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Amperometric-Type Sensor for CO_2 Using $BaCeO_3$-Based Ceramic

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The resistivity of $BaCe_{0.95}Y_{0.05}O_{3-x}$ ceramic element was very sensitive to CO_2 in the moisten atmosphere at 923 K. The reproducible linear relationship between the resistivity and the CO_2 concentration was observed in the range of 200 - 3000 ppm.

In order to monitor carbon dioxide in the atmosphere or to measure its concentration in the exhaust gas from industrial processes, it is necessary to develop a convenient and reliable sensor for CO_2. As a practical sensor, an infrared adsorption method is employed for the detection of CO_2 in the atmosphere, but this apparatus is expensive and spacious. Solid electrolyte-type sensors using alkali metal ion conductors have been examined, and their emfs are selective to CO_2 concentration.[1-3] In addition, a mixed oxide capacitor of CuO-$BaTiO_3$[4] and a Ca^{2+} ion-exchanged A-type zeolite[5] exhibit a high response for CO_2. However, some of above-mentioned sensors are desirable for the use in the dry atmosphere. Here, we report a new type of CO_2 sensor using proton conductive $BaCe_{0.95}Y_{0.05}O_{3-x}$ ceramic as an element. This sensor can detect CO_2 stably in the humid atmosphere.

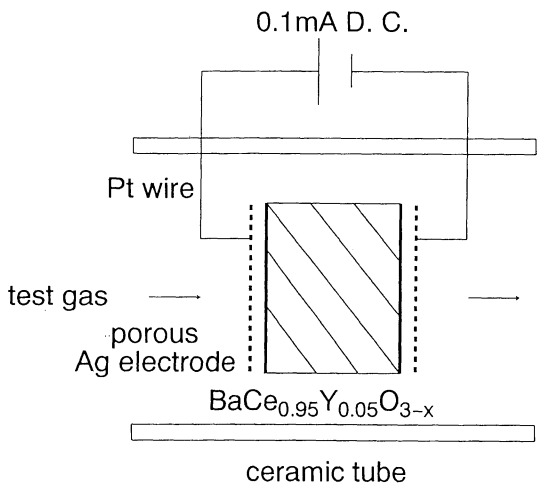

Fig. 1. Structure of sensor element used in the present study.

$BaCe_{0.95}Y_{0.05}O_{3-x}$ ceramic was prepared by solid state reaction of raw materials ($Ba(CH_3COO)_2$, CeO_2 and Y_2O_3), followed by sintering. Further details of preparation were reported in the previous study.[6] For the measurement of resistivity, the cylinder-shaped specimen with 7.2 mm thickness and 2.5 mm diameter was used (Fig. 1). Each face of the cylinder was attached with a porous Ag electrode, which was connected with a Pt lead wire. The measurement of resistivity was carried out in a flow-type apparatus equipped with an electric furnace. The flow rate of wet air or test gas was 70 cm^3/min. Wet air was saturated with water vapor at room temperature. The test gas was prepared by diluting CO_2 with wet air. The concentration of CO_2 was in the range of 200 to 3000 ppm. The direct current of 0.1 mA was sent from a galvanostat, and the resistivity of element was monitored as a voltage by an electrometer. The CO_2 sensitivity was defined as $V_{test\ gas} - V_{air}$, where $V_{test\ gas}$ and V_{air} were voltages in the test gas and wet air, respectively.

Figure 2 (a) shows response transients of $BaCe_{0.95}Y_{0.05}O_{3-x}$ ceramic to 1500 ppm CO_2 under various humidities at 923 K. Here, CO_2 were diluted with air saturated with water vapor at room temperature, air in our laboratory and air passed through molecular sieve 3A at 195 K, respectively. Under any humidity, the resistivity of element increased on introducing CO_2, while it decreased on removing CO_2. Particularly, the response speed to turning-on or -out CO_2 in the humid atmosphere was the shortest, indicating that this element could be sensitive to CO_2 in such an atmosphere.

Figure 2 (b) shows the dependence of response to CO_2 on the operation temperature. As the temperature decreased, the response increased, but the time required to the steady state became longer. Hence, we chose 923 K as an operation temperature in subsequent experiments.

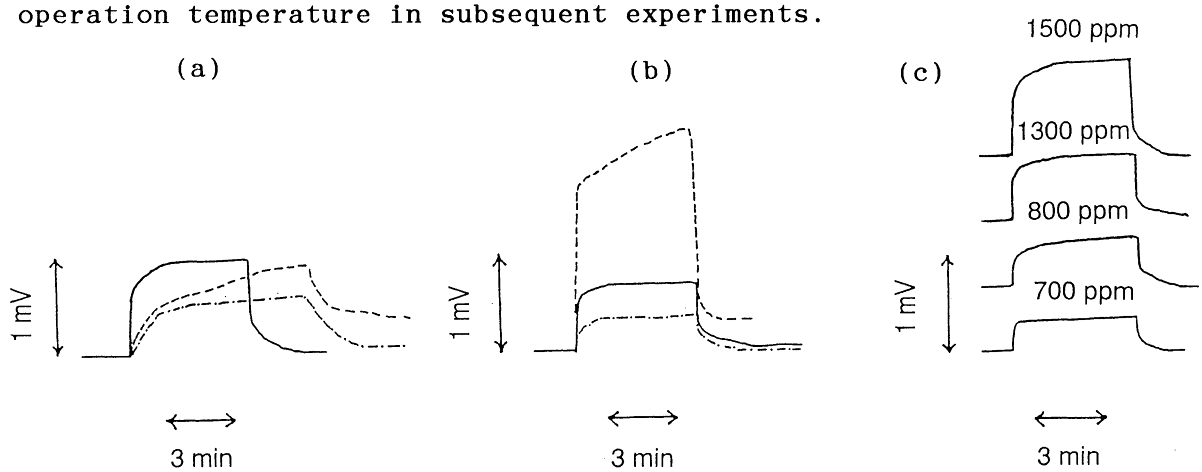

Fig. 2. Response transients of $BaCe_{0.95}Y_{0.05}O_{3-x}$ sensor element to CO_2.
(a) Responses to 1500 ppm CO_2 under various humidities at 923 K; wet (air + CO_2);——— air + CO_2;---- dry (air + CO_2);-·-·-
(b) Responses to 1500 ppm CO_2 at various temperatures in the humid atmosphere; 873 K;-------- 923 K;——— 973 K;-·-·-
(c) Responses to CO_2 at 700, 800, 1300, and 1500 ppm concentrations in the humid atmosphere at 923 K.

In order to evaluate sensing characteristics of this element, the experiment was carried out in the CO_2 concentration from 200 to 3000 ppm. Results are shown in Fig. 2 (c) and Fig. 3. An excellent linear relationship existed between CO_2 sensitivity and its concentration. This means that $BaCe_{0.95}Y_{0.05}O_{3-x}$ ceramic element can sufficiently sense CO_2 in the practical concentration range in the atmosphere. On the other hand, the sensitivity at 0% CO_2 was negative, as shown in Fig. 3. This is probably because wet air includes a small amount of CO_2 as an impurity.

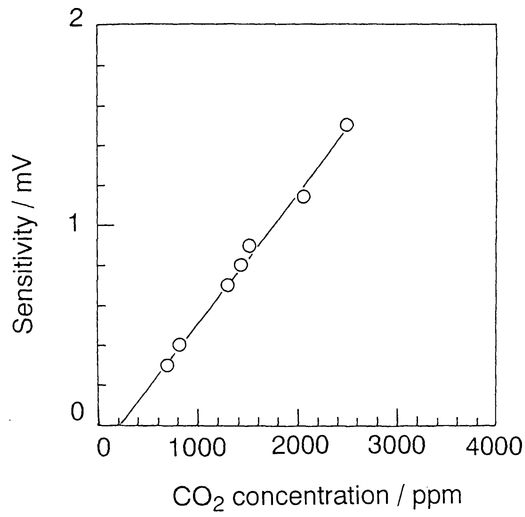

Fig. 3. Sensitivity to CO_2 as a function of its concentration.

As a stability test, this element was exposed to CO_2 for a long time. The sensitivity to CO_2 was not influenced by prolonged exposure to CO_2, as shown in Fig. 4. Furthermore, XRD patterns before and after CO_2 exposure showed no change in the crystalline phase.

Finally, the interference of CO on the sensitivity was studied. Figure 5 shows the change in resistivity as a function of the CO_2 concentration in the test gas containing 200 ppm CO. 200 ppm CO has an appreciable effect on the change in resistivity. This will be ascribed to the oxidation of CO to CO_2 on the Ag electrode and/or the Pt lead wire. Thus, the choice of inert electrode is necessary to solve such a problem.

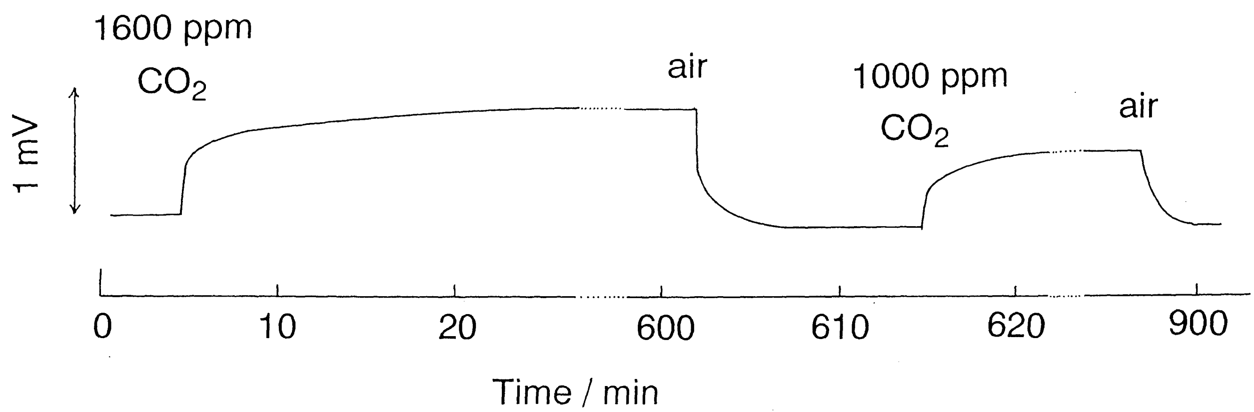

Fig. 4. Stability of CO_2 sensing.

The findings described above revealed that $BaCe_{0.95}Y_{0.05}O_{3-x}$ ceramic element was very sensitive to CO_2 in the moisten- rather than the dry-atmosphere. This can be explained as below. It is known that BaO reacts easily with water vapor to form hydroxide and that CO_2 is adsorbed strongly on the hydroxide. Thus, similar phenomena will occur on the surface of $BaCe_{0.95}Y_{0.05}O_{3-x}$ ceramic. CO_2 adsorbed will form carbonate and lower the protonic and/or p-type electronic conductivities. Further investigations are necessary to understand the sensing mechanism of the present sensor better.

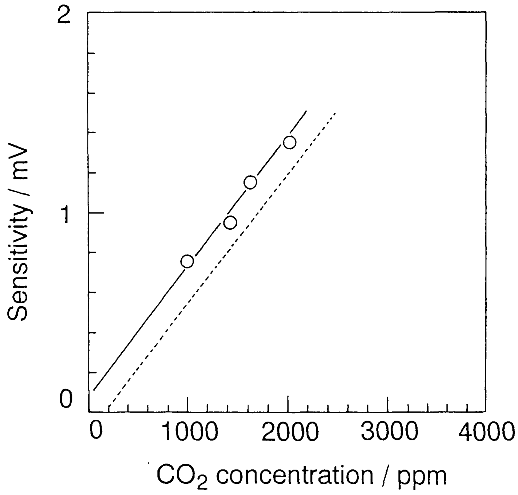

Fig. 5. Influence of 200 ppm CO on sensitivity to CO_2:
none;------
200 ppm CO;———

In conclusion, $BaCe_{0.95}Y_{0.05}O_{3-x}$ ceramic element has the excellent CO_2 sensing property in the humid atmosphere. (1) The response to CO_2 was sufficiently high, and its rate was rather fast. (2) The liner relationship between the CO_2 sensitivity and its concentration was observed. (3) This sensor worked stably for a long time.

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