CHEMISTRY LETTERS, pp. 497-500, 1990.

A Carbon Dioxide Gas Sensor Probe Based on a Lithium Ionic Conductor

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A carbon dioxide gas sensor probe was fabricated by applying a high lithium ionic conductor as a solid electrolyte and a calcium carbonate + calcium oxide mixture as a solid reference electrode, and its ability for CO_2 detection was examined. The electromotive force(EMF) obtained was in excellent agreement with the EMF value calculated from the Nernst's equation for CO_2 gas concentrations from 80 ppm(v/v) to 1 %(v/v).

Accumulation of carbon dioxide produced by the consumption of a fossil fuel has been received great attention as a main reason for the warming of the earth. Instrumental analysis such as an infrared absorption measurement has been widely adopted as a practical method for carbon dioxide detection in the atmosphere. Such apparatus, however,is expensive and complicated since it is necessary to beforehandly remove gases which influence the sensor selectivity to CO_2. As an alternative method for quick carbon dioxide detection with a low cost, an electrochemical sensor based on a solid electrolyte has been eagerly investigated. One of the electrolytes for this purpose is an alkali metal carbonate.[1,2] However, its operation needs high temperature in order to acquire sufficient migration of alkali metal ions. A high Na^+ ionic conductor, NASICON, has also been studied as the electrolyte.[3-5] NASICON is not necessarily the best material for the practical application because of its gradual degradation at high temperature.

In our previous studies,[6,7] a lithium ionic conductor based on lithium titanium phosphate was prepared. Its electrical conductivity was approximately as high as that of NASICON and showed excellent stability in the atmosphere. A

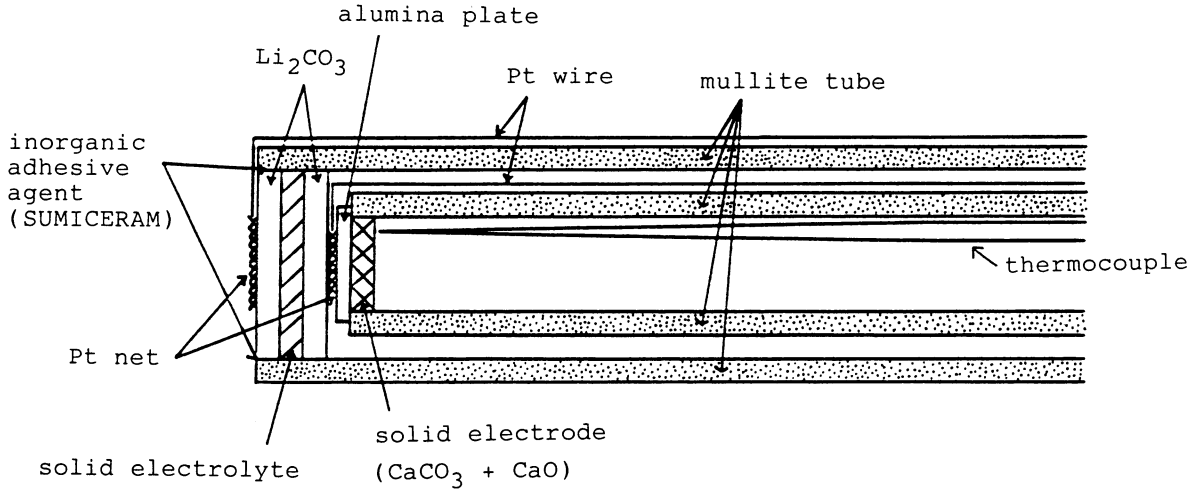

Fig.1. The cross-sectional view of the CO_2 sensor probe.

carbon dioxide sensor probe was fabricated with the lithium conductor and its ability for carbon dioxide detection was investigated.

The lithium solid electrolyte was prepared according to our previous papers.[6,7] The cross-sectional view of the CO_2 sensor probe is presented in Fig. 1. Lithium carbonate pellets were fixed on both surfaces of the electrolytes. The electrolyte and the carbonate pellets were tightly fixed in a mullite tube by an inorganic adhesive agent(SUMICERAM). In order to make the sensor probe more compact, a solid reference electrode produced as an equimolar mixture of calcium carbonate and calcium oxide was utilized. A platinum net was employed as an electrode so as to obtain good contact with the ambient atmosphere. The temperature was measured by a Chromel-Alumel thermocouple. The cell of the CO_2 gas sensor probe is expressed as follows.

$$Pt,\ CO_2,\ O_2 \left| Li_2CO_3 \right|\left| Li_{1.3}Al_{0.3}Ti_{0.7}(PO_4)_3 \right|\left| Li_2CO_3 \right| CO_2,\ O_2,\ Pt$$

In the lower CO_2 pressure compartment, lithium carbonate decomposes into Li^+, CO_2, O_2 and e^-. At the other side, lithium carbonate is produced from ambient CO_2. Therefore, the overall chemical reaction is written as follows,

$$CO_2{}^{I} + 1/2\ O_2{}^{I} \rightarrow CO_2{}^{II} + 1/2\ O_2{}^{II}$$

By applying the Nernst's equation,

$$E = \frac{RT}{2F} \ln \frac{P_{CO_2}{}^{I} \cdot P_{O_2}{}^{I\ 1/2}}{P_{CO_2}{}^{II} \cdot P_{O_2}{}^{II\ 1/2}}$$

Where, R, T, F, and P represent gas constant, temperature, Faraday constant, and partial pressure, respectively. In the atmospheric condition, the next relation is obtained.

$$E = \frac{RT}{2F} \ln \frac{P_{CO_2}{}^{I}}{P_{CO_2}{}^{II}}$$

In the solid reference electrode compartment, the next equilibrium exists.

$$CaCO_3(s) \rightleftarrows CaO(s) + CO_2(g)$$

Therefore, $P_{CO_2}{}^{II}$ is determined at a constant value of a certain temperature. If E, T, and $P_{CO_2}{}^{II}$ are known, the concentration of carbon dioxide($P_{CO_2}{}^{I}$) is calculated.

Figure 2 shows the variation of the EMF response with the CO_2 concentration. The response time for the CO_2 concentration variation was around 4 or 5 min. At least, 4 min is necessary to exchange the atmosphere in the measuring compartment with the detecting gas. Since it seems that the real response time is to be shorter than 1 min, the sensor can detect CO_2 continuously with a quick response.

The EMF variation with the CO_2 concentration is presented in Fig. 3. The measured EMF value was in good agreement with the calculated EMF for the CO_2 gas content ranging from 80 to 1.3×10^4 ppm. For the concentrations lower than 80 ppm,

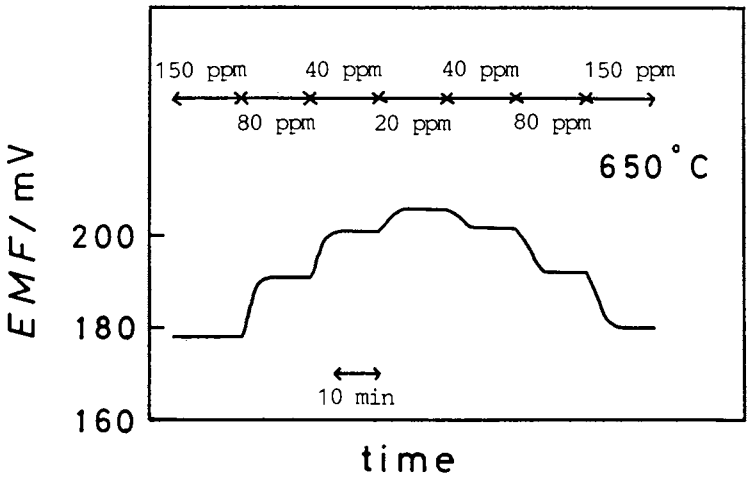

Fig.2. The variation of the EMF response with the CO_2 concentration at 650 °C.

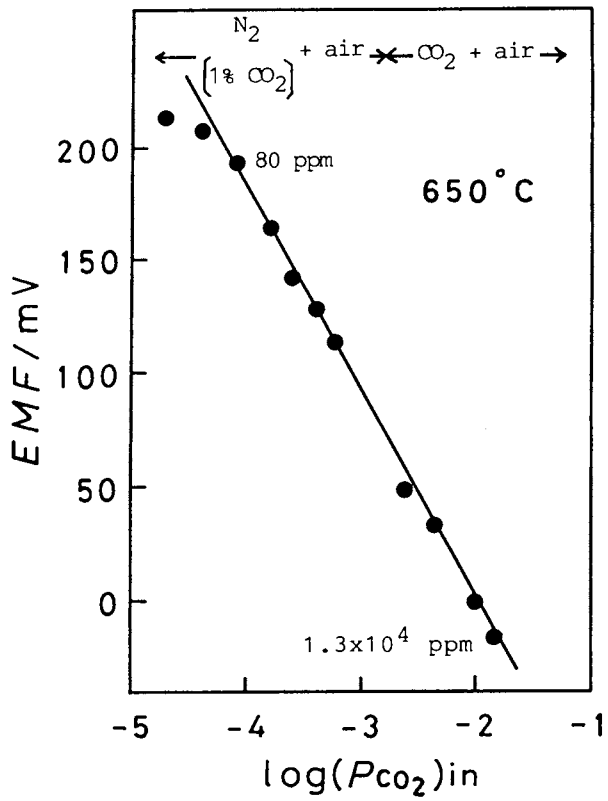

Fig.3. The variation of EMF with the CO_2 concentration at 650 °C.
———— calculated EMF

the measured EMF deviated from the calculated values toward the lower side. In this experiment, the CO_2 gas was diluted with an O_2 and N_2 mixture(1:4). The regulated gas was introduced into an outer mullite tube. The sensor probe was fixed at the one end of the tube with a silicon rubber. The slight permeation of the air atmosphere into the measurement compartment might cause the lowering of the measured EMF value at the low CO_2 concentration ranges.

In conclusion, a carbon dioxide gas sensor probe based on the lithium ionic conductor shows a good response to CO_2 variation. The obtained EMF was almost consistent with those calculated from the Nernst's equation. In addition, the sensor can continuously and rapidly detect CO_2 gas with a low cost. The sensor probe produced, thus, is applicable to CO_2 detection not only in the exhausted gases but also in the atmosphere.

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(Received December 4, 1989)