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# Gas Selectivity Improvement of YSZ-based VOC Sensor via Application of Selective Catalytic Layer over Sensing-electrode

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**Abstract**

A volatile organic compound (VOC) gas sensor which utilizes yttria-stabilized zirconia (YSZ) solid-electrolyte and an NiO sensing-electrode (SE) was fabricated and its sensing properties to VOCs and interfering gases typically found indoors were evaluated. The sensitivity measurements towards $C_7H_8$ (toluene) and common interfering gases ($C_3H_6$, $H_2$, CO, $NO_2$, $C_2H_5OH$ (ethanol)) revealed that toluene detection was strongly affected by high concentrations of ethanol. To overcome this limitation, an $SnO_2$ catalyst layer which selectively oxidizes ethanol was laminated directly onto the NiO layer. The obtained sensor utilizing an $SnO_2$/NiO-SE was capable of sensitive and selective detection of toluene in ppb levels. Sensitivity measurements toward decreasing toluene concentration revealed that the developed sensor was capable of detecting toluene as low as 10 ppb.

**Key words:** Indoor air monitoring, Toluene, YSZ, Mixed potential, Ethanol, VOC

## Introduction

Highly toxic volatile organic compounds (VOCs) such as toluene and formaldehyde cause serious health problems even when inhaled at very low concentrations in ppb levels [1]. For this reason, the development of a high performance VOC sensor, which satisfies the guideline of several tens ppb level concentrations as established by the Japanese government, is strongly required.

Among the several types of VOCs sensors [2-5], solid-state electrochemical gas sensors seem to be an attractive candidate for environmental VOCs monitoring. For example, we reported that the combination of an NiO-SE and a yttria-stabilized zirconia (YSZ) solid-electrolyte enabled the sensitive detection of toluene at ppb levels, with low interferences from $C_3H_6$, $H_2$, CO and $NO_2$ [6]. In addition, the present sensor was also capable of detecting other VOCs such as *m*-xylene, benzene, ethylbenzene, styrene and formaldehyde below the Japanese guideline values [7]. For indoor applications, the evaluation of sensing characteristics against ethanol, which is one of the most interfering gases in present indoor quality measurements, is of great importance for VOC sensing. In this study, the sensing characteristics of YSZ-based sensor utilizing an NiO-SE toward toluene were improved by laminating selective oxidation catalyst on the SE layer.

## Experimental

An oxide (NiO or NiO + 20 wt.% $Al_2O_3$ (NiO: Kishida Chemical, $Al_2O_3$: Sigma)) was thoroughly mixed with α-terpineol, and the resulting pastes as well as a commercial Pt paste (TR-7601, Tanaka Kikinzoku) were separately applied on the outer and inner surface of a YSZ-tube (8 mol.% $Y_2O_3$ doped $ZrO_2$, Nikkato), respectively. Then, the coated YSZ-tube was sintered at 1000°C for 2 h in air to form the oxide-SE and Pt reference-electrode (RE). For the laminated-type SE, a pre-sintered $SnO_2$ (Kojundo Chemical Lab.) layer was applied onto the SE after the sintering process.

The sensing characteristics of the fabricated sensor toward 50 ppb $C_3H_6$, 500 ppb $H_2$, 100 ppb CO, 40 ppb $NO_2$, 50 ppb $C_7H_8$, 80 ppb $C_2H_5OH$ were evaluated at an operational temperature of 450°C under humidified (32% RH, at 25°C) and carbonized (400 ppm $CO_2$) conditions, in order to replicate realistic atmospheric environments. The electromotive force (*emf*) between oxide-SE and Pt-RE was measured in base gas (air) as well as previously described sample gases diluted with base gas, which was recorded as the sensing signal with a digital electrometer (R8240, Advantest). The total gas flow-rate was fixed at 100 $cm^3$ $min^{-1}$.

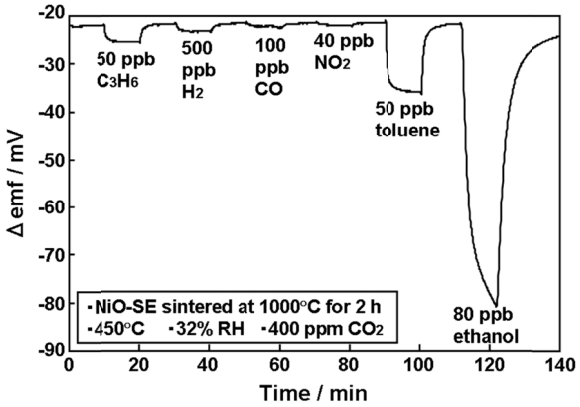


*Fig. 1. Response transients toward different gases for the YSZ-based sensor utilizing NiO-SE at an operational temperature of 450°C under humidified and carbonized conditions (32% RH, 400 ppm $CO_2$).*

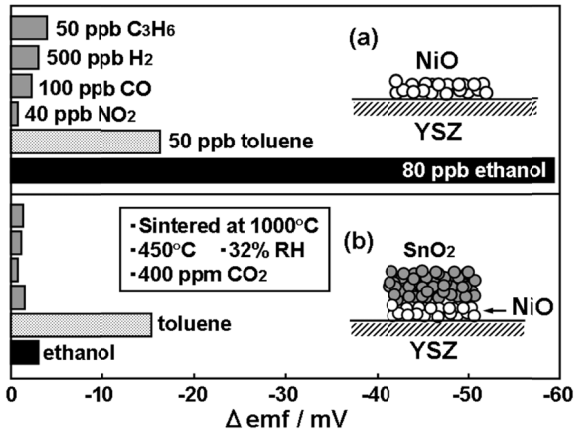


*Fig. 2. Comparison of sensitivity towards different gases for the YSZ-based sensor utilizing NiO-SE and $SnO_2$/NiO(+ 20 wt.% $Al_2O_3$)-SE at an operational temperature of 450°C under humidified and carbonized conditions (32% RH, 400 ppm $CO_2$).*

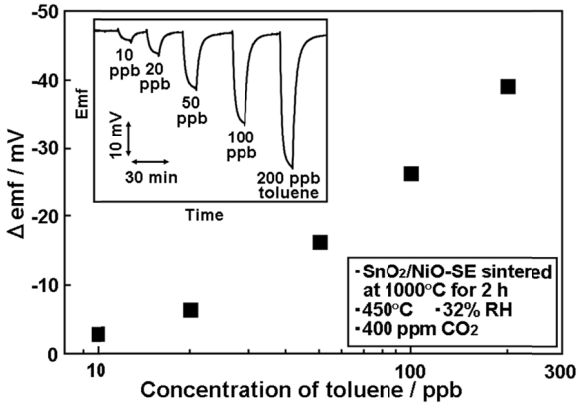


*Fig. 3. Dependence of sensitivity on toluene concentration for the YSZ-based sensor utilizing $SnO_2$/NiO (+ 20 wt.% $Al_2O_3$)-SE at an operational temperature of 450°C under humidified and carbonized conditions (32% RH, 400 ppm $CO_2$).*

The catalytic activities of $Cr_2O_3$, $SnO_2$, ZnO and NiO powders (20 mg each, pre-sintered at 1000°C for 2 h) against gas-phase oxidation of 50 ppb $C_3H_6$, 50 ppb $C_7H_8$ and 80 ppb $C_2H_5OH$ were evaluated by the help of a calibrated YSZ-based sensor utilizing an NiO (+ 20 wt.% nano $Al_2O_3$)-SE operating at 450°C.

**Results and Discussion**

As seen in our previous publications [6,7], a YSZ-based sensor utilizing an NiO-SE exhibited sensitive and selective responses toward ppb levels of VOCs. For indoor VOC sensing applications, the presence of ambient ethanol originating from alcohol consumption and cooking may interfere the sensing performance during measurements, due to irregular fluctuating concentration which sometimes reach ppm levels; an order of magnitude higher than those of the target VOCs [8]. Figure 1 shows the response transients toward 50 ppb toluene and 80 ppb ethanol as well as other interfering gases for the YSZ-based sensor utilizing an NiO-SE at an operational temperature of 450°C under humidified and carbonized conditions (32% RH, 400 ppm $CO_2$). This sensor showed sensitive response toward 50 ppb toluene, with low interferences by 50 ppb $C_3H_6$, 500 ppb $H_2$, 100 ppb CO and 40 ppb $NO_2$. However, the results also indicated that the NiO-SE gave a higher response toward ethanol, rather than the desired toluene; the sensitivity to 80 ppb ethanol and 50 ppb toluene was -59 mV and -16 mV, respectively.

In order to overcome this unfavorable characteristic, the application of an oxidation catalyst over the sensing electrode was investigated. The catalytic activities of $Cr_2O_3$, $SnO_2$, ZnO and NiO powders (20 mg each) toward 50 ppb $C_3H_6$, 50 ppb toluene and 80 ppb ethanol were evaluated at an operational temperature of 450°C. The results indicated that $SnO_2$ demonstrated the most suitable oxidation characteristics for selective toluene detection; the conversion rates for ethanol and $C_3H_6$ were greater than 90%, while that for toluene was only 35%.

To decrease ethanol sensitivity and improve toluene selectively, an $SnO_2$ oxidation layer was formed directly onto the sensing electrode while taking care to avoid contact between the $SnO_2$ and YSZ, which might cause a significant change in sensing performance, as shown in Fig. 2. The mechanical strength of NiO-SE was enhanced by adding 20 wt.% $Al_2O_3$, preventing unwanted mechanical degradation of SE caused in the lamination process. The obtained results in Fig. 2 indicate that the $SnO_2$ lamination affected a notable decrease in overall ethanol sensitivity. Additionally, the

sensitivities to $C_3H_6$, $H_2$, CO and $NO_2$ were also decreased, hence the laminated-type sensor demonstrated enhanced selectivity to toluene.

Figure 3 shows the dependence of sensitivity on toluene concentration in the range of 10 - 200 ppb for the YSZ-based sensor utilizing an $SnO_2$/NiO (+ 20 wt.% $Al_2O_3$)-SE. It is notable that the present sensor was capable of detecting even 10 ppb toluene which was less than one-seventh of the established guildeline value for toluene (70 ppb). The average 90% response and recovery time were in the order of 5 and 8 minutes, respectively; which were acceptable when considering the intended application of the sensor.

## Conclusions

The YSZ-based sensor uitlizing an NiO-SE showed a higher response to the interfering ethanol, rather than that to the desired toluene. By laminating an $SnO_2$ selective oxidation catalyst onto an NiO-SE, the significant decrease in ethanol sensitivity was observed, which enabled sensitive and selective detection of toluene at ppb levels, with a lower detection limit of 10 ppb. The present sensor seems to have a high potential for selective detection of toluene in present indoor environments.

## Acknowledgements

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