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Solid Electrolyte CO_2 Sensor Using NASICON and Perovskite-Type Oxide Electrode

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Abstract

Solid-state electrochemical sensor devices combined with sodium super ionic conductor (NASICON: $Na_{1+x}Zr_2Si_xP_{3-x}O_{12}$) discs and perovskite-type oxide electrodes have been developed for the detection of CO_2 in the range 100-2000ppm. Among the various sensor devices tested, Co-based perovskite-type oxide electrodes were found to show excellent sensing properties to CO_2 at 200-300°C. Especially, $NdCoO_3$- and $La_{0.8}Ba_{0.2}CoO_3$-based elements showed the best CO_2 sensing properties, i.e., the sensor response (EMF) was almost linear to the logarithm of CO_2 concentration in the range between 100 and 2000 ppm, the response time to 500ppm CO_2 was as short as 1-2 min. An open-reference electrode type sensor element, which fitted with $NdCoO_3$ and $La_{0.8}Pb_{0.2}CoO_3$ for sensing and reference electrodes, respectively, showed excellent CO_2 sensing properties and hardly affected with oxygen partial pressure.

Keywords: Perovskite-type oxide, CO_2 sensor, NASICON, Solid electrolyte,

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1. Introduction

There have been increasing the needs for all-solid-state CO_2 sensors which are reliable, inexpensive, and compact, from the recent deepening concern about the emissions of CO_2 as the global warming issue as well as from the growing needs of CO_2 monitoring in various fields and the control of CO_2 in various technologies. So far, many kinds of compact CO_2 sensors using various materials, such as solid electrolyte [1-4], mixed oxide capacitors [5], polymers with carbonate solution [6] and so on, have been investigated. Among them, solid electrolyte-type CO_2 sensors are of particular interest from the view point of low cost, high sensitivity, high selectivity and simple element structure. Recently, it has been reported that the use of metal oxide electrodes, such as SnO_2(with Sb, V) [7] or In_2O_3 [8], instead of conventional metal carbonate for the auxiliary phase of solid electrolyte CO_2 sensors seems to bring about better sensing performance at wide operation temperature as well as chemical and/or thermal stability. Especially, NASICON-based devices seem to be the most promising sensor material from the view point of high conductivity at lower temperature and high chemical stability of NASICON as a solid electrolyte. In our previous study, it was also revealed that La-based perovskite-type oxides have worked as a sensing electrode for NASICON-based solid electrolyte CO_2 sensor [9].

In this paper, we have investigated the sensing properties of various perovskite-type oxides as an electrode for the solid electrolyte CO_2 sensor. As a result, it was turned out that Co-based perovskite-type oxide based device showed excellent sensing properties to CO_2 at 200-300°C. It was further found that an open-reference electrode type [4, 10] CO_2 sensor device fitted with different kinds of electrodes could be fabricated.

2. Experimental

2.1 Electrode materials

Perovskite-type oxides ($Ln_{1-x}A'_xBO_3$: Ln= La, Pr, Nd, Sm, Gd, A'= Ca, Sr, Ba, Ce, Pb, B= Cr, Mn, Fe, Co, Ni; x= 0 - 0.4) and commercial metal-oxides (NiO and Co_3O_4: Kishida Chemical) were used as the electrode material. Perovskite-type oxides were prepared by an amorphous malate precursor (AMP) method [11]. The precursors prepared from malic acid and the nitrates of constituent metal were heated at 650°C for 2h in an ambient atmosphere. X-ray diffraction analysis (XRD: JDX-3500K, JEOL Ltd.) revealed that the oxides thus prepared showed well-crystallized and almost single-phase perovskite-type oxides.

2.2 Sensor devices

Figure 1 shows schematic diagrams of CO_2 sensor devices using perovskite-type oxide electrodes with a conventional closed-reference electrode type (Type A) or an open-reference electrode type (Type B). NASICON ($Na_3Zr_2Si_2PO_{12}$) discs were prepared by a sol-gel method using aqueous solution [12]. A paste prepared with oxides and turpentine oil was painted onto the surface of the NASICON disc, and dried and sintered at 500 °C for 1 h to form a layer of oxide electrode as a sensing or a reference electrode. For the device of Type A, a reference Pt electrode attached on the inside surface of the NASICON disc was always exposed to static atmospheric air. For the device of Type B , on the other hand, both sensing and reference electrodes were exposed to the same gas mixture.

CO_2 sensing experiments were carried out in a conventional flow apparatus equipped with a heating facility at 30-400 °C. Sample gases containing CO_2 was prepared from a parent gas, i.e., CO_2 diluted with a dry synthetic air (N_2+O_2 gas mixture), by mixing it with the air. The sensor response, EMF, was measured with a digital electrometer (Advantest, R8240) at a total flow rate of 100 cm^3/min.

3. Results and Discussion

3.1 Effect of operating temperature

Figure 2 shows CO_2 sensing properties of the device (Type A) attached with $LaCoO_3$ electrode at various temperature. The device showed rather good and reversible EMF responses to CO_2 at the temperatures between 100 and 400°C, as shown in Fig. 2 (a). The each response was rather quick and the 90% response time was within 1 - 5 min for the each temperature. The most highest change of EMF of the $LaCoO_3$-based device was observed at 300°C. The EMF responses were linear to the logarithm of CO_2 concentration ($\log P_{CO2}$) between 100 and 2000 ppm with the slopes of 11 - 33 mV/decade between 100 and 400°C, as shown in Fig. 2 (b).

Most of the devices fitted with perovskite-type oxide electrodes showed highest sensitivities at 300°C. In some cases, such as the devices fitted with $NdCoO_3$ and $SmCoO_3$ showed different temperature dependence, i.e., the highest slope for EMF vs. $\log P_{CO2}$ was seen at 200°C. In the further investigations, it was also found that the devices fitted with $LaMnO_3$ or $NdCoO_3$ also showed CO_2 responses at the low temperature of 30°C, although the slopes for EMF vs. $\log P_{CO2}$ were as low as +13 or +16 mV/decade, respectively.

For the most of the sensor devices tested, the slope of the line for ΔE vs. $\log P_{CO2}$ was not increased with increasing operating temperature as like the case for the $LaCoO_3$ based device as shown in Fig. 2 (b). Thus, the sensing mechanism seems to be come from not the conventional Nernst' type but probably the mixed potential one [13]. However, the sensing mechanisms of the present electrochemical device still need further investigations.

Hereafter, operating temperature was mainly fixed at 300 (or 200)°C.

3.2 Effect of electrode material

As it is well known that the properties of perovskite-type oxides was largely dependent on the kind of B-site metal cation in $LaBO_3$ system, the effects of B-site cation in lanthanum-based perovskite-type oxides ($LaBO_3$, $La_{0.6}Ca_{0.4}CoO_3$; B= Cr, Mn, Fe, Co, Ni) on CO_2 sensing properties were further investigated. Figure 3 shows the effects of B-site cation on CO_2 sensing properties in the La-(Ca)-B-O systems. Although, B=Cr system showed no CO_2 response, the other all devices showed CO_2 responses with different values of the slope and the EMF change. In the $La_{0.6}Ca_{0.4}BO_3$ systems, the electrodes with B=Fe, Co, Ni showed rather high accuracy (slope) and sensitivity (ΔE). In the $LaBO_3$ systems, the electrode with B=Co showed the highest performance. The stability of the sensor response was also dependent on the kind of electrode materials, and it was found that the order for the stability was (B=) Co = Ni (excellent) > Mn (good) >> Fe (poor). Thus, the Co-based perovskite-type oxide seems the most promising material for the sensing electrode of the CO_2 sensor.

Table 1 summarizes the CO_2 sensing performance for the all sensor devices tested. Most of the devices showed rather good sensing performance to CO_2. The EMF responses were linear to the logarithm of CO_2 concentration ($\log P_{CO2}$) between 100 and 2000 ppm with slopes between 24 and 42 mV/decade. Among the various sensor elements tested, those using Ln-Co-O systems showed better sensing properties to CO_2. $NdCoO_3$, and $La_{0.8}Ba_{0.2}CoO_3$ -based devices showed the best results. On the other hand, it was also revealed that the NiO- and the $La_{0.8}Pb_{0.2}CoO_3$- based elements showed no response to CO_2 at 300°C.

The reason for the dependence of the sensor response properties on the electrode material was not clear yet, but it seems come from the electro-catalytic activity and/or sorption-desorption behavior of the reaction gases to the perovskite-type oxide electrodes used. Further investigation is now in progress.

3.3 Effect of oxygen

As the oxide electrode based solid electrolyte device seems to affect with oxygen partial pressure, oxygen sensing properties of the devices were investigated. Figure 4 shows sensing performance to oxygen of CO_2 sensor device using $La_{0.8}Ba_{0.2}CoO_3$ at 300°C. EMF response was linear to the logarithm of oxygen concentration with a Nernst's slope of 31 mV/decade. The 90% response time was about 1 min at 300°C.

It was further found that all sensor devices tested were responded to oxygen and most of the sensor devices except NiO-based one showed almost the same EMF response properties to oxygen, i.e., EMF responses were linear to the logarithm of oxygen concentration with a slope of ca. 30mV/decade, while NiO-based device showed a slope of ca. 60 mV/decade at 300°C. The slopes of ca. 30 or 60 mV/decade for most of the perovskite-type oxides or NiO, respectively, should be considered Nernst's type and they means n=4 or 2, respectively, where n is number of electrons involved in the electrode reaction. In these cases, the electrode reactions of Eq. (1) or (2) could be considered.

$$O_2 + 4e^- = 2O^{2-} \quad (1)$$

$$O_2 + 2e^- = 2O^- \quad (2)$$

Figure 5 shows EMF response behavior to oxygen or carbon dioxide of the various sensor devices attached with some oxide electrodes at 300°C. Most of the devices have the almost same slope for the detection of O_2 as well as CO_2, this means that the CO_2 sensor attached with oxide is easily affected with oxygen partial pressure. On the other hand, NiO- and $La_{0.8}Pb_{0.2}CoO_3$ - based devices, which have less CO_2 sensitivity, also showed oxygen sensitivities with different slopes.

3.4 Open-reference-electrode type sensor device

As shown in the above section, $La_{0.8}Pb_{0.2}CoO_3$ electrode has no CO_2 sensitivity, while it shows good oxygen response of the almost same sensitivity of the other perovskite-type oxides which have high CO_2 sensitivity, such as $La_{0.6}Ca_{0.4}CoO_3$, $NdCoO_3$, and so on. This unique performance of $La_{0.8}Pb_{0.2}CoO_3$ electrode could be applicable as a reference electrode of an open-reference-electrode-type sensor device. Thus, we prepared a sensor device of Type B, which is combining $NdCoO_3$ and $La_{0.8}Pb_{0.2}CoO_3$ for sensing and reference electrodes, respectively. The $NdCoO_3$ and $La_{0.8}Pb_{0.2}CoO_3$ electrodes have high and poor sensitivity to CO_2, respectively, while they have almost the same sensing performance to oxygen. Figure 6 shows CO_2 and O_2 sensing properties of the open-reference electrode type sensor device at 300°C. The sensor still has rather good CO_2 sensing properties, while the sensor hardly affected with oxygen partial pressure, as expected.

4. Conclusion

Solid electrolyte CO_2 sensor devices using NASICON and perovskite-type oxides of Ln-Co-O based electrodes were found to exhibit good performance for the potentiometric sensing of CO_2 at 200-300°C. The EMF responses were linear to the logarithm of CO_2 concentration. A mixed potential should be considered for the sensing mechanism. An open-reference electrode type sensor element, which fitted with $NdCoO_3$ and $La_{0.8}Pb_{0.2}CoO_3$ for sensing and reference electrodes, respectively, showed excellent CO_2 sensing properties and hardly affected with oxygen partial pressure.

Acknowledgments

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Biographies

Youichi Shimizu has been an associate professor at Kyushu Institute of Technology since 1993. He received the B. Eng. degree in applied chemistry in 1983 and the Dr. Eng. degree in 1992 from Kyushu University. His current research interests include the solid-state gas sensors and ion sensors.

Nami Yamashita received her B. Eng. degree in applied chemistry in 1997 and the M. Eng. degree in 1999 from Kyushu Institute of Technology. She is currently working at Ohara Business School.

Figure captions

Fig. 1 Schematic diagrams of solid electrolyte CO_2 sensor devices using perovskite-type oxide electrode.

(a) Closed-reference electrode type, (Type A)

(b) Open-reference electrode type, (Type B)

Fig. 2 Sensing performance to CO_2 of the device attached with $LaCoO_3$ electrode at various temperature (Type A).

(a) Response transient to 300ppm CO_2

(b) ΔE vs. $\log P_{CO2}$

Fig. 3 Sensing performance to CO_2 of the sensor devices attached with various perovskite-type oxide electrodes at 300°C (Type A).

(a) : $La_{0.6}Ca_{0.4}BO_3$ (B=Cr, Mn, Fe, Co, Ni) system

(b) : $LaBO_3$ (B= Mn, Fe, Co, Ni) system

Slope: slope for the line of ΔE vs. $\log P_{CO2}$,

ΔE_{500}: EMF (in 500ppm CO_2)-EMF (in air)

Fig. 4 EMF response behavior to oxygen of the sensor device attached with $La_{0.8}Ba_{0.2}CoO_3$ electrode at 300ºC (Type A).

Fig. 5 EMF response behavior to oxygen or CO_2 of the sensor devices attached with various perovskite-type oxide electrodes at 300ºC (Type A).

Fig. 6 Sensing performance to CO_2 or O_2 of the open-reference electrode type sensor device at 300°C.

(Type B: $NdCoO_3$ | NASICON | $La_{0.8}Pb_{0.2}CoO_3$)

Table 1 Sensing performance to CO_2 of the various sensor devices attached with metal oxide electrodes at 300°C. (Device : Type A)

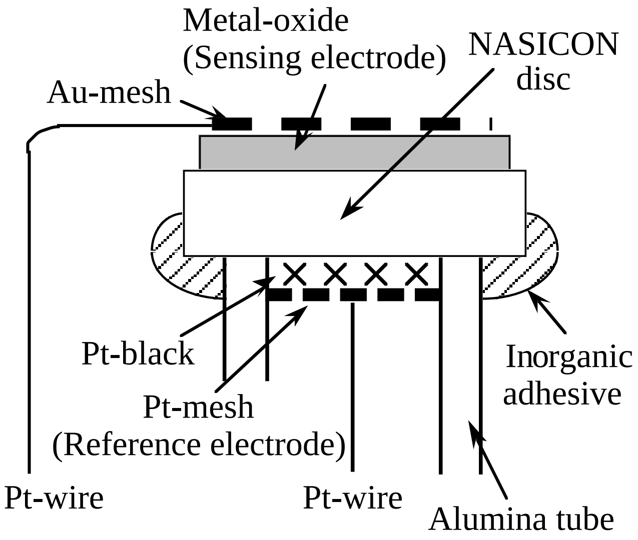
Electrode material	ΔE_{500ppm} [mV] 1)	Slope [mV/dec.]	Stability 2)	90%response time [min] 3)
NiO	0	0	○	—
Co_3O_4	50	25	△	1
$LaCoO_3$	47	33	—	3
$La_{0.6}Ca_{0.4}NiO_3$	33	27	△	1
$La_{0.6}Ca_{0.4}CoO_3$	56	31	○	3(os)
$La_{0.8}Ca_{0.2}CoO_3$	45	26	×	10(os)
$La_{0.8}Sr_{0.2}CoO_3$	47	24	○	9(os)
$La_{0.8}Ba_{0.2}CoO_3$	58	32	○	2
$La_{0.8}Ce_{0.2}CoO_3$	41	26	×	7(os)
$La_{0.8}Pb_{0.2}CoO_3$	0	0	○	—
$NdCoO_3$	42	32	○	9(os)
$NdCoO_3$(200°C)	79	42	○	1
$SmCoO_3$	30	26	×	20(os)
$GdCoO_3$	51	28	△	2

1) $\Delta E_{500ppm} = \Delta E_{500ppmCO_2} - E_{air}$

2) Stability of EMF response; ○ : excellent △ : good × : poor

3) air→500ppmCO_2 ; Responsetime to take within ±10% of the steady value ; (os) : overshoot

(a) Closed-reference electrode type



(b) Open-reference electrode type

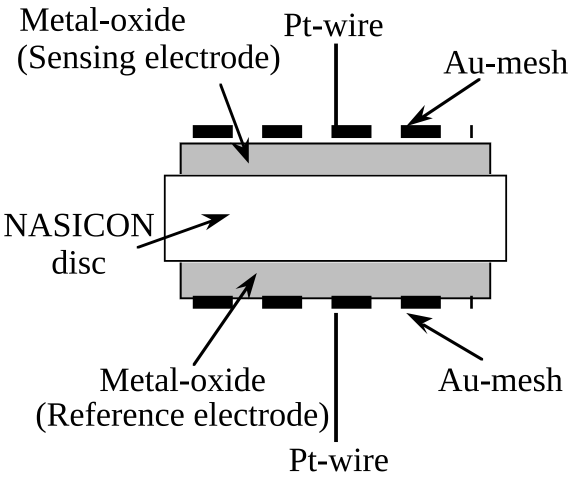


Fig. 1 Schematic diagrams of solid electrolyte CO_2 sensor devices using perovskite-type oxide electrode.
(a) Closed-reference electrode type, (Type A)
(b) Open-reference electrode type, (Type B)

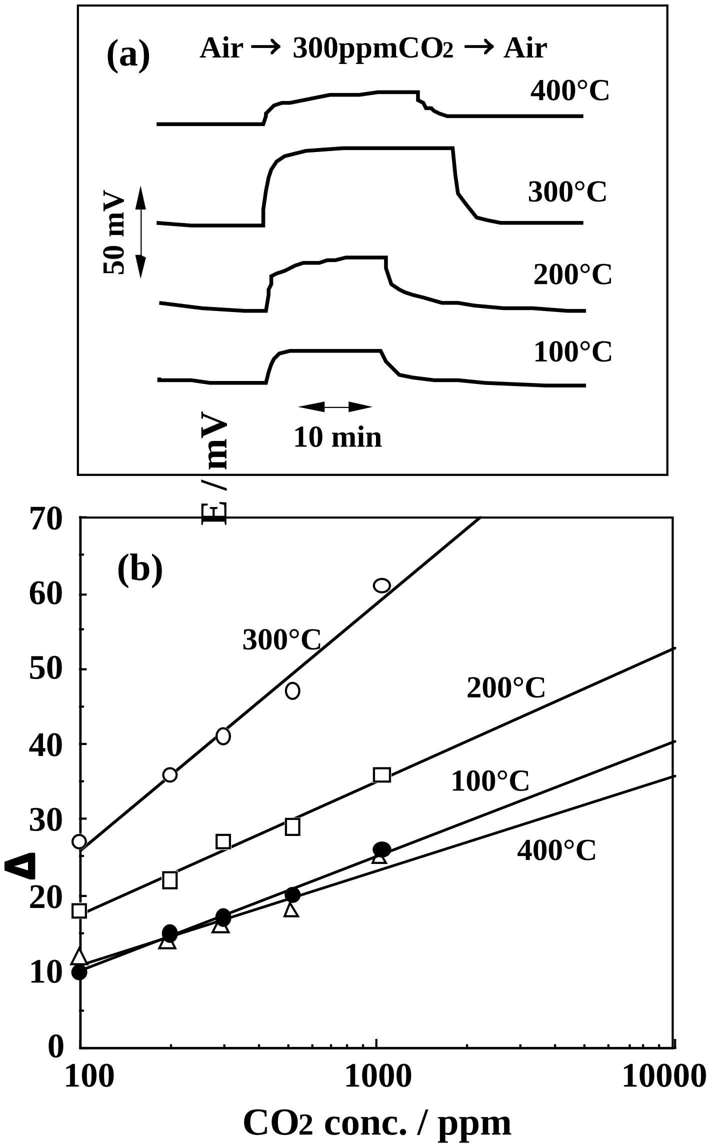


Fig. 2 Sensing performance to CO_2 of the device attached with $LaCoO_3$ electrode at various temperature. (Type A)
(a) Response transient to 300ppm CO_2
(b) ΔE vs. $\log P_{CO_2}$

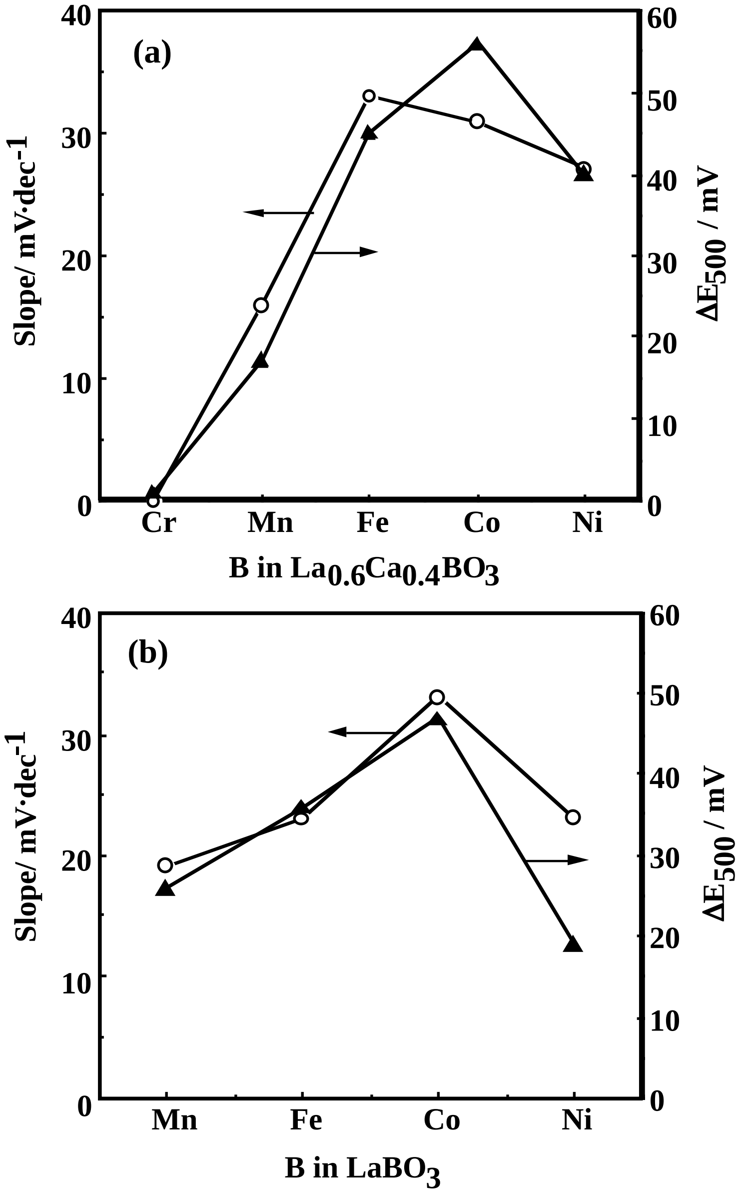


Fig. 3 Sensing performance to CO_2 of the sensor devices attached with various perovskite-type oxide electrodes at 300°C (Type A).
(a) : $La_{0.6}Ca_{0.4}BO_3$ (B=Cr, Mn, Fe, Co, Ni) system
(b) : $LaBO_3$ (B= Mn, Fe, Co, Ni) system
Slope: slope for the line of ΔE vs. $\log P_{CO2}$,
ΔE_{500}: EMF (in $500ppmCO_2$)-EMF (in air)

NEW

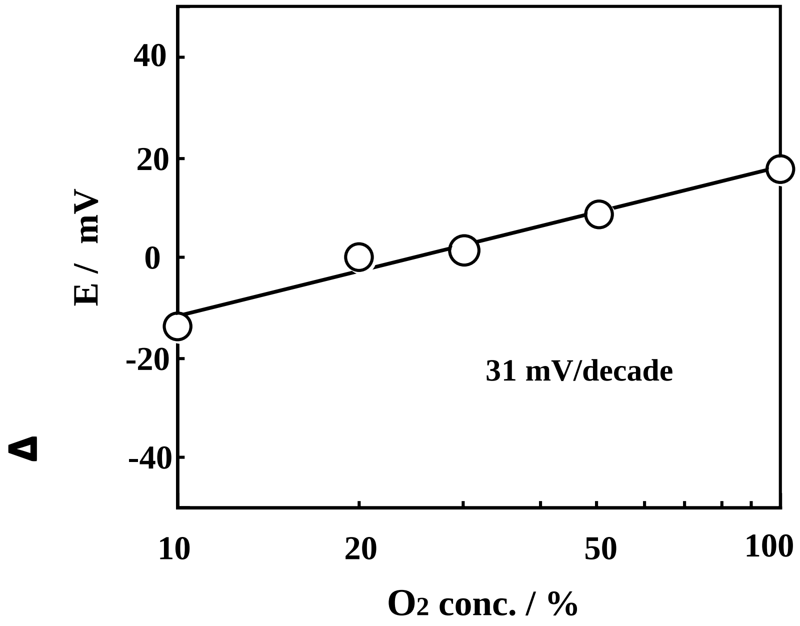


Fig. 4 EMF response behavior to oxygen of the sensor device attached with $La_{0.8}Ba_{0.2}CoO_3$ electrode at 300°C (Type A).

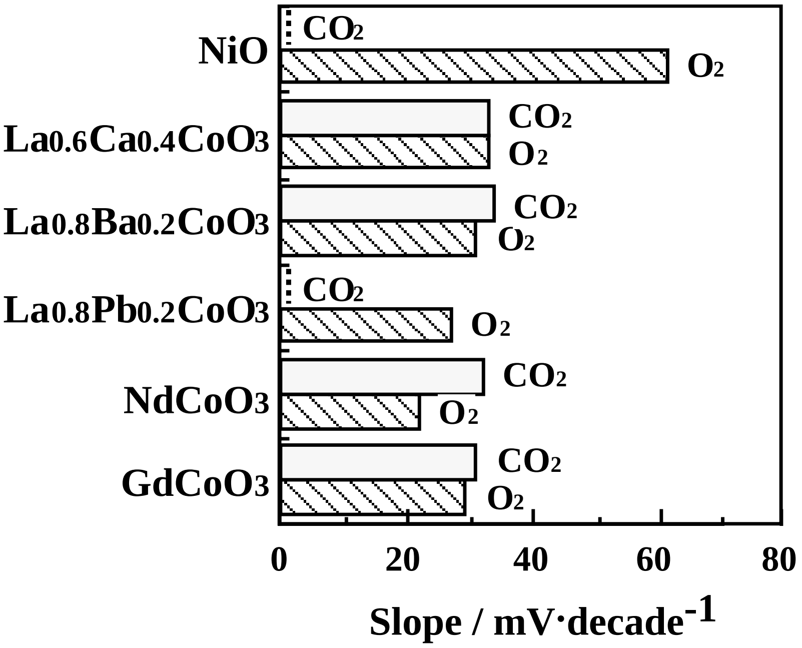


Fig. 5 EMF response behavior to oxygen or CO_2 of the sensor devices attached with various perovskite-type oxide electrodes at 300°C. (Type A)

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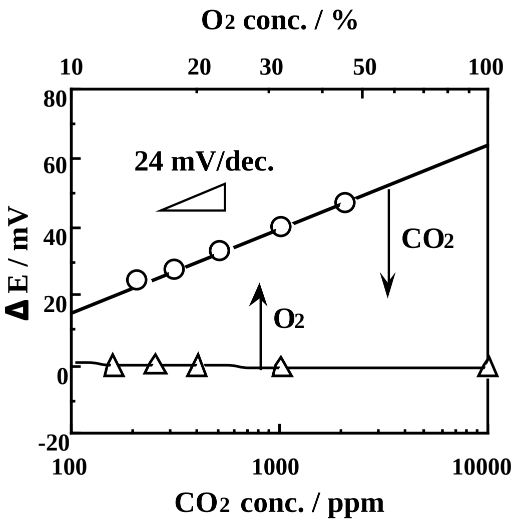

Fig 6. Sensing performance to CO_2 or O_2 of the open-reference electrode type sensor device at 300°C.
(Type B; $NdCoO_3$ | NASICON | $La_{0.8}Pb_{0.2}CoO_3$)

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