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Sensor Properties of Series-connected Mixed-potential H_2 Gas Sensor

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Mixed-potential gas sensors with an anhydrous electrolyte consisting of zinc metaphosphate glass and benzimidazole were fabricated for the detection of hydrogen. Using a combination of similar sensor units connected in series, a strategy for measuring sub-ppm-level hydrogen has been demonstrated. The sensor unit consisted of an electrolyte membrane and an alumina substrate with platinum and gold electrodes. A sensor array with 7 sensors connected in series showed a response to the H_2 gas, even at 1 ppm. The sensitivities of the single sensor and 7-sensor array were −0.57 and −3.54 mV/ppm, respectively. By connecting sensors in series, the sensor response and sensitivity were improved.

1. Introduction

Mixed-potential gas sensors using yttria-stabilized zirconia (YSZ) electrolytes have been studied with the aim of detecting hydrogen, carbon monoxide, nitric oxide, ethanol, and methane in atmosphere.[1–5] These sensors must be operated at high temperatures of 500 °C or higher to ensure sufficient electrical conductivity in the YSZ and to bring about reactions with the detected gases. It is not problematic when operating these sensors in atmosphere above 500 °C, but heaters are required to maintain the temperature of these sensors above 500 °C when operating in atmosphere ranging from room temperature to intermediate temperature, resulting in these sensor devices consuming a large amount of energy. To resolve the aforementioned issue, mixed-potential gas sensors have been developed using proton-conducting electrolytes such as zirconium phosphate hydrate and antimonic acid hydrate, which have high electrical conductivity at room temperature, to reduce the operating temperature.[6–9] However, these electrolytes are crystal hydrates, which makes the gas sensor response characteristics prone to change depending on the humidity in gas atmosphere. Since the proton conduction of these electrolytes is promoted by the dissociation of protons from –OH groups and proton jumping between –OH groups and water molecules, the gas sensor operating temperature is limited to a value below 90 °C.

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We reported a mixed-potential gas sensor using anhydrous electrolytes with high proton conductivity in the intermediate temperature range.[10] These electrolytes use zinc metaphosphate glass and benzimidazole as the starting material and have no water molecules. Therefore, we confirmed that a mixed-potential gas sensor using these electrolytes has no significant difference in sensor response at 100–140 °C in dry and high-humidity atmospheres. This sensor also responded to 250–25000 ppm hydrogen and carbon monoxide, with high hydrogen selectivity against carbon monoxide. However, the sensor sensitivity was low, as the sensor response was problematic at concentrations lower than 250 ppm.

Mondal *et al*. reported that arranging a sensor array connecting mixed-potential gas sensors using YSZ in series increased the sensor sensitivity.[11] Mixed-potential gas sensors utilize the electromotive force generated between the reference electrode and the sensing electrode; thus, the sensor response increases when they are connected in series. If the sensor response increases, the sensor sensitivity at low concentrations would also be expected to increase.

In this study, we conducted an evaluation with a polarization curve to ascertain if a mixed-potential gas sensor using anhydrous electrolytes derived from zinc metaphosphate glass and benzimidazole is a sensing mechanism using mixed potential. Moreover, we also investigated whether the sensor sensitivity is increased by arranging the mixed-potential gas sensor in a series sensor array.

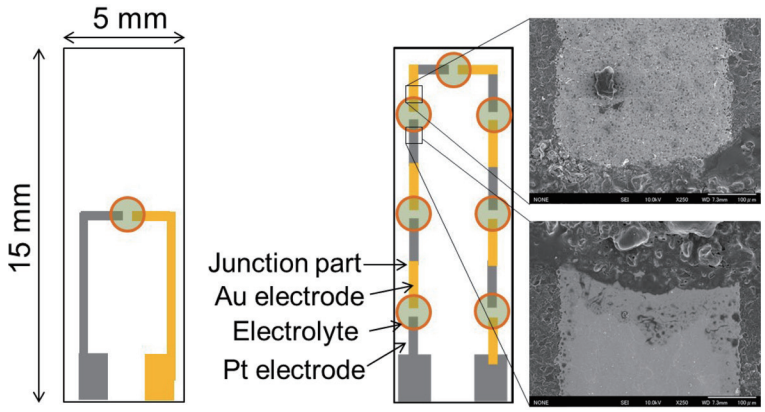
2. Materials and Methods

The electrolyte was obtained as follows. Zinc metaphosphate glass (ZP) was prepared by melting a batch mixture of ZnO and H_3PO_4 in a Pt crucible at 1100 °C in air atmosphere for 30 min. The melt was poured onto an iron plate and quenched by iron pressing to make glass flakes. The glass flakes were milled using an alumina mortar and pestle to a diameter below 100 μm. A powder mixture containing 25 wt% glass powder and 75 wt% benzimidazole (B) was heated at 170 °C for 12 h to prepare the electrolyte (ZP-B) in an airtight vessel. The sample structure was evaluated by ^{31}P magic angle spinning nuclear magnetic resonance (MAS-NMR). The ^{31}P MAS-NMR spectrum was measured at room temperature with a Varian INOVA-300 spectrometer using a Doty probe operating at 121 MHz, with a spinning speed of 7 kHz, a delay time of 60 s, and a pulse length of 5.2 μs.

ZP-B was placed on an alumina substrate (5 × 15 mm^2) with gold and platinum electrodes of 1 mm gap and 1 mm width. The ZP-B-placed substrate was heated at 170 °C, and then a ZP-B membrane was formed on the substrate. Figure 1 shows schematic illustrations of a single sensor and a 7-sensor array. A Au electrode was coated on a Pt electrode in the Pt and Au junction part of the series-connected sensor. The Pt and Au junction part area is about 1 × 1 mm^2.

The sensor element was placed in a test chamber heated to 120 °C in an electrical tube furnace. Synthetic dry air (80 vol% N_2, 20 vol% O_2) was introduced into the chamber for 10 min, and a gas mixture of H_2 in dry air was then injected for 10 min at a flow rate of 200 mL/min. The H_2 gas concentration was controlled to values of 1 to 25000 ppm in dry air.

To clarify the sensing mechanism, polarization curves were measured for 0, 2500, 10000,



(a) (b)

Fig. 1. (Color online) Schematic illustrations of (a) single sensor and (b) 7-sensor array.

17500, and 25000 ppm H_2 in dry air by controlling the potential of the Pt electrode vs the Au electrode with a potentio/galvanostat (VersaSTAT4; Princeton Applied Research). The potential difference [electromotive force (*EMF*)] between the Pt and Au electrodes of the sensor element was also recorded using a potentio/galvanostat. During the measurements, the Pt electrode was always connected to the positive terminal of the potentio/galvanostat. The *EMF*s of the sensor in the air and gas mixtures are denoted as V_a and V_g, respectively. The sensor response (ΔEMF) is defined as $\Delta EMF = V_g - V_a$.

3. Results and Discussion

Figure 2 shows ^{31}P MAS-NMR spectra of ZP and ZP-B. In the spectrum of ZP, a broad peak is confirmed mainly close to −28 ppm, which is assigned to the Q^2 group (the PO_4 tetrahedron bond is the Q^n unit and n is the number of bridging oxygens to the neighboring tetrahedral).[12,13] ZP has a long phosphate chain structure consisting of the Q^2 group. In the spectrum of ZP-B, two peaks are confirmed to be assigned to the Q^0 and Q^1 groups due to the orthophosphate and end phosphate groups, respectively, which were not seen in ZP. In hybrids made of ZP and water, the breaking of the phosphate chain structure occurred because of water molecules resulting in the formation of the Q^0 and Q^1 groups. Since Q^0 and Q^1 increased in the hybrids, the proton conductivity also increased.[14] The flash point of B is 143 °C and the melting point is 170 °C.[15] When a mixture of ZP and B was held at 170 °C for 12 h to obtain ZP-B, the breaking of the phosphate chain structure of ZP occurred because of the liquified B with high proton activity resulting in the formation of the Q^0 and Q^1 groups. These Q^0 and Q^1 enable ZP-B to have a higher proton conductivity than ZP or B alone. Therefore, ZP-B showed a proton conductivity of 10^{-6}–10^{-3} S/cm at intermediate temperatures.[16] The observed high conductivities were suggested to originate from proton conduction due to coexistence with large numbers of acidic P–OH groups and benzimidazole molecules.

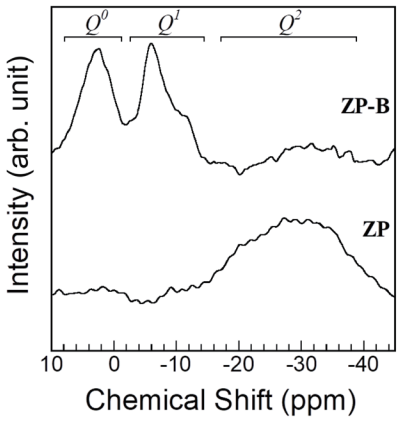


Fig. 2. ^{31}P MAS-NMR spectra of ZP and ZP-B.

Figure 3 shows the 2500–25000 ppm hydrogen gas response characteristics of a mixed-potential gas sensor using ZP-B. The *EMF* of the sensor decreased with the inflow of hydrogen gas and the amount of *EMF* reduction increased with increasing hydrogen gas concentration. The *EMF* is dependent on the following electrochemical oxidation and reduction reactions generated by the Pt and Au electrodes: $H_2 \rightarrow 2H^+ + 2e^-$, $(1/2)O_2 + 2H^+ + 2e^- \rightarrow H_2O$. Mixed potential occurs with the equalization of the electron response rate due to H_2 oxidation and O_2 reduction. The H_2 oxidation response rate differs at the Pt and Au electrodes, and the mixed potential generated at each electrode also differs. Therefore, the *EMF* changes depending on the hydrogen gas concentration. The *EMF* 10 min after the inflow of each hydrogen gas is as follows: 2500 ppm: 84 mV, 10000 ppm: 13 mV, 17500 ppm: −29 mV, and 25000 ppm: −65 mV. Figure 4 shows the polarization curves of the ZP-B gas sensor in air and in 2500–25000 ppm hydrogen gas. When the voltages from the intersection point of the polarization curve in air and the polarization curve in 2500–25000 ppm hydrogen gas were calculated, the results were 2500 ppm: 88 mV, 10000 ppm: 3 mV, 17500 ppm: −23 mV, and 25000 ppm: −66 mV. These voltages are equivalent to the mixed potential given that these values are in good agreement with the *EMF* voltages from the gas sensor response characteristics shown in Fig. 3. Therefore, the operating principle of the gas sensor using ZP-B was similar to that of a typical mixed-potential gas sensor using YSZ.

Figure 5 shows the 1–25 ppm hydrogen gas response characteristics of a single sensor and a 7-sensor array using ZP-B. With the single sensor, there was no response to 1 ppm hydrogen gas. Δ*EMF*s were 10 ppm: −5.5 mV, 17.5 ppm: −9.2 mV, and 25 ppm: −14.1 mV. With the 7-sensor array, a response to 1 ppm hydrogen gas was found. Δ*EMF*s were 1 ppm: −1.8 mV, 10 ppm: −34.4 mV, 17.5 ppm: −60.7 mV, and 25 ppm: −86.8 mV, indicating that the Δ*EMF*s of the 7-sensor array were 6 to 7 times greater than that of the single sensor. Since the gas sensor using ZP-B has the operating principle of a mixed-potential gas sensor, it is considered that the increased sensor response effect appeared because of the series sensor array structure.

Figure 6 shows the relationship between Δ*EMF* and H_2 gas concentration. A good linear relationship between Δ*EMF* and gas concentration was observed in both the single sensor and

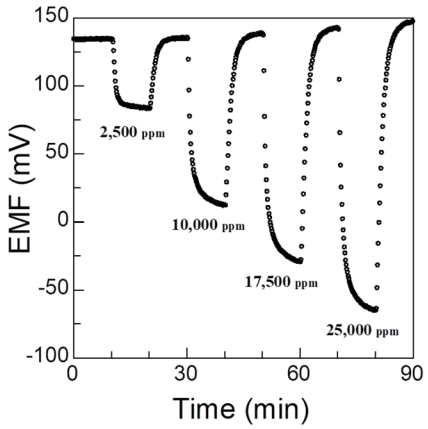


Fig. 3. 2500–25000 ppm hydrogen gas response characteristics of a mixed-potential gas sensor using ZP-B.

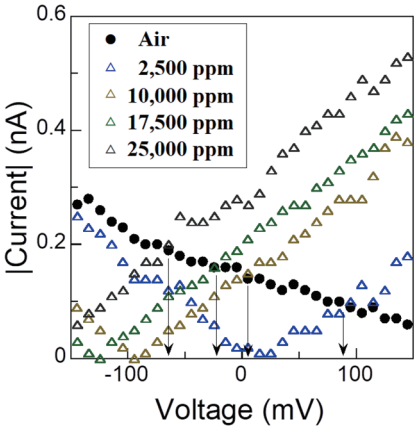
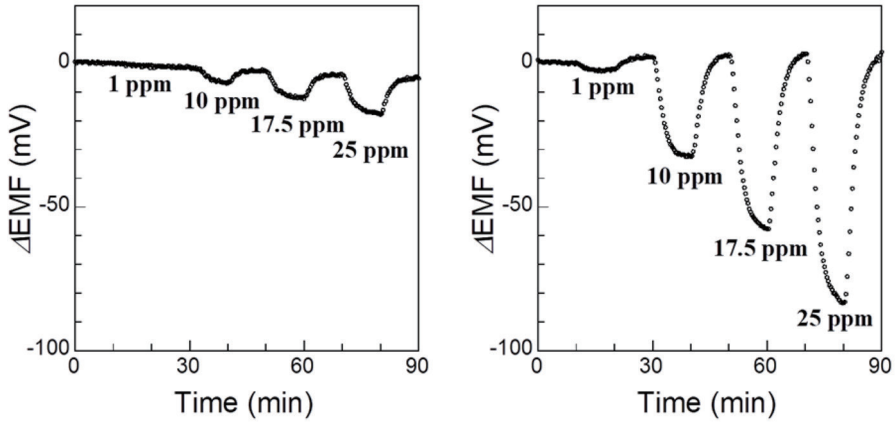


Fig. 4. (Color online) Polarization curves of the ZP-B gas sensor in air and in 2500–25000 ppm hydrogen gas.



(a) (b)

Fig. 5. 1–25 ppm hydrogen gas response characteristics of (a) single sensor and (b) 7-sensor array using ZP-B.

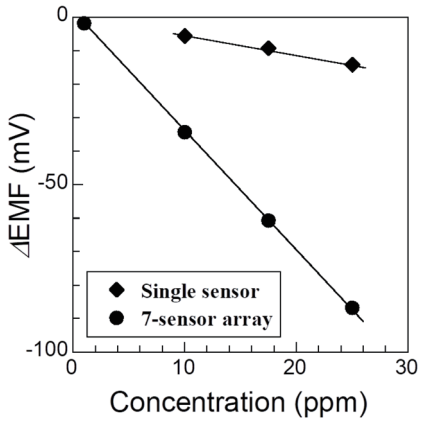


Fig. 6. Relationship between ΔEMF and H_2 gas concentration.

the 7-sensor array. This is considered to be due to the concept of diffusional mass transport limitation proposed by Garzon *et al*.[2] When the sensor sensitivity was calculated from the slope of the straight line, the results were single sensor: −0.57 mV/ppm and 7-sensor array: −3.54 mV/ppm, indicating that the sensor sensitivity of the 7-sensor array is 6.2 times higher than that of the single sensor. The 7-sensor array did not reach the ideal 7-fold sensitivity owing to differences in sensor responsiveness between the single sensors that make up the 7-sensor array. Since the series sensor array used in this study used a method of arranging the ZP-B electrolytes on an alumina substrate with the Pt and Au electrodes, the number of sensors in the series sensor array can be easily controlled. Increasing the number of sensors would be expected to enable gas sensing at even lower concentrations. We will investigate the difference in selectivity between a single sensor and a 7-sensor array in the future.

4. Conclusions

In this study, we have investigated the responses of a series-connected mixed-potential gas sensor using anhydrous electrolytes derived from zinc metaphosphate glass and benzimidazole. ZP-B had orthophosphate and end phosphate groups. The observed high conductivities were suggested to originate from proton conduction due to coexistence with large numbers of P−OH groups and benzimidazole molecules. The 7-sensor array showed a response in the presence of 1 ppm hydrogen. The sensor response and sensitivity of the 7-sensor array were roughly seven times higher than those of the single sensor.

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