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Gas sensing property of the electrochemical cell with a multilayer catalytic electrode

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Abstract

We have developed a planar type NO_X sensor with a dense sensing layer that consists of nano-size grains and a reference electrode buried in an electrolyte by a pulsed laser deposition method, and examined for the mixed-potential-type NO_X sensor. This sensor shows a high NO sensitivity at low temperature (300–450 °C). Electromotive force (EMF) values were almost linear to the logarithm of NO concentration, and the response was reproducible. The magnitude of EMF response was about −90 mV upon exposure to 1000 ppm of NO at 350 °C. And, the 90% response and recovery times were found to be about 5 and 25 s at 450 °C, respectively. This cell opens up the possibilities for development of an integrated electrochemical device for NO_X gas treatment in combustion exhausts.

Keywords: Sensor; Nitrogen oxides; Electrochemical cell; Solid electrolyte

1. Introduction

Nitrogen oxides, NO and NO_2 are emitted together with H_xC_y and CO from diesel and lean-burning engines. Ozone (O_3), which is the principal toxic component of smog in large cities and a greenhouse gas, is produced through a photolytic decomposition of nitrogen oxide radicals (NO_X) by solar irradiation. NO_X is also harmful to the environment as it contributes to the acid rain [1,2]. Therefore, there has been a great demand for an effective method of the purification of the exhaust gases.

Nitrogen oxides (NO_X) gases have a deleterious impact on the environment as well as human and animal health. Lean-burn gasoline and direct-injection diesel engines have been developed to improve fuel efficiency as well as to reduce CO_2 emission form engine, but their development is prevented by their high NO_X emissions. In these engine systems, recently developed NO_X adsorber-catalyst should be used in order to compensate for the low NO_X removal ability of the conventional three-way catalyst under the oxygen rich condition. In a complete control of this catalyst system, a reliable and responsive NO_X sensor for the on-board diagnostic (OBD) system is required to detect the leakage of NO_X from the NO_X adsorber-catalyst in lean exhaust and signal the need for catalyst regeneration, such as its selective catalytic reduction with HC [3,4] or NH_3 [4–6]. The OBD system is a closed-loop system, mounted on each automobile, to continuously monitor the pollutant concentrations in the exhausts. At present, the solid-state NO_X sensor normally uses a two-chamber O_2-pumping potentiometric gas sensor [7–11] for OBD system, which is very expensive in mass production. Meeting the stringent requirements of the automobile industry in terms of manufacturing cost and sensitivity, cheap and innovative gas sensing devices need to be developed.

Recently, we have developed a new type of electrochemical cell with a functional multilayer cathode and achieved drastic improvements of selective NO_X reduction in the presence of excess O_2 [12–16]. This reactor can be represented by the following cell arrangement: YSZ|Pt|NiO-YSZ (Catalytic layer)|YSZ|Pt+YSZ. The multilayer cathode includes a NO_X selective catalytic layer whose structure was designed to generate self-

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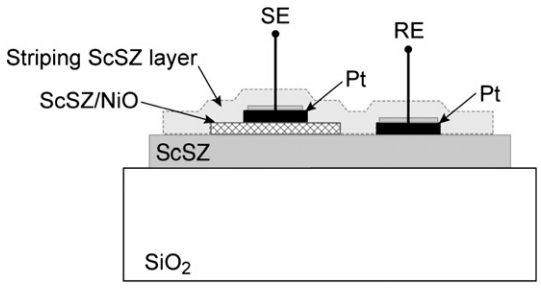

Fig. 1. Schematic image of the prepared electrochemical cell for NO_X detection.

assembled nano-pores and nano-Ni particles in the vicinity of NiO-YSZ interfacial regions by the cell operation. The catalytic layer provides a way to suppress the unwanted reaction of O_2 gas decomposition, resulting in increasing the efficiency of NO decomposition. The cell showed that the decomposition selectivity of NO molecule was over 4.5 times higher than oxygen gas molecule at around 500 °C [14,16]. Taking advantages of the high NO selectivity in the self-assembled catalytic layer for a sensing electrode, we have evaluated the gas sensing properties of the electrochemical cell with simple arrangement of electrodes. As a result, the response speed was slow though the reactor had shown high sensitivity to NO_X [17]. In this research, to improve the response speed, the cell that had a new thin multilayer sensing electrode was fabricated by the pulsed laser deposition method and evaluated.

2. Experimental

The electrochemical cell with an improved configuration of multilayer sensing electrode (ML-SE) for detection of NO gas in the presence of excess O_2 was fabricated as represented in Fig. 1. Electrochemical cells with a ML-SE were deposited on a SiO_2 substrate by the pulsed laser deposition method using a patterned metal mask. ScSZ (10 mol% Sc_2O_3 doped ZrO_2) was selected as a solid electrolyte of the cell. First, ScSZ electrolyte layer was deposited on the surface of SiO_2 substrate. The mixed oxide of ScSZ/NiO with 50 mol% of NiO were deposited on the ScSZ electrolyte layer as the sensing layer with width and spacing of 1 and 1 mm, respectively. Then the Pt electrodes were deposited on the sensing layer and the ScSZ electrolyte layer for sensing electrode and reference electrode (RE) with width and spacing of 0.5 and 0.5 mm, respectively. After that, thin ScSZ cover layer were deposited on the Pt electrodes with width and spacing of 0.4 and 0.6 mm. Finally, ScSZ was deposited as a cover layer to prepare a striped pattern cross over the cells. ScSZ and ScSZ/NiO with 50 mol% of NiO composite target pellets were fabricated from powders synthesized by conventional solid-state reaction. The Pt target (a 99.99% purity metal foil) was used for electrodes. The deposition was performed using a pulsed Nd-YAG laser (λ=355 nm) at a repetition rate of 10 Hz, with the pulse energy ranging from 200 to 210 mJ/pulse. Prior to each irradiation the vacuum chamber was evacuated down to a residual pressure of 2×10^{-6} Torr. All of the depositions were carried out at the same substrate-to-target distance (5 cm). Depending on the targets used for the depositions, the substrate temperature and the deposition environment were modified accordingly. In the case of both electrolyte layer (ScSZ) and catalytic layer (ScSZ/NiO) were deposited under a fixed condition; substrate temperature (T_S)= 600 °C and oxygen partial pressure (P_O)=70 mTorr, whereas, Pt electrode layer was deposited in residual pressure at T_S=200 °C without changing other deposition parameters.

Electrochemical cell was set in the quartz tube placed in the furnace and connected to a digital multimeter (Keithley 2700), which was fitted with an IEEE interface to permit automatic data logging via a computer. The sensing performances of mixed-potential-type gas sensor were evaluated in the temperature range of 300–450 °C. The sample gases containing various concentrations of NO were prepared by diluting parent standard gases (3000 ppm NO in N_2) with dry N_2 and O_2. The total flow rate of the sample gas or the base gas was adjusted at 300 ml/min. Mass flow controllers were employed to obtain an accurate gas mixture of NO, O_2 and N_2. The difference in potential (electromotive force: EMF) between ML-SE and RE was measured by means of a digital multimeter as a sensing signal of the mixed-potential-type sensor when the cell was exposed to the base gas or to the sample gas with different NO_X concentrations. The concentrations of NO and O_2 in the sample gas were monitored using an on-line NO_X (NO, NO_2 and N_2O) gas analyser (Best Instruments BCL-100uH, BCU-100uH) and a gas chromatograph (CHROMPACK Micro-GC CP 2002), respectively.

3. Results and discussion

We have developed a planar type NO_X sensor with a dense sensing layer that consists of nano-size grains and a reference electrode buried in an electrolyte by a pulsed laser deposition method.

Fig. 2 shows a photograph of the sensor array with the ML-SE. The sensor is composed of the translucent thin layer of electrolyte and sensing electrode. In addition, the better part of sensor was covered with striping dense ScSZ layer. Fig. 3 shows the SEM micrograph of the cross-sectional view of the part of ML-SE in the cell. The sensing electrode consists of nano-size

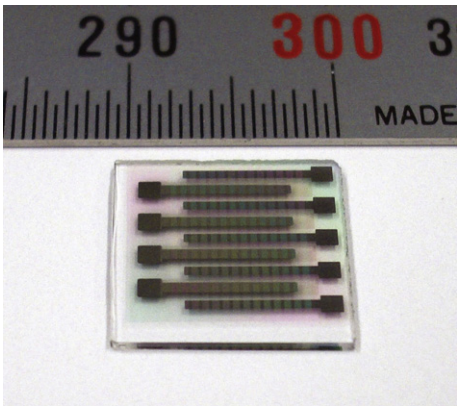

Fig. 2. Photograph of the sensor array with the multilayer sensing electrode.