

High Performance CO_2 Gas Sensing with Combination of Multivalent Ion Conducting Solid Electrolytes with Water-Insoluble Auxiliary Electrode

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A carbon dioxide gas sensor was fabricated by combination of multivalent cation and anion conducting solid electrolytes with a water-insoluble Li and Ba codoped $\text{Nd}_2\text{O}_2\text{CO}_3$ solid solution as an auxiliary electrode. The present sensor shows such a high durability not only in the atmosphere of gas phase water vapor coexistence but also after the exposure to the liquid phase water dew, in addition to persisting the rapid, reproducible response with a high stability from the operation.

Carbon dioxide is mainly released when combustion occurs and water vapor also produces as by-product and when the power is shutdown, the water vapor transforms to the liquid phase of water dew. The durability toward the gas phase water vapor and liquid phase water dew is an essential issue of the gas sensor for in-situ practical application. Furthermore, the stability of the sensor output from the beginning of the operation is highly requested in addition to the rapid, reproducible response.

Among various CO_2 sensing tools proposed, the detecting method to satisfy the requests mentioned above is the sensing with solid electrolyte. As the solid electrolytes, most widely investigated ones are the sensors with alkali metal ion conductors¹⁻⁵ with alkali metal carbonate as the auxiliary electrode. In addition, Mg^{2+} ⁶⁻⁸ Al^{3+} ⁹ and Sc^{3+} ¹⁰ multivalent ion conducting solids have been also investigated. However, the carbonate auxiliary electrode is still soluble in water and this feature becomes a critical disadvantage for practical applications in addition to the considerable output variation from the beginning of the operation. In order to improve the sensing performance at the initial stage, a Mg^{2+} ion conductor was applied with the water insoluble Li and Ba codoped $\text{Nd}_2\text{O}_2\text{CO}_3$ as an auxiliary electrode.¹¹ However, due to the relatively low density (ca. 98%) of the Mg^{2+} ion conducting solid electrolyte, the sensing performance from the beginning is not still satisfactory, because of the gradual immersion of the auxiliary electrode which causes the output deviation.

Recently, we have succeeded in developing the Sc^{3+} ion conductor¹² whose relative density is higher than 99.95%. In this letter, the Sc^{3+} ion conducting solid was combined with oxide anion conducting yttria stabilized zirconia (YSZ) with the water insoluble Li and Ba codoped $\text{Nd}_2\text{O}_2\text{CO}_3$ as the auxiliary electrode and the CO_2 gas sensing performance was investigated.

$\text{Sc}_{1/3}\text{Zr}_2(\text{PO}_4)_3$ was synthesized by a sol-gel method from high purity Sc_2O_3 (99.9%), $\text{ZrOCl}_2 \cdot 8\text{H}_2\text{O}$ (99.95%) and $\text{NH}_4\text{H}_2\text{PO}_4$ (99%) as starting materials. Sc_2O_3 and $\text{ZrOCl}_2 \cdot 8\text{H}_2\text{O}$ were individually dissolved in 3M HNO_3 solution, and then mixed each other. The $\text{NH}_4\text{H}_2\text{PO}_4$ solution (3%) was added dropwise into the mixed nitric acid solution. After white precipitates were obtained, the solution was heated at 75 °C for 24 h to complete the precipitation. Water in the solution was vaporized by heating at 130 °C for 8 h. The dried precipitate was further heated at 300 °C for 24 h and the white powder was made into pellets and sintered

at 850 °C for 24 h. X-ray powder diffraction analysis (Mac Science M18XHF diffractometer) using $\text{Cu K}\alpha$ radiation was carried out. Oxide ion conducting stabilized zirconia (YSZ) was prepared by mixing ZrO_2 and Y_2O_3 in a molar ratio of 9:1 and then heated twice at 1600 °C for 12 h in air. $\text{Nd}(\text{CH}_3\text{COO})_3 \cdot \text{H}_2\text{O}$ and $\text{Ba}(\text{CH}_3\text{COO})_2 \cdot \text{H}_2\text{O}$ were mixed in a molar ratio of 4:1 and then made into pellets. The pelletized samples were heated at 500 °C for 12 h in air and the obtained pellets were pulverized. The pulverized powder was mixed with lithium carbonate in an equimolar ratio and then heated at 600 °C for 12 h in the atmosphere of 10 vol% CO_2 diluted with air to prepare the Li and Ba codoped neodymium oxycarbonate solid solution.

Two pellets of the solid electrolytes were tightly fixed by inorganic adhesive agent (Sumicerm 17-D) and the Li and Ba codoped $\text{Nd}_2\text{O}_2\text{CO}_3$ pellet was fixed on the Sc^{3+} ion conducting solid surface and the temperature was raised up to the operating temperature of 550 °C (Figure 1).¹³ The relative density was measured by Shimadzu AccuPyc 1330.

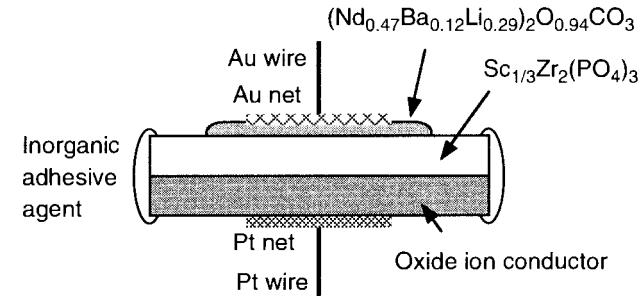


Figure 1. The cross-sectional view of the CO_2 sensor cell with the combination of high dense trivalent Sc^{3+} ion conducting solid and O^{2-} ion conducting stabilized zirconia (YSZ) with the Li and Ba codoped neodymium oxycarbonate solid solution as an auxiliary electrode.

Figure 2 shows the sensor output variation with the logarithm of CO_2 concentration with its typical sensor output response curve (depicted in the inserted figure). A rapid and continuous, and reproducible response was ensured. A linear relationship was clearly observed in the sensor output vs $\log(\text{P}_{\text{CO}_2})$ and the exact CO_2 gas content can be accurately determined only by measuring the sensor output.

One of the great advantages of applying the present high dense Sc^{3+} ion conductor with divalent oxide anion stabilized zirconia is that a considerable high stability can be realized from the beginning of the operation. The EMF output deviation in measuring the CO_2 gas content of 1% is plotted toward the day span in Figure 3. The similar data for the case of applying the conventional monovalent Li^+ ion¹⁴ and divalent Mg^{2+} ion¹⁵ conductor with YSZ are also depicted in the same figure for comparison.

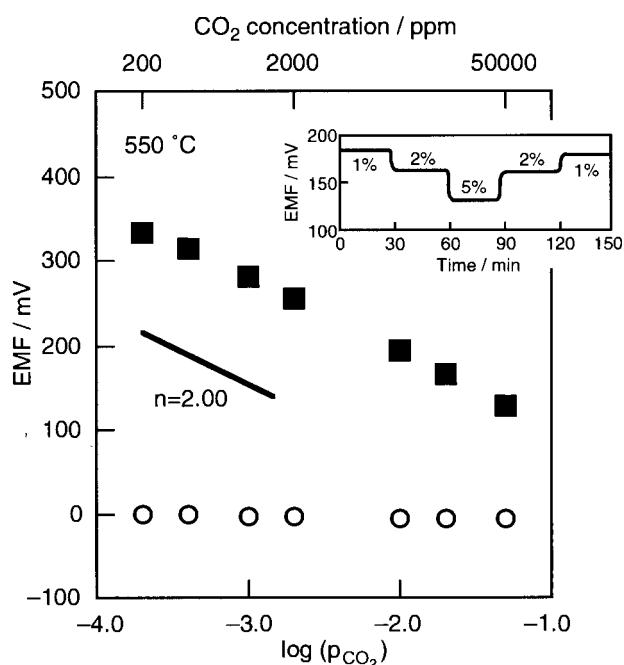


Figure 2. The relationship between the sensor output and the logarithm of CO_2 concentration (■). Typical sensor output response curve with changing the CO_2 gas content (1 to 5 %) is also depicted in the figure inserted. The sensor using only divalent O^{2-} ion conducting YSZ was also fabricated and the result is also presented (○). The theoretical slope ($n=2.00$) calculated from Nernst relation is depicted as solid line.

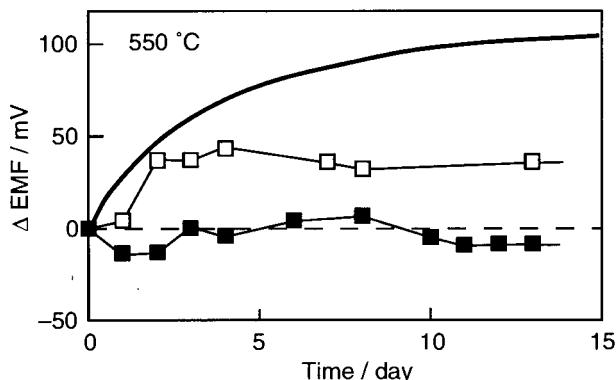


Figure 3. The deviation curve of the sensor output at the CO_2 content of 1 % for the sensor with the combination of the present Sc^{3+} and O^{2-} ion conductors (■) and the Li^+ ¹⁴ (—) or Mg^{2+} ¹⁵ (□) ion conductor with O^{2-} ion conductor reported.

The sensors with Li^+ ion or Mg^{2+} ion conductors show a clear deviation from the start of the operation and especially for the case with Li^+ ion conductor, a serious deviation was observed toward higher EMF output more than 100 mV, which corresponds to the CO_2 content of ca. 0.1% in spite that the present CO_2 gas content in the detecting gas is, in fact, 1%. In contrast, the sensor with the combination of the Sc^{3+} ion conductor and YSZ shows no such an appreciable deviation from the beginning, indicating a high stability of the sensor system from its operation. The sensor using only divalent O^{2-} ion conducting

YSZ was also fabricated and the result is also presented in Figure 2. The sensor with only YSZ solid electrolyte does not show any output at all, clearly demonstrating the necessity of the high dense Sc^{3+} ion conductor with YSZ. In combustion, H_2O , which corresponds to gaseous water vapor and liquid water dew are also formed. The water vapor existence during the monitoring at 550 °C and liquid water dew exposure before monitoring were investigated and it was found that any interference was not observed at all both by the gas phase water vapor appearance¹⁶ and the liquid phase water dew treatment.¹⁷ In addition, the present sensor holds such a merit that the sensor output does not depend on the oxygen concentration as a similar manner as described in our previous paper.¹¹

In conclusions, the prototype CO_2 gas sensor was fabricated by the combination of a high dense Sc^{3+} ion conducting and O^{2-} ion conducting solids with the water insoluble Li and Ba codoped $\text{Nd}_2\text{O}_2\text{CO}_3$ solid solution as an auxiliary electrode. The present sensor shows a considerably high durability both in the atmosphere of water vapor appearance and after exposing to the liquid phase water dew, with demonstrating a satisfactory stability from the operation.

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- 13 The CO_2 gas content of 2000 ppm–1% and 200–2000 ppm was regulated by mixing CO_2 –air and 1% CO_2 diluted with nitrogen–air mixture, respectively. The total flow rate was maintained constant at 100 mL/min and the sensor output was monitored by an electrometer (Advantest R8240).
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- 16 The water vapor content was precisely regulated by firstly bubbling the CO_2 free air gas into the 90 °C water vessel and then passing the gas in the water bath controlled at the temperatures of 30, 50, or 70 °C to attain a saturated water vapor of the individual temperature. The water vapor saturated air was mixed with air + CO_2 dry gas.
- 17 The durability of the exposure to liquid phase water dew was examined in such a manner to expose to the water-vapor saturated air atmosphere at 50 °C for 8 h then decrease the temperature down to room temperature. This process was repeated three times.