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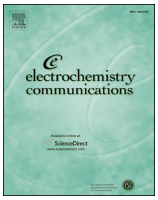

Potentiometric YSZ-based oxygen sensor using $BaFeO_3$ sensing-electrode

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ABSTRACT

Various metal oxides were examined for a sensing-electrode (SE) material of potentiometric yttria-stabilized zirconia (YSZ)-based oxygen sensors. Among the oxides tested, perovskite-type oxides of $Ba_xSr_{1-x}FeO_3$ (x = 1.0, 0.9, 0.5, 0.1, 0) were found to give low responses to various gases (NH_3, H_2, C_3H_6, C_3H_8, CH_4, NO_2, NO, and CO, 100 ppm each) at 600 °C. Particularly, $BaFeO_3$-SE gave the most insensitive behavior to all the gases tested even in the temperature range of 500–600 °C, as the conventional Pt-SE did. Furthermore, the sensor using this inexpensive $BaFeO_3$-SE was found to be quite sensitive to oxygen in the concentration range of 0.05–21 vol.% at temperatures of 500–600 °C, as similar to the case of an expensive Pt-SE. At 600 °C, the number of electron (n) involved in the electrochemical reaction of oxygen for the sensors using each of $BaFeO_3$-SE and Pt-SE was estimated to be 4.2, which was obtained from the slope of linear correlation between potential response and the logarithm of oxygen concentration. The estimated n value was in good agreement with the theoretical value ($n = 4$). The present sensor using $BaFeO_3$-SE was also confirmed to work well as a λ (lambda) sensor at 600 °C, showing similar behavior as the sensor using Pt-SE did.

1. Introduction

Considerable attention has been paid to in-situ measurement of oxygen concentration in combustion processes for improving fuel efficiency as well as reducing air pollutants. Until now, potentiometric, amperometric and conductometric sensors have been developed for oxygen sensing applications at high temperature [1]. As a commercialized λ sensor for controlling air/fuel ratio of automotive engines, a potentiometric YSZ-based oxygen sensor attached with Pt-SE has been used during these four decades [2,3]. Sensing characteristics of the potentiometric oxygen sensor usually depend on not only electrolyte but also SE material. So far, several efforts have been conducted to explore new alternatives to the expensive Pt-SE. Various perovskite-type oxides such as La–Sr–Mn–O [4,5], La–Co–Ni–O [6], La–Sr–Co–Ni–O [7–9], La–Sr–Co–Fe–O [10–12] systems have been used as an SE material for oxygen sensors, in which each of them examined on different solid electrolytes. In these cases, unlike the sensor using conventional Pt-SE, the operating temperature of the oxygen sensor could be lowered largely. However, the above-mentioned studies are mostly limited to investigate only the oxygen responses without checking the cross sensitivities to other interfering gases. In the actual condition, a practical oxygen sensor operating in combustion exhausts as well as a real air-atmosphere must be insensitive to various gases except for oxygen. Therefore, different types of oxides, including but not limited to perovskite-type oxides, were examined here as an SE material for high-performance (sensitive and selective) YSZ-based oxygen sensors.

As the first step of search for a new SE-material, the cross sensitivities to different gases for the YSZ-based sensors using each of the various oxides as an SE material were examined, in order to select an oxide material which is insensitive to the interfering gases. As the second step, by using this insensitive oxide as an SE material, we evaluated the sensing characteristics of the resulted sensor as an oxygen sensor as well as a λ sensor.

2. Experimental

The complex oxides used here were prepared by a metal–nitrate decomposition or a solid-reaction method, and the single-metal oxides were commercially available reagents. The sensor configuration was similar to that of a conventional potentiometric YSZ-based oxygen sensor [1]. Prior to the fabrication of SE, to improve adhesion strength of the metal oxides to a YSZ tube (8 mol% Y_2O_3 doped ZrO_2, one end closed configuration, inside diameter: 5 mm, outside diameter: 8 mm, length: 300 mm, Nikkato, Japan), an intermediate YSZ layer was formed on the outer surface of the YSZ tube by using a YSZ powder mixed with α-terpineol. Subsequently, each of the metal-oxide powders mixed with α-terpineol was applied on the YSZ layer as an SE layer. To fabricate a reference electrode (RE) layer, Pt-paste was applied on the inner surface of the YSZ tube. The YSZ tube attached with the oxide-SE and Pt-RE layers was sintered at 1200 °C for 2 h in air. Meanwhile, a YSZ-based sensor attached with Pt-SE and Pt-RE was fabricated by the similar procedure for sensing characteristic comparison.

The response of the fabricated sensors attached with Pt-RE and each of oxide-SEs were examined in the interference gases such as NH_3, H_2, C_3H_6, C_3H_8, CH_4, NO_2, NO, and CO (100 ppm each, diluted with base

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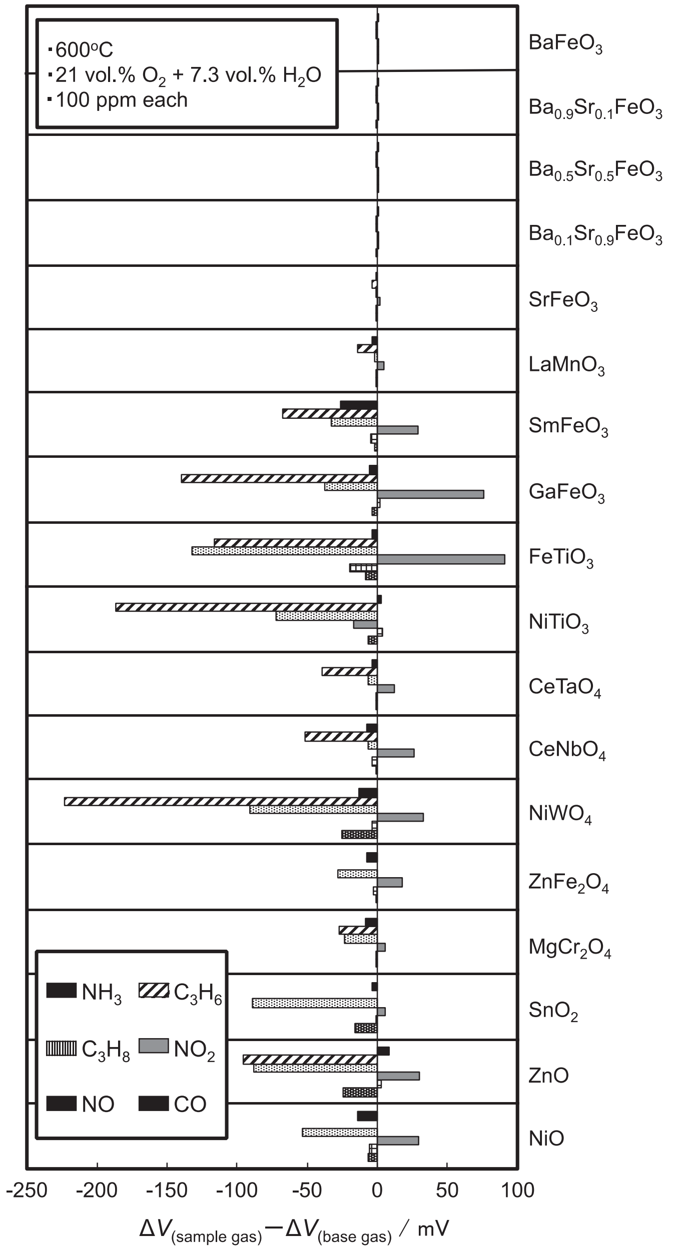

Fig. 1. Comparison of sensitivity (ΔV(sample gas) − ΔV(base gas)) to various gases (100 ppm each, diluted with base gas) at 600 °C, for the YSZ-based sensors attached with each of oxide-SEs.

gas) at temperatures of 400–600 °C. The base gas was composed of 21 vol.% O_2, 7.3 vol.% H_2O and N_2 balance. The total flow-rate of the sample gases and the base gas was kept constant at 100 $cm^3\ min^{-1}$. At the same time, the Pt-RE side of the YSZ tube was always exposed to an ambient air to form Pt/air-RE. The electric potential difference (ΔV) between oxide-SE and Pt/air-RE was measured as a sensing signal by means of a data logger (34970A, Agilent Technologies, USA). The gas sensitivity was defined as |ΔV (sample gas) − ΔV (base gas)|. The oxygen sensing measurements of the fabricated sensors were performed in the oxygen concentration range of 0.05–21 vol.% at 600 °C. The sensing performances of the fabricated sensors as a λ sensor were evaluated in the exhaust gas of an oxidation (combustion) of C_3H_8 (Eq. 1) at 600 °C. The gas mixture (2000 ppm C_3H_8 + variable concentration of O_2 + N_2 balance) was oxidized at 500 °C by using an Mn_2O_3 catalyst located upstream of the sensor testing-cell. In this case, 2.8 vol.% H_2O and 10 vol.% CO_2 were added to the exhaust gas in advance. The resulted exhaust gas was introduced into the sensor testing-cell in which the fabricated sensor had been installed. The response of ΔV was measured as a function of λ which was defined as the concentration (C) ratio of O_2 against C_3H_8 (Eq. 2).

$$C_3H_8 + 5O_2 \rightarrow 3CO_2 + 4H_2O \tag{1}$$

$$\lambda \equiv \frac{C_{(O_2)}}{5 \times C_{(C_3H_8)}} \tag{2}$$

3. Results and discussion

Fig. 1 shows the comparison of cross sensitivities to the interfering gases at 600 °C for the YSZ-based sensors attached with each of various metal-oxide SEs. Among the tested SE materials, $Ba_xSr_{1-x}FeO_3$ (x = 1.0, 0.9, 0.5, 0.1, 0)-SEs exhibited low responses to all examined gases; particularly $BaFeO_3$ brought about the lowest sensitivities (within ±0.2 mV) to the examined gases. In contrast, the other examined oxides gave relatively large responses to the examined gases. These gas sensitivities are considered to be attributed to mixed potential established at the interface of SE/YSZ. It has been reported that a YSZ-based sensor using particular oxide-SE can generate ΔV responses to various gases based on the mixed-potential principle, which is controlled by the catalytic activities against a gas-phase reaction in an SE layer and electrochemical reactions at an SE/YSZ interface [13,14]. By considering the mixed-potential mechanism, we can speculate that the insensitive responses of the $Ba_xSr_{1-x}FeO_3$-SEs against the examined gases are caused by their high catalytic activities to the gas-phase reactions and/or their low catalytic activities to the electrochemical reactions involving these examined gases.

Fig. 2 shows the temperature dependence of cross sensitivities to the interference gases for the YSZ-based sensor using $BaFeO_3$-SE. For

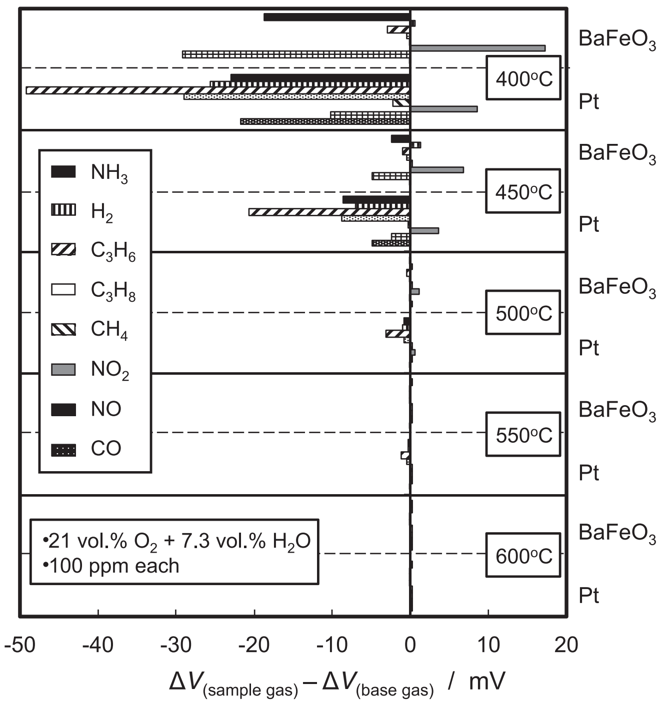

Fig. 2. Cross sensitivities to various gases (100 ppm each, diluted with base gas) measured at different temperatures of 400–600 °C, for the YSZ-based sensors using each of $BaFeO_3$-SE and Pt-SE.