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Solid Electrolyte CO_2 Sensor Using NASICON and Li-based Binary Carbonate Electrode

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A solid electrolyte CO_2 sensor was developed by combining an Na^+ conductor and a Li-based binary carbonate auxiliary electrode represented by Li_2CO_3-$CaCO_3$ (1.8 : 1 in molar ratio: eutectic mixture). It responded to CO_2 quickly and reversibly, following a Nernst equation excellently in the CO_2 concentration range 10^2 - 10^5 ppm. In addition, Li_2CO_3-$CaCO_3$ electrode was found to be stable to deliquescence even when kept under a highly humid condition at 30 °C for more than 700 h.

As the control of CO_2 increases its importance in various technologies, there is an ever growing need for inexpensive CO_2 sensors with high sensitivity and selectivity. Solid electrolyte CO_2 sensors are of particular interest from the viewpoint of low cost, high selectivity and simple element structure.[1-4)] We have proposed the use of binary carbonate electrodes, Na_2CO_3-MCO_3 (M = Ca, Sr, Ba), to improve the sensing characteristics of Na^+-conductor (NASICON)-based CO_2 sensors.[5,6)] These electrodes in fact gave very excellent CO_2 sensing properties at elevated temperatures compared with a conventional pure Na_2CO_3 electrode. Subsequent examinations from a practical viewpoint, however, disclosed that these electrodes were not stable enough during storage at room temperature under extremely humid conditions near 100% relative humidity because of their hygroscopic nature. This situation prompted us to seek for better electrode materials. As a result, Li-based binary carbonate electrodes, Li_2CO_3-MCO_3 (M = Ca, Sr, Ba), were found to be very promising. The use of these electrode for the NASICON based electrochemical cell not only brings about even better CO_2 sensing properties but also makes the sensor very stable to deliquescence during storage in a highly humid atmosphere at room temperature. This paper deals with the sensing characteristics, mechanism, and deliquescence-resistant properties of this newly developed CO_2 sensor.

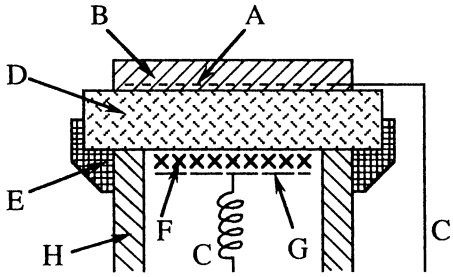

Fig. 1. Structure of CO_2 sensor element.
A: Au-mesh, B: Carbonate electrode,
C: Pt-wire, D: NASICON,
E: Inorganic adhesive, F: Pt-black,
G: Pt-mesh, H: Quartz glass tube.

The sensor elements were fabricated as shown in Fig. 1. A disc of sodium ion conductor (NASICON, NGK Co. Ltd.), 8 mm in diameter and 0.5 mm thick, was fixed on the end of a quartz glass tube with an inorganic adhesive. The sensing electrode was fabricated by fixing a gold mesh (100 mesh) on

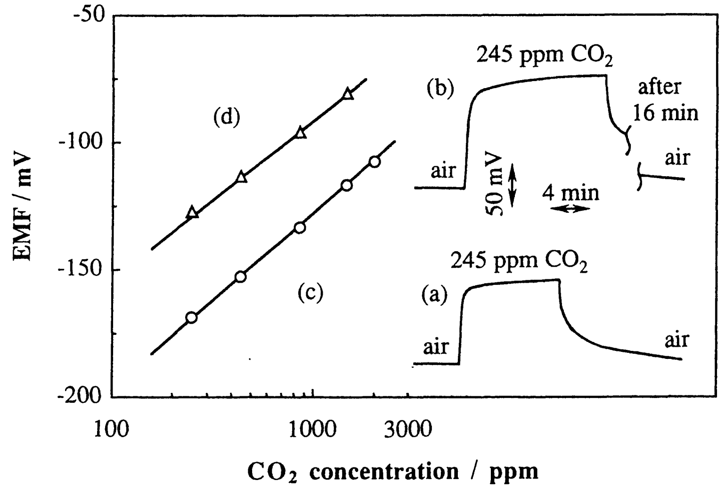

Fig. 2. Sensing performance of the CO_2 sensor element fitted with pure Li_2CO_3.
(a),(b): Response curve to 245 ppm CO_2 in dry air (a) and wet air (P_{H_2O}: 0.86 kPa) (b),
(c),(d): Dependence of EMF on the CO_2 concentration in dry air (c) and wet air (P_{H_2O}: 0.86 kPa) (d).

the outside surface of the disc, followed by covering it with pure Li_2CO_3 or a mixture of Li_2CO_3 and MCO_3 (M = Ca, Sr, Ba) by melting-quenching method. The counter electrode (platinum black) was applied on the inside surface of the disc and mechanically contacted to a platinum mesh attached with a Pt lead. The electrode was always exposed to the atmospheric air. Sensing experiments were carried out in a conventional flow apparatus. Sample gases were prepared from a parent gas, 2000 ppm CO_2 diluted in air or pure CO_2, by mixing it with synthetic air and pure oxygen. The oxygen concentration of the sample gases were always kept constant at 21 vol%. To prepare humid sample gases, dry sample gases were mixed with humid air having bubbled through liquid water. The sensor response, EMF, was measured with a digital electrometer (Advantest, TR 8552) at 500 °C under a total flow rate of 100 cm^3/min. The stability of the carbonates to deliquescence was tested at room temperature in a closed vessel, the atmosphere of which was equilibrated with pure water (relative humidity ca. 100%). The carbonates were melted and quenched in the same way as done for the electrodes, and their weight gains during the storage in the vessel were measured intermittently.

The CO_2 sensing properties of an element fitted with a pure Li_2CO_3 electrode was first examined. As shown in Fig. 2(a), the element responded rather well to switching from dry synthetic air (0 ppm CO_2) to dry CO_2, with the 90% response time of ca. 60 s to 245 ppm CO_2. The EMF response was linear to the logarithm of CO_2 concentration as shown in Fig. 2(c), with a Nernst's slope of 73 mV/decade, or $n = 2.1$ where n is the number of electrons involved in the electrode reaction per CO_2 molecule. In the presence of water vapor, however, the responses were found to be seriously degraded. The rates of response and recovery became smaller, failing to reach steady EMF levels even in 20 min, as shown in Fig. 2(b). In addition, the EMF responses to CO_2 showed large deviations to the positive side in the presence of water vapor as shown in Fig. 2(d), where the EMF levels attained in 20 min after the introduction of wet CO_2 (water vapor pressure 0.86 kPa) are plotted against CO_2 concentrations.

Quite interestingly, the use of a binary electrode, Li_2CO_3-$CaCO_3$ (1.8 : 1.0 in molar ratio), was found to bring about drastic improvements in CO_2 sensing properties. First, it gave very quick responses: the times for 90% response and recovery were both as short as 8 s or shorter for 245 and 860 ppm CO_2, as shown in Fig. 3(a). As compared with the performances of Na_2CO_3-$BaCO_3$ electrode previously reported, the above response time was almost the same, while the recovery time was shortened to about one third.

Second, the responses were totally indifferent of the presence of water vapor up to 1.7 kPa as shown in

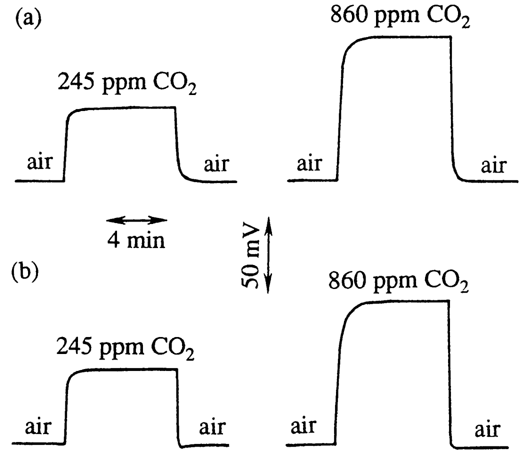

Fig. 3. Response transients of the element using Li_2CO_3-$CaCO_3$ electrode (500 °C).
(a) dry CO_2, (b) wet CO_2 (1.7 kPa-H_2O).

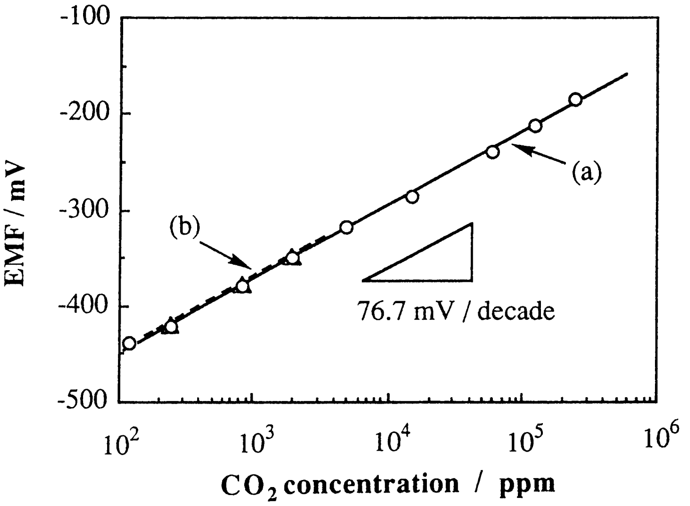

Fig. 4. EMF vs. CO_2 concentration for the element using Li_2CO_3-$CaCO_3$ electrode at 500 °C.
(a) dry CO_2, (b) wet CO_2 (0.86 kPa-H_2O).

Fig. 3(b). As a result, the EMF response was perfectly linear to the logarithm of CO_2 concentration in the whole range tested (120-250000 ppm) without suffering any interference by water vapor, as shown in Fig. 4. The Nernst's slope, 76.7 mV/decade, coincides precisely with a 2-electron reaction of CO_2. It was confirmed by separate experiments that similar performances were also shown by the other binary carbonate systems, Li_2CO_3-$SrCO_3$ and Li_2CO_3-$BaCO_3$.

The present sensors are expressed as a galvanic cell of the form,

air, Pt | NASICON | Au, Li-based carbonate, CO_2 + air.
(Counter electrode) (Na^+conductor) (Sensing electrode)

The cell combines an Na^+ conductor with an Na^+-free carbonate electrode. It is important that despite such an unconventional combination the cell exhibits excellent CO_2 sensing performances. Probably the electrochemical connection between the ionic conductor and the electrode is achieved by a partial ionic exchange between Na^+ of NASICON and Li^+ of the electrode in the vicinity of their interface. On the assumption of such electrochemical connection, the working mechanism of the present sensors is considered to be very similar to that operative in the sensor using Na-based carbonate electrodes.[5,6] The sensing electrode reaction is tentatively assumed to be as follows, although the actual reaction should be investigated in the future study,

$$2Li^+ + CO_2 + (1/2)O_2 + 2e^- = Li_2CO_3 \text{ (in electrode)}. \qquad (1)$$

When the counter electrode reaction is expressed as

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

the overall chemical reaction is written as

$$Li_2CO_3 + 2Na^+ = 2Li^+ + Na_2O + CO_2. \qquad (3)$$

Under the constant activities of Li_2CO_3, Na^+, Li^+ and Na_2O, EMF can be expressed as

$$E = E^o + (RT/2F)\ln P(CO_2). \qquad (4)$$

The experiments have shown that the element fitted with a pure Li_2CO_3 electrode obeys this equation approximately for dry CO_2, whereas water vapor, if present, seriously interferes with its sensing performances.

On the other hand, the element fitted with a Li_2CO_3-$CaCO_3$ electrode has been shown to follow this equation very well irrespectively of the water vapor present, with its Nernst's slope agreeing perfectly with the theoretical value (76.7 mV/decade at 500 °C). The nature of the water vapor interface with the pure Li_2CO_3 electrode as well as that of the drastic improvements brought about by the binary carbonate systems are under investigation.

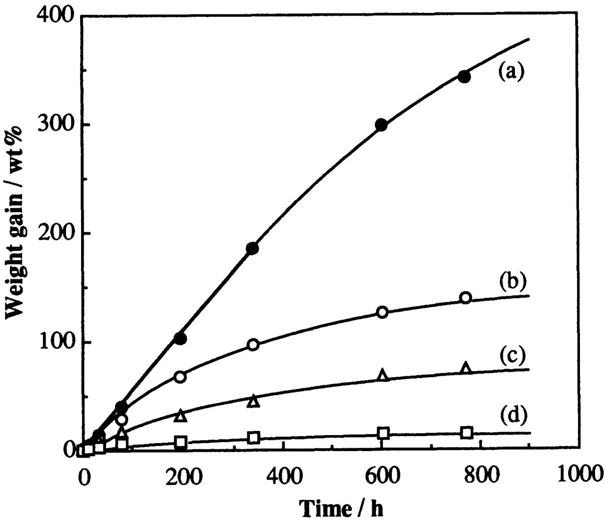

Fig. 5. Weight gains during storage in a very humid atmosphere (R.H.: ca. 100 %) at 30 °C.
(a) pure Na_2CO_3, (b) Na_2CO_3-$BaCO_3$ (1:1.7), (c) pure Li_2CO_3, (d) Li_2CO_3-$CaCO_3$ (1.8:1).

Most important merit of the Li-based binary carbonate electrodes is their remarkable stability to deliquescence. Figure 5 shows weight gains of four carbonate samples, pure Na_2CO_3, Na_2CO_3-$BaCO_3$, pure Li_2CO_3, and Li_2CO_3-$CaCO_3$, during storage under a very humid condition (R. H. : ca. 100%) at room temperature. Because of the high hygroscopicity and large water-solubility of Na_2CO_3, pure Na_2CO_3 and Na_2CO_3-$BaCO_3$ system gained weight most rapidly and began to form a liquid phase in 5 h and 10 h, respectively. Pure Li_2CO_3 gained weight more slowly but still began to form a liquid phase in about 20 h. On the other hand, the weight gain of Li_2CO_3-$CaCO_3$ proceeded very slowly to be almost saturated at about 7% in 200 h, without showing any significant changes in physical appearance of the sample. This implies that the electrode using Li_2CO_3-$CaCO_3$ can stand a very humid atmosphere for a considerable span of time, and thus brings about a great ease in the storage and handling of the sensor in practice.

In conclusion, Li-based binary carbonate electrodes like Li_2CO_3-$CaCO_3$ can be introduced successfully into a NASICON-based electrochemical cell. The resulting CO_2 sensor is excellent in sensing behavior at high temperature (500 °C) and very stable to deliquescence during storage at room temperature.

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