Carbon Dioxide Gas Sensing with the Combination of Divalent Magnesium Ion and Oxide Ion Conducting Solid Electrolytes

Nobuhito Imanaka, Takao Yamamoto, and Gin-ya Adachi*

Department of Applied Chemistry, Faculty of Engineering, Osaka University, 2-1 Yamadaoka, Suita, Osaka 565-0871

The main gas species causing the global warming of the earth is carbon dioxide (CO_2) and the human race must seek for the solution to suppress the continuous increase crisis of the CO_2 concentration in the atmosphere. Here, two types of solid electrolytes were rigidly selected from their thermodynamic stability and reasonably high ionic conducting properties point of view to create the CO_2 practical sensing performance.

Global warming of the earth has been becoming an urgent issue to solve in a worldwide scale. The main gas species causing the warming is carbon dioxide (CO_2) and the suppression of the total CO_2 exhaustion amount into air is becoming an important matter so as to effectively suppress the environmental deterioration. For the purpose of realizing the target, the compact and inexpensive sensing tool is greatly requested to suppress the CO_2 emission at every exhausting site. Up to now, instrumental analyses such as infrared method have been widely utilized. However, the methods are typical analytical apparatuses and are not suitable for controlling the CO_2 emission amount at every site.

Recently, a CO_2 detection with solid electrolytes has been proposed.[1–10] However, the critical disadvantage of the sensor system reported so far is the low reliability of the absolute values of sensor output, including the stability at initial stage and also long-term stability and the reproducibility of the individual sensor output. The above mentioned disadvantage is ascribed to their low stability or appreciably low ionic conducting properties. For example, when the combination of the alkali metal ion and oxide ion conductors reported[9,10] is applied, alkali metal oxide (M_2O) is formed between the interface of the two solid electrolytes. However, M_2O is not stable and the variation of the M_2O activity causes the output baseline deviation. In addition, M_2O easily reacts with gas species existing in ambient atmosphere and this results in a serious deterioration of the sensor performance. In the case of applying the solid electrolytes with a low conductivity, the response becomes sluggish.

In this letter, the oxide, which exists when applying the combination of two solid electrolytes, was selected at first stage from the stability point of view and the cation conductor combined with oxide ion conductor was chosen because of its high ionic conductivity comparable to monovalent cation conductors. Here, magnesium oxide (MgO), which is well known as one of refractory oxides, holding a stoichiometric MgO, showing a high stability in various atmospheres and widely used in high temperature ceramics fields, was selected. Since the cation species in MgO is Mg^{2+}, the divalent Mg^{2+} ion conducting $Mg_{1+x}Zr_4P_6O_{24+x} + xZr_2O(PO_4)_2$ (x = 0.4) composite[11,12] which shows the highest ion conductivity in the magnesium ion conductors reported so far, was employed. In this study, the above mentioned magnesium ion conducting composite and

yttria stabilized zirconia (YSZ), whose performance has been highly guaranteed as the oxygen sensor element and already has prevailed on the market and the stability has been demonstrated, were applied as the combination of the sensor cell.[13]

Mg^{2+} and O^{2-} ion conductors were combined and lithium carbonate was applied as the detecting auxiliary electrode at the operating temperature of 550 °C. The theoretical Nernstian equation is obtained as shown in equation (1) (Details are described in reference 6.).

$$E=C_1(\text{constant}) - (R/nF)T \ln \{(a_{MgO})\cdot(P_{CO_2}{}^{I})\} \quad (n=2.00) \quad (1)$$

Since MgO is very stable in the operating temperature, the activity of MgO (a_{MgO}) is constant and the equation (1) can be finally simplified as follows.

$$E=C_2(\text{constant}) - (R/nF)T \ln (P_{CO_2}{}^{I}) \quad (n=2.00) \quad (2)$$

By measuring the EMF output with some CO_2 content gas as a standard, the constant, C_2, is obtained for the sensor at 550 °C (For the present CO_2 sensor system, C_2 is calculated approximately 0.1 V as shown in Figure 1 (See below)).

The CO_2 content dependencies of the sensor output (○) is presented in Figure 1. A 1:1 relation was exactly observed in the relationship between the EMF output and the logarithm of the CO_2 gas content. The sensor output rapidly changes with the variation in CO_2 content and the reproducible response was clearly observed. The response time defined as the 90% response of the corresponding output was obtained within two min. From the slope of the sensor output, n obtained is 1.92
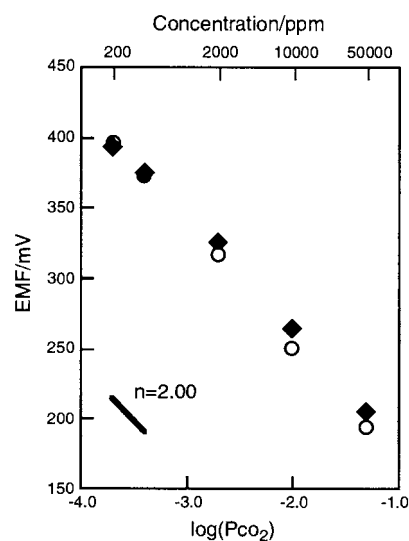
Figure 1. The sensor output comparison of the each CO_2 sensor cell fabricated with the combination of Mg^{2+} and O^{2-} ion conductors.

from the measurements and shows an excellent accordance with the n value calculated from the Nernst equation (n = 2.00) which is depicted in the figure as the solid line. The output variation of the another CO_2 sensor probe similarly built by the combination of Mg^{2+} and O^{2-} ion conductors, is also shown in the same figure. The EMF output (◆) is almost consistent each other with n value of 2.07 and a high reproducibility was demonstrated.

Figure 2(a) shows the deviation of the sensor output at CO_2 concentration of 2000 ppm in air with the day span after the operation of the cell with the present Mg^{2+} ion and O^{2-} ion conductors. The EMF deviation behavior for the CO_2 sensor with the Li^+ ion and O^{2-} ion conductors is also plotted in the same figure as a comparison.[14] The sensor output changes more than 100 mV after 30 days, whose output corresponds to the CO_2 concentration of ca. 250 ppm, while almost no deviation was recognized for the present probe with the combination of Mg^{2+} ion and O^{2-} ion conductors.

a)

b)
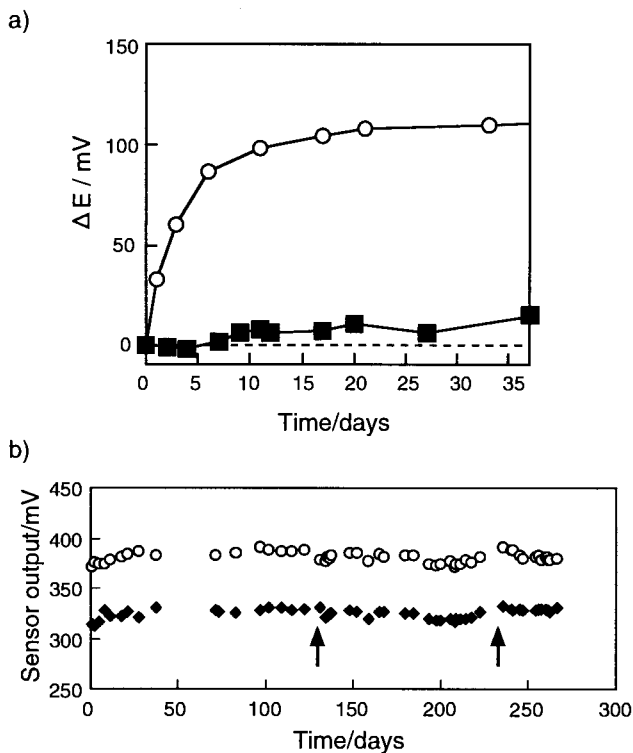
Figure 2. a) The EMF variation with the day span for the CO2 concentration of 2000 ppm in air. ○: with the combination of Li+ and O2- ion conductors, ■: with the combination of Mg2+ and O2- ion conductors. b) Further EMF variation with the long term day span(○: 400 ppm, ◆: 2000 ppm). The arrow indicates the day when the power was shutdown. By the shutdown, the sensor output deviates around 8 mV. However, the output recovers the value before the deviation within several days.

From the measurement of the further day span deviation of the output (up to 270 days) for the sensor with the combination of Mg^{2+} ion and O^{2-} ion conductors (Figure 2(b)), the EMF output was almost constant and any meaningful deviation was not recognized at all. These phenomena clearly indicate that the

sensing system proposed here operates as designed and is well suitable for the on-site CO_2 sensing in practice.

In addition, no interference for the CO_2 sensing was observed in the atmosphere with O_2 (1 to 20 vol%), NO (0 to 500 ppm), NO_2 (0 to 500 ppm), or water vapor (0 to 10 vol%). Even in the case of the water vapor existence up to 30 vol% in the ambient atmosphere, any interference was not recognized for the CO_2 sensing higher than 1000 ppm, indicating that the present sensor is also applicable for the CO_2 sensing in the emitted gas, where both CO_2 and water vapor exist to some higher extent.

In conclusions, a CO_2 sensor was fabricated by the combination of two reasonably high ion conducting solid electrolytes, one is divalent magnesium cation conductor and the other is divalent oxide anion conducting solid electrolyte. Since the oxide formed between the two solid electrolytes is magnesium oxide, which is very stable at elevated temperatures, the sensing performance is reliable and a long-term stability and the reproducibility of the individual sensor output were guaranteed.

References and Notes
1   S. Yao, S. Hosohara, Y. Shimizu, N. Miura, H. Futata, and N. Yamazoe, *Chem. Lett.*, **1991**, 2069.
2   S. Yao, Y. Shimizu, N. Miura, and N. Yamazoe, *Jpn. J. Appl. Phys.*, **31**, L197 (1992).
3   S. Yao, Y. Shimizu, N. Miura, and N. Yamazoe, *Appl. Phys. A*, **57**, 25 (1993).
4   S. Ikeda, S. Kato, K. Nomura, K. Ito, H. Einaga, S. Saito, and Y. Fujita, *Solid State Ionics*, **70/71**, 569 (1994).
5   S. Ikeda, T. Kondo, S. Kato, K. Ito, K. Nomura, and Y. Fujita, *Solid State Ionics*, **79**, 354 (1995).
6   N. Imanaka, M. Kamikawa, S. Tamura, and G. Adachi, *Electrochem. and Solid-State Letters*, **2**, 602 (1999).
7   N. Imanaka, M. Kamikawa, M. Hiraiwa, S. Tamura, and G. Adachi, *Chem. Lett.*, **2000**, 68.
8   N. Miura, S. Yao, S. Nonaka, and N. Yamazoe, *J. Mater. Chem.*, **5**, 1391 (1995).
9   N. Imanaka, T. Murata, and G. Adachi, *Denki Kagaku* (presently, *Electrochemistry*), **61**, 909 (1993).
10 N. Imanaka, Y. Hirota, and G. Adachi, *Sens. Actuators, B*, **24/25**, 380 (1995).
11 N. Imanaka, Y. Okazaki, and G. Adachi, *Chem. Lett.*, **1999**, 939.
12 N. Imanaka, Y. Okazaki, and G. Adachi, *J. Mater. Chem.*, in press.
13 Magnesium zirconium phosphate and zirconium oxygen phosphate composite was prepared by the method described in our previous letter.[11,12] Yttria stabilized zirconia was prepared as described in references.[9,10] Two solid electrolyte pellets were fixed with the inorganic adhesive agent (SUMICERAM-17D from ASAHI). On the surface of the Mg^{2+} ion conductor, a paste of lithium metoxide(purity: 99.9%) diluted with methanol was painted. As a lead, Au or Pt net and wire were applied. The whole sensor cell was heat-treated in the CO_2 (10 vol%) containing air atmosphere to form lithium carbonate on the detecting electrode surface. The content of the CO_2 concentration in the test gas was varied from 200 ppm to 2000 ppm and 1% to 5% by controlling the mixing ratio of air-1% CO_2 diluted with air and air-CO_2, respectively.
14 T. Yamamoto, M. D. Thesis, Osaka University, Osaka, Japan, 1999.