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YSZ-based sensor using Cr-Fe-based spinel-oxide electrodes for selective detection of CO☆

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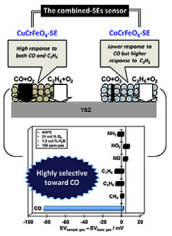
HIGHLIGHTS

- The YSZ-based sensor using $CuCrFeO_4$ and $CoCrFeO_4$ electrodes.
- The sensor could detect CO selectively within 20–700 ppm under humid condition.
- CO response is unaffected by H_2O concentration in the range of 1.3–11.5 vol% H_2O.

GRAPHICAL ABSTRACT



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ABSTRACT

A selective carbon monoxide (CO) sensor was developed by the use of both of $CuCrFeO_4$ and $CoCrFeO_4$ as the sensing electrode (SE) for yttria-stabilized zirconia (YSZ)-based potentiometric sensor. The sensing-characteristic examinations of the YSZ-based sensors using each of spinel oxides as the single-SE sensor showed that $CuCrFeO_4$-SE had the ability to detect CO, hydrocarbons and NO_x gases, while $CoCrFeO_4$-SE was sensitive to hydrocarbons and NO_x gases. Thus, when both SEs were paired as a combined-SEs sensor, the resulting sensor could generate a selective response to CO at 450 °C under humid conditions. The sensor was also capable of detecting CO in the concentration range of 20–700 ppm. Its sensing mechanism that was examined via polarization-curve measurements was confirmed to be based on mixed-potential model. The CO response generated by the combined-SEs sensor was unaffected by the change of water vapor concentration in the range of 1.3–11.5 vol% H_2O. Additionally, the sensing performance was stable during 13 days tested.

1. Introduction

Carbon monoxide (CO) is one of contaminants in our environment and is produced as a by-product of an incomplete-combustion process. The poisonous nature of CO makes its detection an interesting subject to many researchers as well as practitioners in the gas sensor field [1]. When it comes to gas sensing device, the long history of sensors based on yttria-stabilized zirconia (YSZ) has made this kind of sensor to be widely accepted as a promising candidate for high-performance sensing device [2–6].

The sensing mechanism of potentiometric sensor based on YSZ

☆ The experiments of this study were done at Art, Science and Technology Center for Cooperative Research (KASTEC), Kyushu University, Fukuoka, Japan.

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for CO detection has been successfully modeled by mixed-potential theory [3,7–10]. The sensing characteristics of a YSZ-based mixed-potential type gas sensor are controlled by the balance between the catalytic activities to gas-phase oxidation reaction in the sensing electrode (SE) layer and the electrochemical reactions at the SE/YSZ interface [2,3,7,11]. This means that the performance of this type of sensor will be largely governed by the SE materials, hence choosing the appropriate SE material is an important step in obtaining a superior sensing performance.

A spinel-type oxide material (AB_2O_4, where A is a 2+ cation and B is a 3+ cation) is one of the attractive classes of metal oxides for gas sensing application, partly due to its stability under harsh environment [12–15]. In addition, replacing the A (or B) cation that occupies different sites at the crystal lattice with another transition metal may alter the catalytic properties of the resulting spinel oxide material [16,17]. This also makes spinel oxide become interesting to be explored and studied. Up to now, there are many spinel oxides that have been investigated as an SE material for YSZ-based sensors, aiming at detection of NO_x, NH_3 or H_2S [18–21]. However, there are few reports regarding the utilization of spinel oxide for CO detection. Although finding an oxide-SE that can detect CO sensitively is a challenging issue, most of reported YSZ-based CO sensors are using Au either as SE material [9,10] or as an additive [22–24] for oxide-SE material to obtain high CO sensitivity. In this study, the use of spinel oxide is proposed as an alternative material to replace the expensive Au as a CO sensitive SE-material for the YSZ-based sensor.

Detection of CO under harsh condition by using YSZ-based sensor attached with oxide-SE often poses difficulties not only in terms of sensitivity but also selectivity. The sensing signal toward CO generated by YSZ-based sensor is often interfered by the high responses to other gases, especially hydrocarbons [5,10,25–27]. One of the effective ways to obtain a selective CO response has been done by combining two SEs that can cancel out the unwanted responses to interfering gases, as reported before [22,23,28]. These facts have motivated us to study various spinel-oxide SE-materials and to obtain the best material that gives the highest response to CO. As a preliminary result, we have reported that CO selectivity can be achieved by pairing the CO-sensitive-spinel oxide sensing electrode with the appropriate counter electrode [29]. In this study, the detailed sensing characteristics as well as the sensing mechanism of the developed sensor were investigated.

2. Experimental

2.1. Sensor fabrication

The solid electrolyte of the developed sensor is a tubular type open-end YSZ (8 mol.% Y_2O_3-doped ZrO_2, Nikkato, Japan, 300 mm in length; 5 and 8 mm in inner and outer diameter, respectively). An intermediate YSZ (*i*-YSZ) layer that has been previously proposed [30], was fabricated to provide a good mechanical attachment between SE and YSZ. To fabricate this *i*-YSZ layer, the YSZ powder (8 mol.% Y_2O_3-doped ZrO_2, Tosoh, Japan) was mixed with an organic binder (α-terpineol) and the resulting paste was applied onto the surface of the YSZ tube. As for the SE layer, spinel-oxide powders (provided by Riken, Japan) were mixed with α-terpineol and the obtained paste was applied onto the surface of the *i*-YSZ layer. Since the single-SE sensor configuration necessitate a Pt/air reference electrode (RE), Pt paste (Tanaka Kikinzoku, Japan) was applied on the inner surface of the YSZ tube to form an RE layer. To finalize the sensor fabrication, each resulted sensor was dried at 100 °C overnight and sintered at 1000 °C for 2 h in air.

2.2. Evaluation of sensing characteristics

The obtained YSZ-based sensor was set inside a custom-made quartz cell which was connected to a sensor-testing system. A humidified base gas (21 vol% O_2 + H_2O + N_2 balance) or the humidified sample gas (CO, C_3H_8, C_3H_6, CH_4, NH_3, NO or NO_2, diluted with the base gas) at a constant flow-rate of 100 cm^3/min was alternately flowed into the sensor-testing chamber. The gas concentration was always set to 100 ppm, except for the measurements of CO concentration dependence of sensor response. The water-vapor concentration was also set to 1.3 vol%, except for the measurements of water-vapor concentration dependence of sensor response. For the single-SE sensor, the inner Pt electrode (Pt-RE) was always exposed to an ambient atmospheric air to form Pt/air-RE, while SE was exposed to the sample gas or the base gas. On the other hand, for the combined-SEs sensor, both electrodes were exposed to the same atmospheric conditions. The difference in potential between two electrodes (for the single-SE sensor: SE and Pt/air-RE, and for the combined-SEs sensor: SE-1 and SE-2) was recorded as a sensing signal (ΔV). The gas response was defined as follows:

$$\text{Gas response} = \Delta V_{sample\ gas} - \Delta V_{base\ gas} \quad (1)$$

2.3. Evaluation on catalytic properties of SE materials

To investigate the sensing mechanism, the measurements of polarization (I-V) curves were carried out by means of an electrochemical analyzer (Autolab®, PGSTAT30, Eco-Chemie, Netherlands), with a two-electrode configuration at a constant potential scan-rate of 2.5 mV/min. The modified cathodic polarization-curve was obtained by plotting the absolute current value (measured in base gas) against the applied potential. The modified anodic polarization-curve for CO (or C_3H_6) was obtained by subtracting the current value measured in base gas from that in each sample gas (diluted with base gas). In the case of the anodic polarization-curve in CO (or C_3H_6) diluted with N_2, the obtained anodic current value was plotted directly against the applied potential.

The gas-phase catalytic activity of the SE material was evaluated by using a cell with arrangement similar to that reported elsewhere [31]. The SE material powder (50 mg) was packed inside a quartz tube which was positioned as a separate cell (a catalyst cell). This catalyst cell was located at the upstream of the sensing cell. To monitor the change in the sample-gas concentration in the outlet gas exhausted from the catalyst cell, a YSZ-based gas sensor attached with Au-SE was used as a gas detector. This sensor using Au-SE has been reported to be sensitive to both CO and C_3H_6 [32,33].

2.4. Characterization of electrode materials

Each crystal structure of the SE materials was examined by means of an X-ray diffraction analysis system (XRD, RINT 2100VLR/PC, Rigaku, Japan), using Cu Kα X-ray source (λ = 1.5406 Å). To calibrate XRD patterns, an internal Si reference powder (RSRP-43275G, Rigaku, Japan) was incorporated into the powder samples. The morphology was observed by using a field-emission scanning electron microscope (SEM, JSM-6340F, JEOL, Japan), operating at 10 kV. The surface state was investigated by using an X-ray photoelectron spectrometer (AXIS-165, Kratos, UK) and Al Kα as the excitation source. Prior to analysis, the XPS spectra were calibrated with reference to C *1s* at a binding energy of 285 eV. The BET surface area was measured by using an automatic surface area analyzer