A Nasicon CO_2 Gas Sensor With Drift-Detection Electrode

Song Chen, De-Yin Jeng, Hironori Hadano, Yoshiaki Ishiguro, Masakatsu Nakayama, and Kenzo Watanabe

***Abstract*—A Nasicon (sodium super ion conductor) CO_2 gas sensor with a new structure is developed for monitoring CO_2 levels in the atmospheric air. In addition to the sensing and reference electrodes of a conventional Nasicon sensor, an auxiliary electrode, referred to as the base electrode, is provided with the new structure. The principle of CO_2 detection is the same as that of a conventional Nasicon sensor, but the durability is greatly improved by using a nonaqueous carbonate as the sensing material. Characterization has also revealed that the output voltage at the base electrode is closely correlated with the drift at the sensing electrode and is available for the drift compensation.**

***Index Terms*—Carbon dioxide $(CO_2)_2$ gas sensor, drift, durability, equivalent circuit, Nasicon, solid electrolyte.**

I. Introduction

AN INCREASE in energy consumption quickly deteriorates the environmental conditions of the earth. The global warming, acid rains, and atmospheric air pollution due to exhausts are the typical phenomena. Under such circumstances, continuous assessment of air quality in the living and working environments is legislated for human comfort and safety. The gases whose levels should be monitored include carbon monoxide (CO), carbon dioxide (CO_2), and dust. The work described in this paper is concerned with the CO_2 measurement.

A well-acknowledged method for detecting the CO_2 concentration in the atmospheric air is to measure the absorption of the light in the 4.2-μm band due to CO_2 molecules. Such a nondispersive infrared (NDIR) gas detector allows a high-accuracy measurement [1], [2], but is too expensive to prevail. For continuous monitoring of the CO_2 level in schools, hospitals, offices, and homes, much cheaper sensors are desired. To respond to such a request, SnO_2-based sensors are developed [3], [4]. Much effort has been devoted to increase the sensitivity and selectivity, but the accurate measurement is still difficult due to the large dependence on temperature [5]. Another candidate for a low-cost CO_2 sensor is the solid electrolyte sensor based on the sodium super ion conductor (Nasicon) [6]–[8]. The Nasicon CO_2 sensor has such distinct features as the high sensitivity at low concentration and the high gas-selectivity [9]–[11], but the drift and the durability in the course of time bottleneck the practical applications. To resolve these issues, a new structure is exploited. The new structure uses such nonaqueous carbonates as Li_2CO_3 and $CaCO_3$ to improve the durability, and an additional electrode is provided to compensate the drift. In the following, the fabrication process and the performances of the Nasicon sensor will be described.

Manuscript received May 26, 2002; revised June 30, 2003.

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Digital Object Identifier 10.1109/TIM.2003.818561

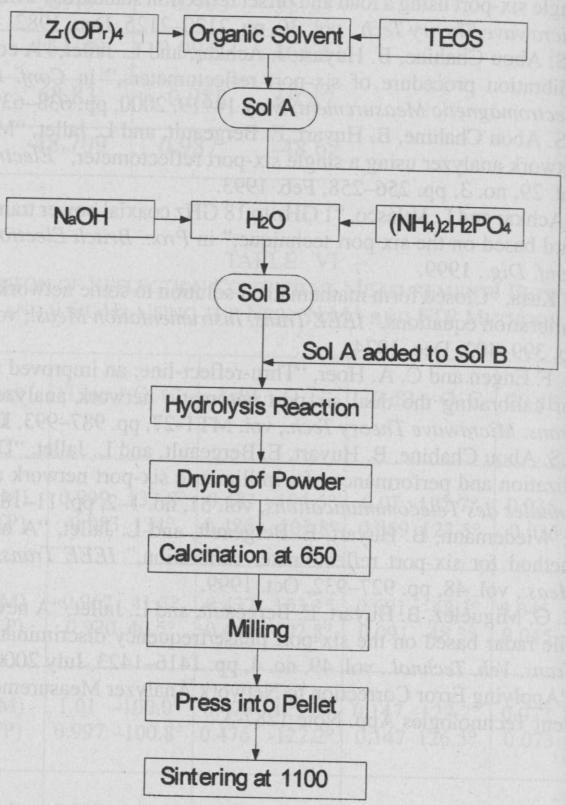


Fig. 1. Sol-gel process to synthesize the Nasicon.

II. Sensor

Fig. 1 shows the sol-gel process used to synthesize the Nasicon. The composition of Nasicon is given by $Na_{(1+x)}Zr_2Si_xP_{3-x}O_{12}$, and zirconium protoxide $Zr(OCH_2CH_3)_4$, $Zr(OPr)_4$ in a conventional notation. TEOS(tetra-ethyl-ortho-silicate $Si(OCH_2CH_3)_4$), sodium hydroxide NaOH, and ammonia phosphoric acid $(NH_4)_2H_2PO_4$ are selected as the starting materials. In weighing each material, $x = 2.1$ is assumed. $Zr(OPr)_4$ and TEOS are solved into an organic solvent[1]. This organic solution is referred to as Sol A. NaOH and $(NH_4)H_2PO_4$ are solved into water. This aqueous solution is referred to as Sol B. Mixing Sol A and Sol B and the subsequent hydrolysis reaction produce the xerogel. The xerogel is dried by a blower and calcined at 650 °C for 2 h. The calcined powder is then milled finely and pressed into the

[1]A proprietary secret for the moment.

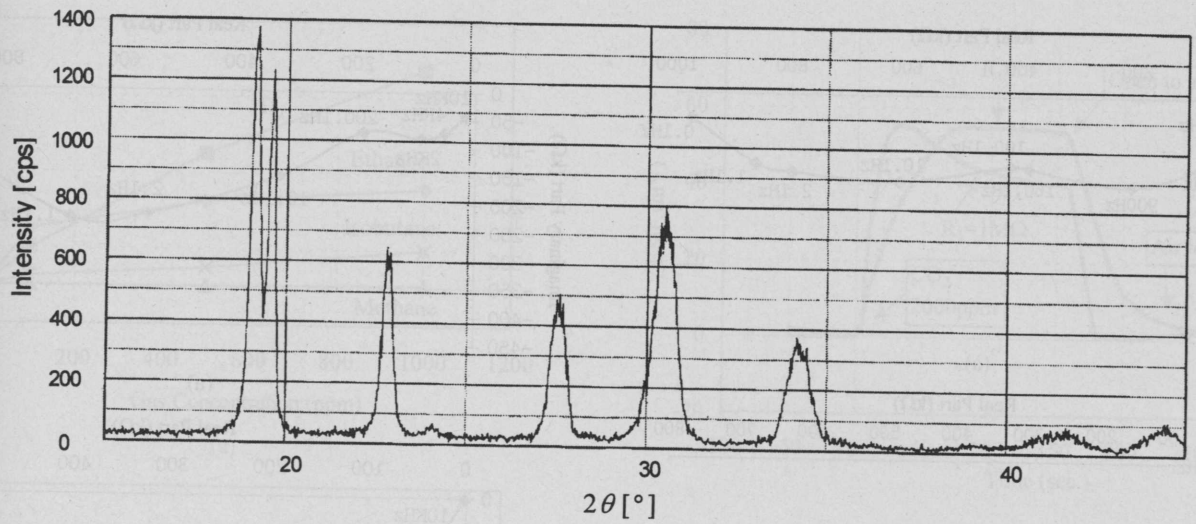


Fig. 2. X-ray diffraction (XRD) pattern of the sintered pellet.

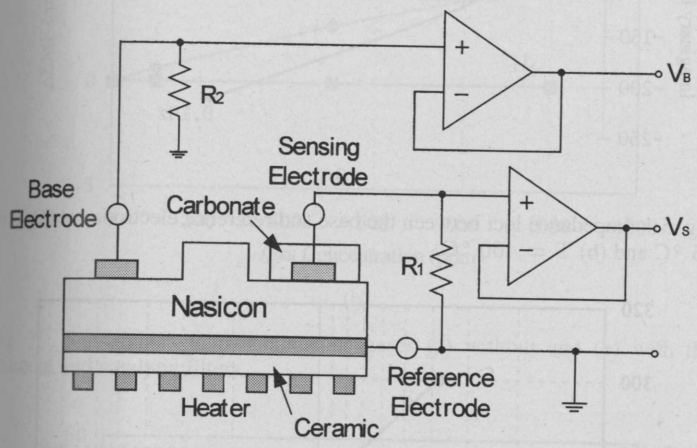


Fig. 3. Three-electrode Nasicon CO_2 gas sensor followed by unity-gain buffers for voltage measurements.

pellet. The pellet is sintered at 1 100 °C. The X-ray diffraction (XRD) pattern of the sintered pellet is shown in Fig. 2. This measured pattern agrees well with that in JCPDS file 35-412, confirming that the Nasicon of the monoclinic structure is synthesized successfully by the sol-gel process shown in Fig. 1.

The pellet is scribed into dies with 3×3 mm^2 dimension. The thickness is 0.5 mm. Fig. 3 shows the structure of the Nasicon CO_2 sensor. Different from a conventional two-electrode structure composed of the sensing and reference electrodes, an auxiliary electrode, referred to hereafter as the base electrode, is provided. All the electrodes are formed by Au screen-printed. The Nasicon barrier is provided between the sensing and base electrodes to prevent the carbonate from diffusing toward the base electrode. The barrier height is 0.2 mm. The carbonates used are Li_2CO_3 and its compounds.

The principle of CO_2 detection is the same as that of the two-electrode device: The CO_2 gas reacts with the carbonate at the sensing electrode, to produce cations and electrons. An interfacial layer of Na_2CO_3 is deduced to be formed by Li_2CO_3 and the Nasicon, and Li^+ ions exchange cations with Na atoms at the interfacial layer. Na^+ ions then drift toward the reference electrode, to generate the electromotive force (EMF) with the reference electrode being the positive polarity. The electrons produced by the reaction between CO_2 gas and the carbonate, on the other hand, flow through an external circuit to the reference

TABLE I
OPERATING CONDITIONS

Item	Specification
Heater voltage (V_H)	3.8V DC
Heater resistance (R_H)	4.5±0.5 Ω (at room temperature) 10.5±0.5 Ω (at 400 °C)
Heater current	Approx. 360 mA
Heater power consumption	Approx. 1.4 W
Environmental conditions	-10 °C ~ +50 °C, 5 ~ 95% RH
CO_2 range	300 ~ 5000 ppm

electrode, to generate the voltage which balances the EMF by the cations. The electrochemical reactions involved in the electrodes are described as follows.

Sensing electrode:

$$2Li^+ + CO_2 + 1/2O_2 + 2e^- \rightleftharpoons Li_2CO_3 \quad (1)$$

Reference electrode: $2Na^+ + 1/2O_2 + 2e^- \rightleftharpoons Na_2O$ (2)

Overall chemical reaction:

$$Li_2CO_3 + 2Na^+ \rightleftharpoons Na_2O + 2Li^+ + CO_2. \quad (3)$$

The EMF E follows the Nernst's equation and is given by

$$E = (RT/2F)\ln\left(PCO_2^S / PCO_2^R\right) \quad (4)$$

where R, T, and F are the gas constant, temperature, and Faraday constant, respectively, and PCO_2^S and PCO_2^R are the partial CO_2 pressure at the sensing and reference electrodes, respectively. PCO_2^R is kept fixed by the dense structure of Nasicon impervious to CO_2 gas.

To enhance the sensitivity, the sensor is heated up to an optimal temperature by the Pt heater deposited onto a ceramic substrate. The operating conditions are listed in Table I.

III. PERFORMANCES

The impedances of the Nasicon sensor were measured and plotted by the swept frequency method using a network analyzer. The finest frequency step was 0.1 Hz. Fig. 4(a) shows the impedance locus between the sensing and reference electrodes measured at $T = 25$ °C. The locus can be decomposed into a semi-circle and an arc. The arc in the frequency range from 0.1

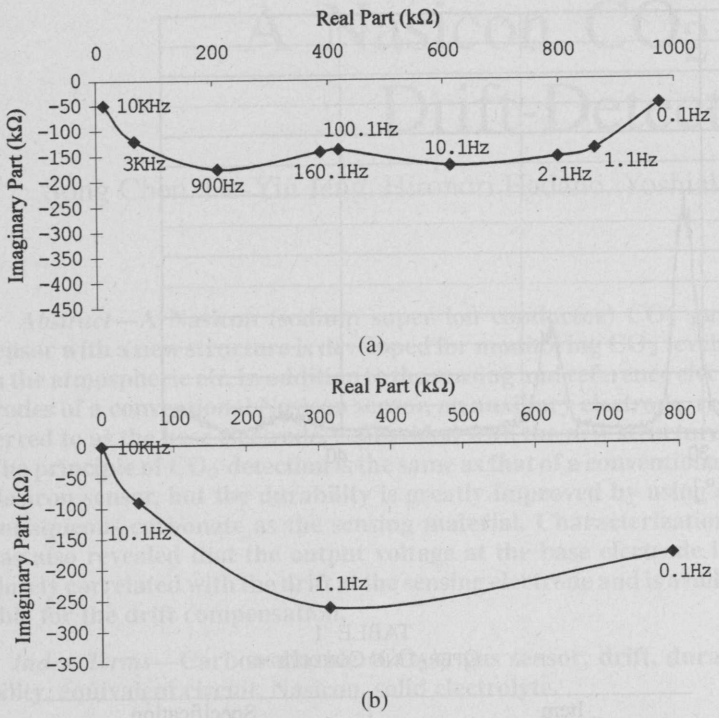


Fig. 4. Impedance loci between the sensing and reference electrodes at (a) T = 25 °C and (b) T = 400 °C.

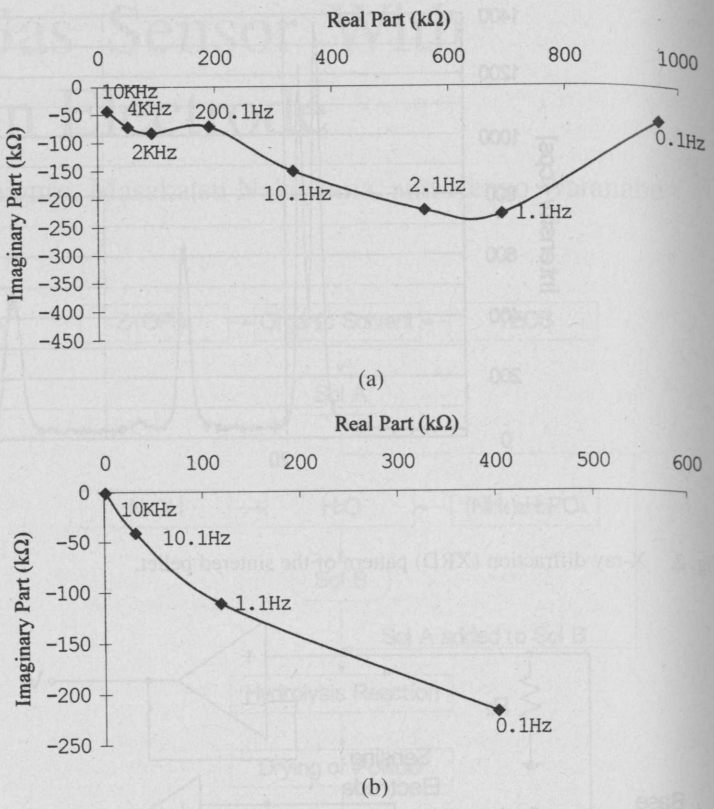


Fig. 5. Impedance loci between the base and reference electrodes at (a) T = 25 °C and (b) T = 400 °C.

to 100 Hz can be further decomposed into the partially overlapped two semi-circles, one of which corresponds to the interfacial impedance, referred to usually as the blocking impedance, of the sensing electrode and the other to that of the reference electrode. Since each semi-circle represents a resistor R and a capacitor C connected in parallel, the electrical impedance between the sensing and reference electrodes consists of three parallel RC circuits connected in series. When the sensor is heated to 400 °C by the Pt heater, the Nasicon impedance decreases with the increasing ion mobility, and thereby the corresponding semi-circle disappears, as shown in Fig. 4(b). Fig. 5 shows the impedance loci measured between the base and reference electrodes. The locus at T = 25 °C is similar to that in Fig. 4(a), though the semi-circle corresponding to the Nasicon impedance is smaller and shifted to the higher frequencies. The impedance locus at T = 400 °C shown in Fig. 5(b), however, is different from that shown in Fig. 4(b). The real and imaginary parts increase in magnitude monotonically with the decreasing frequency. This indicates that the impedance between the base and reference electrodes under operation at T = 400 °C can be represented by a capacitor in series with the series-connected two parallel RC circuits. The impedance between the sensing and base electrode draws almost the same loci as those shown in Fig. 5, and the impedance at T = 400 °C can also be represented by a capacitor in series with the two parallel RC circuits.

Since the internal impedances of the Nasicon sensor are very high, the high input impedance buffers are used for measuring the voltages at the sensing and base electrode, as shown in Fig. 3. Fig. 6 shows the EMF as a function of CO_2 concentration. The measurement was carried out by placing the sensor in an airtight chamber and injecting an appropriate quantity of pure CO_2 gas. A commercial CO_2 monitor based on the nondispersive infrared (NDIR) method is used to measure the CO_2 concentration in the chamber. The operating temperature of the sensor is set 400 °C. It can be seen that the EMF is logarithmically proportional to the

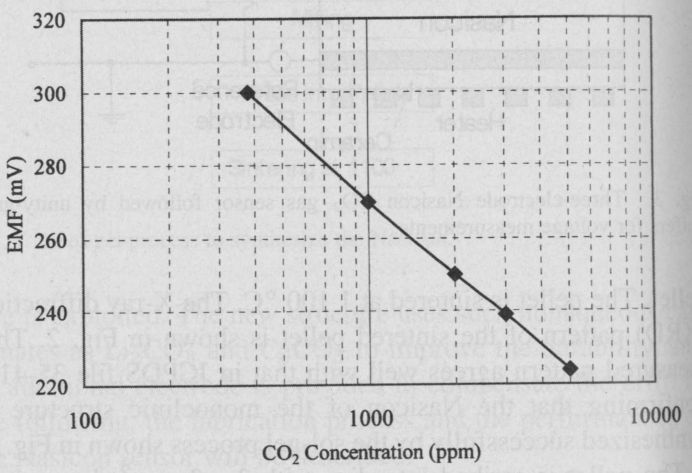
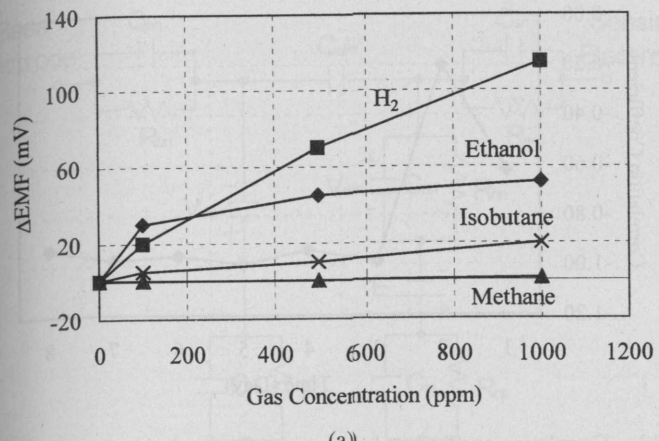


Fig. 6. Sensitivity to CO_2 gas.

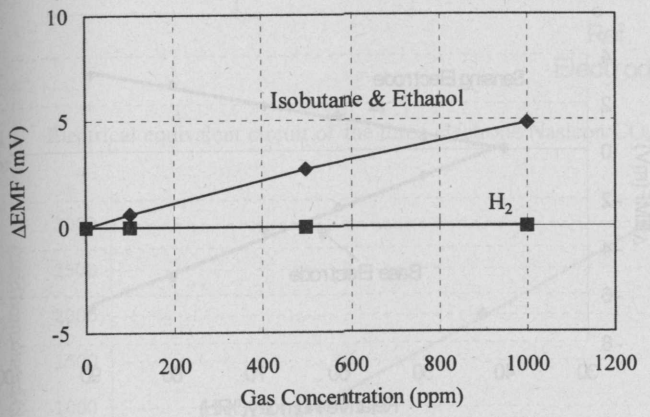
CO_2 concentration, as given by (4). Fig. 7 shows the sensitivities to miscellaneous gases. These sensitivity measurements were also made by means of the airtight chamber. The Nasicon sensor itself has the sensitivity to H_2, ethanol, and isobutene gases, but these effects can be reduced negligibly small by covering the sensor with the charcoal and catalytic filters.

Fig. 8 compares the durability of the carbonates. ΔEMF in the ordinate is the difference in EMF at CO_2 concentrations of 2 000 ppm and atmospheric air level, ca. 380 ppm. The water soluble carbonates such as K_2CO_3 and Na_2CO_3 are unsuited because they are easily dissolved by water vapors in the air [12]. The water solubility of Li_2CO_3 and $CaCO_3$ is 1.24 wt% and 0.71 wt% at 30 °C, respectively. The durability is greatly improved by using these nonaqueous carbonates.

Fig. 9 shows the transient responses. The integrated and differential step responses can be seen depending on the load condition. The impedance between the sensing and reference elec-



(a)



(b)

Fig. 7. Sensitivities to miscellaneous gases (a) without and (b) with the charcoal and catalytic filters.

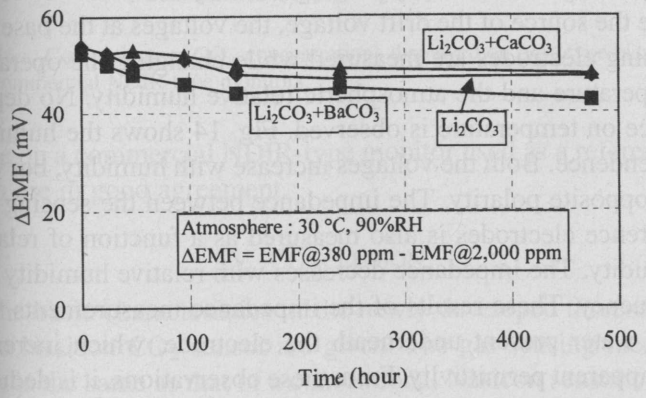


Fig. 8. Durabilities of various carbonates.

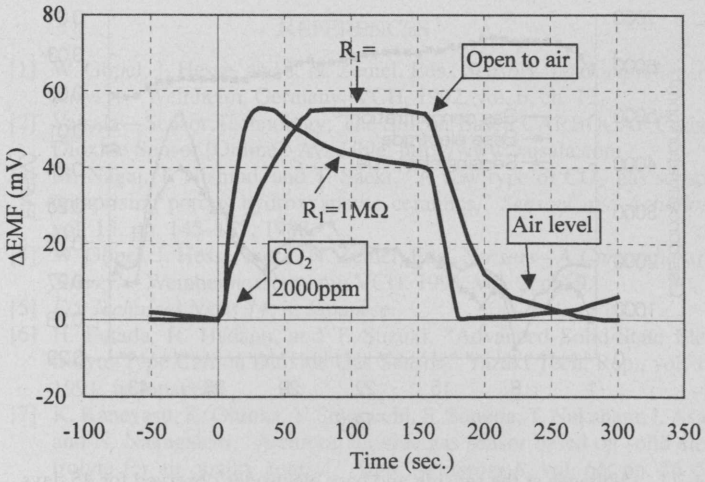
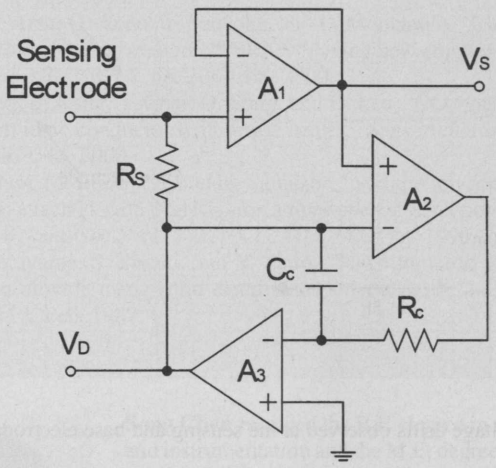
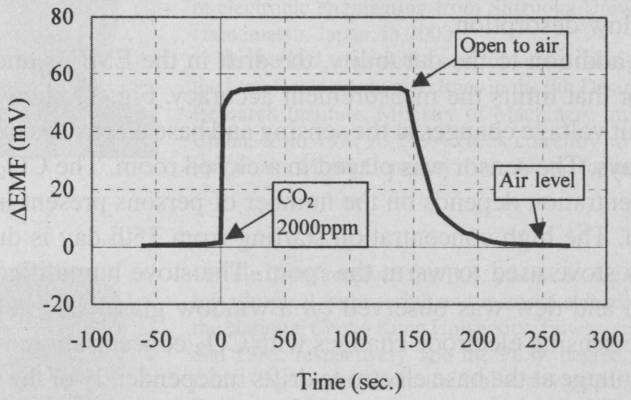


Fig. 9. Transient responses under different load conditions.



(a)



(b)

Fig. 10. (a) Automatic balance circuit and (b) the measured transient response.

trodes can be represented by the third-order RC circuit with three time constants, as described previously. Let the largest time constant be τ_i. Then, the different responses can be explained in terms of the time constants τ_i and τ_e of the internal impedance and the external circuit, respectively: When the load resistor R_1 in Fig. 3 is infinity (open), the time constant τ_e of the external circuit given by $\tau_e = R_i C_i$, where R_i and C_i are the input resistance and capacitance of the buffer, respectively, is larger than τ_i and the step response takes the integrated waveform. When $R_1 = 1\ M\Omega$, on the other hand, τ_e becomes smaller than τ_i and the step response takes the differential waveform. These transient responses validate the equivalent representation of the internal impedance by the parallel RC circuits.

To measure the transient response independently of the time constants, an automatic balance circuit shown in Fig. 10(a) is developed. It consists of a buffer A_1 followed by a high-gain differential amplifier A_2 and an integrator A_3. The response of this circuit is fast because of the high-gain differential amplifier in the feedback loop. The integrator in the feedback loop makes its output equal to the input voltage of the buffer. Therefore, the outputs of the integrator and the buffer quickly follow the EMF of the sensor irrespectively of the resistor R_S. The transient response measured by this circuit is shown in Fig. 10(b). The gas sensing process, consisting of CO_2 gas absorption, chemical reaction at the carbonate, the cation exchange at the interfacial layer, and the drift of cations to the reference electrode, is fast and settles within 15 s. The restoration to the atmospheric level,

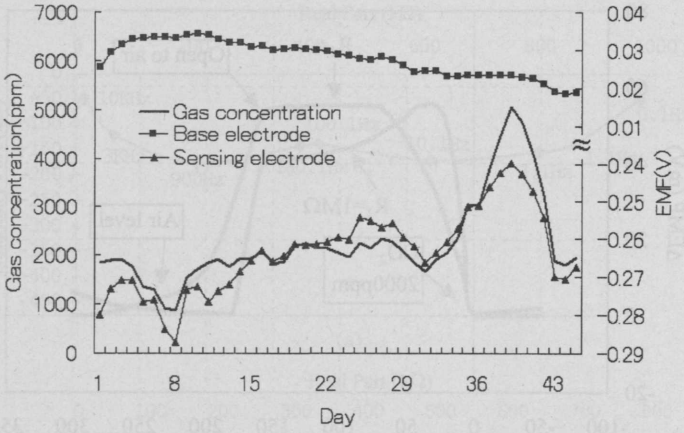


Fig. 11. Voltages at the sensing and base electrodes observed for 45 days.

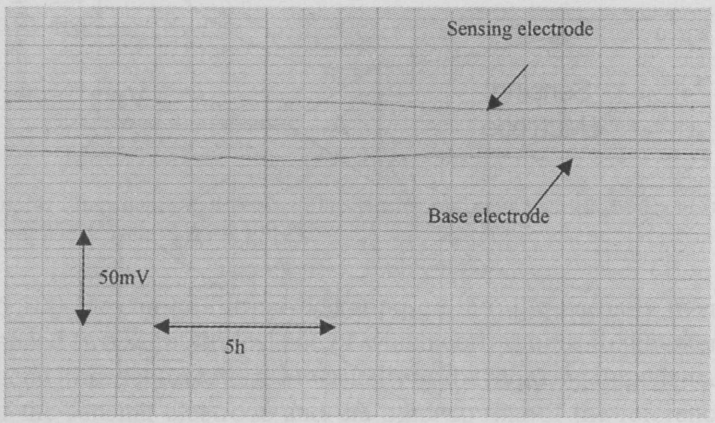


Fig. 12. Voltage drifts observed at the sensing and base electrodes.

however, takes 120 s. The long restoration is attributed due to the slow desorption.

In addition to the durability, the drift in the EMF is another factor that limits the measurement accuracy. Fig. 11 shows the output voltage changes at the sensing and base electrodes during 45 days. The sensor was placed in a closed room. The CO_2 gas concentration depends on the number of persons present in the room. The high concentration starting from 35th day is due to a gas stove used to warm the room. The stove humidified the room and dew was observed on a window glass. The voltage at the sensing electrode changes with CO_2 concentration, while the voltage at the base electrode drifts independently of the CO_2 concentration. To exploit the drift mechanism and the compensation method, the three-electrode Nasicon sensor is exposed to the atmospheric air in a vacant room. The CO_2 concentration is about 380 ppm and is kept constant. Fig. 12 shows the voltages at the sensing and base electrodes thus measured. It can be seen that there exists a close relation between the drifts on the two voltages. Sampling the time-series data every hour, the correlation coefficient γ is calculated daily by

$$\gamma = \frac{\sum_{n=1}^{24} V_S(n)V_B(n)}{\sqrt{\sum_{n=1}^{24} V_S^2(n)}\sqrt{\sum_{n=1}^{24} V_B^2(n)}}. \quad (5)$$

where $V_S(n)$ and $V_B(n)$ are the voltages sampled every hour at the sensing and base electrodes, respectively. Fig. 13 shows the correlation coefficient observed for a week. The correlation

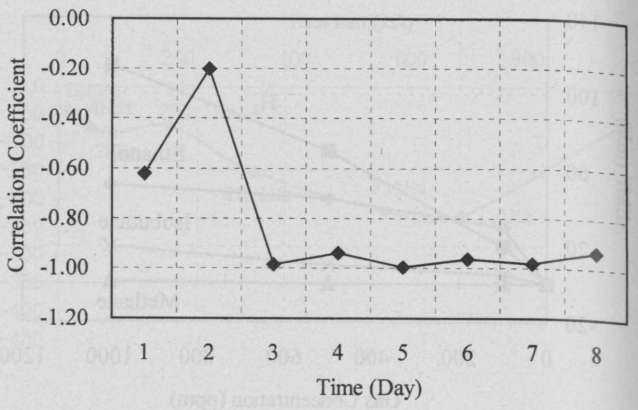


Fig. 13. Correlation coefficients between the sensing and base potentials.

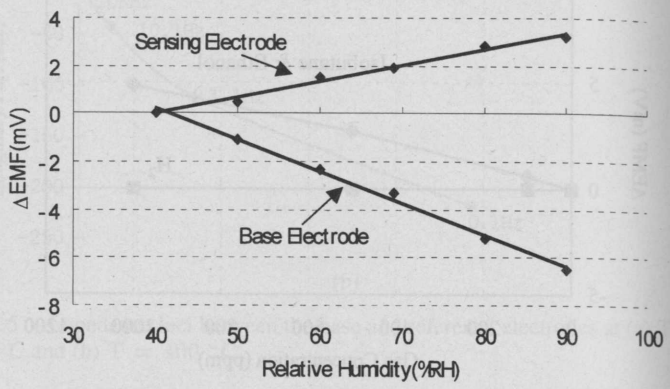


Fig. 14. Change in EMF due to relative humidity.

coefficients after two days' aging are very close to -1. To deduce the source of the drift voltage, the voltages at the base and sensing electrodes are measured while changing the operating temperature and the atmospheric relative humidity. No dependence on temperature is observed. Fig. 14 shows the humidity dependence. Both the voltages increase with humidity, but with the opposite polarity. The impedance between the sensing and reference electrodes is also measured as a function of relative humidity. The impedance decreases with relative humidity and frequency. These results of the impedance measurements suggest water present underneath the electrode, which increases the apparent permittivity. From these observations, it is deduced that the drift voltage is caused by water absorbed into the Nasicon and electrode interface which produces the dipole layer by ionization. The polarity of the dipole layer at the sensing electrode is opposite to that at the base electrode. This polarity reversal is explained to be caused by the electric field generated by the EMF between the sensing and reference electrodes.

Summarizing the measured performances, the electrical equivalent circuit of the three-electrode Nasicon sensor can be represented as shown in Fig. 15. In this representation, V_{db} and V_{ds} denotes the drift voltages due to the humidity dependence of the dipole layers, as deduced above, and E is the EMF due to CO_2 gas. E does not appear at the base electrode because it is blocked by C_{sb}. Since the drift voltages are opposite in the polarity, they can be cancelled by the weighted sum of V_S and V_B, and thereby the true EMF can be detected.

A prototype CO_2 monitor with the new Nasicon sensor has been built for the performance evaluation. Fig. 16 compares the CO_2 concentration displayed on the prototype monitor with

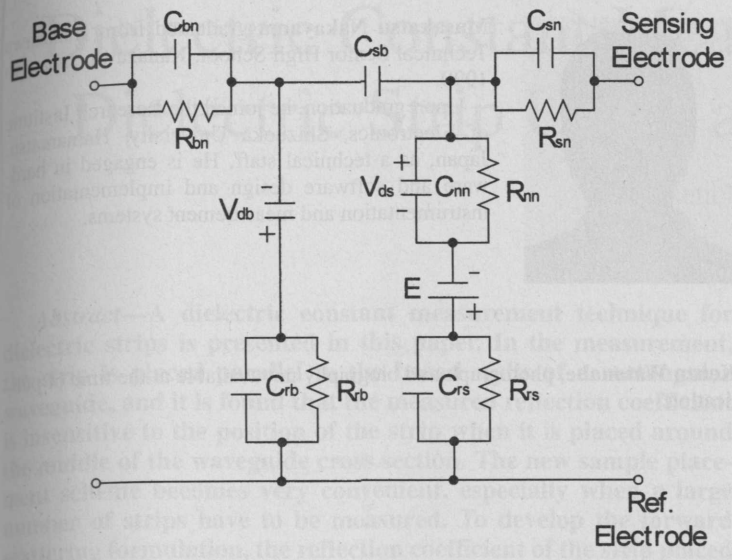


Fig. 15. Electrical equivalent circuit of the three-electrode Nasicon CO_2 gas sensor.

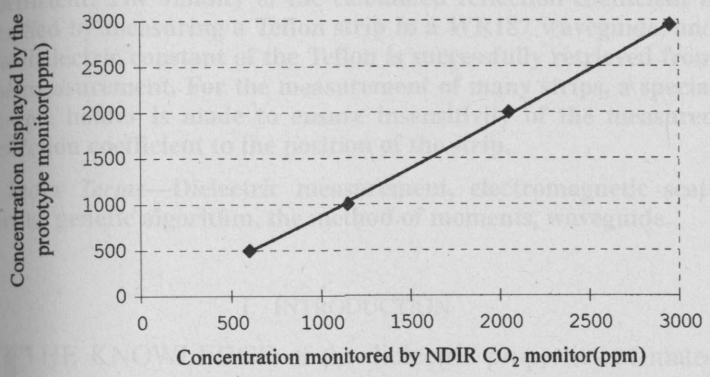


Fig. 16. Comparison of CO_2 concentrations displayed on prototype Nasicon and commercial NDIR-type monitors.

those on a commercial NDIR-type monitor used as a reference. Both are in good agreement.

IV. Conclusion

The basic characteristics of the newly developed three-electrode Nasicon CO_2 sensor are given. The gas sensing mechanism is the same as that of a conventional Nasicon sensor composed of the sensing and reference electrodes, but the durability is greatly improved by using the compound of Li_2CO_3 and $CaCO_3$ as the carbonate. The voltage appeared at the sensing electrode drifts in the course of time even if the CO_2 concentration is kept constant. This drift component is closely related to the voltage at the base electrode and is deduced to be caused by the dipole layer which changes with relative humidity. Based on the characterization, an electrical equivalent circuit of the Nasicon sensor is derived, which suggests that the drift component can be cancelled by summing appropriately the voltages at the sensing and base electrodes.

Not only for atmospheric air quality assessment, the measurement of CO_2 gas concentration is also required for process control in food industry, environment control in greenhouses, diagnoses of patients in hospitals, and so on. The drift cancellation by the three-electrode structure and the durability improvement by nonaqueous carbonates will make the Nasicon CO_2 sensor quite attractive to these applications.

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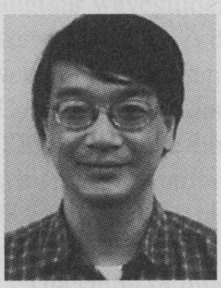

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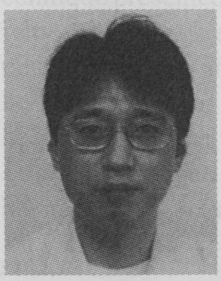
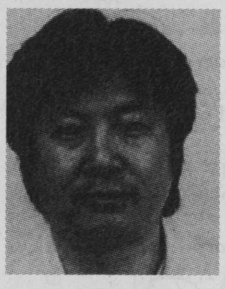
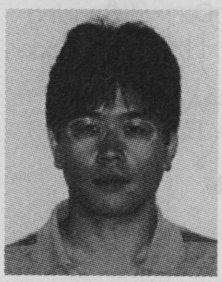


Hironori Hadano received the B.E. degree from Ehime University in 1989. Upon graduation, he joined Yazaki Meter Corp., where he has been engaged in development of chemical sensors. In 1992 he was dispatched to the Graduate School, Toyota Institute of Technology, and received the M.E. degree in 1994. He is now developing solid electrolyte sensors and flow meters at Yazaki Gas Instruments Development Center.



Yoshiaki Ishiguro received the B.E. degree from Nippon University, Japan, in 1981.

Upon graduation, he joined Yazaki Meter Corporation, where he has been engaged in development of chemical sensors, especially catalytic combustion and solid electrolyte sensors. He is now managing the sensor research group at Yazaki Gas Instruments Development Center.



Masakatsu Nakayama graduated from Kanazawa Technical Senior High School, Kanazawa, Japan, in 1990.

Upon graduation, he joined the Research Institute of Electronics, Shizuoka University, Hamamatsu, Japan, as a technical staff. He is engaged in hardware and software design and implementation of instrumentation and measurement systems.

Kenzo Watanabe, photograph and biography not available at the time of publication.