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NASICON-based CO_2 sensor operative at room temperature with Li_2CO_3-based auxiliary as a sensing electrode

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Abstract

A Potentiometric NASICON ($Na_3Zr_2Si_2PO_{12}$)-based CO_2 sensor operative at room temperature was fabricated by combining with a metal oxide (ITO: indium tin oxide) and Li_2CO_3-In_2O_3 (4:1 in molar ratio) auxiliary as a sensing electrode, and its CO_2 sensing properties were examined under 30% RH (relative humidity) in the temperature range of 30 to 100 ^oC. When the Li_2CO_3-In_2O_3–attached sensor was operated in the range of 250 to 2500 ppm CO_2 at 30 ^oC, the EMF (electromotive force) change of the sensor was 30.4 mV. The EMF values were correlated linearly with the logarithm of CO_2 concentration. In addition, to evaluate the interfluence of coexisting NO_2, the Li2CO3-In2O3-attached sensor was measured under 30 %RH in the range of 2 to 7 ppmNO2 between 30 and 100 ^oC. As the result, it was found that the sensor attached with Li_2CO_3-In_2O_3 auxiliary showed the high selectivity to CO_2 as compared with the sensor attached with Li_2CO_3-$BaCO_3$(1:2 in molar ratio) auxiliary phase.

Key words: NASICON, CO_2 sensor, ITO, Li_2CO_3, Operative at room temperature

Introduction

NASICON (Na^+ super ionic conductor: $Na_3Zr_2Si_2PO_{12}$)-based CO_2 sensor using solid-state electrolyte attached with an alkaline metal carbonate or binary carbonate auxiliary phase has been attracted a great deal of attention, because the sensor shows a high sensitivity and fast response [1]. However, the sensor must be operated at elevated above 350 ^oC to advance the electrochemical reaction. The sensor combined with a heater consumes a large amount of electric power. On the other hand, the NASICON-based sensor attached with a metal oxide (ITO: indium tin oxide) and Li_2CO_3-$BaCO_3$ auxiliary phase show the good CO_2 sensing capability at room temperature [2]. If the heater can be eliminated from the sensor, the sensor can be much smaller and simpler, and operated easily with batteries. However, it was pointed out that this type of sensor is unstable by disturbance of NO_2 coexisting in the atmosphere [3]. Recently, it was reported that a CO_2 gas sensor using oxycarbonate-based auxiliary phase was not affected much by NO (0-600ppm) coexisting in the atmosphere [4]. In the present study, we investigated the effects of using Li_2CO_3-based auxiliary phase (Li_2CO_3-In_2O_3) for the NASICON-based CO_2 sensor operative at room temperature.

Experimental method

NASICON powder as a solid-state electrolyte were prepared by a sol-gel technique using $Si(OC_2H_5)_4$, $Zr(OC_4H_9)_4$, $PO(OC_4H_9)_3$ and $NaOC_2H_5$ [2]. After the precursor powder was compacted into a disk (9mm in diameter and 1.2 mm thick), the disk was sintered at 1200 ^oC in air for 5 h. The powder of ITO (10 mol% Sn-doped In_2O_3) was prepared from a mixed solution of $InCl_3$ and $SnCl_4$, by a doping the calcination conditions of 1000 ^oC for 2 h. The Li_2CO_3-based auxilliary (LI_2CO_3-In_2O_3) was prepared from the mixutre of Li_2CO_3 and In_2O_3 (4:1 in molar ratio) and by calcining at 600 ^oC for 1 h. The binary carbonate (Li_2CO_3-$BaCO_3$) were prepared from the mixutre of Li_2CO_3 and $BaCO_3$ (1:2 in molar ratio) and by calcining at 750 ^oC for 10 min.

The sensor was fabricated by combining the NASICON disk with ITO and an auxiliary phase (Li_2CO_3-In_2O_3 and Li_2CO_3-$BaCO_3$), as shown in Fig.1. The reference electrode was prepared by using Au paste, followed by calcination at 800 ^oC in air for 2 h. On top of it, the CO_2 sensing electrode was formed by applying ITO powder assisted with an auxiliary phase. Then, the whole assembly was calcined at 500 ^oC in air for 0.5 h.

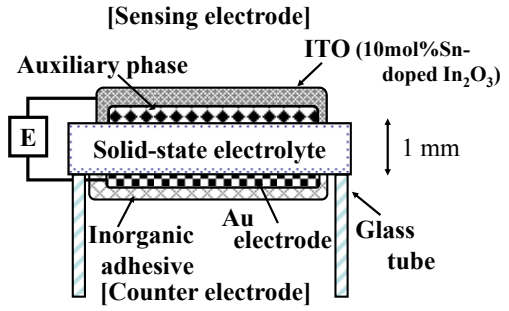

Fig. 1. Schematic drawing of CO_2 sensor.

Gas sensing properties were measured in a conventional gas-flow apparatus equipped with a heating facility. Sample gases consisting of air, CO_2, NO_2 and H_2O were prepared by diluting a parent gas (5000 ppmCO_2 or 10 ppmNO_2 in dry synthetic air) with wet and dry synthetic air. The concentration of CO_2 and NO_2 in the sample gases were varied in the range of 250 - 2500 ppmCO_2 and 2 - 7 ppmNO_2 under 30 % relative humidity (RH). The electromotive force (EMF) of the sensor was measured with a digital electrometer.

Results and discussion

Figure 2 shows the EMF response transients of the Li_2CO_3-In_2O_3-attached sensor to stepwise changing CO_2 concentration under 30 %RH at 30 °C. When CO_2 concentration was increased in the range of 250 to 2500 ppm, the EMF was obtained 30.4 mV. The 90% response time of Li_2CO_3-In_2O_3-attached sensor to stepwise changing CO_2 concentration from 250 to 2500 ppm was estimated to be about 10 min.

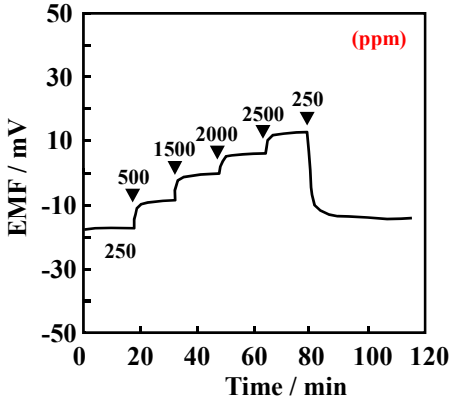

Fig. 2: EMF response transients of the Li_2CO_3-In_2O_3-attached sensor to stepwise changing CO_2 concentration under 30 % RH at 30 °C.

Figure 3 shows the relationship between EMF values and CO_2 concentrations under 30 %RH at various temeperatures for the Li_2CO_3-In_2O_3-attached sensor. The EMF values of the sensor were correlated linearly with the logarithm of CO_2 concentrations at the operation temperature between 30 and 100 °C. The theoretical EMF of the potentiometoric NASICON-based sensor is expressed by using the next Nernstian equation [1]:

$$EMF = (RT/nF)\cdot\ln(P''_{gas}/P'_{gas}) \qquad \textbf{(1).}$$

Where n is the number of electrons associated with the electrode reaction of CO_2 (n= 2), P the partial pressure of target gases, R the gas constant, T the absolute temperature and F the Faraday constant, respectively. Applying to Nernstian equation (1), the n indicated 1.98 (30°C), 2.60 (60 °C) and 3.19 (100 °C), respectively.

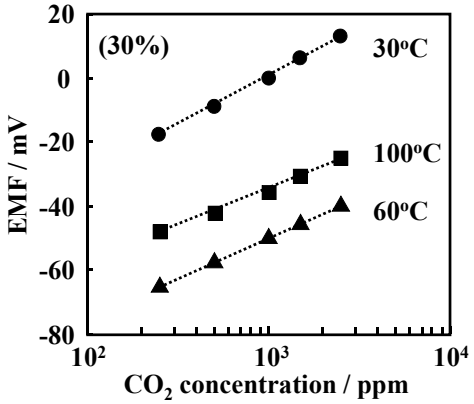

Fig. 3: Relationship between EMF values and CO_2 concentration under 30 % RH at various temperatures for the Li_2CO_3-In_2O_3-attached sensor.

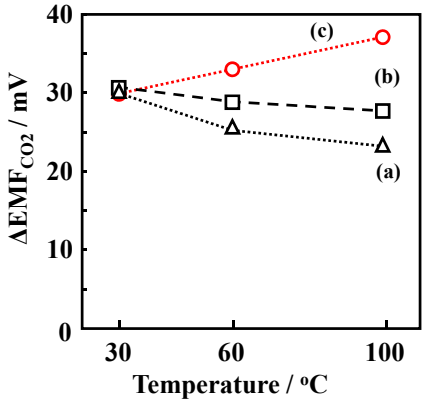

Fig. 4: CO_2 sensitivity under 30 %RH at 30, 60 and 100 °C for the sensors attached with various auxiliary phase: (a) Li_2CO_3-In_2O_3-attached sensor, (b) Li_2CO_3-$BaCO_3$-attached sensor and (c) theoretical values.

Figure 4 shows CO_2 sensitivity of the Li_2CO_3-In_2O_3-attached sensor under 30 %RH at 30, 60 and 100 °C. Here ΔEMF_{CO2} stands for the increments in EMF on increasing the CO_2 concentration from 250 to 2500 ppm. The CO_2 sensitivity of the Li_2CO_3-In_2O_3-attached sensor was a slightly low at higher temperature as compared with the Li_2CO_3-$BaCO_3$-attached sensor.

Subsequently, it was investigated on the influence of NO_2 coexisting in the atmosphere for the Li_2CO_3-In_2O_3-attached sensor. Figure 5 shows the cross-sensitivity to NO_2 in the range of 2 to 7 ppm NO_2 under 30 %RH at 30 °C. As shown in Fig. 5, the sensor was not fluctuated by the change in NO_2 concentration in the range of 2 to 7 ppmNO_2.

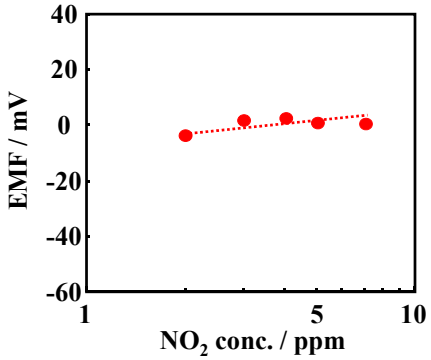

Fig. 5: Cross-sensitivity to NO_2 under 30 %RH at 30 °C for the Li_2CO_3-In_2O_3-attached sensor.

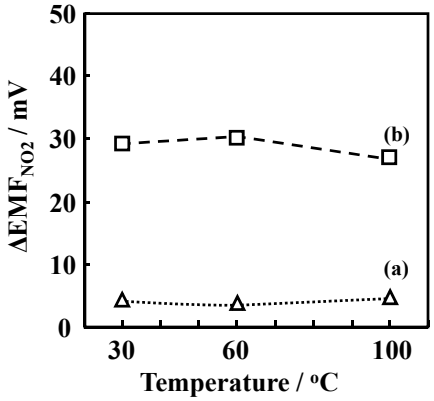

Fig. 6: Comparison of cross-sensitivity to NO_2 under 30 % RH at various temperatures for the sensors attached with (a) Li_2CO_3-In_2O_3 and (b) Li_2CO_3-$BaCO_3$ as an auxiliary phase.

Figure 6 compares a cross sensitivity to NO_2 of the CO_2 sensors attached with (a) Li_2CO_3-In_2O_3 and (b) Li_2CO_3-$BaCO_3$ as an auxiliary phase under 30 % RH at various temperatures. Here ΔEMF_{NO2} stands for the increments in EMF on increasing the NO_2 concentration from 2 to 7 ppm. As shown in Fig. 6, although the Li_2CO_3-$BaCO_3$-attached sensor was disturbed by the NO_2 concentration change, the Li_2CO_3-In_2O_3-attached sensor did not affect the CO_2 detection for the change in NO_2 concentration at the operation temperature between 30 and 100 °C.

Table 1: CO_2 sensitivities and NO_2 cross-sensitivities of the Li_2CO_3-In_2O_3- and Li_2CO_3-$BaCO_3$-attached sensors under 30 %RH at 30 °C.

Gas	Theoretical value / mV	Auxiliary phase	ΔEMF / mV
CO_2	30.1	Li_2CO_3-$BaCO_3$	30.2
		Li_2CO_3-In_2O_3	30.4
NO_2	—	Li_2CO_3-$BaCO_3$	29.0
		Li_2CO_3-In_2O_3	3.7

Table 1 compares ΔEMF_{CO2} and ΔEMF_{NO2} of the sensor attached with the Li_2CO_3-In_2O_3 and Li_2CO_3-$BaCO_3$ as an auxiliary phase to the increase in CO_2 or NO_2 concentration. As shown in Table 1, although Li_2CO_3-$BaCO_3$-attached sensor was largely fluctuated by the NO_2 concentration change, Li_2CO_3-In_2O_3-attached sensor has a high selectivity to CO_2 gas.

Acknowledgements

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