# Potentiometric YSZ-based sensor using NiO sensing electrode aiming at detection of volatile organic compounds (VOCs) in air environment

Sato, Tomoaki
Interdisciplinary Graduate School of Engineering Sciences, Kyushu University

Plashnitsa, Vladimir V.
Research and Education Center of Carbon Resources, Kyushu University

Utiyama, Masahiro
National Institute for Environmental Studies

Miura, Norio
Art, Science and Technology Center for Cooperative Research, Kyushu University



出版情報：Electrochemistry Communications. 12 (4), pp.524-526, 2010-04-28. Elsevier
バージョン：

# Potentiometric YSZ-based sensor using NiO sensing electrode aiming at detection of volatile organic compounds (VOCs) in air environment

Tomoaki Sato [a], Vladimir V. Plashnitsa [b], Masahiro Utiyama [c] and Norio Miura [d,*]

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

[b] *Research and Education Center of Carbon Resources, Kyushu University, Kasuga-shi, Fukuoka 816-8580, Japan*

[c] *National Institute for Environmental Studies, Tsukuba-shi, Ibaraki 305-0053, Japan*

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

**Abstract**

The potentiometric yttria-stabilized zirconia (YSZ)-based sensors using each of various oxide sensing-electrodes (SEs) were fabricated and examined for detection of toluene ($C_7H_8$) in several tens ppb level. As a result, the sensor using NiO-SE was found to exhibit relatively high sensitivity and selectivity to toluene at 450$^{o}$C under the wet condition (1.35 vol.% $H_2O$). The present sensor could respond well to toluene in the concentration range of 10-150 ppb. The response transients to 50 ppb toluene were stable and repeatable, accompanying with the response/recovery time acceptable for an actual environmental monitoring. In addition, the toluene sensitivity was hardly affected by the interference of the other co-existing gases examined.

*Keywords*: gas sensor, environmental monitoring, VOCs, YSZ, toluene, mixed potential

*Corresponding author. Tel.: +81-92-583-8852; fax: +81-92-583-8976.

*E-mail address*: miurano@astec.kyushu-u.ac.jp (N. Miura)

## 1. Introduction

The acceptable levels of volatile organic compounds (VOCs), such as toluene, *m*-xylene, formaldehyde and so on, in an atmospheric air are generally regulated by law because of their toxicity against human. In Japan, for example, Ministry of Health, Labour and Welfare has been setting the maximum permissible indoor concentrations of toluene and formaldehyde to 70 and 80 ppb, respectively. To detect such a very low concentration of VOC, highly precise measuring methods are necessary. Currently, the concentrations of VOCs in air are measured by means of expensive, rather bulky and time-consuming analytical instruments, such as a gas-chromatograph mass-spectroscope (GC-MS) and a high-performance liquid chromatograph (HPLC). However, these instruments are usually employed in stationary laboratories and are not suitable for installation in individual houses and apartments. Thus, the development of a low-cost, compact and reliable VOC sensor is nowadays of great concern for a continuous air-quality monitoring.

Among the various VOC sensors reported so far [1-6], solid-state electrochemical gas sensors based on yttria-stabilized zirconia (YSZ) seem to be attractive candidates for sensitive detection of VOCs, For example, Mori et al. have recently reported that the YSZ-based sensor using the modified-Pt sensing electrode (SE) can detect various VOCs in sub-ppm level [1, 2]. We have also reported that the potentiometric [7] or impedancemetric [8] YSZ-based sensor attached with oxide-SE is capable of rather sensitive and selective detection of propene

($C_3H_6$) in several tens ppb level. Especially, the potentiometric (mixed-potential-type) YSZ-based gas sensor has an advantage that its potential response to a base gas (air) is close to zero volt and rather stable. In addition, the sensitivity to even 50 ppb propene was reported to be as relatively high as about 37 mV, if the oxide-SE material was selected properly [7]. Thus, in the present study, various oxides were examined as SE for the potentiometric YSZ-based sensor so as to detect very low concentrations of toluene as one of representative VOCs. As a result, among oxide-SEs tested, NiO-SE was found to give relatively high sensitivity and selectivity even to several tens ppb toluene, as will be described below.

## 2. Experimental

The YSZ-based sensor was assembled in tubular configuration, as reported elsewhere [7]. Each of various commercial oxides ($SnO_2$, NiO, $Fe_2O_3$, ZnO and $Cr_2O_3$, Kojundo Chemical Lab. & Kishida Chemical, Japan) was thoroughly mixed with α-terpineol and then applied on the outer surface of a YSZ tube (8 mol.% $Y_2O_3$ doped, inside diameter: 5 mm, outside diameter: 8 mm, length: 300 mm, Nikkato, Japan) to form the oxide-SE layer. A commercial Pt-paste (TR-7601, Tanaka Kikinzoku Kogyo, Japan) was applied on the top of inner surface of the YSZ tube to form a reference electrode (RE). Then, the YSZ tube attached with both oxide-SE and Pt-RE was dried at 130°C and sintered at 1000°C for 2 h in air to obtain a final sensing device.

The gas sensing characteristics of the fabricated sensors were evaluated in the temperature range of 400 - 500°C. The oxide-SE was exposed to the base gas (synthetic air + 1.35 vol.% $H_2O$ + 400 ppm $CO_2$) or the sample gases obtained by diluting each parent standard gas with the base gas. The concentration of toluene was varied in the range of 10 – 150 ppb, whereas each concentration of other gases ($H_2$, CO and $NO_2$) was equal to its usually existing concentration in an atmospheric air. The examined concentration of propene was about five times higher than that in an actual air. Pt-RE was always exposed to an atmospheric air. The total flow-rates of the base gas and the sample gas were fixed at 100 $cm^3$/min. Electromotive force (*emf*) between oxide-SE and Pt-RE was measured as a sensor signal by using a digital electrometer (R8240, Advantest, Japan). The polarization (I-V) curves of the sensors were measured in air or in 50 ppb toluene (+air) at 450$^oC$ under potentiodynamic mode at a scan rate of 1 mV/min. The SE potential was controlled by means of a potentiostat (HZ-3000, Hokuto Denko, Japan), by referring to the Pt-RE.

## 3. Results and discussion

Since it is well-known that the sensitivity to a target gas for the mixed-potential-type YSZ-based sensor depends to a large extent on a kind of SE material, each of different oxide-SEs was initially evaluated for detection of toluene. Figure 1 compares the cross sensitivities ($\Delta emf = emf_{sample\ gas} - emf_{base\ air}$) to various gases for the sensors using each of

oxide-SEs operated at 450°C under the wet condition (1.35 vol.% $H_2O$). It is seen that the sensors attached with each of $SnO_2$-, NiO- and $Fe_2O_3$-SEs showed relatively high sensitivity to 50 ppb toluene. In addition, among these SEs, only NiO-SE was found to give the rather selective response to toluene. Thus, the detailed sensing characteristics of the sensor attached with NiO-SE were further examined.

Figure 2 compares the cross sensitivities to various gases examined for the sensor using NiO-SE operating at 400, 450 and 500°C under the wet condition. The gas sensitivity tended to decrease with increasing operation temperature. Such a trend has been usually seen in the mixed-potential-type gas sensors [7, 9, 10]. As also shown in Fig. 2, though the toluene sensitivity was highest at 400°C among the operation temperatures examined, the selectivity and the response/recovery rates at 450°C were better than those at 400°C. Thus, the optimum operation temperature for the present sensor seems to be 450°C.

Figure 3 exhibits the response transients to toluene in the concentration range of 10 - 150 ppb for the sensor attached with NiO-SE operated at 450°C under the wet condition. It is clearly seen that the present sensor is able to detect very low concentrations of toluene even down to 10 ppb which is lower than the value (70 ppb) set up by the legislative Japanese guideline. The present sensor gives stable and repeatable responses to all the toluene concentrations examined, accompanying with the 90% response and recovery times (about 3 min each) acceptable for actual environmental monitoring. In this case, the potential value in

the base gas is close to zero volt and rather stable. The repeatability of the response to 50 ppb toluene was quite good. In addition, since a real atmospheric air is composed of a multi-component gaseous mixture, the interference of other co-existing gases to the response to 50 ppb toluene was examined. As a result, the toluene sensitivity was found to be hardly affected by the presence of each single gas tested or even their mixture, as shown in Fig. 4. Such sensing characteristics are important and suitable for an actual environmental monitoring.

To confirm the sensing mechanism of the present sensor, the polarization (I-V) curves were measured both in the base gas and in the sample gas containing 50 ppb toluene at 450$^{o}$C under the wet condition. The current axis of the cathodic polarization-curve was subtracted from that of the anodic polarization-curve at each potential so as to obtain the modified polarization-curve in which the current axis is shown in absolute scale. As shown in Fig. 5, the potential value (-28 mV) estimated from the intersection of the modified cathodic (for the cathodic reaction of oxygen) and anodic (for the anodic reaction of toluene) polarization-curves was confirmed to be relatively close to the sensor's *emf* value (-22 mV) observed experimentally. This suggests that the present sensor is operating under the sensing mechanism based on mixed-potential model [11], being similar to the several cases reported previously [9, 10]. Moreover, the obtained electric current for the both polarization curves was in the range of a few nA, indicating that the detection of low concentrations of gas is not so easy under the

amperometric mode. Thus, it is a noticeable merit of the mixed-potential-type sensor in which the enough *emf* value of several tens mV can be obtained to the sample gas in the several tens ppb level even when the polarization current is as extremely low as nA level.

## 4. Conclusions

The mixed-potential-type YSZ-based sensor attached with NiO-SE was examined for detection of toluene in the level of several tens ppb. The present sensor was found to respond rather sensitively and selectively to toluene in the concentration range of 10 – 150 ppb at 450°C under the wet condition, accompanying with the response/recovery rates acceptable for an environmental monitoring. In addition, the interference of each of other co-existing gases, such as $C_3H_6$, $H_2$, CO and $NO_2$, or their mixtures was hardly observed on the toluene sensitivity. Since the noticeable *emf* responses were obtained even to the toluene concentrations below the official guideline (< 70 ppb) in Japan, the present sensor seems to have a potential for detection of toluene in air environment, although the detailed sensing performances to various VOCs should be further examined.

## Acknowledgement

This work was partially supported by Kyushu University programs on “Novel Carbon Resource Sciences”.

**References**

1. M. Mori, H. Nishimura, and Y. Sadaoka, Sensor Letters, 6 (2008) 987.

2. M. Mori, H. Nishimura, Y. Itagaki, and Y. Sadaoka, Sens. Actuat. B: Chem., 142 (2009) 141.

3. J. Zosel, K. Ahlborn, R. Muller, D. Westphal, V. Vashook, and U. Guth, Solid State Ionics, 169 (2004) 115.

4. T. Itoh, I. Matsubara, W. Shin, N. Izu, and M. Nishibori, Sens. Actuat. B: Chem., 128 (2008) 512.

5. J. Wang, L. Liu, S. Cong, J. Qi, and B. Xu, Sens. Actuat. B: Chem., 134 (2008) 1010.

6. Q. Qi, T. Zhang, L. Liu, and X. Zheng, Sens. Actuat. B: Chem., 137 (2009) 471.

7. N. Miura, S. Mori, R. Wama, P. Elumalai, V.V. Plashnitsa, and M. Utiyama, Electrochem. Solid-state Lett., 11 (2008) 69.

8. R. Wama, M. Utiyama, V.V. Plashnitsa, and N. Miura, Electrochem. Commun., 9 (2007) 2774.

9. V.V. Plashnitsa, T. Ueda, P. Elumalai, and N. Miura, Sens. Actuat. B: Chem., 130 (2008) 231.

10. N. Miura, J. Wang, M. Nakatou, P. Elumalai, S. Zhuiykov, and M. Hasei, Sens. Actuat. B: Chem., 114 (2006) 903.

11. N. Miura, Y. Yan, G. Lu, and N. Yamazoe, Sens, Actuat. B: Chem., 34 (1996) 367.

**Figure captions**

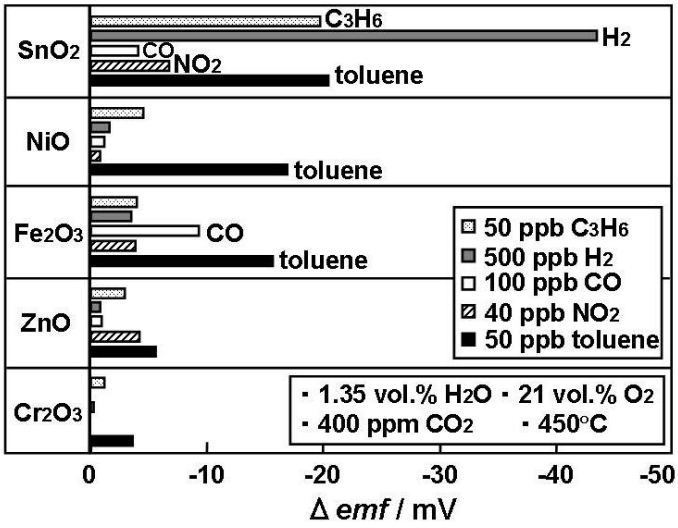
**Fig. 1.** Comparison of the cross sensitivities to various gases for the sensor using each of different oxide-SEs operated at 450°C under the wet condition.

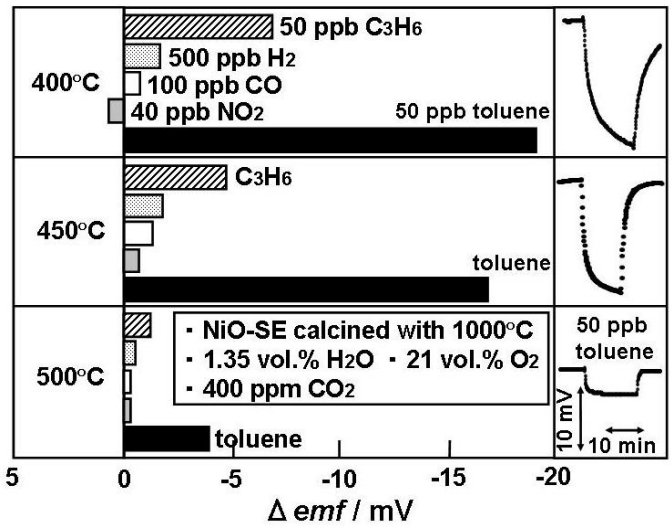
**Fig. 2.** Comparison of the cross sensitivities to various gases for the sensor attached with NiO-SE operated at various temperatures.

**Fig. 3.** Response transients to toluene for the sensor using NiO-SE operated at 450°C under the wet condition.

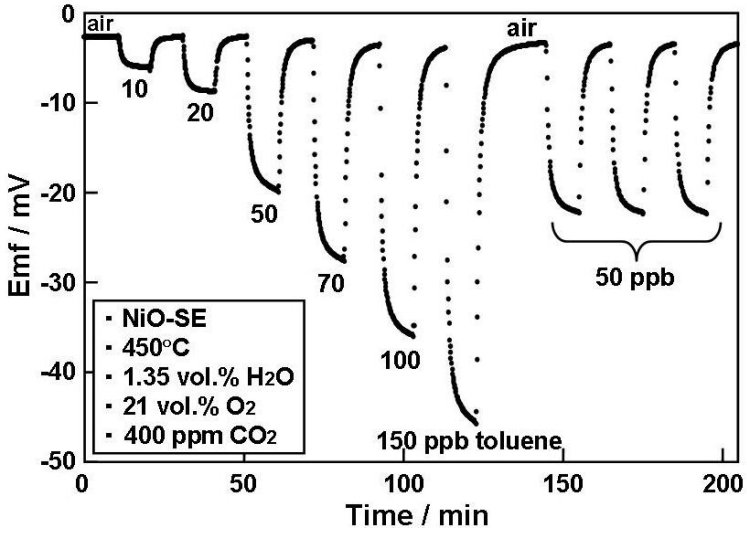
**Fig. 4.** Influence of other co-exiting gases on the response transient to 50 ppb $C_7H_8$ for the sensor using NiO-SE operated at 450$^{o}$C.

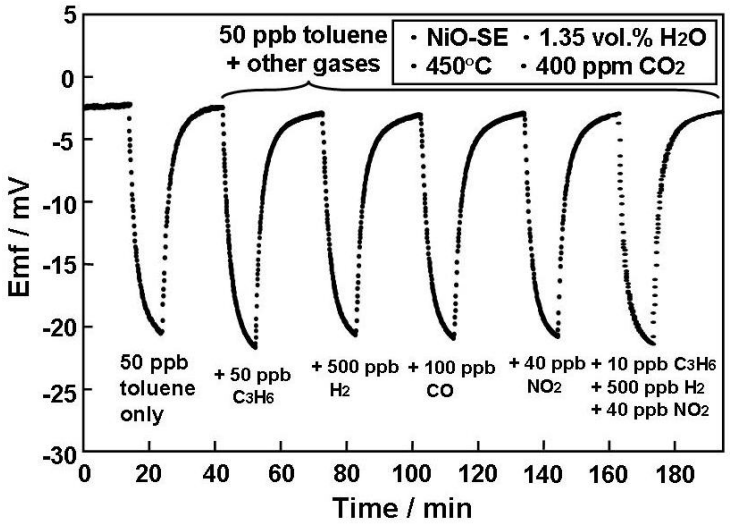
**Fig. 5.** Modified polarization curves measured in the base gas and the sample gas (50 ppb toluene) at 450$^{o}$C for the sensor using NiO-SE.

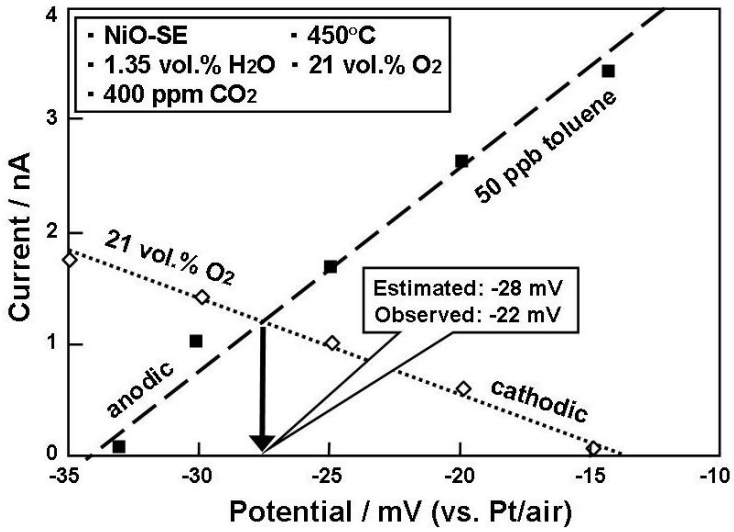

SnO2
C3H6
H2
CO
NO2
toluene
NiO
toluene
Fe2O3
CO
toluene
ZnO
Cr2O3
50 ppb C3H6
500 ppb H2
100 ppb CO
40 ppb NO2
50 ppb toluene
· 1.35 vol.% H2O · 21 vol.% O2
· 400 ppm CO2 · 450°C
0
-10
-20
-30
-40
-50
Δ emf / mV


400°C
50 ppb C3H6
500 ppb H2
100 ppb CO
40 ppb NO2
50 ppb toluene
450°C
C3H6
toluene
500°C
· NiO-SE calcined with 1000°C
· 1.35 vol.% H2O · 21 vol.% O2
· 400 ppm CO2
toluene
50 ppb
toluene
10 mV
10 min
5
0
-5
-10
-15
-20
Δ emf / mV

Sato et al., Fig. 3




50 ppb toluene
+ other gases
· NiO-SE · 1.35 vol.% H2O
· 450°C · 400 ppm CO2
Emf / mV
5
0
-5
-10
-15
-20
-25
-30
0
20
40
60
80
100
120
140
160
180
Time / min
50 ppb toluene only
+ 50 ppb C3H6
+ 500 ppb H2
+ 100 ppb CO
+ 40 ppb NO2
+ 10 ppb C3H6 + 500 ppb H2 + 40 ppb NO2


▪ NiO-SE
▪ 450°C
▪ 1.35 vol.% H2O
▪ 21 vol.% O2
▪ 400 ppm CO2
50 ppb toluene
21 vol.% O2
Estimated: -28 mV
Observed: -22 mV
anodic
cathodic
Current / nA
Potential / mV (vs. Pt/air)
0
1
2
3
4
-35
-30
-25
-20
-15
-10