

NO₂ and CO₂ Sensing Properties of LISICON-Based Sensor Operative at Room Temperature

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Four types of sensor were fabricated by combining solid-state electrolyte (LISICON or NASICON) disks with sensing electrode materials, such as Au, indium tin oxide (ITO), and auxiliary phase (nitrate or carbonate). Their NO₂ and CO₂ sensing properties were examined under 30% relative humidity (RH) in the temperature range of 30 to 100°C. When the NO₂ sensor was operated in the range of 2 to 7 ppm NO₂ at 30°C, the LISICON sensor attached with ITO-NaNO₂ had the highest sensitivity to NO₂ and the electromotive force (EMF) change was 41.4 mV. At 30°C under 30% RH, the EMF values of the LISICON sensor attached with ITO-NaNO₂ were proportional to the logarithm of NO₂ concentration. Also, when the CO₂ sensor was operated in the range of 250 to 2,500 ppm CO₂ at 30°C, the LISICON sensor attached with ITO-Li₂CO₃-BaCO₃ had the highest sensitivity to CO₂ and the EMF change was 20.0 mV. At 30°C under 30% RH, the EMF values of the LISICON sensor attached with ITO-Li₂CO₃-BaCO₃ were correlated linearly with the logarithm of CO₂ concentration. Subsequently, to examine gas selectivity, the NO₂ selectivity of the sensor attached with ITO-NaNO₂ and the CO₂ selectivity of the sensor attached with ITO-Li₂CO₃-BaCO₃ were evaluated at 30°C under 30% RH. As a result, it was found that the LISICON and NASICON sensors attached with ITO-NaNO₂ were fluctuated by the change in CO₂ concentration. On the other hand, although the NASICON sensor attached with ITO-Li₂CO₃-BaCO₃ was affected by the NO₂ concentration change, the LISICON sensor attached with ITO-Li₂CO₃-BaCO₃ showed a high CO₂ selectivity. From thermodynamic calculations, it was considered that the chemical instability of NASICON and NaNO₂ under CO₂ led to the degradation of NO₂ gas selectivity in the ITO-NaNO₂-attached sensor, whereas that of NASICON under NO₂ caused the degradation of CO₂ gas selectivity in the ITO-Li₂CO₃-BaCO₃-attached sensor.

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1. Introduction

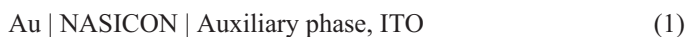
Potentiometric solid-state electrolyte sensors have been reported for the detection of NO_x ⁽¹⁻⁴⁾ and CO_2 .⁽⁵⁻¹⁰⁾ This type of sensor possesses a high selectivity despite its relatively simple structure.⁽¹¹⁻¹³⁾ This is because it detects an objective gas from the electrochemical reaction. However, these potentiometric sensors must be used at a temperature above 150°C to advance the electrochemical reaction smoothly. This denotes that the potentiometric sensor contains a weak point that should be improved in terms of electric power consumption. Also, the sensors combined with a heating element are difficult to downsize. If the target gas sensing at room temperature becomes possible, the heater can be eliminated from the sensor system, so that the sensor can be manufactured as much smaller and simpler, and operated easily with an electric cell.

For the past 10 years, it has been reported that solid-state electrolyte sensors attached with a metal oxide and an auxiliary phase exhibit a gas sensing capability even at room temperature.⁽¹⁴⁻²⁰⁾ In general, this type of sensor was fabricated using NASICON (Na^+ super ionic conductor) that has a high ionic conductivity at room temperature as a solid-state electrolyte. However, in the case of the NASICON-based sensor, it was pointed out that the Na_2O , which is an oxide with a mobile ion species, is unstable under humid condition and easily reacts with NO_2 and CO_2 in ambient atmosphere.^(16,19,20) Also, after being kept in a humid atmosphere at low temperature, Na_3PO_4 eluted from the bulk of the NASICON disk to the surface was related to the degradation of CO_2 sensing properties.⁽²¹⁾ The sensor with NASICON is not suitable for the CO_2 or NO_2 detection due to its chemical instability in the atmosphere. Imanaka *et al.* reported that the gas sensing of the CO_2 gas sensor using LISICON (Li^+ super ionic conductor) was minimally affected by NO_2 .⁽²²⁾ We considered that the LISICON-based sensor operative at room temperature was also effective for improving the influence of coexisting gas.

In this study, the LISICON-based sensor operative at room temperature was fabricated by combining with ITO and auxiliary phase, such as NaNO_2 or $\text{Li}_2\text{CO}_3\text{-BaCO}_3$, and its NO_2 and CO_2 sensing performances were studied in detail in the temperature range of 30 to 100°C under 30% RH. The NASICON-based sensor was also fabricated and its gas sensing properties were compared with those of the LISICON-based sensor.

2. Theory

The solid-state electrolyte sensor attached with a metal oxide and an auxiliary phase detects a target gas concentration from the change in the electrochemical equilibrium state between the gas and an auxiliary phase. For example, an electrochemical cell of the NASICON ($\text{Na}_3\text{Zr}_2\text{Si}_2\text{PO}_{12}$) sensor combined with ITO and an auxiliary phase, such as a carbonate and a nitrate, is expressed as follows.^(17,20)

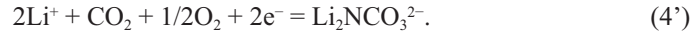


In this type of sensor, the physisorbed water on the surface of the metal oxide such as ITO behaves just like a solvent, and a target gas (NO_2 or CO_2) existing in the atmosphere

is transformed to a chemical ion species (NO_2^- or CO_3^{2-}) involved in the electrode reaction, as written in eq. (2) or (2'), respectively. Furthermore, the electrochemical reaction between a chemical ion species (NO_2^- or CO_3^{2-}) and an auxiliary phase (NaNO_2 or Li_2CO_3) in an equilibrium state may be given by eq. (3) or (3'), respectively.



The total NO_2 and CO_2 sensing reaction is respectively given by



On the other hand, the reference electrode reaction on the Au electrode can be given by



By using the Nernstian equation, the electrode potentials in reactions (4), (4'), and (5) are expressed as eqs. (6), (6'), and (7) in turn,

$$E_1 = C_1 (\text{constant}) + (RT / n_1F) \cdot \ln ((a_{\text{Na}^+}) \cdot P_{\text{NO}_2} / a_{\text{NaNO}_2}), \quad (6)$$

$$E_2 = C_2 (\text{constant}) + (RT / n_2F) \cdot \ln ((a_{\text{Li}^+})^2 \cdot P_{\text{CO}_2} \cdot (P_{\text{O}_2})^{1/2} / a_{\text{Li}_2\text{CO}_3}), \quad (6')$$

$$E_3 = C_3 (\text{constant}) + (RT / n_3F) \cdot \ln ((a_{\text{Na}^+})^2 \cdot (P_{\text{O}_2})^{1/2} / a_{\text{Na}_2\text{O}}), \quad (7)$$

where n_1 , n_2 , and n_3 are respectively the number of electrons associated with the electrode reaction for NO_2 , CO_2 , and O_2 , P the partial pressure, R the gas constant, T the absolute temperature, F the Faraday constant, C the constant of standard electrode potential estimated from Gibbs free energy, and a the activity of chemical species such as Na^+ , NaNO_2 , Li^+ , Li_2CO_3 , and Na_2O (in NASICON). The observed electromotive force (EMF) is given as a potential difference between the sensing and reference electrodes. If P_{O_2} and activity of chemical species (a_{NaNO_2} , $a_{\text{Li}_2\text{CO}_3}$, $a_{\text{Na}_2\text{O}}$, a_{Na^+} , and a_{Li^+}) would be assumed to remain unchanged throughout the measurement, the observed EMF (E_{NO_2} and E_{CO_2}) can be given by the next eqs. (8) and (8').

$$E_{\text{NO}_2} = C_4 (\text{constant}) + (RT / F) \cdot \ln (P_{\text{NO}_2} \cdot a_{\text{Na}_2\text{O}} / a_{\text{Na}^+} \cdot a_{\text{NaNO}_2}) \quad (8)$$

$$E_{\text{CO}_2} = C_5 (\text{constant}) + (RT / 2F) \cdot \ln ((a_{\text{Li}^+})^2 \cdot P_{\text{CO}_2} \cdot a_{\text{Na}_2\text{O}} / ((a_{\text{Na}^+})^2 \cdot a_{\text{Li}_2\text{CO}_3}) \quad (8')$$

When a target gas concentration is varied from P' to P'' , the theoretical EMF change (ΔEMF_{NO_2} and ΔEMF_{CO_2}) is written in eqs. (9) and (9'), respectively. As written in reactions (4) and (4'), n_1 and n_2 are equal to 1 and 2, respectively.

$$\Delta EMF_{NO_2} = (RT/F) \cdot \ln(P''_{NO_2}/P'_{NO_2}) \quad (9)$$

$$\Delta EMF_{CO_2} = (RT/2F) \cdot \ln(P''_{CO_2}/P'_{CO_2}) \quad (9')$$

By applying eqs. (9) and (9') at 30°C, the ΔEMF_{NO_2} value is estimated to be about 32.9 mV in the range of 2–7 ppm, whereas the ΔEMF_{CO_2} value is about 30.1 mV in the range of 250–2,500 ppm.

3. Methods

3.1 Materials preparation

LISICON ($LiTi_2(PO_4)_3$) was prepared from Li_2CO_3 , TiO_2 , and $(NH_4)_2HPO_4$.⁽⁸⁾ These powders were mixed and ground in a ball mill for 24 h by a wet process. The mixture was reacted in a gold crucible at 800°C for 2 h. The precursor powder obtained was mechanically reground with an agate mortar into a fine powder. The precursor was compacted into a disk (10 mm diameter and 1 mm thick), followed by sintering at 900°C in air for 2 h. NASICON ($Na_3Zr_2Si_2PO_{12}$) was prepared by a sol-gel technique using $Si(OC_2H_5)_4$, $Zr(OC_4H_9)_4$, $PO(OC_4H_9)_3$, and $NaOC_2H_5$.⁽²³⁾ These alkoxides were stoichiometrically dissolved in an ethanol solvent containing HNO_3 and allowed to stand for about 20 h under stirring. This operation was carried out in a dry N_2 atmosphere and the ethanol solvent was kept at 60°C. Then, the distilled water was added to the ethanol solution for the hydrolysis. The resulting precipitates were dried at 120°C in air for 24 h. After being calcined at 750°C in air for 1 h, the precursor powder was compacted into a disk (10 mm diameter and 1 mm thick). The disk was sintered at 1,200°C in air for 5 h and polished with sand paper.

3.2 Fabrication of sensor

Four types of sensor were fabricated by combining solid-state electrolyte (LISICON or NASICON) disks with sensing electrode materials, such as Au, ITO, and auxiliary phase ($NaNO_2$ or Li_2CO_3 - $BaCO_3$), as schematically drawn in Fig. 1. The binary carbonate Li_2CO_3 - $BaCO_3$ (1:2 in molar ratio) was used.⁽²⁰⁾ To prepare it, the mixture of Li_2CO_3 and $BaCO_3$ was calcined in air at 750°C for 10 min and the resulting partially molten system was cooled and pulverized in an agate mortar. ITO (10% Sn-doped In_2O_3) was chosen as a metal oxide because the CO_2 sensor using ITO as a sensing material showed excellent sensing capabilities even at room temperature.⁽¹⁶⁾ Ten atomic percent Sn-doped In_2O_3 powders were conventionally prepared from an aqueous mixed solution of $InCl_3$ and $SnCl_4$. Then, the powders were calcined at 1000°C in air for 5 h.

To fabricate a Au-attached sensor, both the reference and sensing electrodes were constructed by using a gold paste, followed by calcining at 800°C in air for 2 h. For the ITO-attached sensor, it was fabricated by using an ITO paste, followed by a calcining

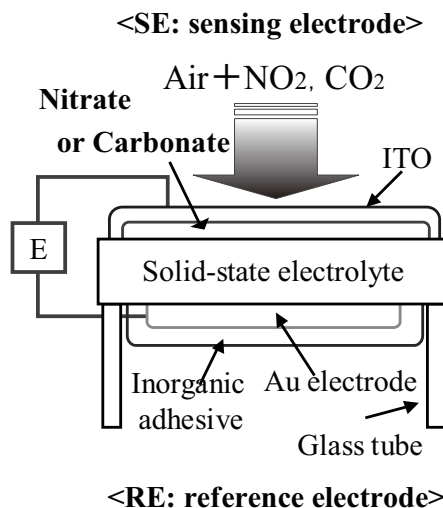


Fig. 1. Schematic of solid-state electrolyte-based sensor.

at 500°C in air for 30 min. The attachment of the ITO- NaNO_2 or ITO- Li_2CO_3 - BaCO_3 sensing electrode was carried out by calcining the whole assembly at 320°C for 5 min and 500°C for 30 min, respectively. On the other hand, the reference electrode (Au) of all the sensors was prepared in the same manner and was covered with an inorganic adhesive (Toagousei Co. Ltd., Aron Ceramic C) as a protective layer to isolate from water vapor, NO_2 , and CO_2 in the atmosphere. The fabricated sensor was fixed on the end of a quartz glass tube (9 mm in diameter) with an inorganic adhesive, as shown in Fig. 1.

3.3 Measurement of gas sensing properties

The gas sensing properties of the sensor were measured in a conventional gas-flow apparatus equipped with a heating facility in the temperature range of 30 to 100°C. Sample gases consisting of air, NO_2 , CO_2 , and H_2O were prepared by diluting a parent gas (10 ppm NO_2 and 5,000 ppm CO_2 in dry synthetic air) with dry synthetic air and/or wet air. The wet air was prepared by allowing the dry air to bubble through water in a flask. The concentrations of NO_2 and CO_2 were varied in the range of 2 to 7 ppm NO_2 and 250 to 2,500 ppm CO_2 . The sample gases were allowed to flow over the sensing electrode at a rate of 0.1 dm^3/min . The EMF of the sensor was measured with a digital electrometer. In this study, the base EMF was defined by measuring EMF to the gas containing 2 ppm NO_2 or 250 ppm CO_2 under 30% RH.

4. Results and Discussion

4.1 NO_2 sensing electrode

Three types of LISICON-based NO_2 sensor using Au, ITO, or ITO- NaNO_2 were tested for the NO_2 sensing capabilities. Figure 2 shows the relationship between the NO_2

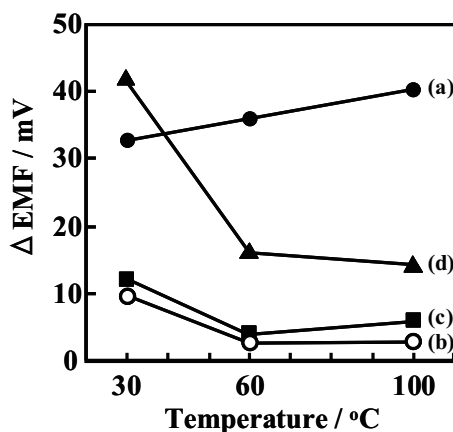


Fig. 2. EMF changes relative to the change in NO₂ concentration under 30% RH between 30 and 100°C: (a) theoretical value, (b) Au-attached, (c) ITO-attached, and (d) ITO-NaNO₂-attached LISICON sensors.

sensitivity (ΔEMF) of the LISICON-based sensor and the measurement temperature. The examination was carried out in the range of 2 to 7 ppm NO₂ under 30% RH between 30 and 100°C for Au-attached, ITO-attached, and ITO-NaNO₂-attached LISICON sensors. Here, ΔEMF_{NO_2} stands for the increase in EMF with increasing NO₂ concentration from 2 to 7 ppm. By applying eq. (9), the theoretical ΔEMF values were calculated to be 32.9, 36.1, and 40.5 mV at 30, 60, and 100°C, respectively. Among the three types of LISICON-based sensors examined, the ITO-NaNO₂-attached sensor had the highest sensitivity to NO₂ at 30°C. However, the NO₂ sensitivity decreased with increasing temperature as shown in Fig. 2. We previously reported that the physisorbed water on the surface of ITO behaves just like a solvent and promotes the gas sensing reaction at room temperature.^(18,20) Thus, it is conceivable that the decrease in ΔEMF originates from the desorption of physisorbed water in the vicinity of the sensing electrode with increasing temperature.

Figures 3(a) and 3(b) show the EMF response curve to stepwise changing NO₂ concentration and the relationship between the EMF value and NO₂ concentration for the ITO-NaNO₂-attached LISICON sensor. The measurement temperatures were 30, 60, and 100°C, and the relative humidity was 30%. When the NO₂ concentration was changed from 2 to 3 ppm in a measurement chamber, the EMF change was 22.4 mV. The EMF change became large as the NO₂ concentration was increased from 2 to 7 ppm and finally reached 41.4 mV. Each 90% response time to stepwise changing NO₂ concentration was estimated to be about 5 min. At each measurement temperature, the EMF value was proportional to the logarithm of NO₂ concentration. By using Nernstian eq. (9), the slope of the ITO-NaNO₂-attached LISICON sensor was evaluated to be $n = 0.79$ at 30°C. Theoretically, the n value should be equal to 1, if the electrochemical reaction in eq. (4) is supposed to take place over the sensing electrode. However, the n value of the measurement at 30°C is far from the theoretical value. It is possible that this is because nitrate easily dissolves in water.

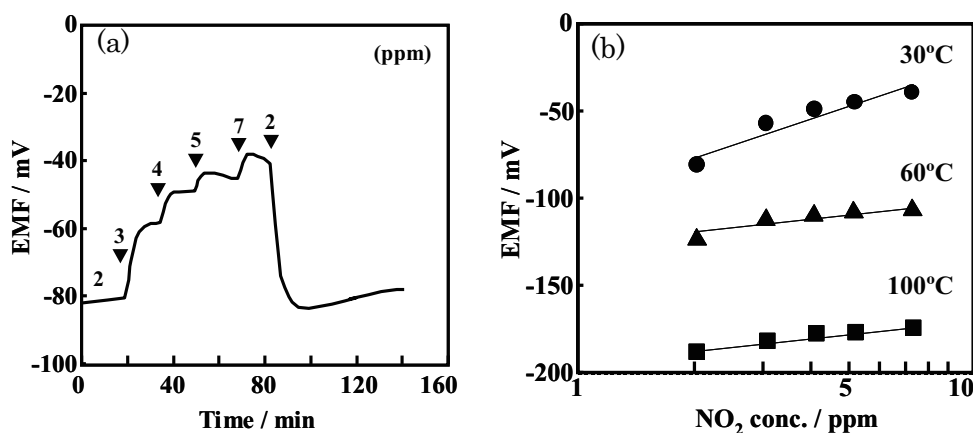


Fig. 3. NO₂ sensing properties under 30% RH at 30°C for the ITO-NaNO₂-attached LISICON sensor: (a) EMF response transients to stepwise changing NO₂ concentration and (b) relationship between EMF values and NO₂ concentration at various temperatures.

4.2 CO₂ sensing electrode

Subsequently, three types of LISICON-based CO₂ sensor using Au, ITO, or ITO-Li₂CO₃-BaCO₃ were examined in terms of CO₂ sensing capabilities. Figure 4 shows the CO₂ sensitivity (ΔEMF_{CO_2}) of the LISICON sensor as a function of measurement temperature. The measurement was carried out in the range of 250 to 2,500 ppm CO₂ under 30% RH between 30 and 100°C for the Au-attached, ITO-attached, and ITO-Li₂CO₃-BaCO₃-attached LISICON sensors. Here, ΔEMF_{CO_2} stands for the increases in EMF with increasing CO₂ concentration from 250 to 2,500 ppm. By applying eq. (9'), the theoretical ΔEMF values were estimated to be 30.1, 33.0, and 37.0 mV at 30, 60, and 100°C, respectively. The ITO-Li₂CO₃-BaCO₃-attached LISICON sensor shows the highest sensitivity to CO₂ among the three types of LISICON-based sensor. However, the CO₂ sensitivity of the sensor also became low with increasing operating temperature as observed in Fig. 2.

Figures 5(a) and 5(b) show the EMF response curve to stepwise changing CO₂ concentration and the relationship between the EMF value and CO₂ concentration for the ITO-Li₂CO₃-BaCO₃-attached LISICON sensor. The measurement was carried out in the same manner. When the CO₂ concentration was changed from 250 to 500 ppm in a measurement chamber, the EMF change was 4.0 mV. The EMF change became large as the CO₂ concentration was increased from 250 to 2,500 ppm and finally reached 20.0 mV. Each 90% response time to stepwise changing CO₂ concentration was estimated to be about 5 min. At each measurement temperature, the EMF value was correlated linearly with the logarithm of CO₂ concentration. According to the Nernstian equation, the slope of the ITO-Li₂CO₃-BaCO₃-attached LISICON sensor indicated $n = 3.01$. The theoretical n value should be equal to 2, if the electrochemical reaction in eq. (4') is supposed to promote the sensing reaction. It is possible that the mobile ion is insufficient

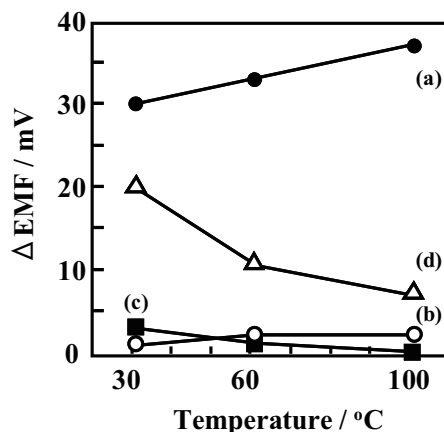


Fig. 4. EMF changes relative to the change in CO₂ concentration under 30% RH between 30 and 100°C: (a) theoretical value, (b) Au-attached, (c) ITO-attached, and (d) ITO-Li₂CO₃-BaCO₃-attached LISICON sensors.

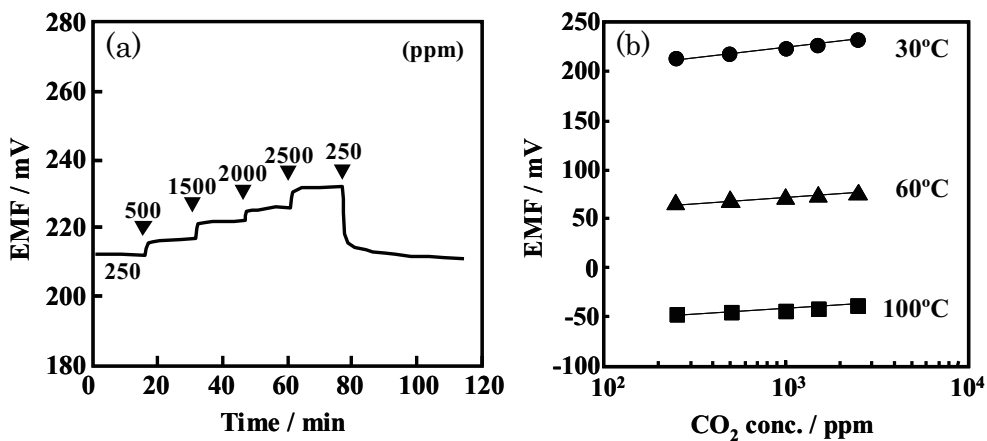


Fig. 5. CO₂ sensing properties under 30% RH at 30°C for the ITO-Li₂CO₃-BaCO₃-attached LISICON sensor: (a) EMF response transients to stepwise changing CO₂ concentration and (b) relationship between EMF values and CO₂ concentration at various temperatures.

to attain the electrochemical chain, since the Li⁺ ion was not exchanged at the interface between LISICON and the auxiliary phase.

4.3 Gas selectivity

To examine gas selectivity, the CO₂ sensitivity of the ITO-NaNO₂-attached sensor and NO₂ sensitivity of the ITO-Li₂CO₃-BaCO₃-attached sensor were evaluated at 30°C under 30% RH. The gas selectivity of the LISICON sensor was evaluated by comparing with the result of the NASICON sensor.

Figures 6(a) and 6(b) show the EMF value as a function of NO_2 or CO_2 concentration at 30°C under 30% RH for ITO- NaNO_2 -attached sensors. As shown in Fig. 6(a), both the LISICON-based and NASICON-based sensors had a Nernst-type response to the change in NO_2 concentration. The EMF values of both sensors were proportional to the logarithm of CO_2 concentration as seen in Fig. 6(b). From the result in Fig. 6, the EMF values of the ITO- NaNO_2 -attached NASICON to below 2,500 ppm CO_2 became negative as compared with those of that to above 2 ppm NO_2 . This means that this type of sensor was not responsive to CO_2 gas. In contrast, the EMF values of the ITO- NaNO_2 -attached LISICON to below 2,500 ppm CO_2 became positive in comparison with those of that to above 2 ppm NO_2 . This result indicates that this sensor was not affected by the change in NO_2 concentration. Table 1 compares ΔEMF (ΔEMF_{NO_2} and ΔEMF_{CO_2}) of ITO- NaNO_2 -attached sensors to the increase in NO_2 or CO_2 concentration. As shown in Table 1, although ITO- NaNO_2 -attached sensors have high NO_2 sensitivities, the sensors were slightly fluctuated by the CO_2 concentration change.

Figures 7(a) and 7(b) show the EMF value as a function of CO_2 or NO_2 concentration at 30°C under 30% RH for ITO- Li_2CO_3 - BaCO_3 -attached sensors. As shown in Fig. 7(a),

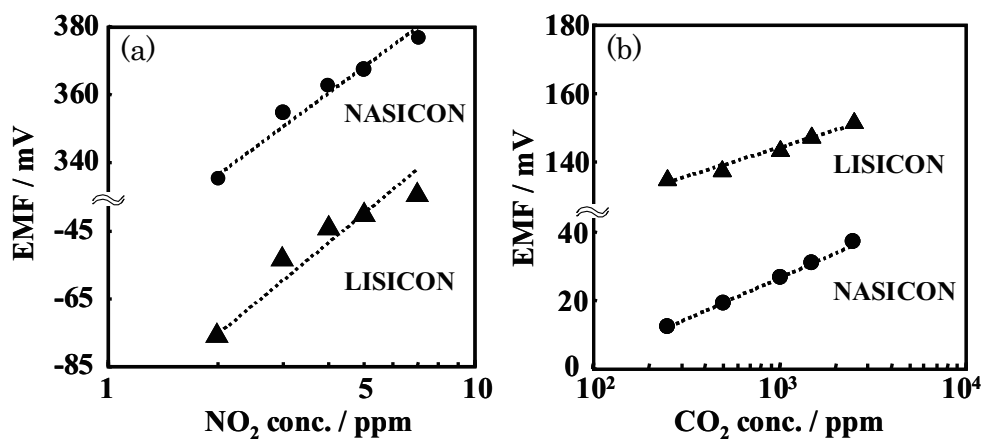


Fig. 6. EMF values of the ITO- NaNO_2 -attached LISICON and NASICON sensors relative to the change in gas concentration under 30% RH at 30°C : (a) NO_2 sensing properties and (b) CO_2 sensing properties.

Table 1
 NO_2 and CO_2 sensitivities of the ITO- NaNO_2 -attached sensors.

Gas	Solid-state electrolyte	$\Delta EMF/\text{mV}$	Theoretical value/ mV
NO_2	NASICON	41.5	32.9
	LISICON	41.4	
CO_2	NASICON	25.2	30.1
	LISICON	17.0	

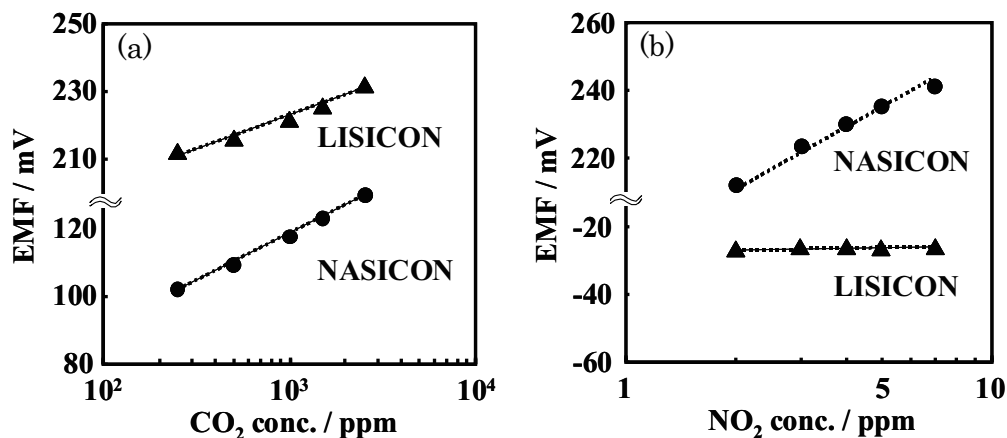


Fig. 7. EMF values of the ITO- Li_2CO_3 - BaCO_3 -attached LISICON and NASICON sensors relative to the change in gas concentration under 30% RH at 30°C: (a) CO_2 sensing properties and (b) NO_2 sensing properties.

both the LISICON-based and NASICON-based sensors had a Nernst-type response to the change in CO_2 concentration. As shown in Fig. 7(b), EMF values of the NASICON-based sensor were correlated linearly with the logarithm of NO_2 concentration, whereas the result of the LISICON sensor was not affected by the NO_2 concentration change. Table 2 compares ΔEMF (ΔEMF_{CO_2} and ΔEMF_{NO_2}) of ITO- Li_2CO_3 - BaCO_3 -attached sensors to the increase in CO_2 or NO_2 concentration. As shown in Table 2, in the case of the ITO- Li_2CO_3 - BaCO_3 -attached LISICON sensor, although the CO_2 sensitivity was lower than the theoretical ΔEMF_{CO_2} , the change in NO_2 concentration did not affect the CO_2 detection. These results indicate that ITO- NaNO_2 -attached sensors and ITO- Li_2CO_3 - BaCO_3 -attached NASICON sensors do not have gas selectivity. In consideration of the relationship between EMF values and coexisting gas in the atmosphere as shown in Fig. 7, the ITO- Li_2CO_3 - BaCO_3 -attached NASICON sensor was responsive to NO_2 gas and the ITO- Li_2CO_3 - BaCO_3 -attached LISICON sensor showed a CO_2 sensing capability. Therefore, it is suspected that the NASICON-based sensor has NO_2 selectivity and the LISICON-based sensor has CO_2 selectivity regardless of auxiliary phase.

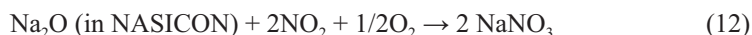
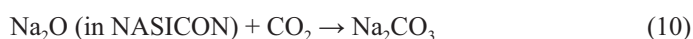
As previously reported, the NaNO_2 -attached NASICON sensor operated at 150°C was not affected by the change in CO_2 concentration.⁽²⁴⁾ In addition, although the Na_2CO_3 - BaCO_3 -attached NASICON sensor operated at 500°C was disturbed by the NO_2 change,⁽²⁵⁾ the Li_2CO_3 -attached LISICON sensor operated at 650°C was not responsive to NO_2 gas.⁽⁸⁾ According to these reports, it was possible that an impurity (a Na-based salt or a Li-based salt), which was eluted from the bulk of the NASICON disk or LISICON disk to the surface, reacted with the coexisting gas. It is assumed that the impurity eluted from the bulk of the solid-state electrolyte reacts with the coexisting gas, and the auxiliary phase, such as nitrate, nitride, and carbonate, was formed on its surface. In this case, if their equilibrium potential for the new auxiliary phase should be more negative than that of the impurity, the sensor could not show a gas sensing capability in

Table 2
CO₂ and NO₂ sensitivities of the ITO-Li₂CO₃-BaCO₃-attached sensors.

Gas	Solid-state electrolyte	$\Delta EMF/mV$	Theoretical value/mV
NO ₂	NASICON	29.0	32.9
	LISICON	1.0	
CO ₂	NASICON	27.6	30.1
	LISICON	20.0	

the negative potential. Therefore, in this type sensor, there are various interfaces, such as ITO/solid-state electrolyte, ITO/auxiliary phase (NaNO₂, Li₂CO₃-BaCO₃), ITO/auxiliary phase (derived from impurity), and auxiliary phase/solid-state electrolyte, and it is important that an interface is electrochemically superior at the operating temperature.

Thus, it was considered that Na₂O in NASICON or nitrite reacts with CO₂ gas, and Na₂CO₃ is spontaneously formed on the NASICON surface, as given in eqs. (10) and (11). Additionally, it was investigated in the same manner on the assumption that Na₂O in NASICON reacts with NO₂ gas, and nitrite is spontaneously formed on the NASICON surface, as given in eq. (12). Since it was difficult to obtain the thermodynamic properties of NaNO₂, the data of NaNO₃ was used in its place.⁽²⁶⁾



The relationship of thermochemical properties with an objective gas (NO₂ or CO₂) and a solid-state electrolyte or an auxiliary phase was investigated. Figures 8(a), 8(b), and 8(c) show the Gibbs free energy change (ΔG) of the reaction in eqs. (10), (11), and (12) in air containing 2 ppm NO₂ and 250 ppm CO₂ at various temperatures, respectively. As seen in Fig. 8(a), ΔG becomes negative between 300 and 500 K, suggesting that Na₂O is rather unstable in the presence of CO₂, and Na₂CO₃ is easily formed at operating temperature. As seen in Fig. 8(b), ΔG is seen to become negative at about 306 K and above. From thermodynamic calculation, it is suspected that NaNO₃ was unstable in dry air containing 250 ppm CO₂ below 33°C and Na₂CO₃ tends to be formed. As shown in Fig. 8(c), ΔG becomes negative between 300 and 500 K, and this result obviously indicates that Na₂O in NASICON is fairly unstable in the presence of NO₂. Although the thermodynamic properties of Li₂O in LISICON have not been verified yet, it is suspected that the thermochemical properties of Li₂O are chemically stable in dry air containing CO₂, in comparison with those of Na₂O in NASICON. These results support the assumption of the formation of an auxiliary phase, such as Na₂CO₃ and NaNO₃, on the surface of NASICON. From thermodynamic calculations, it was considered that the chemical instabilities of NASICON and NaNO₂ in the atmosphere containing CO₂ led to the degradation of NO₂ gas selectivity in the ITO-NaNO₂-attached sensor, whereas

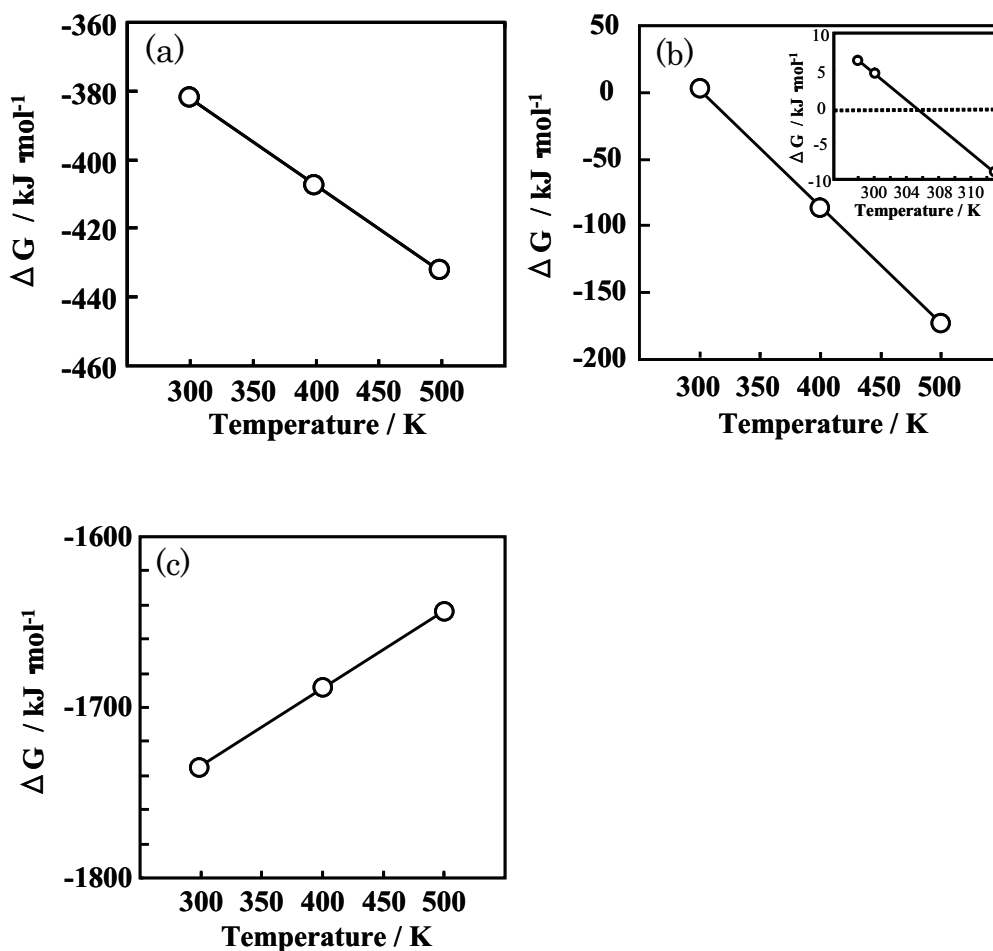


Fig. 8. Gibbs free energy change (ΔG) under dry air condition containing 2 ppm NO_2 and 250 ppm CO_2 at various temperatures for the reactions of (a) Na_2O (in NASICON) + $\text{CO}_2 \rightarrow \text{Na}_2\text{CO}_3$, (b) $2\text{NaNO}_3 + \text{CO}_2 \rightarrow \text{Na}_2\text{CO}_3 + 2\text{NO}_2 + 1/2\text{O}_2$, and (c) Na_2O (in NASICON) + $2\text{NO}_2 + 1/2\text{O}_2 \rightarrow 2\text{NaNO}_3$.

that of NASICON in the atmosphere containing NO_2 caused the degradation of CO_2 gas selectivity for the ITO- Li_2CO_3 - BaCO_3 -attached sensor.

5. Conclusions

In this study, a potentiometric sensor was fabricated by combining solid-state electrolyte (LISICON or NASICON) disks with sensing electrode materials, such as Au, ITO or an auxiliary phase (nitrate or carbonate). Their NO_2 and CO_2 sensing properties

were examined under 30% RH in the temperature range of 30 to 100°C.

- (1) When the NO₂ sensor was operated in the range of 2 to 7 ppm NO₂ at 30°C, the ITO-NaNO₂-attached LISICON sensor had the highest sensitivity to NO₂ and its EMF values were proportional to the logarithm of NO₂ concentration.
- (2) Also, when the CO₂ sensor was operated in the range of 250 to 2,500 ppm CO₂ at 30 °C, the ITO-Li₂CO₃-BaCO₃-attached LISICON sensor had the highest sensitivity to CO₂ and the EMF values of the sensor correlated linearly with the logarithm of CO₂ concentration.
- (3) The ITO-NaNO₂-attached sensors were fluctuated by the change in CO₂ concentration. On the other hand, although the ITO-Li₂CO₃-BaCO₃-attached NASICON sensor was affected by the NO₂ concentration change, the ITO-Li₂CO₃-BaCO₃-attached LISICON sensor showed a high CO₂ selectivity.
- (4) From thermodynamic calculations, it was considered that the chemical instabilities of NASICON and NaNO₂ in the atmosphere containing CO₂ led to the degradation of NO₂ gas selectivity in the ITO-NaNO₂-attached sensor, whereas that of NASICON in the atmosphere containing NO₂ caused the degradation of CO₂ gas selectivity for the ITO-Li₂CO₃-BaCO₃-attached sensor.

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