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Solid-state amperometric CO_2 sensor using a sodium ion conductor

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Abstract

A solid-state amperometric CO_2 sensor was prepared by combining a NASICON (Na^+ conductor, $Na_3Zr_2Si_2PO_{12}$) with a porous Na_2CO_3 auxiliary layer deposited on a sensing electrode. The current between sensing and counter electrodes as a function of CO_2 concentration was approximately linear in the range of 200–2000 ppm at 400 °C. The device could be operated stably during the test period (60 days). The sensing characteristics and long-term stability were discussed in the light of the sensing mechanism.

Keywords: Amperometric CO_2 sensing; Ionic conductivity; Sensors

1. Introduction

The detection of the CO_2 concentration is becoming increasingly important for monitoring the indoor quality as well as global greenhouse gas emissions. Various types of cost-effective sensors have been investigated in an effort to replace the infrared spectroscopic CO_2 sensor.[1–3] Among them, the potentiometric-type sensor, which consists of a Na^+ conductor, metal carbonate and a reference electrode, is attractive because it exhibits a satisfactory EMF (electromotive force) over a wide range of CO_2 concentrations.[4–6]

However, the seal of the reference electrode[4] or the attachment of the Na^+- containing reference electrode material[6] is important in order to avoid drift in the potentiometric signal. Moreover, the sensor EMF is known to decrease after being exposed to a humid atmosphere at low temperatures.[7,8] This paper reports a compact and drift-free amperometric CO_2 sensing device using NASICON (Na^+ conductor, $Na_3Zr_2Si_2PO_{12}$) and a porous Na_2CO_3 layer coated on the sensing electrode, which requires neither gas sealing nor a Na^+-reference electrode. The sensing characteristics and long-term stability are discussed in relationship with sensing mechanism.

2. Experimental

The NASICON powder was prepared by calcining a powder mixture of reagent-grade Na_2CO_3, SiO_2, ZrO_2 and NH_4HPO_4 at 1125 °C for 11 h. After ball milling the powder for 24 h using ethyl alcohol, the dried powder was compacted into a disc at 60 MPa and then sintered at 1220 °C for 14 h. Fig. 1 shows schematic diagram of sensor structure. The Pt paste was applied to both sides of the electrolyte and Pt wires were then attached. A porous Na_2CO_3 layer was formed via the partial melting of a thin Na_2CO_3 powder compact on a Pt|NASICON|Pt cell using a propane torch.

The CO_2 concentration was controlled by changing the mixing ratio between the parent gas (0.2% CO_2 in air balance) and dry synthetic air. At the sensing temperature (400 °C), the current decayed for approximately 1 min after applying the voltage, and the subsequent voltage variation required approximately 30 s to saturate the signal. Therefore, the sensor signal was measured with varying CO_2 concentration 5 min after applying the voltage and the I-V characteristics were attained by measuring the current 1 min after each successive increase in voltage.

3. Results and discussion

Fig. 2 shows the response transient and sensor characteristics measured by varying the CO_2 concentration between 200 and 2000 ppm at 400 °C with an applied voltage of 0.1 V. The response transient was sharp

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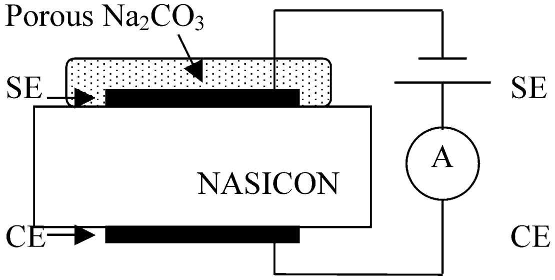

Fig. 1. Schematic diagram of sensor with porous Na_2CO_3 auxiliary layer.

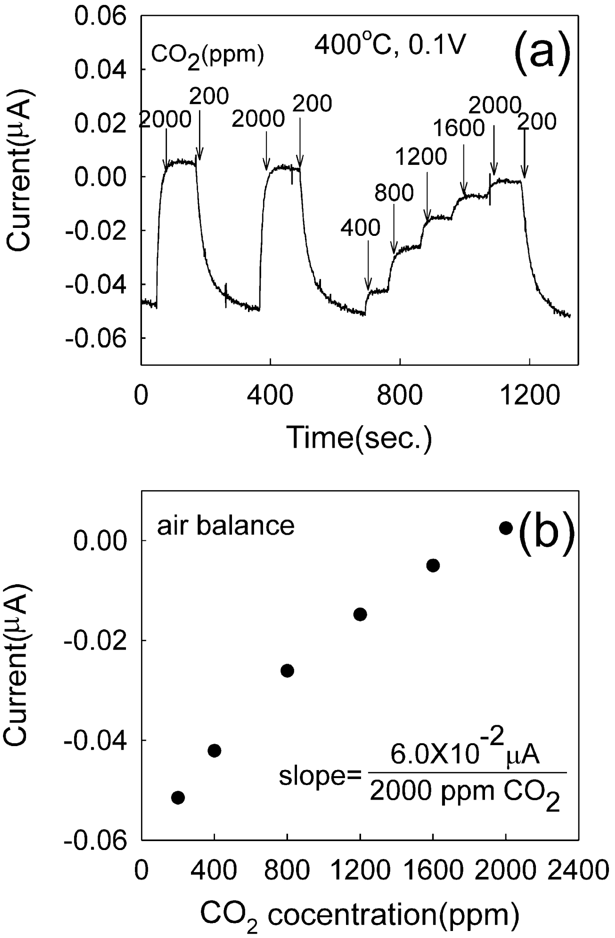

Fig. 2. (a) Response transient and (b) static sensing characteristics.

[Fig. 2(a)] and the current was approximately proportional to CO_2 concentrations ranging from 200 to 2000 ppm. [Fig. 2(b)] The sensor with the dense Na_2CO_3 layer was also fabricated for comparison. The sensing transient was not distinct and the signal at a fixed CO_2 concentration drifted with repeated measurements. This fact suggests that CO_2 diffusion towards the sensing electrode is necessary for amperometric sensing, and it becomes difficult when a dense Na_2CO_3 layer is employed.

The current increased with increasing O_2 concentration and the signal increment was 0.4 nA per 1% increase in oxygen. It is approximately 1/130 of the signal change when the CO_2 concentration varied from 200 to 2000 ppm, which suggests that the present sensor could be used as CO_2 sensor for monitoring the indoor air quality without a significant influence from O_2 concentration.

The I-V characteristics were examined with varying CO_2 concentrations although they are not shown in this paper. No distinct limiting current plateau was found and a negative current was found at 0 V. This means that a limitation in CO_2 diffusion via the porous Na_2CO_3 layer is not the main reason for the CO_2-dependent amperometric signal although CO_2 is necessary for sensing. The net current at 0.1 V was largely negative at lower CO_2 concentrations and increased to slightly positive with increasing CO_2 concentrations upto 2000 ppm. Moreover, the zero-current point decreased to the lower CO_2 concentration with increasing external electric field. It means that the amperometric signal of the present sensor is the result of competition between the Na^+ migration by differences in the Na^+ activity and that by the external electric field. A schematic diagram of the sensing mechanism is shown in Fig. 3. Na^+ ions are known to migrate towards a reference electrode according to the following reactions when the air without CO_2 and H_2O vapor was provided to the gas-sealed reference electrode.[4]

$$Na_2CO_3 \rightarrow 2Na^+ + CO_2 + 1/2O_2 + 2e^- \quad \text{(Sensing electrode)} \tag{1}$$

$$2Na^+ + 1/2O_2 + 2e^- \rightarrow Na_2O \quad \text{(Reference electrode)} \tag{2}$$

Therefore, the Na^+ migrates from the sensing electrode (SE) to the counter electrode (CE). (see the arrow 1 in Fig. 3) On the other hand, the external electric field moves Na^+ toward the SE. (see arrow 2) Therefore, a net negative current (see arrow 3) is observed at low CO_2 concentrations because Na^+ migration by the difference in the Na^+ activity is dominant compared to that caused by the external field. However, at high CO_2 concentrations, a smaller amount of Na^+ migrates toward the CE (arrow 1′) because the reverse reaction of (1) dominates. Therefore, the net current approaches zero and becomes positive with increasing CO_2 concentration because the external field effect is identical.

The long-term stability of the sensor was investigated by monitoring the current at 200 ppm CO_2 for 60 days. (Fig. 4) For this, the sensor was kept in indoor air

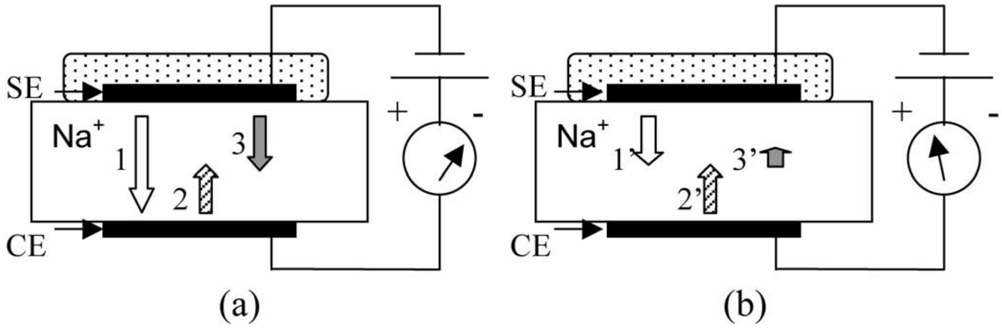

Fig. 3. The schematic diagram of sensing mechanism at (a) low CO_2 concentration and at (b) high CO_2 concentration.

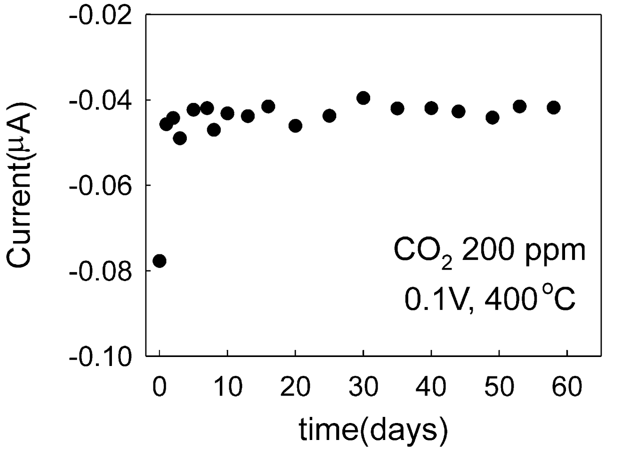

Fig. 4. Long-term stability of the current response to 200 ppm CO_2 at 0.1 V.

containing some humidity (RH 50–80%) and CO_2 (200–2000 ppm) at room temperature (approximately 25 °C) after each measurement. The sensor signal was stable over the test period (60 days) except for the first day, which suggests that the electrode-potential change in both the SE and CE is small. Therefore, the stability of the sensor is discussed in the light of the SE and CE potentials.

Kida et al.[9] investigated the stability of the NASICON-based CO_2 sensor against humidity by monitoring the potentials of the SE and CE after both electrodes had been exposed to a humid atmosphere at low temperatures. They reported that the SE potential covered with a Li_2CO_3–$BaCO_3$ auxiliary phase was stable despite the long exposure to the humid atmosphere. In contrast, the CE potential changed to a large extent and gradually recovered to its original value by sensor operation at 450 °C. The stable SE potential was attributed to the formation of a corrosion layer ($BaZrO_3$) between the auxiliary phase and the NASICON, which protects the NASICON from further attack by water vapor. On the other hand, the change in the CE potential was explained in terms of Na_3PO_4 formation during the exposure to humidity.

In order to conform the existence of a corrosion layer, the Na_2CO_3-covered NASICON without Pt electrodes was placed in the flow of the synthetic air containing humidity (3.5 kPa H_2O) at 50 °C for 3 days. An approximately 10 μm thick layer was observed between the Na_2CO_3 and the NASICON, which was identified as Na_2ZrO_3 by electron probe micro analysis. The corrosion layer similar to $BaZrO_3$ shows that the SE potential in this study is also relatively stable.

Generally, a potentiometric sensor using a Na_2CO_3 auxiliary phase keeps the Na^+ activity at the reference electrode constant by flowing dry air. However, the reaction at the CE in this study might include H_2O vapor and CO_2 because the electrode was not sealed.[9] The following equation illustrates this reaction.

$$2Na^+ + CO_2 + 1/2O_2 + 2e^- \rightarrow Na_2CO_3 \quad \text{(counter electrode)} \tag{3}$$

$$2Na^+ + H_2O + 2CO_2 + 1/2O_2 + 2e^- \rightarrow 2NaHCO_3 \quad \text{(counter electrode)} \tag{4}$$

Besides the above reaction, various other reactions between Na_2O, NaOH, $NaHCO_3$, and Na_2CO_3 are possible. This usually results in a drift in the sensor signal. Sadaoka et al.[10] reported that $NaHCO_3$ forms between the NaOH and CO_2 and decomposes above 300 °C into Na_2CO_3. This means that $NaHCO_3$ and Na_2CO_3 are the most feasible deposits that can be formed in the CE at low and high temperatures, respectively. Because these phases will form more easily at the negative current, the increase in the current level from negative to zero or positive is desirable in order to retard the formation of $NaHCO_3$ and Na_2CO_3 at the CE. In this respect, the application of external electric field opposite to the Na^+ activity gradient might be the reason for the stable sensing character.

In order to investigate the above possibility, a Pt|NASICON|Pt cell without an auxiliary phase was prepared and the current at 0.1 V was measured.

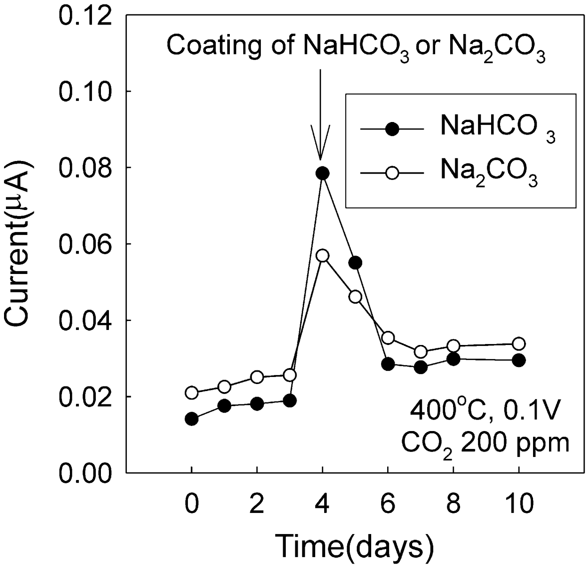

Fig. 5. The influence of $NaHCO_3$ and Na_2CO_3 coatings on the current of Pt|NASICON|Pt cell at 0.1 V (0.014 g of 0.1 M $NaHCO_3$ and 0.009 g of 0.1 M Na_2CO_3 aqueous solutions were coated at the 4th day, respectively.).

(Fig. 5). The current was slightly positive and constant over 3 days. On the 4th day, the $NaHCO_3$ and Na_2CO_3 layers were coated using their aqueous solutions on the (+) electrode and the sensing characters were subsequently measured. The abrupt increase in the current was attributed to the increase in the Na^+ activity by the formation of $NaHCO_3$ and Na_2CO_3 layers. The current values decreased gradually by successive operations at 0.1 V and recovered to approximately their initial value 3 days after being coated. This shows that the formation of $NaHCO_3$ or Na_2CO_3 layers can be inhibited or the formed layers can be decomposed by applying an external electric field.

The Na_2CO_3 layer is less stable to water vapor than binary carbonate layers such as $BaCO_3$–Na_2CO_3[4] and Li_2CO_3–$CaCO_3$.[11] The long-term stability of the present sensor despite employing a Na_2CO_3 layer suggests that a further improvement in the sensor stability is possible. Finally, the retardation of $NaHCO_3$ or Na_2CO_3 formation and the decomposition of a formed layer are expected to be tuned by controlling the external electric field.

4. Conclusion

A compact amperometric CO_2 sensor was prepared by coating a porous Na_2CO_3 auxiliary layer on a Pt|NASICON|Pt cell. The current at 0.1 V between the sensing and counter electrode was largely negative at low CO_2 concentrations and linearly increased with increasing CO_2 concentration from 200 to 2000 ppm. The current was interpreted as a competition between Na^+ migration by the difference in the Na^+ activity and that by the external electric field. Therefore, the long-term stability during the test period (60 days) was attributed to the retardation of $NaHCO_3$ or Na_2CO_3 formation by applying the electric field.

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