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Solid Electrolyte CO_2 Sensor Using Binary Carbonate Electrode

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A simple potentiometric CO_2 sensor based upon a Na^+-conducting solid electrolyte (NASICON) was found to be greatly improved in response time and water vapor-resistance by using a binary carbonate electrode of $BaCO_3$-Na_2CO_3. For a wide range of CO_2 concentration from 4 to 400000 ppm, the electromotive force examined at 823 K followed a Nernst's equation excellently, with a 90% response time of as short as 8 s. Water vapor hardly affected the sensor characteristics, in contrast to the case of a pure Na_2CO_3 electrode.

From the global issue of CO_2 emission as well as growing importance of CO_2 control in advanced technology, there have been ever increasing needs for CO_2 sensors. Among the CO_2 sensors[1,2] so far investigated those using solid electrolytes[3-5] are of particular interest from a viewpoint of inexpensive all solid-state structure. The sensors based on β-alumina[6] and NASICON[7,8] were reported to respond to CO_2 potentiometrically, following Nernst's equations, with the 90% response times of about 6 min at temperatures such as ca. 500 °C. A serious problem of them seems to be the strong interference of water vapor. We have found that the interference is associated with the use of an Na_2CO_3 electrode, and that a binary carbonate electrode of $BaCO_3$ and Na_2CO_3 not only eliminates the interference almost completely but also increases the response rates quite remarkably, as described below.

The sensor elements were fabricated as shown in Fig. 1. A disc of a sodium ion conductor (NASICON), 14 mm in diameter and 0.5 mm thick, was fixed on the top of a quartz glass tube (10 mm in diameter) with an inorganic adhesive (Sauereisen). The counter electrode (platinum black) was applied on the surface of the disc inside the tube, on which a platinum mesh connected to a Pt wire was pressed mechanically to secure the electrical contact. The sensing electrode was fabricated by applying platinum black on the outside surface of the disc, followed by covering it with a platinum mesh and finally with a carbonate layer of Na_2CO_3 or an eutectic mixture of $BaCO_3$ and Na_2CO_3 (1.7 : 1 in molar ratio). The carbonate layer was fixed to the disc tightly by melting and crystallizing method. CO_2 sensing experiments were carried out in a conventional flow apparatus. Sample gases were prepared by mixing 1 vol% CO_2 diluted in nitrogen or pure CO_2 with air (wet or dry) and pure oxygen. Humid air was prepared by allowing air to bubble through a water phase. The electromotive force (EMF) of the sensor was measured with a digital electrometer (Advantest, TR 8552) at 550 °C

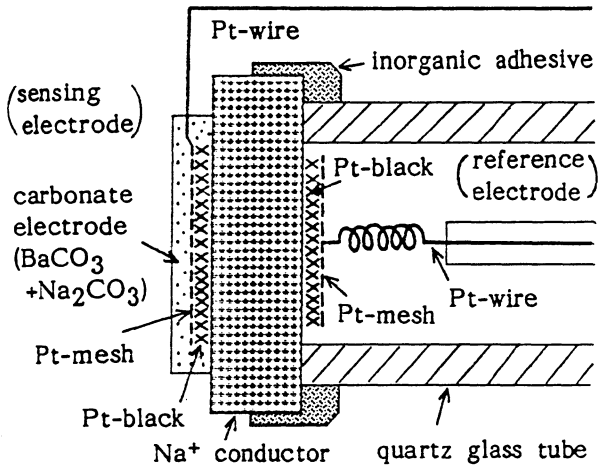

Fig. 1. Structure of CO_2 sensor element using Na^+ conductor.

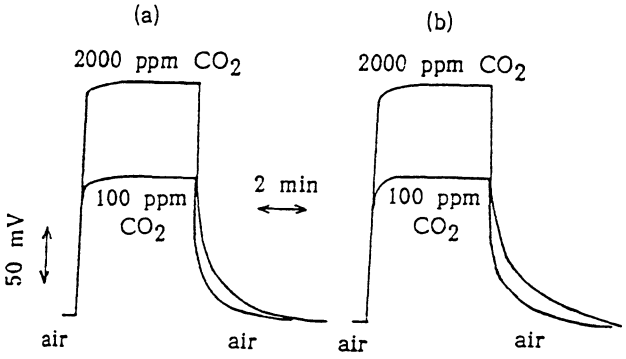

Fig. 2. Response transients to 100 and 2000 ppm CO_2 for the element using $BaCO_3$-Na_2CO_3 electrode at 550 °C.
(a) dry CO_2, (b) wet CO_2(2720 Pa-H_2O)

under constant oxygen concentration of 21 vol% and a total flow rate of 100 cm^3/min.

Typical response transients of the sensor element fitted with a binary carbonate electrode are shown in Fig. 2. On switching from a dry air flow to a CO_2-containing flow, EMF increased quickly up to a steady value. On switching back, EMF returned to the initial value also rather quickly. The observed 90% response time for the increase of CO_2 concentration was as short as 8 s in each case for the tested concentration range up to 400000 ppm. Quite notably the transients were hardly affected by humidity (Fig. 2(b)). As shown in Fig. 3, EMF was perfectly linear to the logarithm of CO_2 concentration in the whole range tested (4-400000 ppm) with a Nernst's slope of 81 mV/decade. This slope indicates that the electrode reaction is a 2-electron reduction per a CO_2 molecule. It is again noted that the presence of water vapor hardly gave significant effects on the data.

For comparison, the sensor element fitted with a Na_2CO_3 electrode was subjected to the same examinations. As shown in Fig. 4 its response transients in the absence of water vapor were rather reasonable, although the 90% response time of about 60 s was far larger than in the above case. However, the transients were seriously affected by humidity. Even at a low level of 20.4 Torr (2720 Pa) H_2O, the 90% response times were greatly elongated to ca. 10 min, while the steady EMF values attained were far larger than those observed for dry CO_2, as seen from Fig. 4(b). Figure 5 shows EMF vs. CO_2 concentration relations for the Na_2CO_3 electrode. Here, EMF was taken relative to the values in air flow (base EMF), because the base EMF was not stable enough. For dry CO_2, ΔE followed a Nernst's equation with a slope of 61 mV/decade, while it increased greatly with the coexistence of water vapor and became far less dependent on or totally independent of CO_2 concentration at 6.3 (840) and 20.4(2720) Torr(Pa)-H_2O, respectively. It is thus too obvious that the element with the Na_2CO_3 electrode can not operate in the presence of water vapor.

The sensing mechanisms of these sensors are considered as follows, although many speculations are inevitable at this moment. The sensor elements are galvanic cells of the following form.

O_2, Pt | NASICON | Pt + carbonate, CO_2 + O_2
(counter electrode) (Na^+ conductor) (sensing electrode)

In the case where only Na_2CO_3 is utilized in the sensing electrode, the sensing electrode reaction

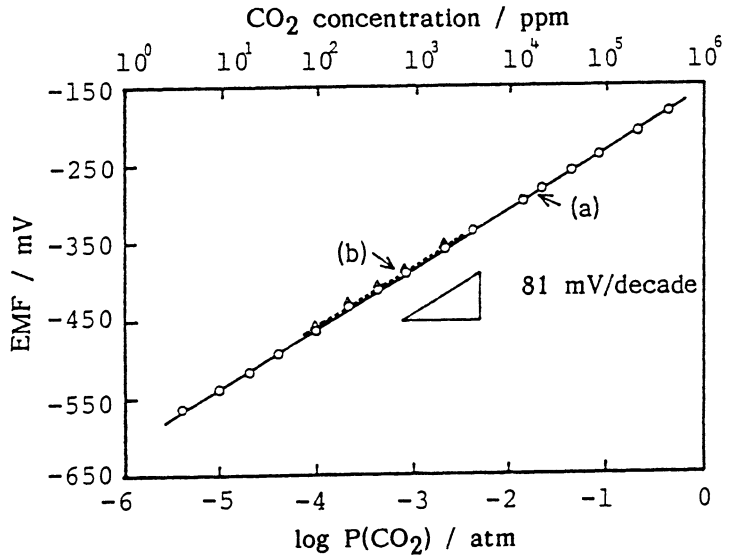

Fig. 3. EMF of the element using $BaCO_3$-Na_2CO_3 electrode as a function of CO_2 concentration at 550 °C.
(a) dry CO_2, (b) wet CO_2(2720 Pa-H_2O)

is conventionally written by the equation;

$$2Na^+ + CO_2 + (1/2)O_2 + 2e^- = Na_2CO_3 \quad (1)$$

whereas the counter electrode reaction is assumed to be

$$2Na^+ + (1/2)O_2 + 2e^- = Na_2O \text{ (in NASICON)} \quad (2)$$

The overall chemical reaction is reduced to $Na_2CO_3 \rightarrow Na_2O + CO_2$. When the activities of Na_2CO_3 and Na_2O are kept constant, EMF can be expressed as

$$E = E° - (RT/2F)\ln P(CO_2) \quad (3)$$

where $P(CO_2)$ is the partial pressure of CO_2, E° is a constant, and RT/F has the usual meaning. The observed Nernst's slope for dry CO_2, 61 mV/decade, is not too much inconsistent with the theoretical value (81.6 mV/decade). As just observed, however, the same electrode is subject to serious interference of water vapor. Suspectedly the interference occurs because Na_2CO_3 tends to deteriorate to other compounds such as NaOH, $NaHCO_3$ and $Na_2CO_3 \cdot xH_2O$ in the presence of water vapor. If NaOH is formed, for example, reaction (1) may change to

$$Na^+ + (1/4)O_2 + (1/2)H_2O + e^- = NaOH \quad (4)$$

Thus EMF can be even independent of CO_2 concentration.

The remarkable stability of the binary carbonate electrode is likely to be ascribable to the stability of $BaCO_3$ against water vapor. In this case $BaCO_3$ seems to play a dominant role in the sensing electrode reaction although its detail is unclear yet. It is important that the Nernst's slope observed in this case (81 mV/decade) is in excellent agreement with Eq. 3. Another merit of the use of the binary carbonate system is to lower the melting point. The eutectic mixture of $BaCO_3$ and Na_2CO_3 utilized in the present study has a melting point of 686 °C, and thus was easily adaptable to electrode preparation by the melting-crystallizing method.

As mentioned above, the use of the binary carbonate electrode is quite effective to upgrade a solid electrolyte CO_2 sensor in both stability against water vapor and rate of response to CO_2, although the mechanisms for these improvements are still to be elucidated. It is emphasized that

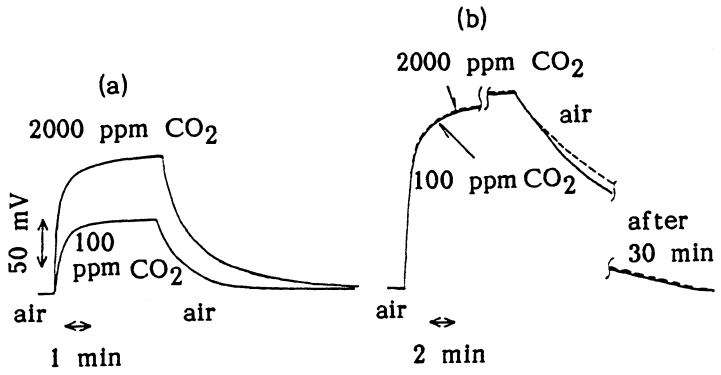

Fig. 4. Response transients to 100 and 2000 ppm CO_2 of the element using Na_2CO_3 electrode at 550 °C.
(a) dry CO_2, (b) wet CO_2(2720 Pa-H_2O)

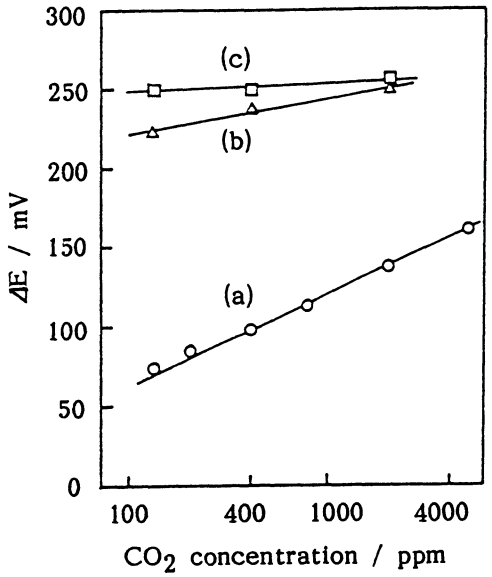

Fig. 5. Dependence of ΔE of the element using Na_2CO_3 electrode on CO_2 concentration at 550 °C.
Water vapor pressure (Pa) : (a); 0, (b); 840, (c); 2720.

the same effects were observed when Na^+-β/β''-alumina or other Na^+ conductor[9] was utilized as a solid electrolyte. Other binary systems such as $CaCO_3$-Na_2CO_3 and $SrCO_3$-Na_2CO_3 also showed similar effects. Based on these results, the effects are not specific to the combination of NASICON and $BaCO_3$-Na_2CO_3 investigated in this study but likely to be a rather common phenomenon to binary carbonate electrodes.

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