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Stabilized Zirconia Based CO_2 Sensors Combined with Carbonate Auxiliary Phase

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A solid-state electrochemical CO_2 sensor was fabricated by combining an MgO-stabilized zirconia (MSZ) tube and Li_2CO_3 auxiliary phase. The sensor responded very well to 100-1000 ppm CO_2 in air at 400-600 °C, with its EMF responses following the Nernst's equation for the 2-electron reduction of CO_2. It was also possible to fabricate an MSZ-based planar-type sensor, which gave stable EMF responses to CO_2 regardless of variations in O_2 concentration. The CO_2 sensing mechanism of these sensors was briefly discussed.

Recently it has become very important to develop high-performance solid-state CO_2 sensors which are reliable, inexpensive and compact, in relation to conservation of the global environment, control of air quality in houses, and control of various chemical- and bio-processes. Among the CO_2 sensors so far investigated, those using solid electrolytes$^{1-11)}$ are of particular interest from the viewpoints of low cost, simple structure, and high sensitivity. We have reported that the combination of a NASICON ($Na_3Zr_2Si_2PO_{12}$) disc-based electrochemical cell with a binary carbonate auxiliary phase, such as Na_2CO_3-$BaCO_3$$^{7, 11)}$ and Li_2CO_3-$CaCO_3$,$^{8)}$ provides a CO_2 sensor device which has excellent characteristics such as wide detection range, quick response, and no interference by water vapor. Although NASICON is an excellent Na^+ conductor, its long-term stability is still questionable under some particular conditions. In this respect, stabilized zirconia (a typical oxide ion conductor) has been widely used for oxygen sensors as a basic material which is very reliable and chemically stable even under severe conditions. Actually we have proposed a new-type SO_2 sensor using an MgO-stabilized zirconia (MSZ) tube and a metal sulphate (auxiliary phase),$^{12, 13)}$ which exhibits good SO_2 sensing properties together with excellent chemical and mechanical stability. Moreover, we have discovered very recently that an LaF_3 single crystal, a typical anion (F^-) conductor, can also be incorporated into a CO_2 sensor if combined with a metal carbonate.$^{14)}$ These situations prompted us to try to fabricate a CO_2 sensor which utilizes a combination of stabilized zirconia (anion conductor) / carbonate (poor cationic conductor) instead of the conventional one of a NASICON disc (cation conductor) / carbonate. Stabilized zirconia has already been incorporated into some CO_2 sensors such as those based on alkaline ion conductors, e.g., K_2CO_3 (K^+),$^{15)}$ NASICON (Na^+),$^{3, 16)}$ and lithium phosphate compound (Li^+),$^{17)}$ but it has been used as a solid reference electrode material, not as a main solid electrolyte material of the sensors. We have found that the use of an MSZ tube provides a CO_2 sensor which is simple in structure and easy for fabrication as well as installation. Moreover, it has also been possible to fabricate a planar-type CO_2 sensor (probe-type sensor) which is insensitive to the variations of coexistent O_2.

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This paper deals with the CO_2 sensing characteristics and mechanisms of these stabilized zirconia-based devices.

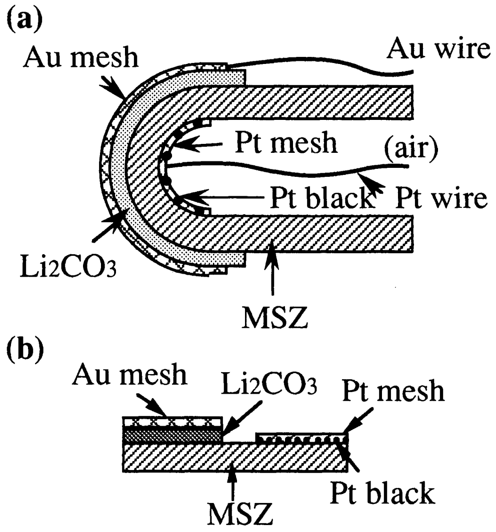

Fig. 1. CO_2 sensor devices using MgO-stabilized zirconia (MSZ) and Li_2CO_3 auxiliary phase. (a) Tubular-type sensor. (b) Planar-type sensor.

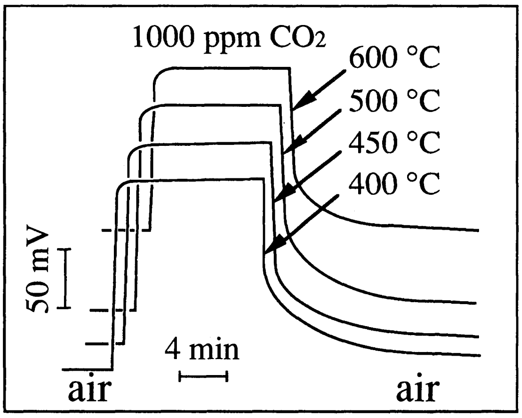

Fig. 2. Response transients to 1000 ppm CO_2 of the tubular-type device at various temperatures.

A schematic view of the investigated sensor devices is shown in Fig. 1. The tubular-type device (Fig. 1 (a)) was fabricated by using an MSZ tube with a closed end (ZR-15M, NKT, 5 and 8 mm in inner and outer diameter, respectively). The reference Pt electrode was attached at the inside bottom of the tube by applying Pt black powder, followed by annealing it at about 900 °C. This electrode was connected to a Pt lead through a mechanically pressed Pt mesh, and was always exposed to atmospheric air. The coating of Li_2CO_3 (auxiliary phase) was fixed on the outside bottom of the tube by dipping that part of the tube in the molten Li_2CO_3, followed by cooling it rapidly in atmospheric air. Then it was covered with an Au mesh (sensing electrode) connected to an Au lead. The planar-type device (Fig. 1 (b)) was actually fabricated by using the MSZ tube: after attaching the Li_2CO_3 coating and the Au sensing electrode in the same way as mentioned above, the counter electrode (Pt black and Pt mesh) was also attached on the outside surface of the tube. CO_2 sensing experiments were carried out in a conventional gas flow apparatus equipped with a heating facility in the temperature range 400-600 °C. The sample gases containing different concentrations of CO_2 under a constant oxygen concentration of 21 vol% were prepared by diluting a parent gas (2000 ppm CO_2 in air) with dry synthetic air. In some cases, the oxygen concentration was varied under a fixed concentration of CO_2 (200 or 400 ppm) by means of an N_2 (or O_2) balance. On changing the gas flow (100 cm^3/min) between air and the sample gas, EMF of the sensor was monitored with a digital electrometer (Advantest, TR8652).

Figure 2 shows the response transients of the tubular-type device to 1000 ppm CO_2 in air at various temperatures (400-600 °C). The responses to switching-on CO_2 were sharp and stable, with 90% response times of several tens seconds in all cases. The recovery on switching-off CO_2 was somewhat slow, e.g., 90% recovery time of about 8 min at 550 °C. It is rather surprising that the simple electrochemical device incorporating a "heterojunction" between an anion conductor (MSZ) and a cation conductor (Li_2CO_3) can give such stable CO_2 responses as demonstrated above. As for stabilized zirconia, calcia-stabilized zirconia (CSZ) and yttria-stabilized zirconia (YSZ) were also tested, but no such stable responses to CO_2 were obtained. Only MSZ was thus acceptable, although the reason is not clear.

As shown in Fig. 3, EMF of the tubular-type device varied logarithmically with the CO_2 concentration at

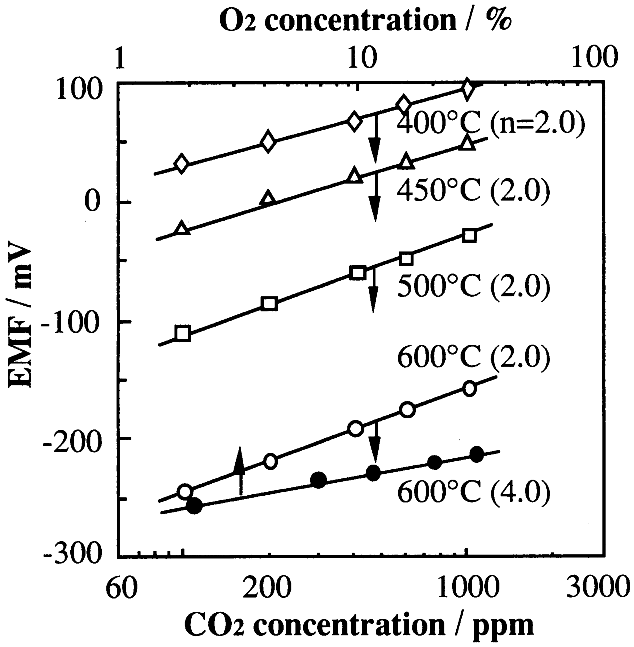

Fig. 3. Dependence of EMF on gas concentration for the tubular-type device.
Open marks: dependence on CO_2 (at 21 vol% O_2).
Full marks: dependence on O_2 (at 200 ppm CO_2).

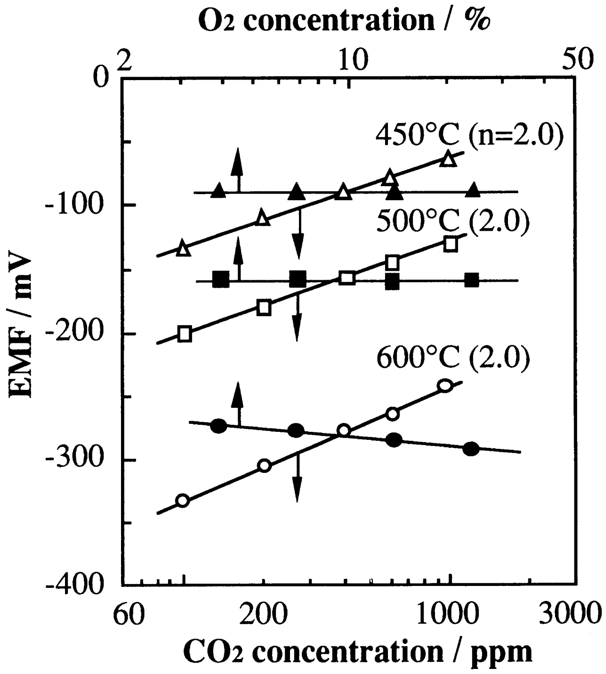

Fig. 4. Dependence of EMF on gas concentration for the planar-type device.
Open marks: dependence on CO_2 (at 21 vol% O_2).
Full marks: dependence on O_2 (at 400 ppm CO_2).

each temperature in the range of 400-600 °C, following the Nernst's equation for the 2-electron reduction of CO_2 (n=2). It was further found that EMF was also linearly correlated with the logarithm of coexistent O_2 concentration (2-30%) at a fixed CO_2 concentration of 200 ppm at 600 °C, being coincident with the 4-electron reduction of O_2 (n=4) as also shown in Fig. 3. These results are consistent with the following sensing electrode reaction.

$$2Li^+ + CO_2 + \frac{1}{2}O_2 + 2e^- = Li_2CO_3 \qquad (1)$$

It is evident that this device can operate as a CO_2 sensor under a fixed O_2 concentration.

The planar-type device was designed to eliminate the O_2-dependence of EMF observed above. In this case, the Pt counter electrode was also exposed to the sample gas. Figure 4 shows EMF of the new device as a function of the concentration of CO_2 or O_2 at 450, 500, and 600 °C. The Nernst's behavior to CO_2 (n=2) was the same as seen in the previous device, but the response behavior to O_2 was totally different. That is, EMF at a fixed CO_2 concentration (400 ppm) was hardly dependent on coexistent O_2 concentration. In the planar-type device, both of the sensing (Au) and counter (Pt) electrode potentials are dependent on O_2, following the same Nernst's behavior (n=4). As a whole electrochemical device, the O_2-dependence is canceled out between the respective electrodes, leading to the O_2-almost independent EMF. Imanaka et al.[17)] have obtained similar results with a lithium phosphate compound (Li^+ conductor)-based CO_2 sensor of more complex device structure.

The present sensor devices are composed of the following electrochemical cell:

CO_2+air, Au | Li_2CO_3 || MgO-ZrO_2 (MSZ) | Pt, air (+CO_2) (2)
(sensing electrode) (Li^+ conductor) (O^{2-} conductor) (counter electrode)

The auxiliary phase of Li_2CO_3 is assumed to work as an Li^+ conductor. The sensing electrode reaction has been shown to be Eqn. (1), while the counter electrode reaction is well known to be

$$O_2 + 4e^- = 2O^{2-}. \qquad (3)$$

To achieve an electrochemical junction between Li_2CO_3 and MSZ, one has to assume the presence of a solid phase containing Li^+ and O^{2-} at the interface, which acts as a so called "ionic bridge". As such a phase we tentatively assume the formation of Li_2ZrO_3, although a compound which contains Mg^{2+} simultaneously (Li-Mg-Zr-O) may be better, judging from the result that only MSZ can provide a reasonable CO_2 sensor.

$$2Li^+ + O^{2-} + ZrO_2 = Li_2ZrO_3 \qquad (4)$$

From (1), (3) and (4), EMF is expressed as

$$E = E_0 + \frac{RT}{4F}\ln\left(\frac{P^s_{O_2}}{P^c_{O_2}}\right) + \frac{RT}{2F}\ln P_{CO_2}\,. \qquad (5)$$

The superscripts s and c mean sensing- and counter-electrode, respectively. When $P^c_{O_2}$ is fixed, EMF is linearly related to the logarithm of both CO_2 and O_2 concentrations, being in agreement with the experimental results. In the case of the planar-type device, $P^s_{O_2}$ and $P^c_{O_2}$ are always equal to each other, so that Eqn. (5) is further simplified to the following equation (6) which explains well the O_2-independent nature of the EMF responses to CO_2.

$$E = E_0 + \frac{RT}{2F}\ln P_{CO_2} \qquad (6)$$

In conclusion, a unique CO_2 sensing device was fabricated by combining an MSZ tube (O^{2-} conductor) with an Li_2CO_3 auxiliary phase (Li^+ conductor). It was also possible to fabricated an MSZ-based planar type CO_2 sensor, which produced the O_2-almost independent EMF responses to CO_2 as designed.

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