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NASICON based CO_2 gas sensor with an auxiliary electrode composed of $LiCO_3$-metal oxide mixtures

Yoshihiko Sadaoka*

Department of Materials Science and Biotechnology, Graduate School of Science and Engineering,
Ehime University, 3 Bunkyo-cho, Matsuyama, Ehime 790-8577, Japan

Abstract

Stability of CO_2 sensing performance was strongly influenced by additives to the auxiliary electrode layer for the sensor with CO_2,Pt/Li_2CO_3/$Na_3Zr_2Si_2PO_{12}$/Pt structure. Use of a mixture of Li_2CO_3 with some metal oxide was effective to stabilize the response behavior, and a stable response was achieved in a shorter period for the as-prepared sensor. It is proposed that a layer composed of the oxide particles covered with carbonates acts as a stable diffusion boundary layer to separate an auxiliary electrode and the NASICON phase. The formation of the metal oxide covered with carbonate was also effective to increase the activity in the auxiliary electrode phase. The increase in the activity is contributed to the balance of the chemical potential and the electrostatic forces for the ions in the diffusion boundary layer.

Keywords: Rare earth oxide; NASICON; Lithium carbonate; CO_2 gas sensor

1. Introduction

The increasing need of reliable and continuous monitoring of CO_2 levels in the atmosphere has promoted the development of potentiometric sensors using an alkali ion conducting solid electrolyte and an auxiliary phase on the measuring electrode [1–5]. A potentiometric CO_2 sensor with a Li_2CO_3 layer as an auxiliary electrode shows satisfactory performances with a fast response, appreciable sensitivity and gas selectivity. However, a lack of reproducibility and long-term stability was observed [6–8]. In some cases, additional compounds were formed in the fabrication process and under humid conditions. The formation of Li_2ZrO_3, Li_3NaSiO_4, Li_2SiO_3, $Na_2SiO_3{\cdot}9H_2O$ and $LiOH{\cdot}H_2O$ with Au,CO_2/Li_2CO_3/NASICON ($Na_3Zr_2Si_2PO_{12}$)/Au (shielded by dense alumina) structure [7] and $BaZrO_3$ for a CO_2 gas sensor with Au,CO_2/Li_2CO_3–$BaCO_3$/NASICON/O_2,Pt structure have been reported [6]. To fabricate reproducible and durable CO_2 sensors, how to stabilize the ionic activity in the sensing and reference electrodes is the most important technique. It has been reported that a use of Na_2CO_3 as an auxiliary electrode is not preferable for potentiometric CO_2 gas sensor, since the Na_2CO_3 layer is unstable especially under humid conditions. To minimize the effect of humidity, the use of lithium carbonate and/or the eutectic point composition of the mixture of carbonates have been proposed instead of Na_2CO_3 [2,9–11]. Imanaka et al. reported that the CO_2 gas sensor using Li- and Ba-doped $Nd_2O_2CO_3$ auxiliary electrodes showed a reversible CO_2 response and high stability against water vapor, since the $Nd_2O_2CO_3$ has very low solubility [12,13]. Even under dry conditions, some drift phenomena were also observed and, in most cases, the EMF decreased with time. It seems that these observed phenomena are due to the third interlayer formation between an auxiliary electrode and the electrolyte, NASICON. If the interlayer is well formed and stable, a preferable stability and reversibility of the sensing performance may be achieved. To form a stable interlayer between an auxiliary electrode and the electrolyte, adding of some metal oxide to an auxiliary electrode is considered. In experimental, it was observed that the use of the mixture of Li_2CO_3 and Al_2O_3 was effective to stabilize the sensing performances.

In this work, we studied about the adding effects of metal oxides on the sensing performances of the sensor with CO_2,Pt/Li_2CO_3//NASICON/Pt structure.

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* Tel.: +81 89 927 8543; fax: +81 89 927 8543.
E-mail address: sadaoka@eng.ehime-u.ac.jp.

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2. Experimental

2.1. Preparation of NASICON and CO_2 sensor

For preparation of NASICON ($Na_3Zr_2Si_2PO_{12}$), a stoichiometric mixture of Na_2CO_3, $ZrSiO_4$, Na_2HPO_4 and H_3PO_4 (0.705:1.34:0.30:0.37 in molar ratio) was heated at 400 °C for 2 h and then at 1000 °C for 8 h, and then the ground powders were heated again at 1000 °C for 8 h. After that a proper amount of a 3% polyvinyl-alcohol solution was added to the dried powders as a binder. The mixtures were pressed into a disc at a pressure of 1×10^8 Pa. The disc for a CO_2 gas sensor was prepared by sintering at 1150 °C for 12 h. Pt paste (Tanaka Metals Co.) as porous electrode was painted on both sides of the surface together with Au wire and then heated at 600 °C. An auxiliary electrode layer was formed on the porous Pt electrode. Mixtures of Li_2CO_3 and a metal oxide of a 1:1 molar ratio were pulverized and mixed under dry conditions by ball milling with a nylon pot and Y-stabilized ZrO_2 balls. The treated mixture with vaseline for an auxiliary electrode material was coated on the surface and then dried in air. The structure of the CO_2 sensing device is illustrated in Fig. 1.

2.2. Measurements

Thermal studies for the mixture of Li_2CO_3 (99.9%) with commercially available oxides were carried out with thermogravimetrical analysis (TGA) and differential thermal analysis (DTA) in standard-air (<0.5 ppm CO_2) and 100% CO_2 at a heating and cooling rate of 5 °C/min. For the examinations with XRD (Cu Kα) and SEM, the mixtures were heated in the range of 300–1000 °C for 2 h in standard-air and 100% CO_2 atmospheres. EMF response was observed with a digital electrometer at 460 °C in ambient air ($CO_2 = 370$ ppm) supplied from an air compressor and in standard 10,000 ppm CO_2 gas. This test using ambient air is suitable to examine the stability of CO_2 gas sensors. Two test gases were alternately introduced into the test chamber in an interval of 30 min with a flow rate of 200 ml/min. The ambient air was naturally exposed to the reference electrode. Ionic conductivity of the 1:1 mixture of Li_2CO_3 and a metal oxide in disc form was determined with an impedance analyzer.

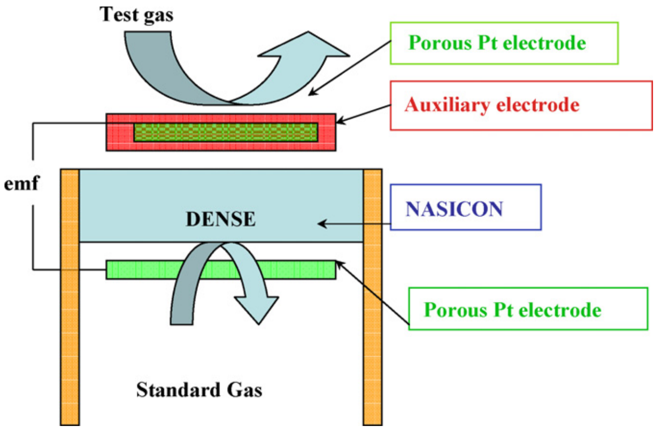

Fig. 1. Schematic illustration of the sensor structure.

3. Results

3.1. Sensing characteristics

We considered the electrochemical cell for the sensor.

Auxiliary electrode (a):

$$Li_2CO_3 \rightarrow 2Li^+ + CO_2 + \tfrac{1}{2}O_2 + 2e^- \tag{1}$$

NASICON (r):

$$2Na^+ + \tfrac{1}{2}O_2 + 2e^- \rightarrow Na_2O \tag{2}$$

Assuming that equilibrium is reached at each phase, the following expressions can be derived.

Auxiliary electrode:

$$\mu_{aLi_2CO_3} = 2\mu_{aLi^+} + \mu_{aCO_2} + \tfrac{1}{2}\mu_{aO_2} + 2\mu_{ae^-} \tag{3}$$

NASICON:

$$2\mu_{rNa^+} + \tfrac{1}{2}\mu_{rO_2} + 2\mu_{re^-} = \mu_{rNa_2O} \tag{4}$$

The difference in the electrochemical potential of the electrons is as follows:

$$\mu_{ae^-} - \mu_{ce^-} = \tfrac{1}{2}\mu_{aLi_2CO_3} - \mu_{aLi^+} - \tfrac{1}{2}\mu_{aCO_2} - \tfrac{1}{4}\mu_{aO_2} - \tfrac{1}{2}\mu_{rNa_2O} + \mu_{rNa^+} + \tfrac{1}{4}\mu_{rO_2}$$

The resulting EMF of the cell is expressed by

$$\mathrm{EMF} = \frac{-\Delta G^\circ}{2F} - \frac{RT}{2F}\ln\left[\frac{a^2_{aLi^+}P_{aCO_2}a^{0.5}_{aO_2}a_{rNa_2O}}{a_{aLi_2CO_3}a^2_{rNa^+}a^{0.5}_{aO_2}}\right] \tag{5}$$

where $-\Delta G^\circ$ is the standard free energy of the reaction. For the separate type structure with a thick NASICON, the activities in the electrolyte are controlled by the ambience in the reference and the EMF change as a function of the activities of the auxiliary electrode;

$$\mathrm{CV} = \mathrm{EMF} + \frac{RT}{2F}\ln[P_{aCO_2}] \tag{6}$$

$$= -\frac{RT}{2F}\ln\left[\frac{a^2_{aLi^+}a_{rNa_2O}}{a_{aLi_2CO_3}a^2_{rNa^+}}\right] + \text{constant} \tag{6}$$

Fig. 2 shows the characteristic value, CV, of the CO_2 gas sensor with sole Li_2CO_3 and mixtures of Li_2CO_3 and metal oxides as auxiliary electrode at 370 and 10,000 ppm CO_2. The measurements were started at the programmed temperature, 460 °C, and then continued over 15,000 min. In the initial period, an increase in the EMF was observed. During the testing, the temperature intentionally dropped down to room temperature and then elevated again in some periods. When the temperature was raised again, a large drift was no more observed. The large drift toward an increase in the EMF was only observed for the