Water Vapor Influence on Carbon Dioxide Detection of the Sensor Based on Lithium Conducting Solid Electrolyte

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The influence of the water vapor on the CO_2 selectivity of the sensor based on a lithium ionic conductor has been investigated. In a CO_2 gas concentration higher than 1000 ppm, the sensor was able to detect the CO_2 content continuously even when the vapor coexisted up to 222.8 g/m³. In a CO_2 concentration lower than 1000 ppm, EMF deviated lower with the increase of the water vapor content. This might be attributed to the lithium hydroxide formation on the solid electrolyte surface by the chemical reaction between the $\mathrm{Li}_2\mathrm{CO}_3$ + $\mathrm{Li}_2\mathrm{O}$ electrode and water vapor in the atmosphere.

Carbon dioxide produced by fossil fuel combustion has been appreciably increasing since the Industrial Revolution. The control of carbon dioxide emission into the environment is a serious theme these days. Several ${\rm CO_2}$ sensing methods have been proposed to measure the ${\rm CO_2}$ gas concentration. The detection is carried out by measuring the potentiometric, $^{1-4}$) or amperometric 5) response, and resistance, 6) or capacitance change. 7,8) In every method except for Ref.4, the influence of the other coexisting gases emitted on the ${\rm CO_2}$ selectivity, has not been made clear yet. In our previous letter, 4) the influence of ${\rm NO_2(100~ppm)}$, ${\rm SO_2(<20~ppm)}$, ${\rm CH_4(1000~ppm)}$ and a small amount of water(2000~ppm) on the selec-

tivity was investigated and we clarified the excellent ${\rm CO}_2$ selectivity in the existence of these other gases. Among the coexisting gases, however, water vapor, which is one of the main resultants by the combustion of the fuel, is expected to exist in the atmosphere in various amounts. In this letter, the influence of the water vapor on the ${\rm CO}_2$ selectivity of the sensor based on a lithium ionic conductor was investigated.

The preparation of the lithium ionic conductor $^{9)}$ and the fabrication of the sensor $^{2,4)}$ have been already shown in our previous letters. The inlet of water vapor was conducted in two ways. One was to introduce liquid decarbonated water directly at one time (3.5 ml for 1min) to vaporize immediately into the compartment where the sensor was settled (method 1). The other was to mix the dried CO_2 containing air with the moisturized air at the high temperature region of the compartment (method 2). Since carbon dioxide gas is easily absorbed in water, water should be mixed with the CO_2 gas containing air at the temperature where water vaporizes.

Figure 1 presents the electromotive force(EMF) response of the ${\rm CO}_2$ gas sensor with various ${\rm CO}_2$ concentration before and after the exposure to water(method 1). In the ${\rm CO}_2$ gas concentration range from 600 ppm to 0.5%, the ${\rm CO}_2$ gas sensor can detect the gas precisely after the exposure to such a high humidity atmosphere. However, in a content lower than 600 ppm, the EMF value deviated lower from the calculated EMF. Several microcracks, which might be produced by the instant vaporization of the water, appeared in the inorganic adhesive agent of the sensor probe after the measurements. The inlet gas permeation from the detecting compartment to the reference occurred and resulted in the decrease of the EMF value.

Figure 2 shows the EMF results for the ${\rm CO_2}$ sensor with the variation of the moisture in the inlet gas(method 2). The difference between the measured and the calculated EMF became clear in the ${\rm CO_2}$ gas content lower than 1000 ppm. The higher the water content would be, the lower the EMF value became. Lithium hydroxide might be produced on the surface of the lithium carbonate and lithium oxide electrode which was settled on the

electrolyte surface by the introduction of fumed air, and suppressed the electrode reaction of lithium carbonate decomposition. With the increase of the CO_2 concentration, the driving force of the lithium carbonate decomposition at the detecting compartment decreased. Then, the formation of LiOH on the electrode surface has a diminishing influence on the detection up to a CO_2 content of 0.1%. At CO_2 content higher than 0.1%, LiOH formation has almost no influence on the CO_2 detection. After stopping the water vapor introduction, the EMF gradually increased and became stable at the EMF value just obtained before the water vapor

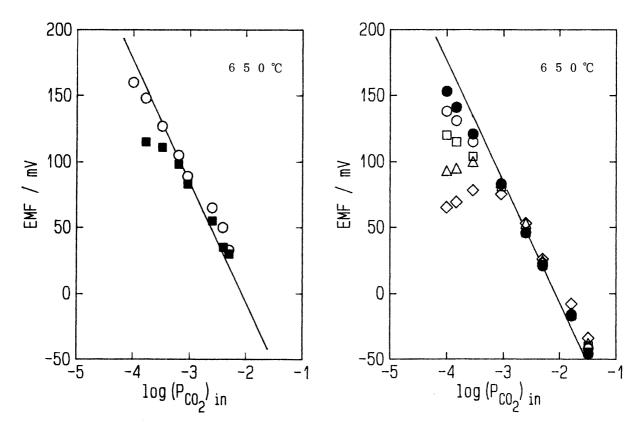


Fig.1. The EMF response of the ${\rm CO}_2$ sensor with various ${\rm CO}_2$ concentration before and after the exposure to water vapor.

○ :before

:after

--: calculated EMF

Fig.2. The EMF results for the ${\rm CO}_2$ sensor with the variation of the moisture.

 \bullet :none \bigcirc :4.73 g/m³

 $\square:30.34 \text{ g/m}^3 \qquad \triangle:88.22 \text{ g/m}^3$

 \diamondsuit :222.8 g/m³

--: calculated EMF

introduction. The lithium hydroxide compound produced by the water vapor exposure, reacted with carbon dioxide in the atmosphere to form $\rm Li_2CO_3$ on the electrode surface.

In conclusion, the CO_2 gas sensor based on a lithium ionic conductor is able to measure the gas concentration continuously in the CO_2 concentration higher than 1000 ppm even when water vapor coexists up to 222.8 g/m 3 . In the CO_2 content lower than 1000 ppm, lithium hydroxide might be formed on the $\mathrm{Li}_2\mathrm{CO}_3$ + $\mathrm{Li}_2\mathrm{O}$ electrode surface and the sensor cannot detect the precise CO_2 content. However, the sensor recovers the CO_2 detectability when the water vapor is removed.

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