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Square-surface nanostructured tungsten oxide for a highly selective NO_2 gas sensing electrode in a YSZ mixed-potential sensor

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Abstract:

In this work, a YSZ mixed-potential sensor was fabricated utilising square-surface nanostructured tungsten oxide (WO_3) as an NO_2 gas sensing-electrode. YSZ (ZrO_2+8% mol Y_2O_3) was used as the high temperature electrolyte layer of the sensor. The square-surface nanostructured WO_3 was synthesised by a hydrothermal treatment and used to fabricate the NO_2 gas sensing-electrode. The sensor with a configuration of Pt/YSZ/(Pt-WO_3) was investigated at operating temperatures ranging from 320 to 600°C to monitor sensing performance to NO_2, NO, CO, CH_4, and CO_2 gases. The Pt/YSZ/(Pt-WO_3) sensor presented a high selectivity to NO_2 gas. This behaviour is suggested to occur due to the specific high catalytic activity of the square-surface nanostructured WO_3 to NO_2 gas. The highest gas-sensing response (ΔU_{emf}) of the sensor was about 40.9 mV for 50 ppm NO_2 at 450°C. The sensor also had a short response time and recovery time (τ_{90}) of approximately 15 and 39 s, respectively, for 50 ppm NO_2 at 450°C.

Keywords: **gas sensing-electrode, mixed-potential gas sensors, square-surface nanostructured tungsten oxide (WO_3), YSZ (Yttria-stabilised zirconia).**

Classification number: **2.1**

Introduction

Highly toxic gases such as NO_2, NO, CO, and SO_2, etc., are typically released from fuel combustion. These gases can cause adverse human health effects and severe air pollution. In fuel combustion, nitrogen oxides (NO_x = NO_2 + NO) are mainly formed from a chemical-reaction between N_2 and O_2 in high temperature conditions. Therefore, in-situ or direct analysis of NO_2 concentration from exhaust gas environments plays an important role in the feedback control of fuel combustion process to not only reduce toxic gas emission into the air but also optimise fuel consumption. Two typical types of gas sensors for analysing NO_x gases in combustion environments include electrochemical gas sensors and optical gas sensors (e.g., a nondispersive infrared gas sensor or NDIR). However, the NDIR gas sensor has been met with major difficulties in selectivity due to the partial overlap of the IR absorption band of H_2O vapour and that of NO_x gases [1]. Moreover, it is also difficult to design the NDIR gas sensor for direct or in-situ operation in the high temperature processes of fuel combustions. In contrast, a high temperature electrochemical sensor like the YSZ-based gas sensor can directly operate in these hazardous environments, thus it has been considered as a promising candidate [1, 2]. Actually, some commercial YSZ-based electrochemical sensor devices have been developed to directly measure NO_2 gas in high temperature processes [2, 3].

High temperature electrochemical sensors using the solid electrolyte YSZ (Yttria-stabilised zirconia) and a metal-oxide sensing electrode to detect various gases (such as NO_2, NO, CO, HC, NH_3) have been explored in hazardous environments with high temperature and corrosive agents. In this case, the YSZ mixed-potential gas sensors with a metal-oxide auxiliary sensing electrode have been of great interest to NO_2 gas detection. Numerous metal-oxides such as NiO, WO_3, ZnO, SnO_2, In_2O_3, CeO_2, Nb_2O_5, $LaFeO_3$, and $MnCr_2O_4$, etc., have been mostly investigated with the aim of finding highly selective gas-sensing electrodes for NO_2 (as reviewed in Refs. [3-5]). Potentiometric sensors based a configuration of WO_3/YSZ/Pt for high NO_2 sensing responses have

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been reported in Refs. [6, 7]. A. Dutta, et al. (2003) [8] also indicated that the WO_3 electrode of a YSZ-based gas sensor had the high sensing performance to NO_2 gas. Most of the WO_3 nanostructures for the sensing electrode of the YSZ-based electrochemical sensor were used with a type of nanoparticles. However, the NO_2 gas sensing electrode-based YSZ sensor remains in need of sensitivity and selectivity improvement to achieve the best performance in application requirements.

Additionally, WO_3 nanostructure-based conductive sensors have been reported to possess the highest sensing performance to NO_2 gas [9-14]. Square-surface WO_3 nanostructures were especially reported to exhibit very high or even ultra-high sensitivity to NO_2 gas. This characteristic was considered to occur due to the contribution of well-oriented crystalline structure of tungsten oxide after square-surface nanostructuring to NO_2 catalytic activity. For example, L. You, et al. (2011) [13] synthesised square-like nanosheets of WO_3 by hydrothermal treatment and reported having a very high selectivity and sensitivity to NO_2 gas with R_g/R_a=92 for 100 ppb at 125°C when compared to various gases including Cl_2, SO_2, H_2S, NH_3, and C_2H_5OH. Similarly, nanosheets assembled from hierarchical flower-like WO_3 nanostructures fabricated by hydrothermal treatment presented a high sensing performance to NO_2 gas when compared with Cl_2, CO, H_2S, NH_3, acetone, and ethanol were proposed by C. Wang, et al. (2015) [14]. A. Boudiba, et al. (2012) [10] also reported two-dimensional WO_3 nanostructures synthesised by hydrothermal treatment for very high sensitivity in ppb of NO_2.

In this work, square-surface nanostructured WO_3 was investigated as the NO_2 sensing electrode in a YSZ (ZrO_2 doped 8% mol Y_2O_3) mixed-potential sensor. The main ideal of this work is utilizing the high NO_2 catalytic activity of the square-surface WO_3 nanostructures for the auxiliary sensing electrode of a YSZ mixed-potential sensor to obtain high NO_2 selectivity performance.

Experimental design

The square-surface nanostructured WO_3 used to fabricate the auxiliary sensing electrode was synthesized by a hydrothermal process as shown in detail in our previous work [15]. Briefly, $(NH_4)_{10}W_{12}O_{41}\cdot 5H_2O$ was dissolved in distilled water and then $(NH_2)_2CO$ solution was added and stirred continuously at 80°C for 1 h to achieve a homogeneous solution. Hydrochloric acid (1.5 M) was gradually dropped into the homogeneous solution until the appearance of a light-yellow precipitate. After that, this mixture was transferred to a Teflon autoclave for hydrothermal treatment at 180°C for 24 h. Finally, the precipitate after hydrothermal treatment was filtered and washed by distilled water and then calcined at 300°C for 2 h to achieve a powder of square-surface nanostructured WO_3. The WO_3 nanostructured powder was mixed with an organic binder (α-terpineol) to achieve a paste for creating the thick sensing electrode film.

Powder YSZ (ZrO_2 doped 8% mol Y_2O_3), as shown in Ref. [16], synthesised by a sol-gel citric route was used to fabricate the electrolyte substrate. Therein, the powder YSZ was pressed at 5 tons/cm^2 and then sintered at 1300°C for 4 h to realise YSZ plate. Then, the YSZ plate was sharpened and laser-cut into square substrate with widths of 3×3 mm and thickness of 0.1 mm.

To fabricate the mixed-potential sensor, two Pt porous electrodes (size of each electrode was width of 1×1 mm and thickness about 3 μm, as similarly reported in our previous work [16]) were created by screen-printing on two sides of the YSZ substrate using the Pt paste (ESL 5545) and then sintered at 1000°C for 1 h to obtain a structure of Pt/YSZ/Pt. One Pt electrode of the Pt/YSZ/Pt structure was coated by the paste of square-surface

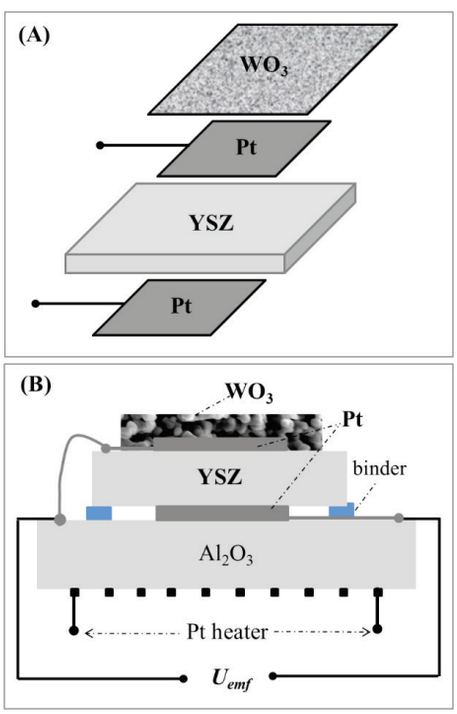

Fig. 1. (A) Illustration of compositional layers and (B) Cross-sectional view structure of the mixed-potential sensor Pt/YSZ/(Pt-WO_3) on Al_2O_3 substrate.

nanostructured WO_3, after that sintered at 700°C for 10 h to get the sensing electrode with WO_3 thick film of approximately 2×2 mm in size and 5 µm in thickness. The structure Pt/YSZ/(Pt-WO_3) was adhered on the front side of an Al_2O_3 substrate integrated with a Pt heater on its rear side to control the operating temperature. Pt wires with a diameter of 25 µm were connected to both Pt and Pt-WO_3 electrodes by sealing with the Pt paste (ESL 5545). The complete mixed-potential sensor consists of the electrode (Pt), electrolyte layer (YSZ), and NO_2 auxiliary sensing electrode (Pt-WO_3). Fig. 1 illustrates this configuration including the compositional layers (Fig. 1A) and structure of the mixed-potential sensor Pt/YSZ/(Pt-WO_3) on Al_2O_3 substrate (Fig. 1B).

Gas sources (including NO_2 and NO from Air Liquide America Specialty Gases - LLC and CO, CH_4, and CO_2 from Singapore Oxygen Air Liquide Pte Ltd.) were used in mixture with dry air (80% N_2+20% O_2) by using the flow-through mixing method [17] for gas-sensing performance. A measuring chamber of 50 ml in volume was used and the total gas flow rate through the chamber was fixed at 300 ml/min. Changes in electromotive force or mixed-potential voltage (U_{emf}) between the electrodes of the sensor Pt/YSZ/(Pt-WO_3) were recognised by a voltmeter (Keithley, model 2700). The gas sensing response (ΔU_{emf}) was calculated with the following equation:

$$\Delta U_{emf} = U^{g}_{emf} - U^{a}_{emf} \quad (1)$$

where U^{g}_{emf} and U^{a}_{emf} are the mixed-potential voltages measured between the two electrodes of the sensor in air containing the desired gases and pure air, respectively.

Scanning electron microscopy (SEM, Hitachi S-4800), X-ray diffractometry (Miniflex Rigaku) with a Cu-Kα radiation source (λ=1.5405 Å), and transmission electron microscopy (TEM, JEOL 2100) were used to examine morphologies and crystalline structures of the sensing electrode of the square-surface nanostructured WO_3.

Results and discussion

Figs. 2A and 2B show TEM images of the as-synthesised WO_3 nanoparticles and WO_3 nanoparticles originating from the sensing electrode after sintering at 700°C, respectively. The results indicate that the synthesised WO_3 nanoparticles from the hydrothermal treatment presented square-surface nanostructures approximately 60×80 nm in size. It can also be seen that the WO_3 nanoparticles almost retain their morphological structure after sintering at 700°C (Fig. 2B). This characteristic is further defined by the SEM image of the surface of the WO_3 sensing electrode as shown in Fig. 2C. The thickness of the WO_3 sensing electrode on the YSZ substrate was defined to be about 5 µm by the cross-sectional SEM image in Fig. 2D.

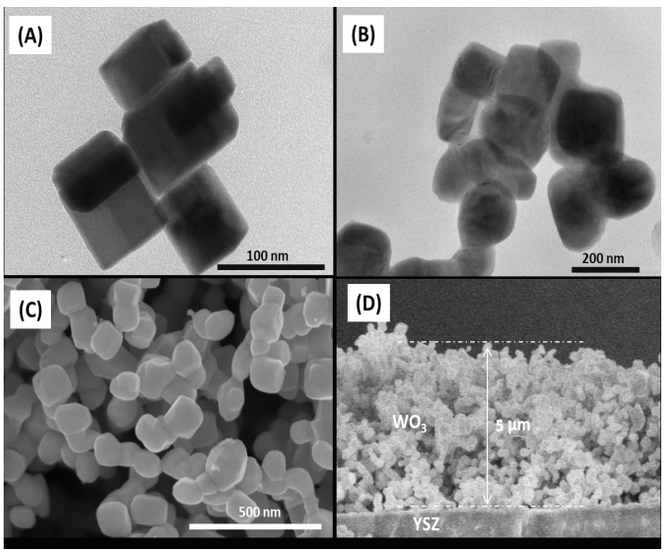

Fig. 2. (A) TEM images of as-synthesised WO_3 nanoparticles, (B) WO_3 nanoparticles originated from the sensing electrode after sintering at 700°C, (C) SEM images of surface, and (D) Cross-sectional view of the WO_3 sensing electrode on YSZ substrate.

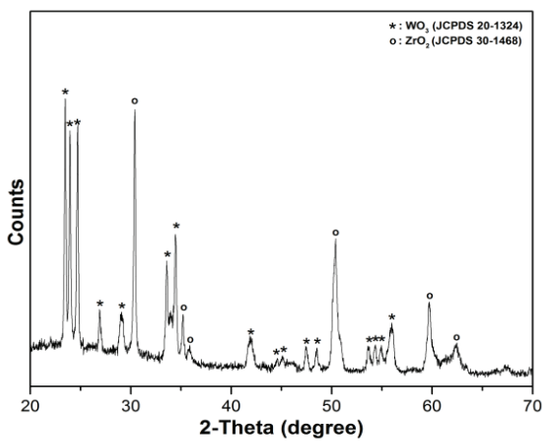

Fig. 3. XRD pattern of the WO_3 square-surface nanostructure-based sensing electrode on YSZ substrate after sintering process at 700°C.

The X-ray diffraction pattern of the WO_3 nanoparticle sensing electrode on YSZ substrate after the sintering process at 700°C is shown in Fig. 3. The result indicated that the peaks of the pattern likely belong to the typical crystalline structures of orthorhombic WO_3 (JCPDS 020-1324, denoted '*') and cubic zirconia (JCPDS 30-1468, denoted 'o').

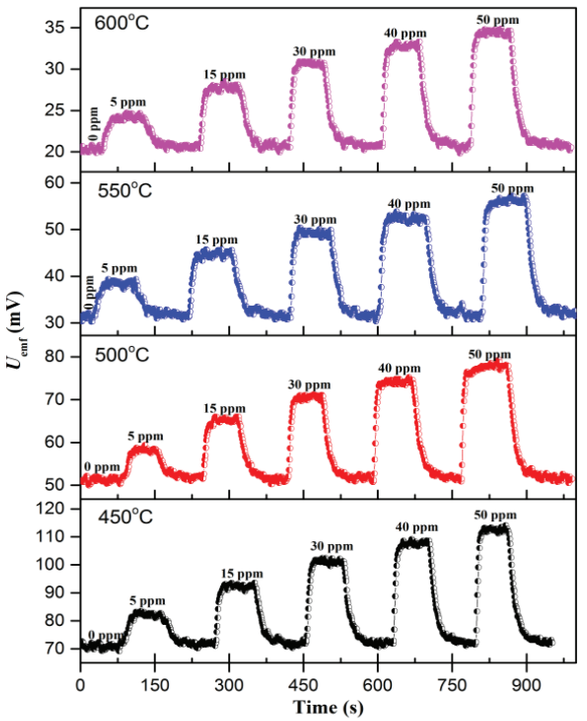

Fig. 4. Electromotive voltage (U_{emf}) of the sensor Pt/YSZ/(Pt-WO_3) responding to 5, 15, 30, 40, and 50 ppm NO_2 at operating temperatures of 450, 500, 550, and 600°C.

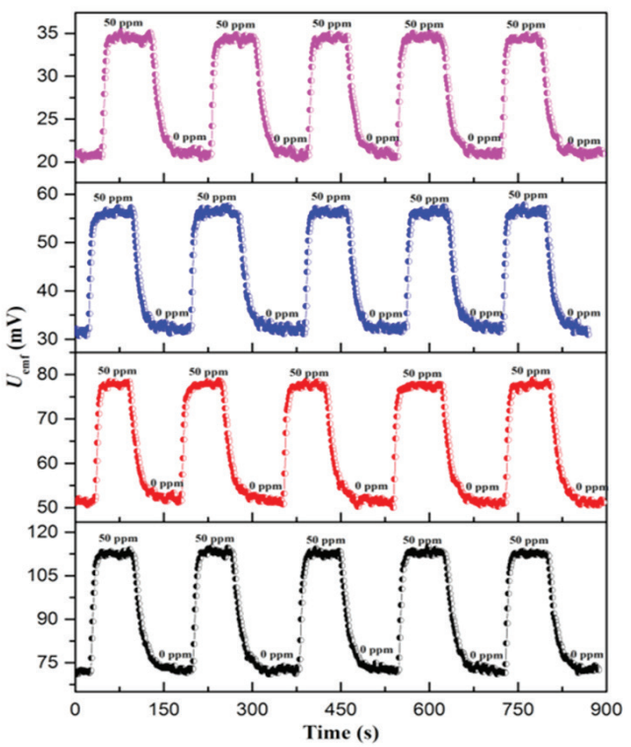

Fig. 5. Electromotive voltage (U_{emf}) of the sensor Pt/YSZ/(Pt-WO_3) responding to 50 ppm NO_2/air cycles at operating temperatures of 450, 500, 550, and 600°C.

For the gas sensing investigation, the Pt/YSZ/(Pt-WO_3) sensor was examined when responding to NO_2 gas at different operating temperatures of 320, 390, 450, 500, 550, and 600°C. From this measured data, the sensing response (ΔU_{emf}) and the response-recovery times (τ_{90}) were calculated. Fig. 4 shows typical results of electromotive voltage (U_{emf}) of the Pt/YSZ/(Pt-WO_3) sensor responding to 5, 15, 30, 40, and 50 ppm NO_2 at operating temperatures of 450, 500, 550, and 600°C. It was observed that the electromotive voltage U_{emf} clearly changed according to the cycles of exposure to different NO_2 gas concentrations. Fig. 5 shows highly repeatable and stable characteristics of the electromotive voltage U_{emf} responding to 50 ppm NO_2/air cycles under working temperatures of 450, 500, 550, and 600°C.

With the each NO_2 concentration, the sensing response ΔU_{emf} of the Pt/YSZ/(Pt-WO_3) sensor slightly increased with operating temperatures from 320 to 450°C and then strongly reduced from 450 to 600°C.

For example, ΔU_{emf} values for 50 ppm NO_2 of the sensor Pt/YSZ/(Pt-WO_3) were found about 35.2, 39.9, 40.9, 27.6, 25.2, and 13.7 mV for operating temperatures of 320, 390, 450, 500, 550, and 600°C, respectively. These values were significant for YSZ mixed potential gas sensor as compared with recent reports [4]. In more detail, Table 1 showed a typical gas sensing performance of the Pt/YSZ/(Pt-WO_3) sensor to 50 ppm NO_2 when operating at 320, 390, 450, 500, 550, and 600°C. The highest response was about 40.9 mV for 50 ppm NO_2 at 450°C. The sensor presented quite short response/recovery times (τ_{90}) of only approximately several tenths of seconds. Fig. 6 indicates the dependences of the sensing response ΔU_{emf} on NO_2 gas concentration when operating at 320, 390, 450, 500, 550, and 600°C. The dependences presented a similar shaped curve with the sensing response ΔU_{emf} increasing with the increase of NO_2 gas concentration. However, one disadvantage was found: the sensing response (ΔU_{emf}) sharply reduced in the high operating temperature region. This behaviour presents an obstacle for high temperature applications.

Table 1. Gas sensing performance of the sensor Pt/YSZ/(Pt-WO_3) to 50 ppm NO_2.

Operating temperature	Gas sensing response (ΔU_{emf})	Response time (τ_{90})	Recovery time (τ_{90})
320°C	35.2 mV	17 s	40 s
390°C	39.9 mV	16 s	39 s
450°C	40.9 mV	15 s	39 s
500°C	27.5 mV	14 s	37 s
550°C	25.2 mV	13 s	35 s
600°C	13.7 mV	13 s	34 s

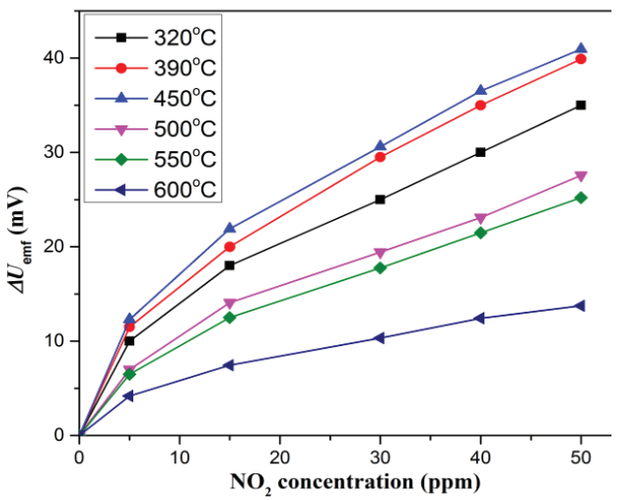

Fig. 6. Dependence of sensing response (ΔU_{emf}) of the Pt/YSZ/(Pt-WO_3) sensor on NO_2 concentration at operating temperatures of 320, 390, 450, 500, 550, and 600°C.

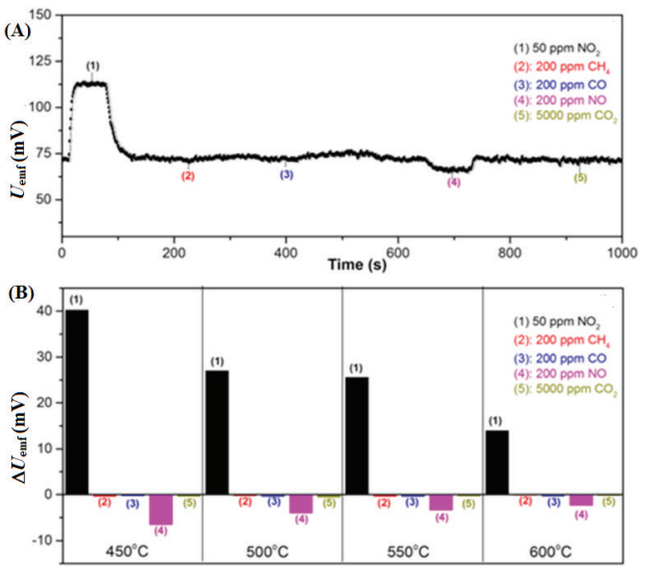

Fig. 7. (A) Typical electromotive voltage (U_{emf}) of the Pt/YSZ/(Pt-WO_3) sensor responding to 50 ppm NO_2, 200 ppm CH_4, 200 ppm CO, 200 ppm NO, and 5000 ppm CO_2 450°C and (B) Comparison of the sensing response (ΔU_{emf}) for these gas concentrations at operating temperatures of 450, 500, 550, and 600°C.

To evaluate selectivity, we have investigated and compared the gas sensing responses of the Pt/YSZ/(Pt-WO_3) sensor to some common combustion gases including NO_2, NO, CO, CH_4, and CO_2. The selective gas sensing characteristics of the Pt/YSZ (Pt-WO_3) sensor are shown in Fig. 7. Typically, the electromotive voltage U_{emf} responding to 50 ppm NO_2, 200 ppm CH_4, 200 ppm CO, 200 ppm NO, and 5000 ppm CO_2 at operating temperatures of 450°C are illustrated in Fig. 7A. A comparison chart of the gas sensing response (ΔU_{emf}) for these gas concentrations at different operating temperatures of 450, 500, 550, and 600°C is presented in Fig. 7B. The result indicated that the gas sensing response ΔU_{emf} of the Pt/YSZ/(Pt-WO_3) sensor was small for NO gas and almost negligible for CO, CH_4, and CO_2 gases. It was concluded that the Pt/YSZ/(Pt-WO_3) sensor presented a very high selectivity to NO_2 gas in compared with the gases of NO, CO, CO_2, and CH_4.

The gas sensing mechanism of the mixed potential sensor Pt/YSZ/(Pt-metal-oxide) when exposed to gas mixtures occurs by simultaneous electrochemical reactions at the triple phase boundary of the gas-electrolyte-electrode and then reaches an equilibrium state resulting in the formation of the mixed potential or electromotive force (U_{emf}) as proposed in Refs. [3, 18, 19]. The triple phase boundary, considered as a key factor explaining the NO_2 sensing performance of the Pt/YSZ/(Pt-metal-oxide) mixed potential sensor, can be described as:

In air: O_2, Pt/YSZ/(Pt-metal-oxide), O_2

In air containing NO_2: $O_2 + NO_2$, Pt/YSZ/(Pt-metal-oxide), $O_2 + NO_2$

The electrochemical reactions can be assumed as following:

Anodic for O_2: $O^{2-} \rightarrow \frac{1}{2}O_2 + 2e^-$ (2)

Cathodic for NO_2: $NO_2 + 2e^- \rightarrow NO + O^{2-}$ (3)

The changes of ionic (O^{2-}) and electronic (e^-) forms the electrochemical potentials (U_{emf}) at the electrodes. Differences in the cathodic/anodic catalytic reactions in the interfaces of Pt/YSZ and (Pt-metal-oxide)/YSZ makes the sensing response (ΔU_{emf}) change in correspondence with the NO_2 gas concentration. The magnitude of the sensing response (ΔU_{emf}) is mainly dominated by the catalytic activity properties of (Pt_metal-oxide)/YSZ interfaces with reducing/oxidising gases. Thus, in this work, the specific characteristic of the high catalytic activity to NO_2 gas of the square-surface nanostructured WO_3, as mentioned in Refs. [10, 13-15], could play an important role in the high selectivity performance of the Pt/YSZ/(Pt-WO_3) sensor to NO_2 gas.

Conclusions

In summary, the mixed-potential gas sensor Pt/YSZ/(Pt-WO_3) exhibited very high selectivity to NO_2 in comparison with NO, CO, CO_2, and CH_4 gases. The high sensing selectivity of the Pt/YSZ/(Pt-WO_3) mixed-

potential gas sensor to NO_2 could be related to the high catalytic activity of the square-surface nanostructured WO_3. The sensor Pt/YSZ/(Pt-WO_3) exhibited the high NO_2 sensing performance with the gas sensing response (ΔU_{emf}) and response/recovery times (τ_{90}) of 40.9 mV and 15/39 s, respectively, for 50 ppm at 450°C. It can be expected that the square-surface nanostructured WO_3 will be developed for the gas sensing electrode of YSZ-based gas sensors for the detection of NO_2.

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COMPETING INTERESTS

The authors declare that there is no conflict of interest regarding the publication of this article.

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