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Challenges for the Development of Toxic Gas Sensors by Employing Semiconductors and Solid Electrolytes

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Abstract

The present paper reports at first our recent research work directed to improving NO_2 sensing properties of In_2O_3 sensors by controlling pore structure inside In_2O_3 particles by fully utilizing ultrasonic spray pyrolysis of its precursor solution containing a polymer template. Other research results to be pronounced are high CO sensing performance of two kinds of solid electrolyte gas sensors, potentiometric anion-conducting polymer and NASICON sensors. For both sensors, high CO response and CO selectivity against H_2 at room temperature even in humid environment could be achieved by the compositional design of the sensing electrodes.

Key words: NO_2 sensor, CO sensor, In_2O_3, Anion-conducting polymer, NASICON

Introduction

Quick detection of toxic gases, such as NO_2 and CO, is of primary importance from the viewpoint of safety in many industrial processes as well as our daily life. We have so far been trying several approaches to improve toxic gas sensing properties. The present paper reports our recent research results on semiconductor NO_2 sensors fabricated with porous In_2O_3 powder [1] and solid electrolyte CO sensors fabricated with an anion-conducting polymer [2] or NASICON [3].

Experimental

Porous In_2O_3 (pr-In_2O_3) powders were prepared by ultrasonic spray pyrolysis of precursor $In(NO_3)_3$ aqueous solutions containing given amounts of commercially available or our own synthesizing polymethylmethacrylate (PMMA) microspheres as a template. Microstructure of pr-In_2O_3 was controlled by the size of PMMA microspheres used and the spray pyrolysis conditions [1]. Typical microstructure of pr-In_2O_3 particles is shown in Fig. 1. Thick film sensors were fabricated by screen printing of the pr-In_2O_3 paste on an alumina substrate equipped with a pair of interdigitated Pt electrodes, followed by calcination at elevated temperature. NO_2 gas response properties were measured in a flow apparatus. The magnitude of NO_2 response was defined as the ratio (R_g/R_a) of the sensor resistance in NO_2 balanced with air (R_g) to that in air (R_a).

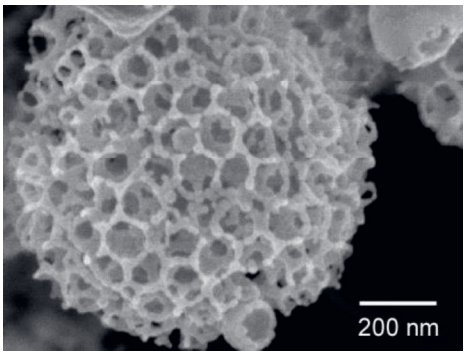

Fig. 1 SEM photograph of pr-In_2O_3 particles.

Anion-conducting polymer (ACP) sensors were fabricated by applying the noble metal-loaded oxide paste, as sensing and counter electrodes, on the surface of both sides of an ACP membrane, followed by drying at 50°C in air [2]. The sensor fabricated was sandwiched with Au meshes as a current collector, and then the electromotive force (E) generated between two electrodes was measured by exposing the sensing electrode to the CO or H_2 sample gases balanced with air at 30°C, whereas the counter electrode was always kept in air environment. The effect of relative humidity on the CO response properties was tested.

NASICON-based sensors were fabricated basically by applying both Pt paste mixed with a metal oxide and pristine Pt paste on the same side of the NASICON disc as a sensing and a

counter electrode, respectively, followed by annealing at 700°C in air [3]. The change in electromotive force generated between two electrodes induced by the exposure of both two electrodes to CO or H_2 sample gases from base air was measured under different conditions. The effect of relative humidity on the CO response properties was also tested.

Results and Discussion

Figure 2 shows variations in NO_2 response and 90% response time of two kinds of pr-In_2O_3 sensors with operating temperature [1]. Here, pr-In_2O_3(*1100*) and pr-In_2O_3(*1100*)S were fabricated with the powders prepared with ca. 77 and 26 nm diameter PMMA microspheres, respectively, but at the same pyrolysis temperature of 1100°C. For comparative purpose, results obtained with the sensor (c-In_2O_3(*1100*)) fabricated with solid In_2O_3 particles prepared without PMMA microspheres, but under the same pyrolysis conditions, are also depicted in the same figure. From the results shown in Fig. 2, we could confirm the usefulness of the introduction of porous structure inside the In_2O_3 particles in enhancing the NO_2 response especially around 200°C, along with improved response time. Further improvement of gas sensing properties may be realized by the simultaneous introduction of mesopores into the skeleton of the macroporous In_2O_3 particles (see Fig. 1).

The ACP sensor {EC(Au/SnO_2(400air))} equipped with 2 wt% Au loaded SnO_2 (fired at 400°C in air) showed high CO response and excellent CO selectivity against H_2 at 30°C even in wet air environment, as shown in Fig. 3, along with acceptable response and recovery behavior. The selection of both the kinds of metal oxides and noble metals used for

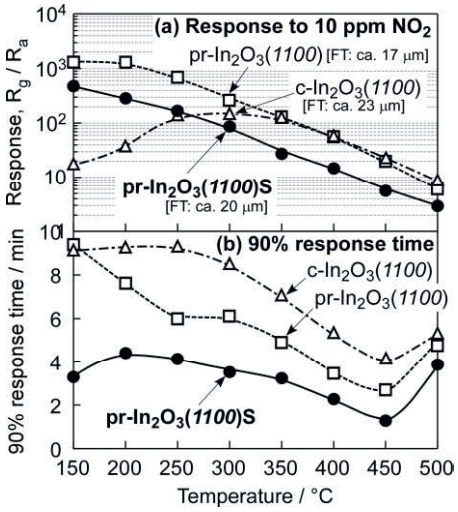

Fig. 2 Variations in (a) response to 10 ppm NO_2 and (b) 90% response time of threel In_2O_3 sensors with operating temeprature. FT: thickness of In_2O_3 films.

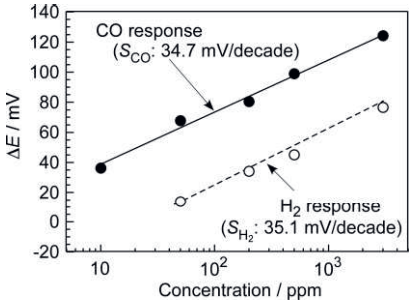

Fig. 3 Concentration dependece of CO and H_2 responses of EC(Au/SnO_2(400air)) in wet air (57%RH) at 30°C.

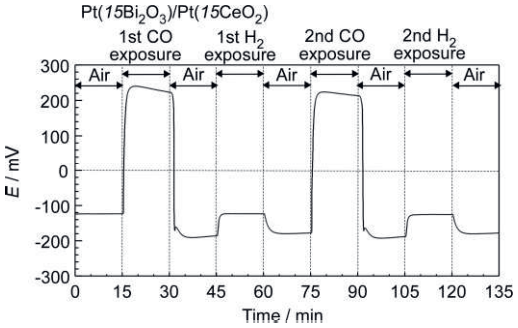

Fig. 4 Response tramsients of Pt(15Bi_2O_3)/ Pt(15CeO_2) to 300 ppm CO and 300 ppm H_2 at 25°C.

electrodes and strict control of their preparation conditions were found to be key factors in determining CO sensing performance. The measured potential is considered to be determined by the mixed potential resulting from anodic and cathodic reactions.

The direction of a potential shift (positive or negative) of NASICON-based sensors upon exposure to CO was dependent upon the kind of metal oxides added to the Pt-based sensing electrodes, while the pristine Pt counter electrode remained unchanged. The positive shift was observed by the addition of Bi_2O_3 or La_2O_3, but the negative shift in the case of CeO_2 or V_2O_5. By considering these results, we could realize much improved CO response and then CO selectivity against H_2 with the sensor {Pt(*15*Bi_2O_3)/Pt(*15*CeO_2)} equipped with 15 wt% Bi_2O_3 added Pt sensing and 15 wt% CeO_2 added Pt counter electrodes, as shown in Fig. 4. Other pronounced futures of this type of sensors will be delivered in the presentation.

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