Electrochimica Acta 155 (2015) 8–15

Contents lists available at ScienceDirect

Electrochimica Acta

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

CO-sensing properties of a NASICON-based gas sensor attached with Pt mixed with Bi_2O_3 as a sensing electrode

Hirotaka Takeda, Taro Ueda, Kai Kamada, Katsuhide Matsuo, Takeo Hyodo, Yasuhiro Shimizu *

Graduate School of Engineering, Nagasaki University, 1-14 Bunkyo-machi, Nagasaki 852-8521, Japan

ARTICLE INFO

Article history:
Received 9 October 2014
Received in revised form 23 December 2014
Accepted 30 December 2014
Available online 3 January 2015

Keywords:
gas sensor
carbon monoxide
solid electrolyte
NASICON

ABSTRACT

NASICON ($Na_3Zr_2Si_2PO_{12}$)-based gas sensors capable of detecting various gases (CO_2, NO_2, Cl_2, VOC and so on) have so far been developed by many researchers. In this study, planar-type gas sensors using a NASICON disc attached with Pt mixed with Bi_2O_3 as a sensing electrode (Pt($n$$Bi_2O_3$), n (*0.01~30*): the amount of Bi_2O_3 addition (wt%)) and Pt as a reference electrode were fabricated, and their sensing properties to CO and H_2 were examined in the operating temperature range of 25~300 °C in dry and wet air. The sensors obtained were denoted as Pt($n$$Bi_2O_3$)/Pt. All Pt($n$$Bi_2O_3$)/Pt sensors fabricated responded to CO at all operating temperatures tested, and the magnitude of CO response increased with a decrease in the operating temperature. In addition, the magnitude of CO response largely depended on the additive amounts of Bi_2O_3 to the Pt sensing electrode. The increase in the additive amount of Bi_2O_3 to the Pt sensing electrode ($0.01 \leq n \leq 1$) enhanced markedly the magnitude of CO response, 90% response time and CO selectivity against H_2. The Pt(*1*Bi_2O_3)/Pt sensor showed a linear relationship between the CO response and the logarithm of CO concentration (1~3000 ppm) in dry air at 25 °C and the CO selectivity against H_2 was enhanced in wet air, in comparison with those observed in dry air. The interfacial layer, which was formed between the NASICON and the Pt(*1*Bi_2O_3) electrode, was suggested to play an important role in improving of the CO-sensing properties.

1. Introduction

Various types of gas sensors (e.g., semiconductor type [1,2], diode type [3–5], catalytic-combustion type [6] and solid-electrolyte type [7–23]) have been widely investigated and developed to detect various gases such as volatile organic compounds (VOCs) [7,8], carbon monoxide (CO) [1,2,6,9,10] and hydrogen (H_2) [5,11,12] under different atmospheres. They have contributed to forestall various serious troubles to human beings, such as sick building syndrome (for VOC), difficulty of breathing (for CO) and explosion accidents (for H_2). Among them, the solid-electrolyte gas sensors have advantages, since they can detect some kinds of gases selectively and sensitively, by optimization of the composition and microstructure of the gas-sensing electrodes as well as the electrolyte. NASICON ($Na_3Zr_2Si_2PO_{12}$) is well-known as a promising electrolyte which shows relatively high ionic conductivity at low temperatures (e.g., 5.2×10^{-2} S m^{-1} at RT [24]), and thus many efforts have recently directed to developing the NASICON-based gas sensors which can detect various gases, such as SO_2 [13], CO_2 [14–16], NO_2 [17,18], VOCs, [8], NH_3 [19] and Cl_2 [20]. For example, Obata et al. have demonstrated that a NASICON-based gas sensor using $NaNO_2$-Li_2CO_3 mixed with ITO powders as a sensing electrode material showed stable response to NO_2 without interference of humidity even at RT and the response to NO_2 was proportional to the logarithm of NO_2 concentration [18]. Kida et al. reported that a NASICON-based gas sensor using $Bi_2Cu_{0.1}V_{0.9}O_{5.35}$ as an electrode material could detect VOCs such as ethanol, formaldehyde and toluene [8]. Lu et al. have reported that a NASICON-based gas sensor using Cr_2O_3 as a sensing-electrode material showed the high sensitivity to Cl_2 at 300 °C [20]. We have also reported that the compositional and morphological optimizations of the Li_2CO_3-$BaCO_3$ auxiliary layer coated onto the sensing electrode of NASICON-based gas sensors were quite effective in improving the CO_2 sensitivity [15,16]. As described above, different NASICON-based sensors have been already investigated for the detection of various gases, but little effort has been directed to developing NASICON-based CO gas sensors. CO is colorless, odorless and badly hazardous to human health, and especially it exerts a negative impact on the respiratory system due to its strong associativity with hemoglobin in the blood [25]. Namely, even the

* Corresponding author. Tel.: +81 95 819 2642; fax: +81 95 819 2643.
E-mail address: shimizu@nagasaki-u.ac.jp (Y. Shimizu).

http://dx.doi.org/10.1016/j.electacta.2014.12.168
0013-4686/

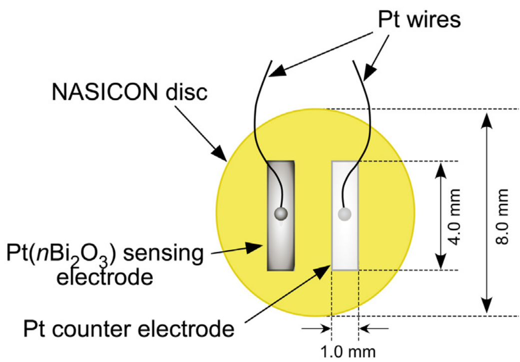

Fig. 1. Schematic structure of a NASICON-based planar gas sensor.

small amount of CO (500 ppm) causes various symptoms such as headache, dizziness and nausea, and an increase in the CO concentration more than 1500 ppm possibly results in death for almost animate beings. Such CO is easily produced from incomplete combustion of fossil fuels used in automobiles, power plants and industrial plants, and therefore high-performance CO sensors, which can detect the low concentration of CO sensitively and selectively, are indispensable for operating them safely and effectively. Recently, we have found that the NASICON-based gas sensor attached with Pt- and/or Au-based electrodes can detect CO at low temperatures and the addition of Bi_2O_3 powder to the electrodes was the most important factor for the detection of CO [21,22].

In this study, therefore, the effects of the addition of Bi_2O_3 powder to a Pt electrode on the CO sensitivity and selectivity of the NASICON-based gas sensors have been investigated in detail at 25~300 °C in dry and wet air.

2. Experimental

2.1. Synthesis of NASICON and Bi_2O_3 powders

NASICON powder was synthesized from $Si(OC_2H_5)_4$, $Zr(OC_4H_9)_4$, $PO(OC_4H_9)_3$ and $NaOC_2H_5$ by sol-gel process [15,16,26]. The above metal alkoxides in stoichiometric ratios were first dissolved in pure water, together with an equimolar amount of citric acid. The mixture was subjected to heat treatment at 80 °C to prepare an organic metal complex, followed by an overnight drying at 120 °C. Then, the resultant solid was pyrolyzed at 750 °C for 5 h. The precursor obtained was finally calcined in air at 1100 °C for 4 h. Bi_2O_3 powder was synthesized by using the procedure reported in the literature [23] as follows. After $Bi(NO_3)_3{\cdot}5H_2O$ was fully dissolved in 1.12 M HNO_3 aqueous solution, polyvinyl pyrrolidone was added to the solution as a stabilizing agent and then they were stirred for 15 min. The resultant solution was slowly and continuously dropped into 0.2 M NaOH solution under constant stirring, until the pH reached 11. After further stirring for 5 min, the resultant suspension was sonicated at 28 kHz for 30 min. The precipitate was centrifuged and washed with pure water for several times. The resultant product was dried at 80 °C for 2 h and then annealed at 500 °C for 2 h.

Crystal structure of these materials synthesized was analyzed by X-ray diffraction (XRD, RINT2100; Rigaku Corp.) with CuKα radiation. And their crystallite size was calculated from Scherrer equation. Specific surface area of the Bi_2O_3 powder was measured by Brunauer–Emmett–Teller (BET) method using a N_2 adsorption isotherm (Micromeritics Instruments Corp., Tristar3000), and its microstructure was observed by scanning electron microscopy (SEM; JEOL Ltd. JSM-7500F).

2.2. Sensor fabrication

The schematic structure of a NASICON-based planar sensor is shown in Fig. 1. Both Pt paste (Tanaka Corp., TR-7907) mixed with the Bi_2O_3 powder and just Pt paste were applied on the same surface of the NASICON disc as a sensing and a counter electrode by screen printing, respectively, and then they were annealed at 700 °C for 30 min. The electrode fabricated from the Pt paste mixed with the Bi_2O_3 powder was denoted as Pt(nBi$_2$O$_3$) (the amount of the Bi_2O_3 added to Pt (n): *0.01~30* wt%), and the sensor obtained was denoted as M/N (M: Pt(nBi$_2$O$_3$) sensing electrode, N: Pt counter electrode). The secondary electron image (SEI) and backscattered electron image (BEI) of the cross-section of the Pt (nBi$_2$O$_3$)/Pt sensors were observed by SEM, and the composition of the electrode/NASICON interface was analyzed with the energy-dispersed spectroscope (EDS; JEOL Ltd. JED-2300) equipped with SEM.

2.3. Measurement of gas-sensing properties

Gas response of the sensors obtained was measured to 1~3000 ppm CO and 300 ppm H_2 balanced with dry or wet (relative humidity: 30 or 60%RH on a basis of the saturated water vapor value at 25 °C) air in a flow apparatus (gas-flow rate: 100 cm^3 min^{-1}) at 25 °C, 100 °C and 300 °C. The electromotive force (EMF, mV) of the sensors was measured with a digital electrometer as a sensing signal. The magnitude of response was defined as the difference in EMF between in a sample gas and in base air (ΔEMF_{Gas}, Gas: CO or H_2). The CO selectivity against H_2 was defined as the ratio of CO response to H_2 response ($\Delta EMF_{CO}/\Delta EMF_{H2}$).

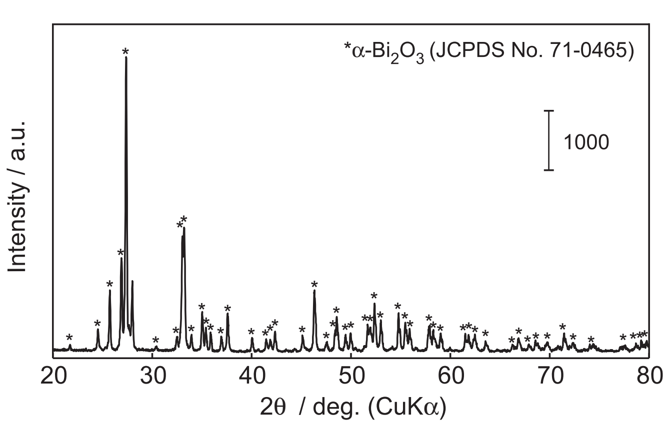

Fig. 2. XRD pattern of the Bi_2O_3 powder annealed at 500 °C for 2 h.

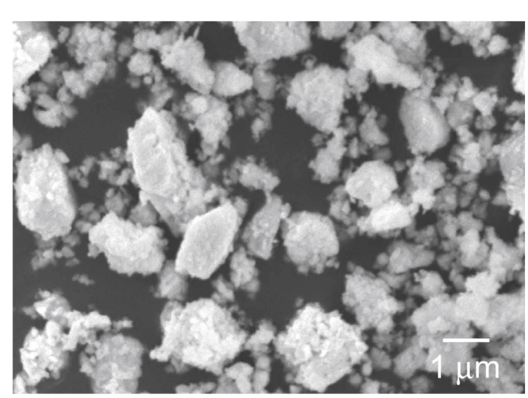

Fig. 3. SEM photograph of the Bi_2O_3 powder annealed at 500 °C for 2 h.