Carbon Dioxide Gas Sensor with Li$_2$TiSiO$_5$ Solid Electrolyte and NiO–Li$_2$CO$_3$ as Sensing Electrode

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NiO–Li$_2$CO$_3$ 検知極と Li$_2$TiSiO$_5$ を用いた炭酸ガスセンサー
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Sodium ionic conductors such as NASICON (Na$_3$Zr$_2$Si$_2$PO$_{12}$) have been used as a solid electrolyte for electromotive force (EMF) CO$_2$ sensor. However, it has been difficult to obtain a sufficiently high quality for this type of sensor. In general, when the EMF CO$_2$ sensor is left in an atmosphere having a high water concentration, such as a high-humidity atmosphere or condensation atmosphere, the EMF of the sensor greatly decreases. For the purpose of improving the humidity-resistance of the CO$_2$ sensor, Li$_2$TiSiO$_5$ is employed as the solid electrolyte material of the following electrochemical cell: CO$_2$-Air/Au–Li$_2$CO$_3$/Li$_2$TiSiO$_5$/Au–CO$_2$-Air. The electrochemical reaction is in good agreement with the Nernst equation, and the reaction constant, 2.04, is preserved and the EMF of the sensor does not change after exposure to high humidity atmosphere. Au–NiO–Li$_2$CO$_3$//Li$_2$TiSiO$_5$/Au can be considered to serve as a high humidity-resisting system for solid electrolyte CO$_2$ sensors.

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1. Introduction

In recent years, along with a growing interest in environmental problems, monitoring sensors for controlling a concentration of carbon dioxide gas (CO$_2$) discharged into an atmosphere have been attracting much attention. Out of the sensors, a solid electrolyte CO$_2$ sensor element making use of a change in electromotive force (EMF) of a solid electrolyte is small in size, simple in structure and inexpensive. Therefore, the implementation of this solid electrolyte CO$_2$ sensor element has been strongly desired. In general, the solid electrolyte of this CO$_2$ sensor is formed of a sodium ionic conductor such as NASICON (Na$_3$Zr$_2$Si$_2$PO$_{12}$). $^{1,2,3}$ However, the above solid electrolyte CO$_2$ sensor in which an alkali metal carbonate is used as a sensing electrode material has such a problem that when it is left in an atmosphere having a high water concentration such as a high-humidity atmosphere or condensation atmosphere after heating is stopped to suspend the operation of the sensor and then its operation is resumed, the EMF greatly falls below a value before it is left. $^{4,5}$ In such a case, it is actually impossible to measure the CO$_2$ concentration in the air. Therefore, the development of a solid electrolyte CO$_2$ sensor whose EMF does not change even when it is left in an atmosphere having a high water concentration such as high humidity and condensation for a long time without being heated has been strongly desired.

This phenomenon seems to be caused by fundamental properties of sodium ionic conductors. Therefore, in order to improve the humidity resistance of the solid electrolyte CO$_2$ sensor, lithium ionic conductors are investigated instead of sodium ionic conductors. In this experiment, lithium silicates and lithium titanium silicate are tried to use as the solid electrolytes. The lithium silicates may be regarded as basic materials for the lithium ionic conductors. Consequently, these compounds are at first examined for the sensing materials.

2. Experimental

2.1 CO$_2$ Sensor

The lithium silicates (Li$_2$SiO$_3$, Li$_2$SiO$_5$, and Li$_2$SiO$_7$) were prepared through the hydrolysis of lithium methoxide and tetraethyl orthosilicate. The lithium titanium silicate (Li$_2$TiSiO$_5$) was prepared through the hydrolysis of lithium methoxide, titanium tetra-n-butoxide, and tetraethyl orthosilicate. After hydrolyzing, each gel was heated at 800°C in the air for 2 h. The resulting powders of lithium silicates were pressed into small pellets (3.5 mm in diameters and 0.5 mm in thickness), and then were calcined at 1000°C for 6 h. In the case of Li$_2$TiSiO$_5$, the powders were pressed into the same form, and then were calcined at 1100°C for 6 h.

The structure of the sensor at this time is shown as Fig. 1. The sensing electrode was formed by kneading gold powders as an electron conducting material and Li$_2$CO$_3$ (75 mass% Au + 25 mass% Li$_2$CO$_3$) into a terpinolene solution containing 5 mass% of ethyl cellulose to prepare paste, applying this paste to one side of the solid electrolyte by screen printing, drying and baking it at 650°C in the air for 30 min.
The reference electrode was formed by kneading gold powders as an electron conducting material into a terpineol solution containing 5 mass% of ethyl cellulose to prepare paste, applying this paste to a surface opposite to the sensing electrode of the solid electrolyte by screen printing, drying and baking it at 650°C in the air for 30 min.

The sensor is composed of the following electrochemical cell:

\[
\text{CO}_2 + \text{Air}/\text{Au} + \text{Li}_2\text{CO}_3/\text{Li}^+ \text{ conductor}/\text{Au}/\text{CO}_2 + \text{Air} \tag{1}
\]

In this case, the left-hand side acts as the sensing electrode and the right-hand side acts as the reference electrode. The respective electrode reaction is given by the following equations:\(^5\)

Sensing electrode: \(\text{Li}_2\text{CO}_3\)
\[
= 2\text{Li}^+ + \text{CO}_3^2-(1/2)\text{O}_2 + 2e^- \tag{2}
\]

Reference electrode: \(2\text{Li}^+ + (1/2)\text{O}_2 + 2e^- = \text{Li}_2\text{O} \tag{3}\)

As the sensing and reference electrodes are exposed to the same atmosphere, the pressure of \(\text{O}_2\) closing to the two electrodes is the same. Therefore, the overall reaction can be described as the follows.

\[
\text{Li}_2\text{CO}_3 = \text{CO}_2 + \text{Li}_2\text{O} \tag{4}
\]

When the activity of \(\text{Li}_2\text{CO}_3\) is kept constant, the EMF of the cell can be expressed as:

\[
\text{EMF} = C - \left(\frac{RT}{nF}\right) \ln \left(\frac{a(\text{Li}_2\text{O})P(\text{CO}_2)}{a'}\right) \tag{5}
\]

where \(C\) is a constant, \(R\) is the gas constant, \(T\) is the absolute temperature, \(n\) is the reaction constant, \(F\) is the Faraday constant, \(a\) is the activity, and \(P\) is the partial pressure.

2.2 Humidity resistance test

Right after the manufacture of the \(\text{CO}_2\) sensors, they were placed in a chamber which can control the concentration of \(\text{CO}_2\), and DC voltage was applied to a heater from a power source to heat the sensor elements at 450°C.

While the temperature of each of the sensor elements was maintained at 450°C, the EMF was measured and taken as initial EMF. After the measurement of the initial EMF, the sensor elements were taken out from the chamber and placed in a thermostatic chamber maintained at a temperature of 60°C and a relative humidity of 90% without heating. After that, the sensor elements were taken out from the thermostatic chamber and the EMF was measured in the same manner as in the above methods for measuring the initial EMF.

3. Results and discussion

3.1 Sensing characteristic and humidity resistance of the sensor constructed of lithium silicates

Figure 2 shows the EMF (\(\text{CO}_2 = 350\) ppm) and the sensitivity of the sensors constructed of lithium silicates as the solid electrolyte. The sensitivity of the sensor is calculated from the slopes of the EMF with \(\text{CO}_2\) concentration between 350 ppm and 3500 ppm.

The structure of the lithium silicates varies with a ratio of lithium to silicon. For example, when lithium over silicon is 1, \(\text{Li}_2\text{SiO}_3\) is formed. In the other case, when lithium over silicon is 2, \(\text{Li}_4\text{SiO}_4\) is formed. With increasing the ratio of lithium to silicon from 0.5 to 4, the EMF of the sensor decreases continuously as shown in Fig. 2(a). On the other hand, the \(\text{Li}_4\text{SiO}_4\) sensor takes a maximum sensitivity among these sensors. But the sensitivity of the \(\text{Li}_2\text{SiO}_3\) sensor is 53.0 mV/decade and does not reach the theoretical value (71.7 mV/decade) calculated from the Eq. (5).

The humidity resistance of the sensors is evaluated while they are exposed to an atmosphere of 90% relative humidity at 60°C for 12 and 24 h. The EMF of the lithium silicates sensors drops suddenly with exposure time except for that of \(\text{Li}_2\text{SiO}_3\) as shown in Fig. 3(a). In the case of the changes in the sensitivity of the sensors exposed to the same atmosphere, only \(\text{Li}_2\text{SiO}_3\) maintains the constant value with exposure time as shown in Fig. 3(b). Judging from the results in these experiments, the humidity resistance of \(\text{Li}_2\text{SiO}_3\) is superior to that of the other lithium silicates. \(\text{Li}_2\text{SiO}_3\) has the shortest Li–O bond length suggesting the strongest bond among the lithium silicates. It can be assumed that the strong bond enhances the humidity resistance of the \(\text{Li}_2\text{SiO}_3\) sensor.

However, as mentioned before, the sensitivity of the \(\text{Li}_2\text{SiO}_3\) sensor does not reach the theoretical value. It may be responsible for the bond-structure through lithium ions.

3.2 Humidity-resistance of \(\text{Li}_2\text{TiSiO}_5\) sensor

In order to transform the bond-structure through lithium ions, \(\text{Li}_2\text{TiSiO}_5\) has been tried to use for the sensor. The layered [TiSiO\(_4\)]\(^2-\) anions are bound by planes of Li\(^+\) cations\(^6\) in \(\text{Li}_2\text{TiSiO}_5\).

Figure 4(a) shows the changes in the EMF of the \(\text{Li}_2\text{TiSiO}_5\) sensor as a function of \(\text{CO}_2\) concentration. At the same time, the changes in the EMF of the sensor exposed to an atmosphere of 90% relative humidity at 60°C for 24 h are illustrated. The sensitivity of this sensor is 70.3 mV/decade and the reaction constant calculated from the Eq. (5) is 2.04.

The electrochemical reaction of the \(\text{Li}_2\text{TiSiO}_5\) sensor is in good agreement with the Nernst equation. After exposure to the high humidity atmosphere, the sensitivity and the reaction constant are not altered. On the other hand, the sensitivity of \(\text{Na}_2\text{CO}_3\) or \(\text{Li}_2\text{CO}_3\)/NASICON sensors was greatly decreased.\(^7\) These experiments results make it possible to use \(\text{Li}_2\text{CO}_3/\text{Li}_2\text{TiSiO}_5\) sensor in the practical en-
proved, it is not perfect. The EMF of the Li$_2$CO$_3$/Li$_2$TiSiO$_5$ sensor decreases slightly as shown in Fig. 4(a). The slightly drop in the EMF needs to be reduced to zero for the completion of the sensor.

In order to investigate the reason why the EMF of the Li$_2$TiSiO$_5$ sensor decreases under the high humidity atmosphere, the reaction between the solid electrolyte and the sensing electrode was examined. At first, Li$_2$TiSiO$_5$ powder was mixed with Li$_2$CO$_3$ powder (Li$_2$TiSiO$_5$: Li$_2$CO$_3$ = 1:1 (molar ratio)). And then, the mixture was heated at 650°C for 30 min. As noted above, this heating is required for the bonding of the sensing electrode to the solid electrolyte. Figure 5(a) shows X-ray diffraction patterns for the mixture heated at 650°C. After heating, the mixture is exposed to the atmosphere of 90% relative humidity at 60°C for 24 h. Figure 5(b) shows the X-ray diffraction patterns for the mixture exposed to the high humidity atmosphere. In this case, new compound such as Li$_2$SiO$_3$ is detected. The EMF and the sensitivity of the Li$_2$SiO$_3$ sensor decrease with exposure time as shown in Fig. 3, so this compound seems to deteriorate the humidity resistance of the Li$_2$TiSiO$_5$ sensor.

**3.3 Effect of NiO as sensing electrode**

For the purpose of prevention the drop in the EMF of the Li$_2$TiSiO$_5$ sensor, several oxides such as Al$_2$O$_3$, SiO$_2$, ZrO$_2$, and NiO were tried to mix with the sensing electrode. Within these oxides, NiO was the most promising addition. The other compounds had no effect on properties of the Li$_2$TiSiO$_5$ sensor.

Therefore, NiO powder was mixed with Li$_2$CO$_3$ and Li$_2$TiSiO$_5$ powder (NiO: Li$_2$TiSiO$_5$: Li$_2$CO$_3$ = 1:5:5 (molar ratio)). Figure 6(a) shows X-ray diffraction patterns for the mixture of NiO, Li$_2$TiSiO$_5$, and Li$_2$CO$_3$ heated at 650°C for 30 min. After heating, the mixture is exposed to the atmosphere of 90% relative humidity at 60°C for 24 h. Figure 6(b) shows the X-ray diffraction patterns for the mixture exposed to the high humidity atmosphere. In this case, even when the mixture is exposed to the high humidity atmosphere, new compounds are not detected. It is supposed that NiO prevents the reaction between Li$_2$TiSiO$_5$ as the solid electrolyte and Li$_2$CO$_3$ as the sensing electrode.

Figure 4(b) shows the changes in the EMF of the Li$_2$TiSiO$_5$ sensor fabricated with Li$_2$CO$_3$–NiO (Li$_2$CO$_3$: NiO = 5:1 (molar ratio)) as the sensing electrode. At the same time, the changes in the EMF of the sensor exposed to the atmosphere of 90% relative humidity at 60°C for 24 h are

Although the humidity resistance of the sensor is im-

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**Fig. 3.** EMF (a) and sensitivity (b) of the sensors fabricated with Li$_2$SiO$_3$ (○), Li$_2$SiO$_3$ (△), and Li$_2$SiO$_3$ (●) after exposure to an atmosphere of 90% relative humidity at 60°C.

**Fig. 4.** EMF of the sensor fabricated with (a) Li$_2$CO$_3$/Li$_2$TiSiO$_5$ and (b) (NiO+Li$_2$CO$_3$)/Li$_2$TiSiO$_5$ system. ○: fresh, ●: after exposure to the atmosphere of 90% relative humidity at 60°C for 24 h.

**Fig. 5.** XRD patterns for Li$_2$TiSiO$_5$–Li$_2$CO$_3$ calcined at 650°C for 30 min (a) and exposed to the atmosphere of 90% relative humidity at 60°C for 24 h after calcining (b). ○: Li$_2$TiSiO$_5$; △: Li$_2$CO$_3$; ●: Li$_2$SiO$_3$.
illustrated. The reaction constant, 2.04, is preserved and the EMF of the sensor does not change after exposure to the high humidity atmosphere. NiO can be said to serve as the high humidity-resisting material for the solid electrolyte carbon dioxide gas sensor.

Like the humidity resistance, a quick response of the EMF is required for the CO₂ sensor. The initial 90% response of the EMF of this sensor is steadied within 4 min. These experimental results satisfy the conditions for use in the practical environments.

4. Conclusions

(1) The electrochemical reaction of the sensor fabricated with Li₂Ti₃SiO₈ is in good agreement with the Nernst equation, and the reacted electron is calculated as 2.04.

(2) The EMF of the Li₂Ti₃SiO₈ sensor decreases slightly when it is exposed to the atmosphere of 90% relative humidity at 60°C after heating is stopped to suspend the operation of the sensor.

(3) The humidity resistance of the Li₂Ti₃SiO₈ sensor is enhanced by NiO addition as the sensing electrode.

References