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High sensitivity and selectivity of mixed potential sensor based on Pt/YSZ/$SmFeO_3$ to NO_2 gas

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ABSTRACT

Yttria-stabilized zirconia (YSZ) ceramic has been well known as a solid electrolyte in electrochemical gas sensors working at high temperature. In this work, YSZ-8 (ZrO_2 doped 8 mol% Y_2O_3) powder was synthesized by a sol–gel method. Crystalline structure of the synthesized powder YSZ-8 was analyzed by X-ray diffraction. The impedance spectroscopy investigation showed that the pressed plate YSZ-8 sintered at 1300 °C had good ionic conductivity at high working temperature. The gas sensing properties of the mixed potential sensor Pt/YSZ-8/$SmFeO_3$ were investigated by exposing to NO_2, CO, CH_4, C_3H_8 and C_6H_{14} at the operating temperatures from 300 to 500 °C. The experimental results indicated that the sensor Pt/YSZ-8/$SmFeO_3$ presented very good sensitivity and selectivity to NO_2 gas. The high sensitivity of the sensor Pt/YSZ-8/$SmFeO_3$ to NO_2 was suggested by relation to high catalytic activity of the oxide $SmFeO_3$ to NO_2.

1. Introduction

It has been known that many dangerous gases such as carbon oxides (CO, CO_2), nitrogen oxides (NO, NO_2), and sulfur dioxide (SO_2) are released from high temperature combustion processes. These gases cause adverse human health effects and air pollutions. Among these gases, the nitrogen oxides are highly chemical active gases and their acceptable concentration limits in the air are very small about several parts per million. There are some devices commonly used to identify or control the nitrogen oxides concentrations, such as metal oxides semiconductor gas sensors [1–3], IR gas sensors [4,5] and electrochemical gas sensors [6–9]. The electrochemical gas sensors based on solid-state electrolytes (for example, yttria-stabilized zirconia or YSZ) have exhibited advantages in numerous parameters like sensitivity, selectivity and stability, particularly in operating ability in high-temperature and hazardous conditions [6,10]. In yttria-stabilized zirconia, ZrO_2 doped 8 mol% Y_2O_3 has been reported to have the best ionic conductivity electrolyte for electrochemical gas sensors [8,11,12].

Recently, mixed potential zirconia-based sensors, a type of electrochemical gas sensor that both sensing and reference electrodes exposed to same gas mixture, have been greatly interested in research for detecting NO_x [6,8,13]. The sensing electrodes of the mixed potential sensors have mostly used metal oxides such as WO_3, NiO, ZnO and SnO_2 while the reference electrodes based on noble metals like Pt, Au [6,8,14]. Furthermore, perovskite type oxides $LnFeO_3$ (Ln = La, Nd Sm, Gd, etc.) have been known as high catalytic activities to reducing/oxidizing gases [15] are expected for designing the sensing electrode of the electrochemical gas sensors. For example, Yoon et al. [7] reported that the mixed potential sensors based on Pt/YSZ/$LaFeO_3$(Pt) had very high sensitivity to NO_2 at the operating temperature near 500 °C. Bartolomeo et al. [16] also investigated the Pt/YSZ/($LaFeO_3$, $La_{0.8}Sr_{0.2}FeO_3$) sensors and showed that these sensors exhibited good performance to NO_2 and CO gases. In addition, the electrochemical sensor Pt/YSZ/Pt modified with catalytic layer $SmFeO_3$ was demonstrated very high sensitivity to VOCs at sub-ppm levers by Mori et al. [17]. According to the review by Zhuiykov and Miura [6], the complex or multi-metal oxides have been attracted more attention for gas-sensing electrodes of the zirconia-based sensors. Especially, it was also observed from this review that the sensors with multi-metal oxide sensing-electrodes commonly worked at low temperatures in compared with the sensors with single-metal oxide sensing-electrodes.

In this work, the mixed-potential planar sensor based on electrolyte YSZ-8 (ZrO_2 doped 8 mol% Y_2O_3) and the sensing electrode $SmFeO_3$ was investigated. In the perovskite oxides $LnFeO_3$, $SmFeO_3$ has been reported to have the optimum of Sm—O bond in crystalline lattice structure leading to high concentrations of adsorbed oxygen (O^{2-}) and the $SmFeO_3$ thick-film sensor also presented the highest sensitivity to NO_2 in compared to other the oxides with rare earth elements such as La, Nd and Gd [1]. Thus, the main purpose of this work is that the high catalytic activity of $SmFeO_3$ to NO_2 is used for

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sensing electrode of the mixed potential sensor based on zirconia to intensify the sensitivity and selectivity to NO_2.

2. Experimental

2.1. Synthesizing and analyzing the YSZ-8 electrolyte

YSZ-8 (ZrO_2 doped 8 mol% Y_2O_3) was synthesized by sol–gel citric method and reported in our previous work [18]. Briefly, $ZrOCl_2{\cdot}8H_2O$ (99.95%) and Y_2O_3 (99.95%) were used as precursors. Stoichiometric amounts of $ZrOCl_2{\cdot}8H_2O$ and Y_2O_3 were weighted and dissolved with HNO_3 solution, and then added citric acid. The pH of the solution was always kept at about 7 by NH_4OH. The homogeneous solution was continuously stirred and heated at 80 °C for 10 h to obtain a white gel. After that, the gel was dried at 100 °C in air for 24 h to get a solid black resin and then calcined at 700 °C in air for 3 h to obtain a white powder YSZ-8.

To get the density oxide expected to have high ion conductivity for designing electrolyte layer in electrochemical gas sensor, the synthesized powder YSZ-8 was pressed at 5 ton/cm^2 to get a round pellet YSZ-8 with 1 cm in diameter. The pellet was sintered at 1300 °C for 4 h. The effect of sintering temperatures on ionic conductivity of the synthesized powder YSZ-8 was reported in our other paper [18]. Then, the sintered pellet was cut into a plate YSZ-8 with thickness of 0.2 mm. For the evaluation of ionic conductivity, the Pt paste (ESL 5545 – ElectroScience) was covered on the two sides of the plate YSZ-8 to get a cell of Pt/YSZ-8/Pt (widths of the each Pt electrode = 1 mm × 1 mm). The schematic of the cell Pt/YSZ-8/Pt was shown in Fig. 1a. The impedances of this cell Pt/YSZ-8/Pt were measured by AutoLab PGSTAT-30 with scanning frequency range from 10 mHz to 1 MHz.

2.2. Sensor fabrication and gas-sensing measurement

In this work, the mixed potential planar sensor consists of the two parallel electrodes (widths of each electrode: 0.3 mm × 0.5 mm; separation between two electrodes: 0.3 mm) on the top surface of the pressed and sintered plate YSZ-8. One of the electrodes was created by coating the Pt paste (ESL 5545 – Electro-Science) as the reference electrode. The nano-powder $SmFeO_3$ [19] synthesized by the sol–gel method was mixed with an organic binder (mixture of α-terpineol, antarox and ethyl-cellulose at weight percent ratio of 95:2:3, respectively) to create the sensing electrode. After that, the configuration was sintered at 700 °C for 8 h to get a device Pt/YSZ-8/$SmFeO_3$. The device Pt/YSZ-8/$SmFeO_3$ was adhered on a front-side of an Al_2O_3 substrate integrated Pt microheater. Finally, the Pt wires with 25 μm in diameter were connected on top of the both electrodes by sealing Pt paste to get the sensor Pt/YSZ-8/$SmFeO_3$ as illustrated in Fig. 1b.

The gas sources (NO_2 from Air Liquide America Specialty Gases – LLC; CO, CH_4, C_3H_8 and C_6H_{14} from Singapore Oxygen Air Liquide Pte Ltd.) were used for analyzing the gas sensing characteristics. The sensor was investigated in a chamber of 50 ml in volume, the total flow rate of gases through the chamber was fixed at 500 ml/min. The change in electromotive force of the sensor Pt/YSZ-8/$SmFeO_3$ was calculated as following equation: $\Delta EMF = |V_{air} - V_{gas}|$, where V_{air} and V_{gas} were the voltages measured between the two electrodes of the sensor in the pure air and the air containing desired gases, respectively.

X-ray diffraction (Siemens D5000) with Cu Kα radiation and scanning electron microscope (SEM, HITACHI S-4800) were used for analyzing the crystalline structures and morphologies of the YSZ-8 and $SmFeO_3$ materials.

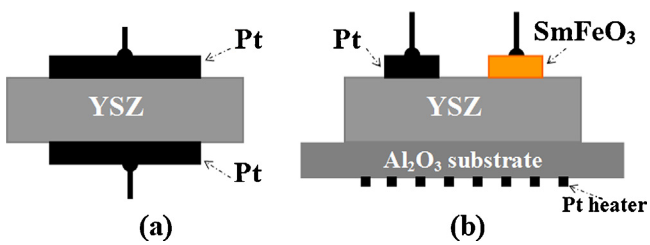

Fig. 1. Schematics of the cell Pt/YSZ-8/Pt (a) and the sensor Pt/YSZ-8/$SmFeO_3$ (b).

3. Results and discussion

3.1. Electrolyte and electrodes

Fig. 2 shows X-ray diffraction patterns of the synthesized powders YSZ-8 and $SmFeO_3$. The results indicated that all the peaks of the pattern YSZ-8 could belong to cubic symmetry of the crystalline structure of the zirconia oxide with space group of *Fm3m*, indexed according to JCPDS 30-1468. The nano-powder $SmFeO_3$ had orthorhombic perovskite structure as reported in our previous work [19].

The surface morphology of the pressed pellet YSZ-8 after sintering at 1300 °C is shown in Fig. 3a. The result showed that this pellet YSZ-8 exhibited high density and homogeneous surface. The electrode of thick-film $SmFeO_3$ sintered at 700 °C for 8 h express porous surface in which the grains with 50–60 nm associated together (Fig. 3b). The thickness of the $SmFeO_3$ film electrode on YSZ layer of the sensor Pt/YSZ-8/$SmFeO_3$ is about 10 μm (Fig. 3d) while that of the Pt electrode is 3 μm (Fig. 3c). It was also observed that the $SmFeO_3$ electrode was higher porous in compared with the Pt electrode.

Fig. 4 shows impedances of the cell Pt/YSZ-8/Pt at different temperatures 400, 500 and 600 °C. At low temperature (400 °C), the impedance curve had a small semi-circle at high frequency region (1.32–1000 kHz) and a long tail at low-frequency region (10 mHz to 1.32 kHz). Ionic conductivity of the solid electrolyte YSZ relates to ionic mobility and effects of both bulk-grain and grain-boundary. Thus, it could be observed in Fig. 4 that the high-frequency semicircle nearly disappeared and the low-frequency tail gradually changed into the small semi-circles when the cell Pt/YSZ-8/Pt worked at the high temperatures (500 and 600 °C). From the results in Fig. 4, it was concluded that the plate YSZ-8 represented an ionic conductivity materials for electrochemical gas sensor working at the high temperature. The characteristics of surface morphology

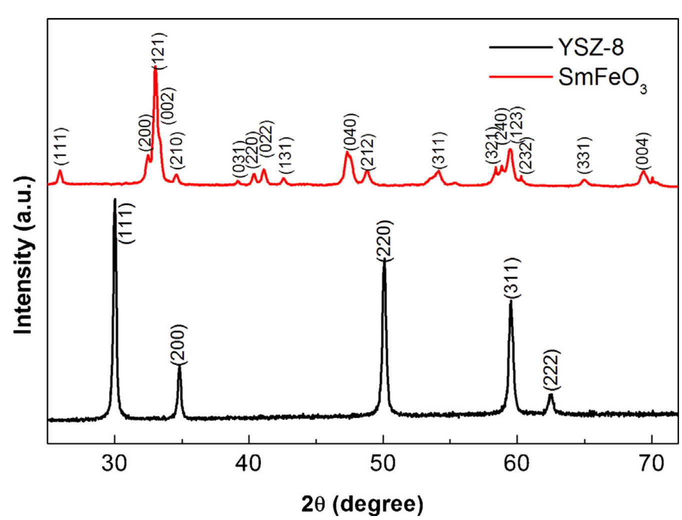

Fig. 2. X-ray diffraction patterns of the synthesized powders YSZ-8 and $SmFeO_3$.