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The Operating Temperature Lowering for CO_2 Gas Sensor with a Lithium Conducting Solid Electrolyte

Nobuhito IMANAKA, Toshihide MURATA, Takeshi KAWASATO, and Gin-ya ADACHI*
Department of Applied Chemistry, Faculty of Engineering,
Osaka University, 2-1 Yamadaoka, Suita, Osaka 565

The lowering of the operating temperature for the CO_2 gas sensor with the lithium conducting solid electrolyte was examined by applying a ductile solid of a Li_2CO_3+Li_2O mixture or a Li_2CO_3-K_2CO_3-Na_2CO_3 eutectic. In the case of the eutectic solid, the CO_2 sensor can detect the gas content precisely from 100 ppm to 1% at as low a temperature as 350 ^oC. The ductilities of the solid greatly enhanced the reactivity between Li_2CO_3 in the eutectic and the CO_2 gas in the atmosphere.

The increase of carbon dioxide content in the atmosphere has become a serious problem around the world. The on-line CO_2 monitoring in the exhaustion and the regulation of the carbon dioxide emitted in air is an appropriate way of suppressing the green house effect. As a practical method for the detection, infrared analyses have been widely utilized. However, the apparatus is difficult to set up at each site because of its high price. Recently, several electrochemical methods have been extensively investigated. One is to obtain the content by a potentiometric method using a solid electrolyte.[1-4] The other is to measure the concentration from the capacitance,[5,6] resistance[7] or current[8] change. However, the selectivity of the sensor with several gases in a coexisting atmosphere has not been made clear in the latter case. As the candidates for the electrolyte, β-Alumina,[1] lithium conducting solid electrolyte,[2,4] and NASICON[3] have been investigated for a practical utilization.

In our previous letter,[2,4] the CO_2 sensor based on lithium titanium phosphate, which shows excellent properties; both ionic conductivity and stability in the atmosphere,[9] was fabricated. The influence of the several gases in the coexisting atmosphere on the CO_2 selectivity was investigated and clarified that no influence to the detectability of CO_2 existed. However, the measuring temperature for the CO_2 detection with the solid electrolyte should be still controlled at 400 °C,[1] 650 °C,[2,4] and 550 °C[3] in the case of β-Alumina, lithium phosphate based electrolyte, and NASICON, respectively. Since this type of CO_2 sensor has a merit in its simplicity and compactness, it can be set up at every site with various temperatures.

In this letter, the lowering of the measuring temperature for the CO_2 sensor with the lithium conducting solid electrolyte was examined by applying a lithium containing ductile solid on the electrolyte surface.

In our previous measurements, lithium carbonate was fixed on the electrolyte surface. The measuring temperature was controlled at 650 °C, where the decomposition and formation of Li_2CO_3 proceed smoothly. In this study, two kinds of solid pellets were fixed on both surfaces of the electrolyte so as to make the operating temperature lower. One was a lithium carbonate and lithium oxide mixture prepared by heating lithium methoxide at 650 °C. By this heat treatment, we can get a thin layer of Li_2CO_3+Li_2O on the electrolyte surface. An excellent contact between the Au electrode and the solid electrolyte was obtained. The other was the eutectic mixture of Li_2CO_3-K_2CO_3-Na_2CO_3(47.6:25.4:27.0). This eutectic melts as low a temperature as around 390 °C[11] and is also expected to lower the contact resistance between the electrode and the electrolyte.

The EMF variation for the CO_2 gas sensor with Li_2CO_3+Li_2O at 450 °C is shown in Fig.1. In the CO_2 gas concentration from 100 ppm to 0.5%, the measured EMF was almost consistent with the calculated EMF(—). Lithium carbonate and the products prepared by the partial decomposition of the carbonate are found to make some kind of eutectic around 410 °C.[10] The electrode reaction of the formation and decomposition of Li_2CO_3 on the Li_2CO_3+Li_2O surface proceeds well even at this temperature. The EMF variation with the CO_2 gas concentration at 400 °C is also presented in Fig.1. The measured EMF was considerably decreased in comparison with the calculation(--). It is mainly attributed to the decrease of the decomposition reaction on the CO_2 detecting surface because Li_2CO_3+Li_2O is not reactive enough to promote the electrode reaction of the Li_2CO_3 decomposition.

Figure 2 shows the EMF variation with Li_2CO_3-K_2CO_3-Na_2CO_3 on the electrolyte surface instead of the Li_2CO_3+Li_2O mixture. Almost the same EMF value was obtained between the measured and calculated EMF even at 350 ^{o}C, which is 100 ^{o}C lower than the lowest operating temperature of the CO_2 sensor with Li_2CO_3+Li_2O on the surface. The time taken for 90% response in the CO_2 detection was around a half minute, which compared favorably to the time for the previous measurements at 650 ^{o}C.[2,4] Because the melting point of the Li_2CO_3-K_2CO_3-Na_2CO_3 eutectic was around 390 ^{o}C,[11] the eutectic solid is still ductile even at this temperature. This ductility greatly contributes to start the decomposition reaction of Li_2CO_3 smoothly on the eutectic surface as well as to decrease the

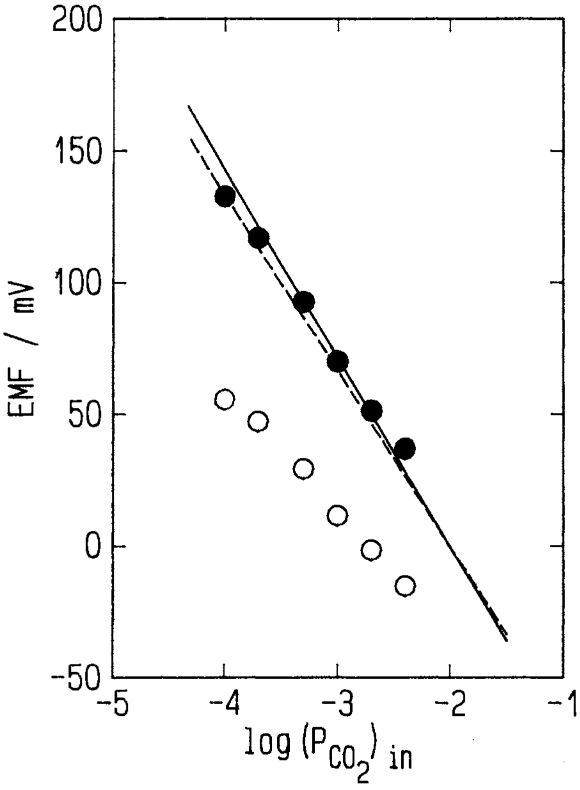

Fig.1. The EMF variation for the CO_2 gas sensor with Li_2CO_3-Li_2O.
● : 450 ^{o}C
○ : 400 ^{o}C
——,- - - : calculated EMF[2)]

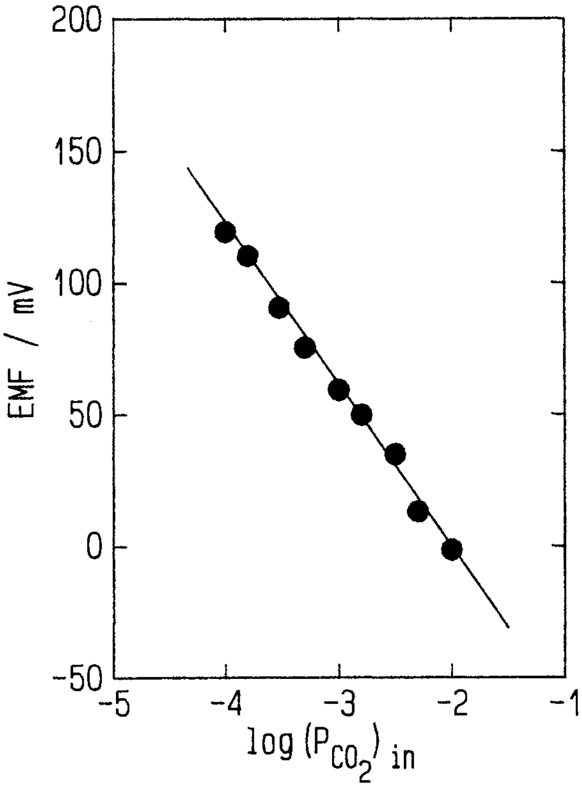

Fig.2. The EMF variation for the CO_2 gas sensor with Li_2CO_3-K_2CO_3-Na_2CO_3 at 350 ^{o}C.
—— : calculated EMF[2)]

contact resistance between the electrolyte and the electrode.

In conclusion, the application of the Li_2CO_3+Li_2O mixture or the Li_2CO_3-K_2CO_3-Na_2CO_3 eutectic solid with a lithium conducting solid electrolyte in the fabrication of the CO_2 sensor is appreciably effective by lowering the operating temperature. Especially, in the case of the eutectic solid, the sensor can detect the CO_2 concentration exactly from 100 ppm to 1% at a temperature as low as 350 ^{o}C, which is appreciably lower than the operating temperature for the solid electrolyte type CO_2 sensor reported before.

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