO<sub>3</sub>-added NiO-SE, and 50 wt % WO<sub>3</sub>-added NiO-SE.

observed values in each case confirms that the sensing mechanism of the present sensor is also based on the mixed-potential model, as reported before. <sup>4-7,10,19-21,38-41</sup>

The increase or decrease in the catalytic activity to the cathodic reaction of NO<sub>2</sub> caused by the addition of WO<sub>3</sub> to NiO-SE was also substantiated by the results of complex-impedance measurements. Figure 11 gives Nyquist plots measured in the base gas (5 vol %  $O_2 + N_2$  balance) and in the sample gas containing 400 ppm NO<sub>2</sub> (+ the base gas) at 800°C under wet conditions for the sensor attached with pure NiO-SE, 10 wt % WO<sub>3</sub>-added NiO-SE, and 50 wt % WO<sub>3</sub>-added NiO-SE. It is seen that, in all cases, the complex-impedance plots are in the form of a compressed semicircle in the examined frequency range. The Nyquist plots in the base gas obtained for the sensors attached with both 10 wt % WO<sub>3</sub>-added NiO-SE and 50 wt % WO<sub>3</sub>-added NiO-SE are almost



Figure 11. (Color online) Complex impedance plots obtained in (a) 5 vol %  $O_2$  and (b) 100 ppm NO<sub>2</sub> at 800°C for the planar sensors attached with pure NiO-SE, 10 wt % WO<sub>3</sub>-added NiO, and 50 wt % WO<sub>3</sub>-added NiO-SE.



Figure 12. (Color online) Temperature dependence of  $NO_2$  conversion to NO for the gas-phase reaction on pure NiO, 10 wt % WO<sub>3</sub>-added NiO, and 50 wt % WO<sub>3</sub>-added NiO samples sintered at 1400°C.

the same as that of the sensor using pure NiO-SE. This suggests that the rate of the anodic reaction of O<sub>2</sub> occurring at the interface of WO3-added NiO-SE/YSZ is the same as that of pure NiO-SE/YSZ. The Nyquist plot in the sample gas shrinks when the SE changes from pure NiO to 10 wt % WO3-added NiO and expands when the SE changes to 50 wt % WO<sub>3</sub>-added NiO. This suggests that the rate of cathodic reaction of NO2 at the interface of 10 wt % WO3-added NiO-SE/YSZ is higher than that at the interface of pure NiO-SE/ YSZ. Thus, such an increased rate of cathodic reaction of NO<sub>2</sub> at the interface between 10 wt % WO\_3-added NiO-SE and YSZ is one of the contributing factors for enhancing the NO<sub>2</sub> sensitivity of the present sensor. At the interface of 50 wt % WO<sub>3</sub>-added NiO-SE/ YSZ, the rate of cathodic reaction of NO<sub>2</sub> seems to be much lower than that for pure NiO. Such a lower reaction rate might be because the number of reaction sites at the interface (50 wt % WO<sub>3</sub>-added NiO-SE/YSZ) is significantly less than those at the interface of pure NiO-SE/YSZ. It is evident from the SEM images (Fig. 4 and 5) that the surface of 50 wt % WO3-added NiO-SE is composed of many bald surfaces throughout the SE matrix. At these bald surfaces, the electrochemical reaction of NO2 would hardly proceed. In this case, there is also a possibility that the Pt-current collectors may contact with YSZ to some extent and influence the emf response of the sensor. Thus, as a result, the sensor using 50 wt % WO<sub>3</sub>-added NiO-SE exhibited the diminished NO2 sensitivity compared with the sensors using both pure NiO-SE and 10 wt % WO<sub>3</sub>-added NiO-SE.

We have already reported that the catalytic activity to the gas-phase NO<sub>2</sub> conversion to NO also plays an important role in deciding the NO<sub>2</sub> sensitivity of the mixed-potential-type sensors.  $^{31,32,36-41}$  Thus, it is essential to examine the gas-phase NO<sub>2</sub> conversion to NO on pure NiO, 10 wt % WO3-added NiO, and 50 wt % WO<sub>3</sub>-added NiO samples sintered at 1400°C. Figure 12 shows the temperature dependence of NO<sub>2</sub> conversion to NO for all the samples. It is quite interesting that the 10 wt % WO<sub>3</sub>-added NiO exhibits lower NO2 conversion than pure NiO at each temperature examined. Such a lower gas-phase catalytic activity of SE layer also plays an important role for the increment of NO<sub>2</sub> sensitivity by the 10 wt % WO<sub>3</sub> addition, because the undecomposed NO<sub>2</sub> can reach the interface of SE/YSZ in this case. The lower gas-phase catalysis is mainly due to increased porous NiO matrix (less fewer reaction sites) due to evaporation of WO<sub>3</sub>, as seen from SEM images (Fig. 4). The gas-phase catalytic activity of 50 wt % WO<sub>3</sub>-added NiO was much lower than those of pure NiO and 10 wt % WO3-added NiO, probably due to bigger pores and more bald surface. However, the contribution of such a lower catalytic activity to the lower NO<sub>2</sub> sensitivity is not cleared yet in this case.

It should be noted here that the initial content of WO<sub>3</sub> was varied from 5 to 50 wt %, and only 10 wt % WO<sub>3</sub> addition gives a large improvement in NO<sub>2</sub> sensitivity. If a trace amount of WO<sub>3</sub> would present on the NiO surface and affect the NO<sub>2</sub> sensitivity drastically, the same influence (improvement) should be observed in all the WO<sub>3</sub>-added samples. But it was not so, as seen from Fig. 3. For example, 20 and 50 wt % WO<sub>3</sub>-added samples gave even a diminished sensitivity. Thus, only in the case of 10 wt % WO<sub>3</sub> addition, an appropriate morphology of NiO matrix can be obtained, which leads to the large improvement in sensitivity.

Based on the above-mentioned results obtained from the measurements of the polarization curves, the complex-impedance plots, and the gas-phase NO<sub>2</sub> decomposition catalysis, the improved NO<sub>2</sub> sensitivity by the addition of 10 wt % WO<sub>3</sub> to NiO can be attributable to increased porosity, which in turn leads to the improved kinetic effect on the cathodic reaction of NO<sub>2</sub> and the lower gas-phase catalytic activity.

# Conclusions

The mixed-potential-type planar sensors based on a YSZ plate and NiO-based SEs were fabricated and examined for detection of NO<sub>2</sub> at high temperatures. Among the several examined metal-oxide additives (WO<sub>3</sub>, ZnO, Ta<sub>2</sub>O<sub>5</sub>, SnO<sub>2</sub>, In<sub>2</sub>O<sub>3</sub>, Cr<sub>2</sub>O<sub>3</sub>, Fe<sub>2</sub>O<sub>3</sub>, CuO, Nb<sub>2</sub>O<sub>5</sub>, and CeO<sub>2</sub>) to NiO-SE, WO<sub>3</sub> was found to give rather large improvement in NO2 sensitivity. The maximum enhancement was observed when the initial WO3 content in NiO before sintering at 1400°C was 10 wt %. The sensitivity ( $\Delta emf$ ) to 50 ppm NO<sub>2</sub> was as high as about 70 mV for the sensor using the 10 wt % WO<sub>3</sub>-added NiO-SE at 800°C in the presence of 5 vol % H<sub>2</sub>O and 5 vol % O<sub>2</sub>. The coexistence of H<sub>2</sub>O and CO<sub>2</sub> gave no influence on the NO<sub>2</sub> sensitivity. Based on the results of measurements for the polarization curves, the complex-impedance plots, and the gas-phase catalysis, the improvement effect in NO<sub>2</sub> sensitivity by the addition of 10 wt % WO3 to NiO was speculated to be attributable to the modification of morphology, which lead to the improved kinetic effect on the cathodic reaction of NO<sub>2</sub> and the lower gas-phase NO<sub>2</sub> conversion rate.

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#### References

- 1. F. Menil, V. Coillard, and C. Lucat, Sens. Actuators B, 67, 1 (2000).
- 2. N. Docquier and S. Candel, Prog. Energy Combust. Sci., 28, 107 (2002).
- 3. J. W. Fergus, Sens. Actuators B, 121, 652 (2006).
- N. Miura, G. Lu, N. Yamazoe, H. Kurosawa, and M. Hasei, J. Electrochem. Soc., 143, L33 (1996).
- N. Miura, H. Kurosawa, M. Hasei, G. Lu, and N. Yamazoe, *Solid State Ionics*, 86–88, 1069 (1996).
- 6. N. Miura, G. Lu, and N. Yamazoe, Sens. Actuators B, 52, 169 (1998).
- 7. G. Lu, N. Miura, and N. Yamazoe, Ionics, 4, 16 (1998).
- T. Hibino, Y. Kuwahara, T. Otsuka, N. Ishida, and T. Oshima, *Solid State Ionics*, 107, 213 (1998).
- T. Hibino, Y. Kuwahara, T. Otsuka, N. Ishida, and T. Oshima, *Solid State Ionics*, 107, 217 (1998).
- 10. N. Miura, G. Lu, and N. Yamazoe, Solid State Ionics, 136-137, 533 (2000).
- W. Geopel, G. Reinhardt, and M. Rosch, *Solid State Ionics*, **136–137**, 19 (2000).
  E. D. Bartolomeo, E. Traversa, M. Baroncini, V. Kotzeva, and R. V. Kumar, *J. Eur. Ceram. Soc.*, **20**, 2691 (2000).
- T. Ono, M. Hasei, A. Kunimoto, T. Yamamoto, and A. Noda, JSAE Rev., 22, 49 (2001).
- S. Zhuiykov, M. Muta, T. Nakano, M. Hasei, N. Yamazoe, and N. Miura, *Electro-chem. Solid-State Lett.*, 4, H19 (2001).
- J. W. Yoon, M. L. Grilli, E. D. Bartolomeo, R. Polini, and E. Traversa, Sens. Actuators B, 76, 483 (2002).
- N. F. Szabo, H. Du, S. A. Akbar, A. Soliman, and P. K. Dutta, *Sens. Actuators B*, 82, 142 (2002).

- 17. N. F. Szabo, H. B. Du, S. A. Akbar, A. Soliman, and P. K. Dutta, Sens. Actuators B, 82, 142 (2002)
- 18. E. L. Brosha, R. Mukundan, D. R. Brown, and F. H. Garzon, Sens. Actuators B, 87, 47 (2002) 19. N. Miura, S. Zhuiykov, T. Ono, M. Hasei, and N. Yamazoe, Sens. Actuators B, 83,
- 222 (2002). 20. S. Zhuiykov, T. Ono, N. Yamazoe, and N. Miura, Solid State Ionics, 152-153, 810
- (2002). 21. T. Ono, M. Hasei, A. Kunimoto, and N. Miura, Electrochemistry (Tokyo, Jpn.), 71,
- 405 (2003). 22. R. Mukundan, E. L. Brosha, and F. H. Garson, J. Electrochem. Soc., 150, H279
- (2003).
- 23. D. C. Skelton, R. G. Tobin, D. K. Lambert, C. L. Di Maggio, and G. B. Fisher, Sens. Actuators B, 96, 46 (2003).
   L. P. Martin, A. Q. Pham, and R. S. Glass, Sens. Actuators B, 96, 53 (2003).
   A. Dutta, N. Kaabbuathong, M. L. Grilli, E. Di Bartolomeo, and E. Traversa, J.
- Electrochem. Soc., 150, H33 (2003).
- 26. S. Kading, S. Jakobs, and U. Guth, Ionics, 9, 151 (2003).
- W.-F. Zhang, P. Schmidt-Zhang, and U. Guth, *Solid State Ionics*, 169, 121 (2004).
  U. Guth and J. Zosel, *Ionics*, 10, 366 (2004).
- 29. N. F. Szabo and P. K. Dutta, Solid State Ionics, 171, 183 (2004).

- 30. D. Y. Wang and E. Detwiler, Sens. Actuators B, 99, 571 (2004).
- 31. T. Ono, M. Hasei, A. Kunimoto, and N. Miura, Solid State Ionics, 175, 503 (2004).
- 32. N. Miura, K. Akisada, J. Wang, S. Zhuiykov, and T. Ono, Ionics, 10, 1 (2004). 33. R. Ramamoorthy, S. A. Akbar, and P. K. Dutta, Sens. Actuators B, 113, 162
- (2006).
- 34. E. L. Brosha, R. Mukundan, R. Lujan, and F. H. Garzon, Sens. Actuators B, 119, 398 (2006).
- 35. S. W. Song, L. P. Martin, R. S. Glass, E. P. Murray, J. H. Visser, R. E. Soltis, R. F. Novak, and D. J. Kubinski, J. Electrochem. Soc., 153, H171 (2006).
- 36. P. Elumalai, J. Wang, S. Zhuiykov, D. Terada, M. Hasei, and N. Miura, J. Electrochem. Soc., 152, H95 (2005).
- 37. N. Miura, J. Wang, M. Nakatou, P. Elumalai, and M. Hasei, Electrochem. Solid-State Lett., 8, H9 (2005).
- 38. P. Elumalai and N. Miura, Solid State Ionics, 176, 2517 (2005).
- 39. N. Miura, J. Wang, M. Nakatou, P. Elumalai, S. Zhuiykov, and M. Hasei, Sens. Actuators B, 114, 903 (2006).
- 40. J. Wang, P. Elumalai, D. Terada, M. Hasei, and N. Miura, Solid State Ionics, 177, 2305 (2006).
- 41. P. Elumalai, V. V. Plashnitsa, T. Ueda, M. Hasei, and N. Miura, Ionics, 12, 331 (2006).