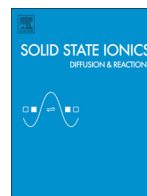




Contents lists available at ScienceDirect

Solid State Ionics

journal homepage: www.elsevier.com/locate/ssi

Sensing performance of zirconia-based gas sensor using titania sensing-electrode added with palladium

Yuki Fujio^{a,b,1}, Tomoaki Sato^{a,b}, Norio Miura^{c,*}

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

^b Japan Society for the Promotion of Science, Chiyoda-ku, Tokyo 102-8471, Japan

^c Art, Science and Technology Center for Cooperative Research, Kyushu University, Kasuga-shi, Fukuoka 816-8580, Japan

ARTICLE INFO

Article history:

Received 15 May 2013

Received in revised form 20 August 2013

Accepted 25 August 2013

Available online xxx

Keywords:

Potentiometric sensor

YSZ

Hydrocarbon

Mixed potential

TiO₂

Pd

ABSTRACT

The sensing characteristics of a yttria-stabilized zirconia (YSZ)-based sensor using a sensing electrode (SE) consisting of rod-shaped TiO₂ added with 1 wt.% of nano-sized Pd particles (abbreviated as TiO₂(+Pd)-SE) were evaluated, aiming at selective detection of hydrocarbons. The rod-shaped TiO₂-SE without Pd addition (TiO₂-SE) was found to give high sensitivities to both C₃H₈ and C₃H₆ which were used as representatives of alkane and alkene groups, respectively, in hydrocarbons (HCs), while TiO₂(+Pd)-SE gave selective detection of C₃H₈. The evaluation of catalytic activity to the gas-phase oxidation of HCs for the SE materials revealed that the oxidation of C₃H₆ was largely promoted by the Pd addition, leading to the high selectivity to C₃H₈ for the sensor using TiO₂(+Pd)-SE. From the results of polarization-curve measurements, the current value for the cathodic reaction of O₂ was found to be slightly decreased by the Pd addition, while those for the anodic reaction of C₃H₈ and C₃H₆ were largely decreased. This is presumably due to the decrease in the actual concentration of C₃H₈ and C₃H₆ at the SE/YSZ interface owing to the promoted gas-phase oxidation of these HCs through the TiO₂(+Pd)-SE layer. XRD measurements as well as SEM observations confirmed that the added Pd particles were existing as PdO particles on the surface of the rutile-type TiO₂ rods after the SE fabrication process. The stability test revealed that the C₃H₈ sensitivity of the sensor using TiO₂(+Pd)-SE gradually increased and reached the stable value after the 12 day operation. By considering the results of the complex-impedance analysis, we believed that this gradual increase in sensitivity was due to the decrease in the catalytic activity against the gas-phase oxidation of C₃H₈ in the TiO₂(+Pd)-SE layer.

© 2013 Elsevier B.V. All rights reserved.

1. Introduction

Recently, the strict regulations for the automobile exhausts such as hydrocarbons (HCs), carbon monoxide (CO) and nitrogen oxide (NOx) have been settled in various advanced countries. The regulations are becoming more severe year by year. In order to meet such stringent regulations, automobile companies have been trying to develop the advanced engine systems equipped with new catalyst systems, such as selective catalytic reduction (SCR) [1] and NOx storage/reduction (NSR) catalyst [2]. To make such engine systems operate efficiently, high-performance and reliable gas sensors need to be developed for monitoring the concentrations of various exhaust gases upstream and/or downstream of the catalysts. So far, there have been many reports on yttria-stabilized zirconia (YSZ)-based exhaust gas sensors which are classified into three categories based on sensing modes; potentiometric (mixed-potential type) [3–8], amperometric [9–11] and

impedancemetric [12–14]. In general, selection of a SE material is one of the most important points to achieve high-performance of solid-state electrochemical gas sensors.

It has been reported that YSZ-based sensors using composite (oxide + metal)-SE can give sometimes specifically excellent sensing performances toward various exhaust gases even at rather high temperatures [15–17]. Recently, we have also found that the use of composites, such as ZrCr₂O₄(+Au) and NiO(+Au), as an SE material resulted in high sensitivity and/or high selectivity to CO [18] and C₃H₆ [19], respectively. Thus, in this study, the YSZ-based sensor using such a composite (oxide + metal) SE material, especially rod-shaped TiO₂ added with nano-sized palladium (Pd) particles was fabricated and its sensing characteristics were evaluated, aiming at sensitive and selective detection of HCs.

2. Experimental

2.1. Sensor fabrication

The rod-shaped TiO₂ powders (Ishihara Sangyo, Japan) were drizzled with the commercial colloidal solution consisting of nano-sized Pd

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

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

¹ Present address: National Institute of Advanced Industrial Science and Technology, Tosu, Saga 841-0052, Japan.

particles of 3–8 nm (Tanaka Kikinzoku, Japan) and was added to a proper amount of distilled water, followed by agitation for 2 h. Then, the solution was dried at 130 °C overnight and the resulting TiO₂(+Pd) composite powder was sintered at 700 °C for 2 h in air. The final SE material was obtained by thoroughly pulverizing the sintered powder in a mortar.

The obtained composite material was mixed with α -terpineol in a weight ratio of 1:1 and the obtained SE paste was applied on the outer surface of a YSZ tube (8 mol% Y₂O₃ doped ZrO₂, length: 300 mm, inside diameter: 5 mm, outside diameter: 8 mm, Nikkato, Japan). A commercial Pt paste (Tanaka Kikinzoku, Japan) was painted on the inner and outer surfaces of the YSZ tube, respectively. The painted YSZ tube was then sintered at 900 °C for 2 h in air to fabricate TiO₂(+Pd)-SE, Pt reference-electrode (RE) and Pt counter-electrode (CE).

2.2. Evaluation of sensing performance

The electromotive force (*emf*) between SE and RE was measured as a sensing signal by means of a digital electrometer (R8240, Advantest, Japan). SE was exposed to a base gas (21 vol.% O₂ + 5 vol.% H₂O + N₂ balance) or sample gases (CO, NO, NO₂, C₃H₈, C₃H₆: 100 ppm each, diluted with the base gas), while RE was always exposed to air atmosphere. The total gas flow-rate was fixed at 100 cm³ min⁻¹.

The polarization (current–voltage) curves of the fabricated sensors were measured in the base gas and in the sample gas (100 ppm C₃H₈ or 100 ppm C₃H₆, diluted with the base gas). The potential scan was carried out in a potentiodynamic mode at a scan rate of 5 mV min⁻¹ by means of an automatic polarization system (HZ-3000, Hokuto Denko, Japan), based on a 3-terminal method.

The complex-impedance of the sensor using TiO₂(+Pd)-SE was measured in the base gas and in 100 ppm C₃H₈ (diluted with the base gas) by means of a complex-impedance analyzer (1255WB, Solartron, UK), based on a 2-terminal method at 0 mV potential difference between SE and RE. The frequency was changed from 0.1 to 10⁶ Hz, and the amplitudes of the AC potential and the applied DC potential were fixed at 50 mV and 0 mV, respectively.

2.3. Characterization of SE material

The crystal structures of TiO₂ and TiO₂(+Pd) powders after sintering at 900 °C for 2 h in air were examined by the use of an X-ray diffractometer (XRD, RINT 2100VLR/PC, Rigaku, Japan) with Cu K α radiation ($\lambda = 1.5406$ Å) at angle step of 1° min⁻¹. The morphology of the TiO₂(+Pd)-SE material formed on YSZ was observed by a field-emission scanning electron microscope (FE-SEM, JSM-6340 F, JEOL, Japan).

The catalytic activities to the gas-phase oxidation reaction of 700 ppm C₃H₈ (or 700 ppm C₃H₆, diluted with synthetic air) for the TiO₂ and TiO₂(+Pd) powders (20 mg each) were evaluated by using a gas-chromatography-mass spectroscopic analysis (GC: GC-17A, Shimadzu, Japan; column: RT-m sieve 5A, Restek, USA; MS: MSQP5050A, Shimadzu, Japan) in the temperature range of 25–800 °C. Helium was used as a carrier gas at a column-head pressure of 100 kPa. The scanned mass-to-charge (*m/z*) ratio was fixed at 39, 41, 42 for C₃H₆ and 27, 29, 43 for C₃H₈ detection.

3. Results and discussion

3.1. Evaluation of SE materials by XRD and SEM

The crystal structures of the TiO₂ and TiO₂(+Pd) powders were investigated by means of XRD and the observed diffraction patterns are given in Fig. 1. The peaks appearing around 36, 39 and 41° observed in the patterns of the both powders revealed that the TiO₂ used in this study has a rutile-type crystal structure (JCPDS no. 73-1765). Only in the patterns of the TiO₂(+Pd) powder, a peak around 34° was seen.

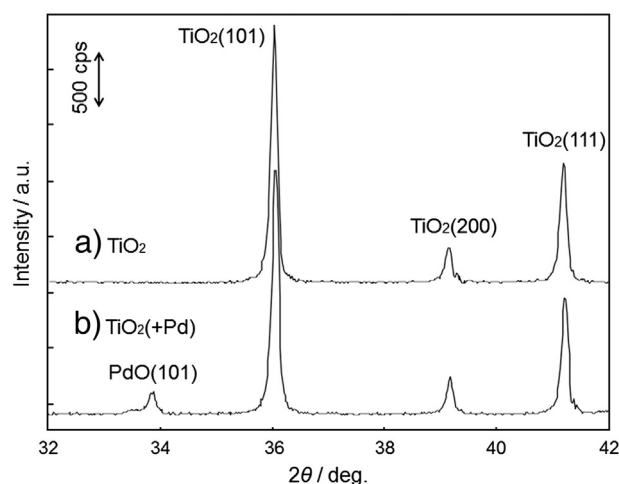


Fig. 1. XRD patterns of (a) TiO₂ powder and (b) TiO₂(+Pd) powder, after calcination at 900 °C for 2 h in air.

This is confirmed to be a (101) peak of palladium oxide (PdO, tetragonal, JCPDS no. 41-1107). Since the strongest (111) peak of metal palladium (Pd) around 40° was not found in the pattern (Fig. 1 (b)), the added Pd is believed to be oxidized to PdO in the sintering process.

To observe the morphology of TiO₂(+Pd)-SE, the SEM measurements were performed and the obtained images are shown in Fig. 2. It

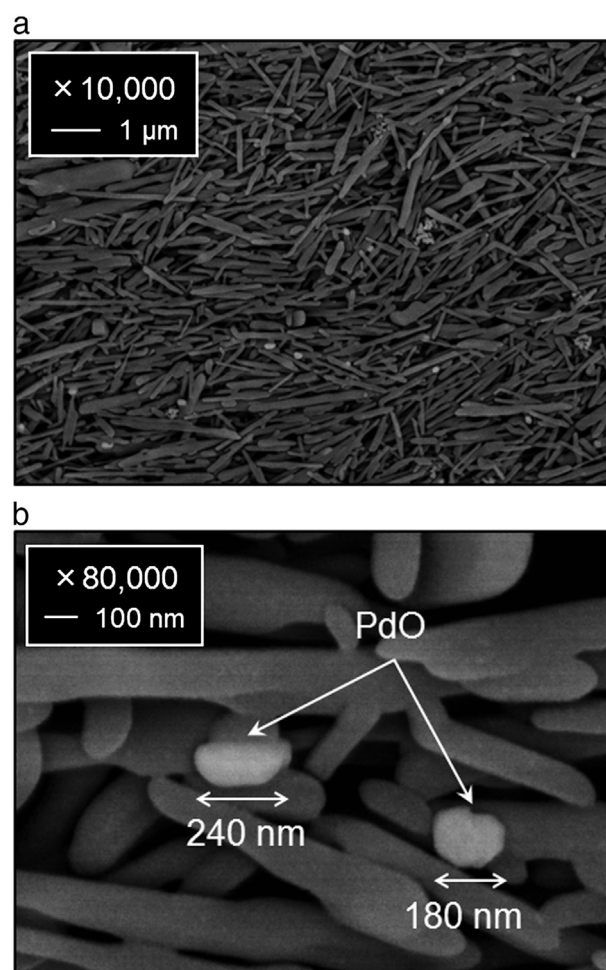


Fig. 2. SEM images (top views, (a): $\times 10,000$, (b): $\times 80,000$) of TiO₂(+Pd)-SE.

Download English Version:

<https://daneshyari.com/en/article/7746193>

Download Persian Version:

<https://daneshyari.com/article/7746193>

[Daneshyari.com](https://daneshyari.com)