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Effects of Electrode Materials on CO₂ Sensing Properties of Solid-Electrolyte Gas Sensors

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The effect of oxide powder addition to a carbonate auxiliary electrode on the CO₂-sensing properties of Na₃Zr₂Si₂PO₁₂ (NASICON) gas sensors has been investigated. CO₂ was adsorbed on the surfaces of most of the oxides tested after treatment at 400°C in dry air, while the coexistence of H₂O reduced the amount of adsorbed CO₂. However, the amount of CO₂ adsorbed on the oxides was not correlated with the CO₂ response of the NASICON sensors equipped with an electrode containing the oxide. The CO₂ response increased and the humidity cross response decreased with a decrease in the resistance of the oxides. This result suggests that the strict conductivity control of auxiliary electrodes is an important factor for achieving high-performance potentiometric CO₂ sensors.

1. Introduction

CO₂ sensors with high sensitivity and selectivity that can operate stably under various severe conditions are required in various fields such as environmental monitoring, life science, agricultural industry and automotive technology. Among various CO₂-sensing systems proposed, potentiometric sensors coupled with a solid electrolyte and a metal carbonate auxiliary electrode are the most practical in terms of the CO₂ selectivity.^(1–3) Therefore, considerable effort has so far been directed to improving the CO₂-sensing performance and operating stability of such sensors.^(4–8) Among them, Obata and coworkers have reported that potentiometric CO₂ sensors employing Na₃Zr₂Si₂PO₁₂ (NASICON) as a solid electrolyte and two kinds of metal carbonates (Li₂CO₃ and BaCO₃) and In₂O₃ as detecting auxiliary electrode materials operated stably with high CO₂ sensitivity even at room temperature (RT) and that the In₂O₃ played a particularly

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important role in the stable operation under various conditions.⁽⁹⁻¹¹⁾ However, the mechanism for the stabilization of sensor operation was insufficiently elucidated in their papers. In this study, therefore, 13 metal oxides including In_2O_3 were selected as an additive to the metal-carbonate-based auxiliary electrode material of the potentiometric NASICON-based CO_2 sensor, and the effect of the CO_2 adsorption-desorption properties and the resistance of these oxide additives on the sensor performance were investigated in detail.

2. Materials and Methods

NASICON powder was prepared from $\text{Si}(\text{OC}_2\text{H}_5)_4$, $\text{Zr}(\text{OC}_4\text{H}_9)_4$, $\text{PO}(\text{OC}_4\text{H}_9)_3$ and NaOC_2H_5 by a conventional sol-gel technique.⁽¹²⁾ They were mixed in ethanol then heated at 70°C for 12 h with a small amount of nitric acid and water under nitrogen atmosphere, and therefore they could be hydrolyzed gradually. The gel obtained was dried at 120°C for 24 h and then heated at 750°C for 1 h. Figure 1 shows XRD patterns of the powder obtained before and after heating at 750°C for 1 h. The as-prepared powder was amorphous, whereas it crystallized to a single NASICON phase after the heating. The powder obtained was pressed into a disc (10 mm in diameter and about 1.0 mm thick), and the disc was sintered at 1100°C for 5 h in air.

A conventional planar sensor structure attached to both a working electrode and a counter electrode on the same side of the NASICON disc was adopted in this study.⁽⁹⁻¹¹⁾ A pair of Au electrodes was first attached by screen printing Au paste, followed by heating at 800°C for 2 h. An Au counter electrode was completely coated with a Na-free glass,

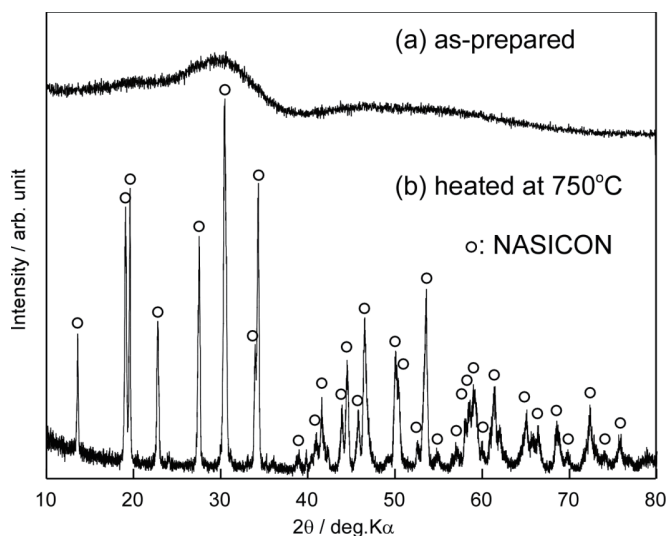


Fig. 1. XRD patterns of NASICON powder as-prepared by sol-gel technique and heated at 750°C for 1 h.

so as to prevent contact with ambient gas. An auxiliary electrode consisting of Li_2CO_3 , BaCO_3 and an oxide was fabricated on the Au working electrode by the following procedure. Li_2CO_3 and BaCO_3 ($\text{Li}_2\text{CO}_3 : \text{BaCO}_3 = 1 : 2$ in molar ratio) were mixed with a terpeneol solvent, and the slurry obtained was screen printed on the working electrode. After it was dried at 150°C , another slurry prepared with an oxide powder and terpeneol was screen printed on the porous mixed-carbonate film. The oxide slurry could penetrate into the prefabricated porous mixed-carbonate film during the second screen printing, and therefore an auxiliary electrode consisting of a mixture of the carbonates and the oxide could be fabricated by this procedure. The oxide powders used are listed in Table 1. Thereafter, the sensor elements obtained were annealed at 600°C for 3 h in air.

Table 1
Sensor properties and some characteristics of various oxides tested in this study.

Oxide powder	Maker or preparation method	Chemical grade, trade name or model number	CO_2 response	Humidity cross response	Spectra intensity by TPD / a.u.				CO ₂ spectrum intensity measured by FT-IR***	
					Treated in dry atmosphere		Treated in wet atmosphere		Physi-sorbed	Chemisorbed
					CO ₂	H ₂ O	CO ₂	H ₂ O		
In_2O_3	Junsei Chemical	Special	53	0	304.0	10.0	135.0	115.0	○	×
$5\text{Sn-In}_2\text{O}_3^*$	Kojundo Chemical	Special	66	0	20.4	2.0	20.6	38.0	○	×
$10\text{Sn-In}_2\text{O}_3^*$	Sumitomo Chemical	SUFR-HX	45	1	15.0	16.0	11.1	172.0	×	×
$15\text{Sn-In}_2\text{O}_3^*$	Douwa Chemical	TD-33	44	2	236.0	11.0	134.0	169.0	△	×
SnO_2	Prepared by pyrolysis (600°C) of tin oxalate		44	0	85.8	19.3	31.3	183.3	△	×
0.5Sb-SnO_2^{**}	Prepared by pyrolysis (600°C) of a mixture of tin oxalate and SbCl_3		27	0	100.6	8.5	36.4	145.0	△	×
1.5Sb-SnO_2^{**}			25	0	98.3	9.5	58.3	124.0	△	×
CuO	Kishida Chemical	For Chemicals	30	2	7.1	2.3	8.8	47.0	○	×
NiO	Wako Chemical	For Chemicals	39	4	10.4	11.9	10.9	55.0	○	×
ZnO	Wako Chemical	For Chemicals	29	5	23.4	1.3	4.7	51.0	○	×
Pr_6O_{11}	Wako Chemical	For Chemicals	40	4	344.0	12.0	316.0	88.0	◎	◎
$\gamma\text{-Al}_2\text{O}_3$	Taimei Chemical	TM-300D	0	7	394.6	58.0	237.0	614.0	○	○
Zeolite	Catalyst & Chemicals	JRC-Z-Y5.3	0	8	90.0	100.0	148.4	501.0	○	×

*nSn-In₂O₃: In₂O₃ doped with n wt% SnO₂

**nSb-SnO₂: SnO₂ doped with n wt% Sb₂O₃

*** ◎ : large, ○ : medium, △ : small, × : undetected

The CO₂ responses of the sensors were measured at 400°C under gas flows with 30, 50 and 70% relative humidity (RH) at 20°C. The magnitude of the CO₂ response was defined as the difference between electromotive force (EMF) in 500 ppm CO₂ and that in 5000 ppm CO₂, both of which were balanced with air (30%RH). On the other hand, the magnitude of the humidity cross response was defined as the difference between EMF in air with 50%RH and that with 30%RH, while maintaining the same CO₂ concentration of 5000 ppm, in order to investigate the influence of water vapor on the CO₂ response.

Some properties of the 13 oxides listed in Table 1 were investigated by the following methods. The desorption behavior of CO₂ and H₂O from various oxides was measured by a conventional temperature-programmed desorption (TPD) technique.⁽¹³⁾ After 40–60 mesh granules of each oxide were set in the glass reactor of a flow apparatus and pretreated at 600°C for 2 h in a dry air stream, they were treated for 30 min in a 1.4% CO₂ stream balanced with dry air or wet air with saturated water vapor at 20°C. The atmosphere was changed to a He stream (10 cm³ min⁻¹), and then the granules were quenched to RT. Thereafter, they were heated to 400°C at a heating rate of 4°C min⁻¹ in a He stream. The desorbed CO₂ and H₂O were analyzed using a gas chromatography mass spectrometer (GC-MS, Shimadzu, QP-5000) with a CP-PoraPLOT Q (Varian Inc.).

The adsorption state of CO₂ was estimated by diffuse reflectance Fourier transform infrared spectroscopy (FT-IR, JASCO Corp., FT/IR-680 plus). After each oxide powder was set in a special container in a flow system, it was pretreated at 600°C for 2 h in a dry air stream. Then, it was treated at 400°C for 30 min in a dry 100% CO₂ stream or wet 100% CO₂ stream saturated with water vapor at 20°C. In some cases, the treatment was also performed at RT and 100°C. After the atmosphere was changed to an Ar stream and the powder was quenched to RT, it was characterized by diffuse reflectance FT-IR under the same conditions.

The resistance of each oxide was measured by employing a general measurement technique for semiconductor gas sensors.⁽¹⁴⁾ Each oxide powder was mixed with a printing oil (Goo Chemical Co., Ltd., OS-4530) as an organic binder, and then screen printed on an alumina substrate with interdigitated Pt electrodes (electrode gap: 200 μm), followed by drying at 80°C for 30 min. After firing at 600°C for 3 h in air, the resistance was measured at 400°C in dry air.

3. Results and Discussion

Figure 2 shows the CO₂ response transients of representative solid-electrolyte sensors attached to the mixed-carbonate-based auxiliary electrode containing In₂O₃, ZnO or γ-Al₂O₃ at 400°C under flowing air with 30, 50 and 70%RH. Hereafter, the sensor attached to the electrode containing In₂O₃ is denoted as an In₂O₃-based sensor. The CO₂ response of the In₂O₃-based sensor (the magnitude at 30%RH: *ca.* 53 mV) was sufficiently stable, irrespective of the humidity. This means that the humidity cross response was hardly noticeable in 5000 ppm CO₂ balanced with air. The ZnO-based sensor also showed a reasonable response to CO₂ and recovery behavior, but the magnitude of the CO₂ response (*ca.* 30 mV at 30%RH) was much smaller than that of the In₂O₃-based sensors. In addition, the humidity cross response was clearly noticeable. On

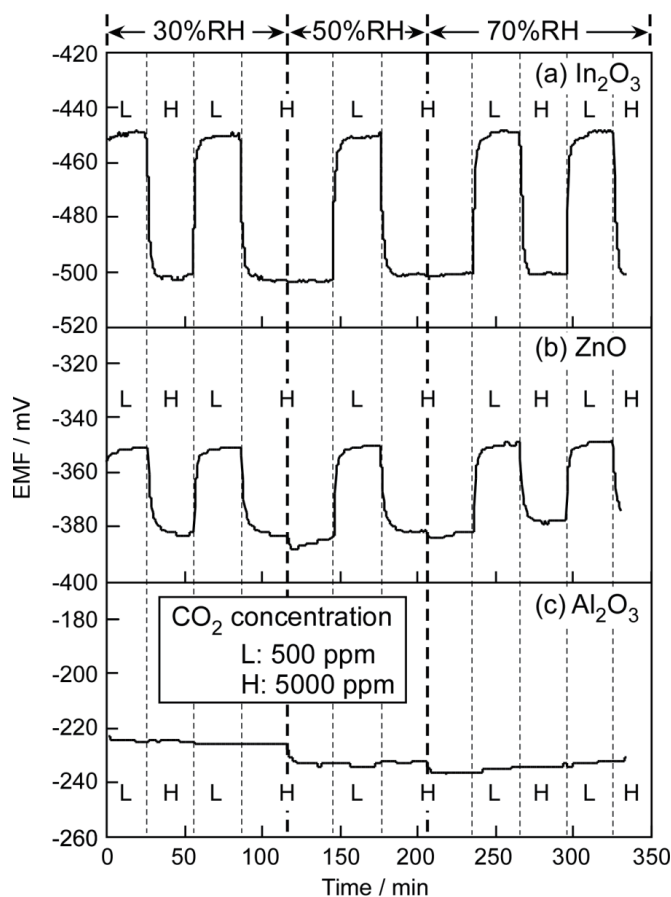


Fig. 2. CO_2 and humidity dependences of EMF at 400°C for solid-electrolyte sensors attached to the mixed-carbonate-based auxiliary electrode containing (a) In_2O_3 , (b) ZnO and (c) $\gamma\text{-Al}_2\text{O}_3$.

the other hand, the $\gamma\text{-Al}_2\text{O}_3$ -based sensor showed no response to CO_2 , but the humidity cross response was the largest among the three sensors. The magnitudes of the CO_2 response and humidity cross response of all the sensors investigated are listed in Table 1. Four kinds of In_2O_3 -based sensors, namely, sensors attached to the electrode containing In_2O_3 or SnO_2 -doped In_2O_3 , showed a relatively large response to CO_2 . In particular, the magnitude of the CO_2 response of $5\text{Sn-In}_2\text{O}_3$ (In_2O_3 doped with 5 wt% SnO_2) was the largest among the four sensors without a humidity cross response. Three kinds of SnO_2 -based sensors also showed a good CO_2 response, but the magnitude of the CO_2 response is smaller than that of the In_2O_3 -based sensors. Transition-metal-oxide (CuO , NiO and ZnO)-based sensors also showed moderate CO_2 -sensing properties, while the humidity cross response increased considerably in comparison with In_2O_3 - and SnO_2 -based sensors. The behavior of the Pr_6O_{11} -based sensor was comparable to those of the transition-metal-oxide-based sensors. On the other hand, the zeolite-based sensor

showed no CO₂ response but a large humidity cross response, similar to a γ -Al₂O₃-based sensor.

It is well known that the use of carbonate species (Li₂CO₃ and BaCO₃ in this case) as the main auxiliary electrode material for solid-electrolyte CO₂ sensors is essential for detecting CO₂ sensitively and selectively, as described in previous studies.⁽¹⁻¹¹⁾ However, the CO₂-sensing properties depended largely on the kind of oxide mixed with the carbonate species, as noted above. Therefore, in the present study, attempts were made to clarify the most important factor, i.e., the property of the oxide that determines the CO₂-sensing properties.

First, the desorption behavior of CO₂ and H₂O molecules adsorbed on the surfaces of all the oxide powders was measured by TPD. Figure 3 shows representative TPD spectra

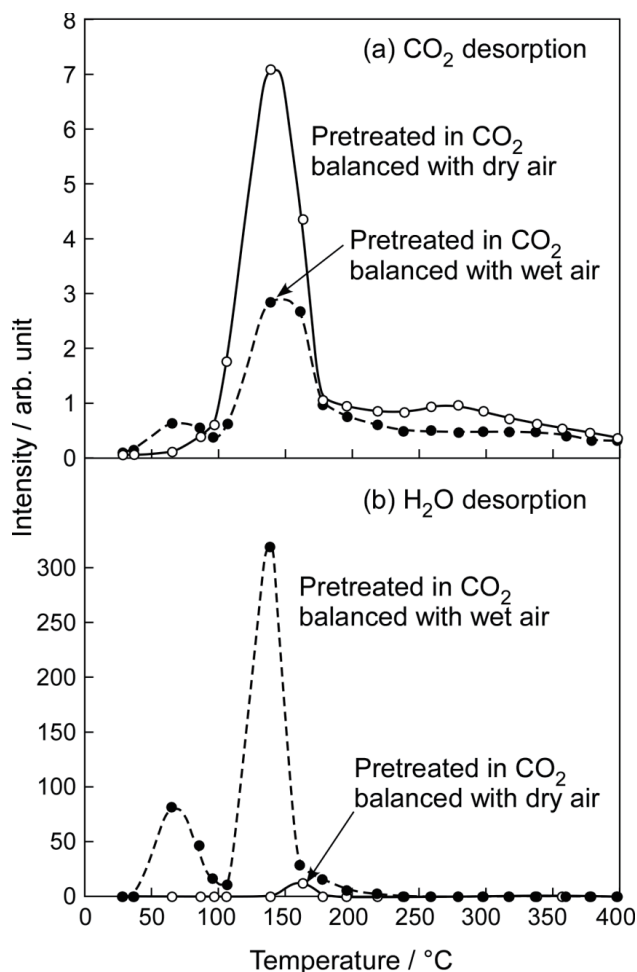


Fig. 3. TPD spectra of (a) CO₂ and (b) H₂O from In₂O₃ powder pretreated at 400°C for 30 min in 1.4% CO₂ balanced with dry or wet air.

of CO_2 and H_2O obtained from In_2O_3 powder. A large amount of CO_2 was adsorbed on the surface of In_2O_3 during pretreatment at 400°C for 30 min in 1.4% CO_2 balanced with dry air, and an intense peak in the CO_2 desorption spectrum around 150°C was observed, while hardly any H_2O was desorbed naturally because it was pretreated in dry air. On the other hand, the amount of CO_2 desorbed from In_2O_3 pretreated in wet air was much lower than that upon pretreatment in dry air, whereas H_2O was largely coadsorbed on the oxide surface. The amounts of CO_2 and H_2O desorbed from all the oxides tested are also listed in Table 1. In addition to In_2O_3 , $15\text{Sn-In}_2\text{O}_3$ and basic oxides such as Pr_6O_{11} and $\gamma\text{-Al}_2\text{O}_3$ showed much larger amounts of CO_2 adsorbed than other oxides. Meanwhile, the desorption of a large amount of H_2O was observed in the cases of $\gamma\text{-Al}_2\text{O}_3$ and zeolite, which have high specific surface areas (200 and $723\text{ m}^2\text{ g}^{-1}$, respectively). The CO_2 response in air with 30%RH was plotted against the amount of CO_2 desorbed from oxides pretreated in CO_2 balanced with dry or wet air in Fig. 4, but no important correlation could be confirmed. Therefore, the adsorption state of CO_2 on the surfaces of all the

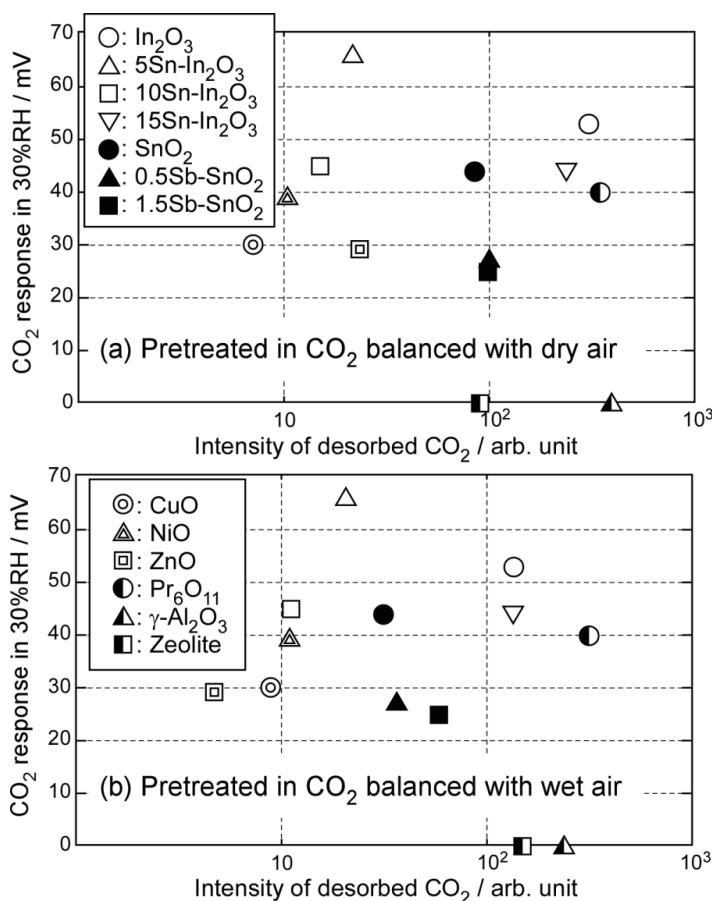


Fig. 4. Variation in CO_2 response in air with 30%RH with the amount of CO_2 desorbed from various oxides.

oxide powders was investigated by diffuse reflectance FT-IR. Several peaks (1200–1700 cm^{-1}) ascribed to different chemisorbed CO_2 species on In_2O_3 ^(15–17) were clearly observed after pretreatment in dry CO_2 at RT, as shown in Fig. 5(a-i). Even after pretreatment in wet CO_2 at RT, almost the same spectra could be observed, but the intensity was slightly weaker than that obtained by pretreatment in dry CO_2 (compare Fig. 5(b-i) with Fig. 5(a-i)). When CO_2 was adsorbed at 100°C, however, the spectra of chemisorbed CO_2 species disappeared, as shown in Figs. 5(a-ii) and 5(b-ii). Figure 6 shows FT-IR spectra of Pr_6O_{11} and SnO_2 after pretreatment in dry CO_2 at 400°C. Chemisorbed CO_2 species on the surface of SnO_2 were not observed, as shown in Fig. 6(b). A similar phenomenon was observed for almost all the oxides tested, as listed in Table 1. However, Pr_6O_{11} clearly showed strong peaks even after pretreatment under the same conditions, probably due to the strong basicity of the oxide surface. On the other hand, a peak ascribed to physisorbed CO_2 species was observed at 2400–2500 cm^{-1} for almost all the oxides, except for $10\text{Sn-In}_2\text{O}_3$ (see Table 1). The spectral intensity of the physisorbed CO_2 appears to be strongly correlated with the amount of CO_2 desorption measured by TPD. This suggests that the desorbed species shown in the TPD profiles are physisorbed CO_2 species, which have little electronic interaction with the oxide surfaces. This may be the main reason for there being no correlation between the CO_2 response and the amount of CO_2 desorption measured by TPD, as shown in Fig. 4.

Figure 7 shows the variation in humidity cross response with the amount of H_2O desorbed from all the oxides tested. The humidity cross response tends to increase with increasing amount of H_2O desorbed after pretreatment in CO_2 balanced with both wet and dry air. However, In_2O_3 - and SnO_2 -based oxides showed a relatively low humidity cross response, even though they desorbed a medium amount of H_2O . Therefore, other factors must be considered for the explanation of their humidity cross response.

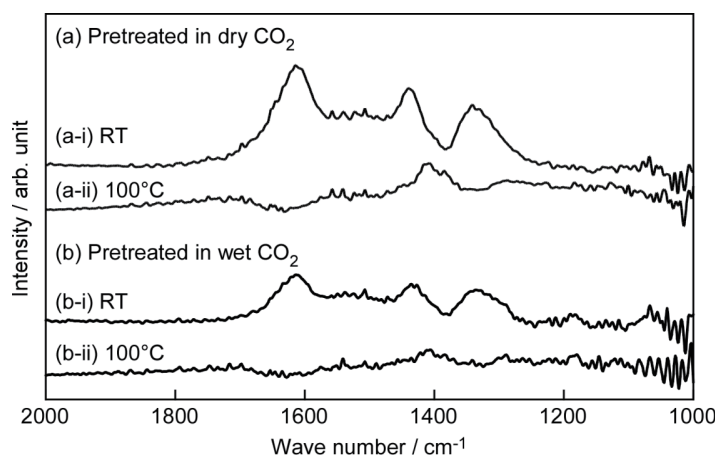


Fig. 5. FT-IR spectra of In_2O_3 after CO_2 adsorption at RT and 100°C in (a) dry and (b) wet atmosphere.

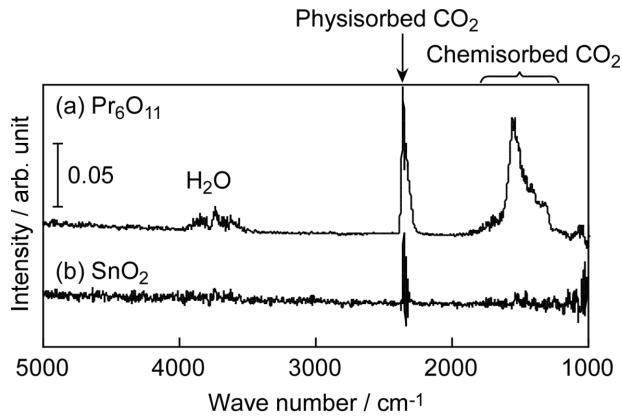


Fig. 6. FT-IR spectra of (a) Pr_6O_{11} and (b) SnO_2 after CO_2 adsorption at 400°C in dry atmosphere.

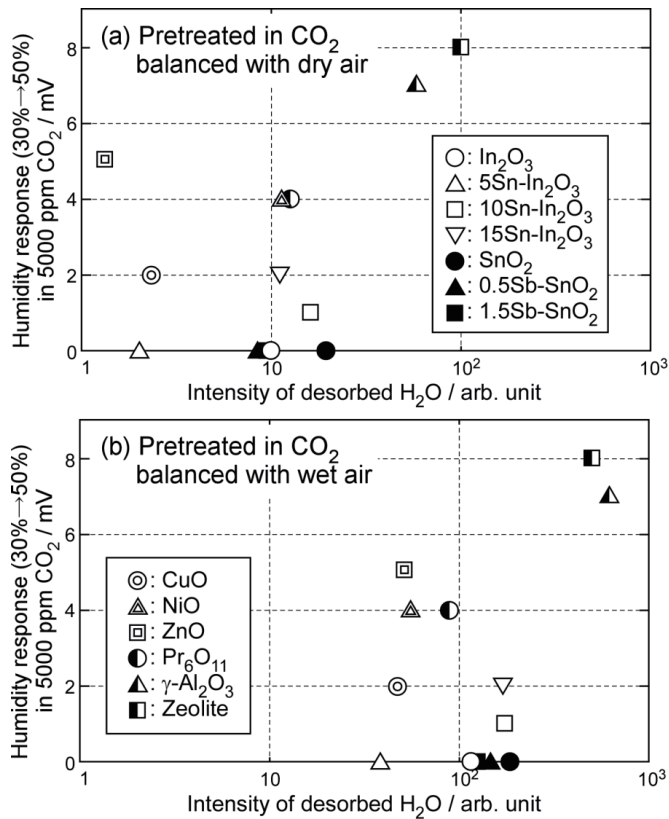


Fig. 7. Variation in humidity cross response with the amount of H_2O desorbed from various oxides.

Figure 8 shows the CO_2 response and humidity cross response as a function of resistance for all the oxides measured at 400°C . The CO_2 response decreased with increasing oxide resistance, while the humidity cross response showed an inverse tendency. This result indicates that the strict conductivity control of auxiliary electrodes including the oxide additive is the most important among the possible factors tested in the present study for determining the performance of potentiometric CO_2 sensors. Since the carbonate species (Li_2CO_3 and BaCO_3) used as the main auxiliary electrode material have low electric conductivity, the formation of a different electron pathway between the carbonates and the Au working electrode should be indispensable for achieving effective electron transfer (e.g., $2\text{Li}^+ + (1/2)\text{O}_2 + \text{CO}_2 + 2e^- \rightleftharpoons \text{Li}_2\text{CO}_3$) on the surface of the carbonate species. Therefore, the coexistence of a high-electron-conductivity oxide in the auxiliary electrode is considered to allow the possibility of the formation

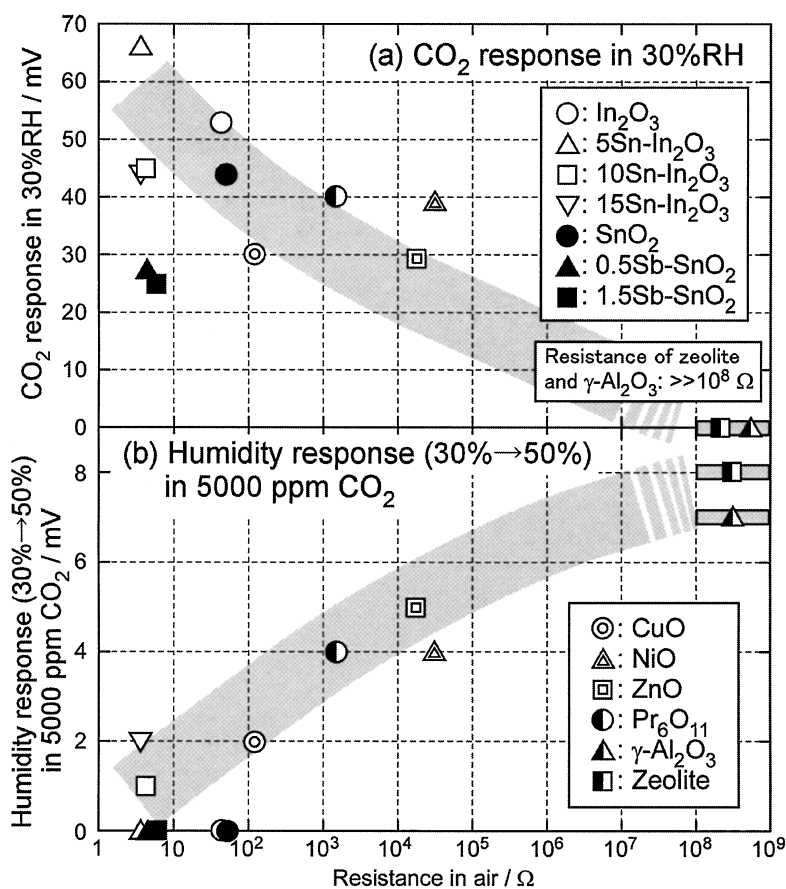


Fig. 8. CO_2 response and humidity cross response as a function of resistance for various oxides at 400°C .

of an important electron pathway. This scenario also supports the fact that γ -Al₂O₃- and zeolite-based sensors showed almost no CO₂ response due to the lack of an electron pathway. On the other hand, the introduction of water vapor to the atmosphere may improve the ion conductivity of the oxide surface due to the partial weak hydration. This may have an effect on the electrode potential, particularly for low-electron-conductivity electrodes having a large ohmic resistance loss. Therefore, the effect of water vapor on the sensors containing low-electron-conductivity oxides is thought to be much larger than that on the sensors containing high-electron-conductivity oxides. This may be the reason for the high humidity cross resistance of the γ -Al₂O₃- and zeolite-based sensors. Further efforts are now being directed to collecting more information so that the mechanism of the humidity cross response can be simply explained. Such an approach is believed to be useful for improving the long-term stability of the carbonate-based auxiliary electrode to water vapor.

4. Conclusions

Various oxide powders were used as an additive to the Li₂CO₃-BaCO₃ auxiliary electrode for NASICON-based CO₂ sensors, and their CO₂ response and humidity cross response were investigated. The CO₂ response was independent of the amount of CO₂ adsorbed on the oxides, probably due to the small amount of chemisorbed CO₂ species on the surface of almost all the oxides. On the other hand, the CO₂ response decreased and the humidity cross response increased with an increase in the resistance of the oxides tested. Therefore, it is considered that the improvement of the conductivity of the auxiliary electrode is the most important factor for achieving high-performance potentiometric CO₂ sensors.

References

- 1 T. Maruyama, S. Sasaki and Y. Saito: *Solid State Ionics* **23** (1987) 107.
- 2 N. Imanaka, T. Kawasato and G. Adachi: *Chem. Lett.* **19** (1990) 497.
- 3 S. Yao, Y. Shimizu, N. Miura and N. Yamazoe: *Chem. Lett.* **19** (1990) 2033.
- 4 H. Futata and K. Ogino: *Sens. Actuators B* **52** (1998) 112.
- 5 K. Kaneyas, K. Otsuka, Y. Setoguchi, S. Sonoda, T. Nakahara, I. Aso and N. Nakgaichi: *Sens. Actuators B* **66** (2000) 56.
- 6 T. Kida, Y. Miyachi, K. Shimanoe and N. Yamazoe: *Sens. Actuators B* **80** (2004) 28.
- 7 P. Pasierb, S. Komornicki, S. Kozinski, R. Gajerski and M. Rekas: *Sens. Actuators B* **101** (2004) 47.
- 8 Y. Sadaoka: *Sens. Actuators B* **121** (2007) 194.
- 9 K. Obata, S. Kumazawa, K. Shimanoe, N. Miura and N. Yamazoe: *Sens. Actuators B* **76** (2001) 639.
- 10 K. Obata, K. Shimanoe, N. Miura and N. Yamazoe: *Sens. Actuators B* **93** (2003) 243.
- 11 K. Obata, S. Kumazawa, K. Shimanoe and N. Yamazoe: *Sens. Actuators B* **108** (2005) 352.
- 12 D.-D. Lee, S.-D. Choi and K.-W. Kee: *Sens. Actuators B* **24–25** (1995) 607.
- 13 Y. Shimizu, N. Matsunaga, T. Hyodo and M. Egashira: *Electrochemistry* **69** (2001) 109.
- 14 T. Hyodo, N. Nishida, Y. Shimizu and M. Egashira: *Sens. Actuators B* **83** (2002) 209.

- 15 M.-I. Baraton: *Sens. Actuators B* **31** (1996) 33.
- 16 O. Seiferth, K. Wolter, B. Dillmann, G. Klivenyi, H.-J. Freund, D. Scarano and A. Zecchina: *Surf. Sci.* **421** (1999) 176.
- 17 D. H. Gibson: *Coordin. Chem. Rev.* **185** (1999) 335.