

# Influence of H<sub>2</sub>O, CO<sub>2</sub> and various combustible gases on the characteristics of a limiting current-type oxygen sensor

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Received 4 January 1988; revised 11 April 1988

Current-voltage characteristics of limiting current-type oxygen sensors were investigated. The sensor showed a two-stage current plateau in current-voltage characteristics in H<sub>2</sub>O-O<sub>2</sub>-N<sub>2</sub> and CO<sub>2</sub>-O<sub>2</sub>-N<sub>2</sub> mixtures. The sensor current in the first stage corresponded to O<sub>2</sub> concentration and was practically independent of H<sub>2</sub>O and CO<sub>2</sub> concentration in the gas mixtures. The sensor current in the second stage increased linearly with the H<sub>2</sub>O or CO<sub>2</sub> concentration, for a sensor with high electrode activity. The behavior of the sensor suggests that the deoxidization of H<sub>2</sub>O or CO<sub>2</sub> occurs at the sensor cathode. For nonequilibrium gas mixtures containing combustible gas and O<sub>2</sub>, the sensor current in the first stage decreased linearly with combustible gas concentration. The decrease of the sensor current differed from that corresponding to the O<sub>2</sub> concentration consumed by the reaction of these gases in the ambient gas, depending on the kind of combustible gas. The reduction of the sensor current is explained by a model assuming that the reaction of these gases occurs at the cathode, and the diffusion of the combustible gas in the porous coating is a rate-limiting step.

## 1. Introduction

Recently, limiting current-type oxygen sensors have attracted much interest in the automobile industry. The sensor is used for detecting oxygen concentration in the exhaust gas of a lean combustion engine system, which is capable of improving fuel efficiency and of reducing pollutant emissions of automobiles [1, 2]. The sensor utilizes limiting current characteristics that appear in a zirconia oxygen pumping cell with a diffusion barrier covering the cathode of the cell [3-5]. The limiting current of the sensor is determined by gaseous diffusion of oxygen in the diffusion barrier. Therefore, the sensor shows a linear output current with respect to O<sub>2</sub> concentration. For the sensor with a porous coating as the diffusion barrier, a very weak temperature dependence and a fast response of the sensor output were achieved [4]. These characteristics are suited for the precise control of air-to-fuel ratio over a lean range in the combustion system.

In the sensor with the porous coating, limiting current,  $I_l$ , is given by

$$I_l = \frac{4FD_{O_2}S}{l} C_{O_2} \quad (1)$$

where  $F$  is the Faraday constant,  $D_{O_2}$  is the diffusion coefficient of O<sub>2</sub> within the porous coating,  $S$  and  $l$  are the area of the cathode and the thickness of the coating, respectively, and  $C_{O_2}$  is O<sub>2</sub> concentration in the ambient gas of the sensor.

Although the sensor is based on oxygen pumping, the sensor output depends on other gas species, such as H<sub>2</sub>O, CO<sub>2</sub> and combustible gas. The effects of these gases on the sensor output have been reported by several authors [3, 6-8]. Dietz [3] observed a sensor output corresponding to equilibrated O<sub>2</sub> concentration for CO and O<sub>2</sub> mixtures. He reported limiting current due to the reduction of H<sub>2</sub>O and CO<sub>2</sub> also. The influence of gas composition on the sensor output should be taken into account when the sensor is used in combustion exhaust gas, since it contains H<sub>2</sub>O, CO<sub>2</sub>, and various combustible gases in addition to O<sub>2</sub> and N<sub>2</sub>. The present paper reports detailed experimental and analytical results on the influence of H<sub>2</sub>O, CO<sub>2</sub> and various combustible gases on the sensor output.

## 2. Experimental details

The construction of the sensor used in experiments is shown in Fig. 1. The sensor element was made of an 8 mol % Y<sub>2</sub>O<sub>3</sub>-stabilized ZrO<sub>2</sub> electrolyte disk with sputtered platinum electrodes. These were covered with a porous spinel coating whose porosity was approximately 9%. The diameter of the element was 3 mm, and the thickness of the electrodes and the porous coating on the cathode side were approximately 1 μm and 600 μm, respectively. The element was heated up to a constant temperature of several hundred °C by a small heater. The current-voltage characteristics of the sensor were examined in H<sub>2</sub>O-

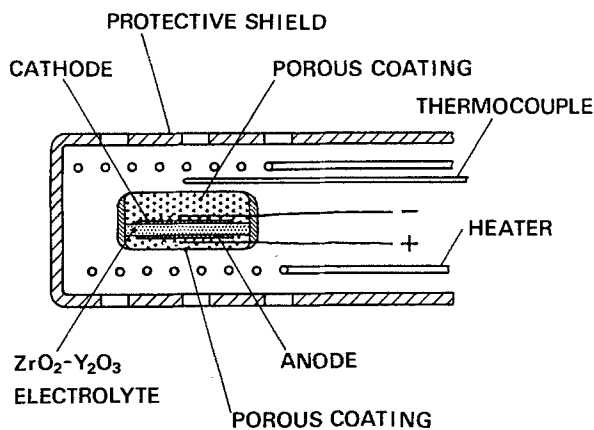


Fig. 1. Schematic sectional structure of the sensor.

$O_2-N_2$ ,  $CO_2-O_2-N_2$  and combustible gas- $O_2-N_2$  mixtures.

### 3. Results and discussion

#### 3.1. Limiting current due to the decomposition of $H_2$ and $CO_2$

The sensor showed two-stage saturation current characteristics in  $H_2O-O_2-N_2$  mixtures at a temperature of  $720^\circ C$ , as shown in Fig. 2. In the first stage, the magnitude of the limiting current corresponds to  $O_2$  concentration in the gas mixtures, and is practically independent of the presence of  $H_2O$ . On the other hand, the sensor current in the second stage increases linearly with  $H_2O$  concentration.

The effects of  $H_2O$  on the sensor characteristics may be caused by the variation in the diffusion coefficient of  $O_2$  in the porous coating and by the formation of  $O_2$  due to the decomposition of  $H_2O$  in the cathode. However, it is seen in Fig. 2 that the former effect is not significant, since the sensor current in the first stage is not varied by  $H_2O$  concentration. For the latter, if the formation of  $O_2$  from  $H_2O$  is very fast,  $H_2O$  concentration at the cathode becomes much lower than that in the ambient gas owing to the limit-

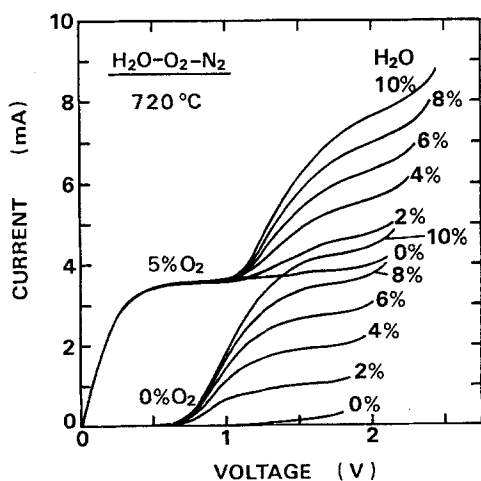


Fig. 2. Current-voltage characteristics of the sensor in  $H_2O-O_2-N_2$  mixtures at  $720^\circ C$ .

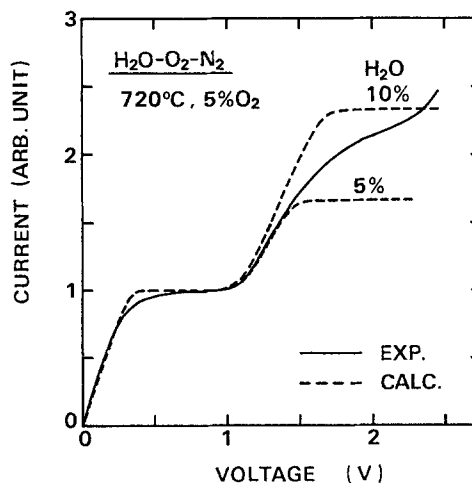


Fig. 3. Comparison of current-voltage curve between calculated and experimental results shown in Fig. 2 for  $H_2O-O_2-N_2$  mixtures at  $720^\circ C$ . Sensor current is normalized by the magnitude of limiting current due to  $O_2$ , and the resistance of the sensor is assumed to be 290 ohm.

ing effect of the porous coating. Consequently, the decomposition rate of  $H_2O$  is determined by  $H_2O$  diffusion in the porous coating. In this case, limiting current,  $I_{l,H_2O}$ , due to the decomposed oxygen will be given by

$$I_{l,H_2O} = \frac{2FD_{H_2O}S}{l} C_{H_2O} \quad (2)$$

In Equation 2,  $D_{H_2O}$  is the diffusion coefficient of  $H_2O$  in the porous coating, and  $C_{H_2O}$  is  $H_2O$  concentration in the ambient gas of the sensor. This linear relationship between  $I_{l,H_2O}$  and  $C_{H_2O}$  can be seen in the second stage of the current-voltage characteristics shown in Fig. 2.

On the other hand, the relationship between sensor voltage,  $V$ , and current,  $I$ , is written as

$$V = IR_b + \frac{RT}{4F} \ln \frac{C_{O_2}}{C_{O_2,c}} \quad (3)$$

where  $R_b$  is the resistance of the electrolyte, and  $C_{O_2,c}$  is  $O_2$  concentration at the cathode. In Equation 3,  $C_{O_2,c}$  can be regarded as the equilibrium  $O_2$  concentration of the reaction,  $H_2O \rightleftharpoons H_2 + \frac{1}{2}O_2$ , at the cathode when the reaction occurs very rapidly. From these relationships, the current-voltage characteristics were numerically calculated, as described in the Appendix. In the calculation,  $R_b$  and the magnitude of limiting current for  $O_2$  were fitted to experimental results, and the relationship for Knudsen diffusion  $D_{H_2}/D_{O_2} \sim \sqrt{M_{O_2}/M_{H_2O}}$  is assumed, where  $M_{O_2}$  and  $M_{H_2O}$  are the molecular weights of  $O_2$  and  $H_2O$ , respectively. The experimental results shown in Fig. 2 are compared with calculated results in Fig. 3. In the comparison, sensor current is normalized with respect to the magnitude of limiting current due to  $O_2$  diffusion. The comparison indicates that the magnitude of the calculated sensor current in the second stage is somewhat larger than the experimental results. This discrepancy may be caused by insufficient gas permeability of the cathode. However, as can be seen in Fig. 3, the cal-

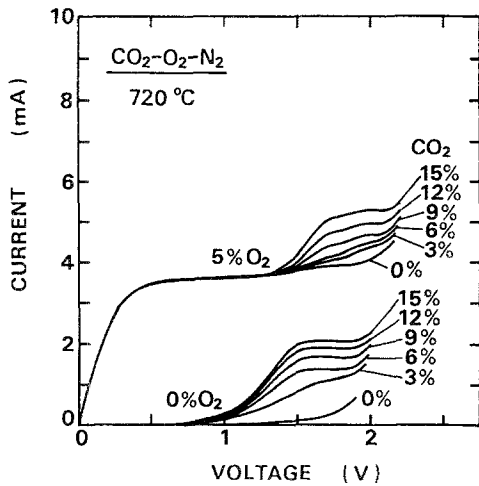


Fig. 4. Current-voltage characteristics of the sensor in CO<sub>2</sub>-O<sub>2</sub>-N<sub>2</sub> mixtures at 720°C.

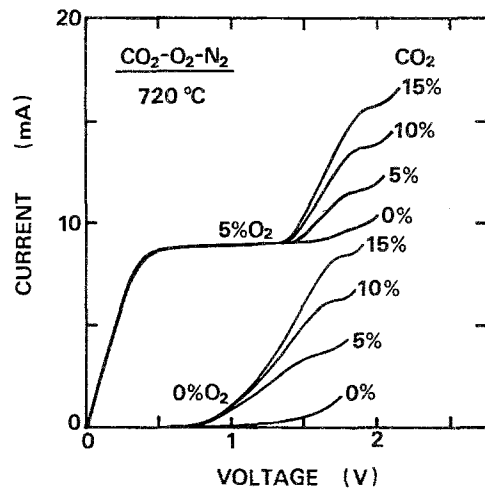


Fig. 5. Current-voltage characteristics of a sensor with a high electrode activity, in CO<sub>2</sub>-O<sub>2</sub>-N<sub>2</sub> mixtures at 720°C.

culated onset of sensor current due to the decomposition of H<sub>2</sub>O is in good agreement with the experimental results, where the calculated onset voltage is approximately 0.68 V\* at 720°C for a 5% O<sub>2</sub>-10% H<sub>2</sub>O-N<sub>2</sub> mixture. This agreement suggests that H<sub>2</sub>O readily decomposes at the cathode.

For CO<sub>2</sub>-O<sub>2</sub>-N<sub>2</sub> mixtures, the second stage current was also observed. Figures 4 and 5 are the results for the different sensors having previously been operated at 800°C and at 720°C for ~ 10 h, respectively. If CO<sub>2</sub> is decomposed by the reaction CO<sub>2</sub> → CO + ½ O<sub>2</sub>, the magnitude of the limiting current, *I*<sub>l,CO<sub>2</sub></sub>, may be expressed, similarly to Equation 2, as

$$I_{l,CO_2} = \frac{2FD_{CO_2}S}{l} C_{CO_2} \quad (4)$$

where *D*<sub>CO<sub>2</sub></sub> is the diffusion coefficient of CO<sub>2</sub> in the porous coating, and *C*<sub>CO<sub>2</sub></sub> is CO<sub>2</sub> concentration in the ambient gas. The experimental sensor current in the second stage shown in Fig. 4 is, however, nonlinear with CO<sub>2</sub> concentration. On the other hand, the second stage current shown in Fig. 5 is approximately linear with CO<sub>2</sub> concentration. This difference in the second stage current is considered to be caused by the previous operation of the former sensor at a high temperature of 800°C. Therefore, the difference in the characteristics for CO<sub>2</sub> suggests the variation of electrode activity for the decomposition of CO<sub>2</sub>. The variation of the electrode activity may be ascribed to morphological changes at high temperatures above 800°C, which were observed by Pizzini *et al.* [9]. However, in the case of the sensor showing the linear relationship with CO<sub>2</sub>, the magnitude of sensor current in the second stage is somewhat lower than that given by Equation 4, as can be seen in Fig. 6. Moreover, in this figure, it can also be seen that the experimental onset voltage of the second stage is considerably greater than the calculated magnitude of 0.75 V\*

at 720°C for a 5% O<sub>2</sub>-10% CO<sub>2</sub>-N<sub>2</sub> mixture. From the difference in the onset voltage of the second stage current between the experimental results shown in Figs 3 and 6, it is suggested that CO<sub>2</sub> is not as easily decomposed as H<sub>2</sub>O. Therefore, the decomposition rate of CO<sub>2</sub> in this case is considered to be affected not only by gaseous diffusion, but also by the activity of the cathode, particularly in the case of the results shown in Fig. 4.

### 3.2. The influence of combustible gas on sensor output

Figures 7-9 show experimental results measured at 720°C in H<sub>2</sub>-O<sub>2</sub>-N<sub>2</sub>, CO-O<sub>2</sub>-N<sub>2</sub> and iC<sub>4</sub>H<sub>10</sub>-O<sub>2</sub>-N<sub>2</sub> mixtures with combustible gas concentration as a parameter. The results indicate that the magnitude of the limiting current decreases linearly with increasing combustible gas concentration. To explain the decrease in sensor current, the following two cases were examined.

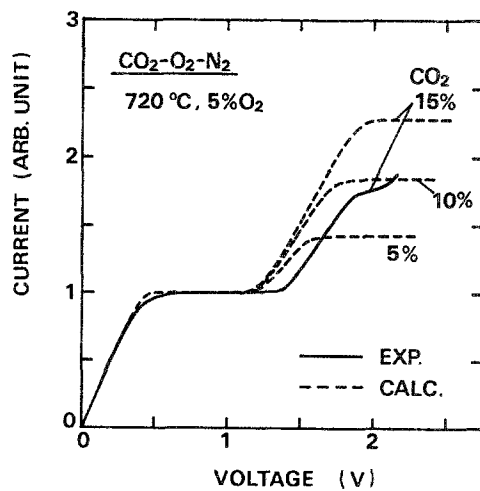


Fig. 6. Comparison of current-voltage curve between calculated and experimental results shown in Fig. 5 for CO<sub>2</sub>-O<sub>2</sub>-N<sub>2</sub> mixture at 720°C. Sensor current is normalized by the magnitude of limiting current due to O<sub>2</sub>, and the resistance of the sensor is assumed to be 380 ohm.

\* The onset voltage is defined by the overvoltage at which the sensor current increases by 1% of the magnitude of the limiting current for O<sub>2</sub>. The overvoltage is given by the second term in the right-hand side of Equation 3.

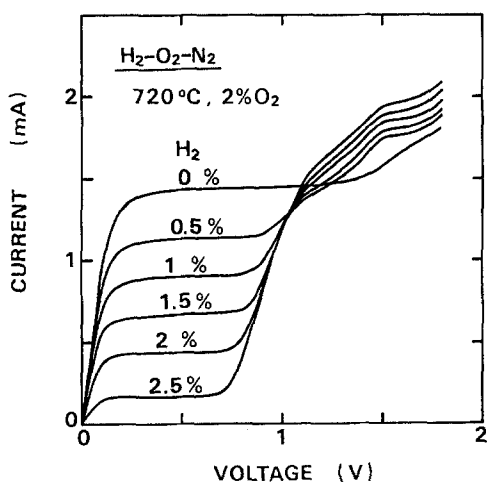


Fig. 7. Effect of H<sub>2</sub> in H<sub>2</sub>-2% O<sub>2</sub>-N<sub>2</sub> mixtures on the current-voltage characteristics of the sensor at 720°C.

Case I: when combustible gas fully reacts with O<sub>2</sub> before reaching the sensor surface, the limiting current will be decreased by an amount corresponding to the reacted O<sub>2</sub> concentration. In the reaction, if the stoichiometric mole ratio of O<sub>2</sub> against the combustible gas is assumed to be  $n$ , the magnitude of the limiting current will be given by

$$I_l = \frac{4FD_{O_2}S}{l} (C_{O_2} - nC_x) \quad (5)$$

where  $C_x$  is the combustible gas concentration in the gas mixture.

Case II: it is assumed that combustible gas reacts readily with O<sub>2</sub> at the cathode, not in other places, due to the catalytic activity of the cathode. In this situation, the combustible gas concentration at the cathode is much lower than in the ambient gas and, consequently, the diffusion of the combustible gas in the porous coating can be regarded as being rate determining. In this case, the diffusion rates of these gases are given by

$$J_{O_2} = \frac{D_{O_2}S}{l} C_{O_2} \quad (6)$$

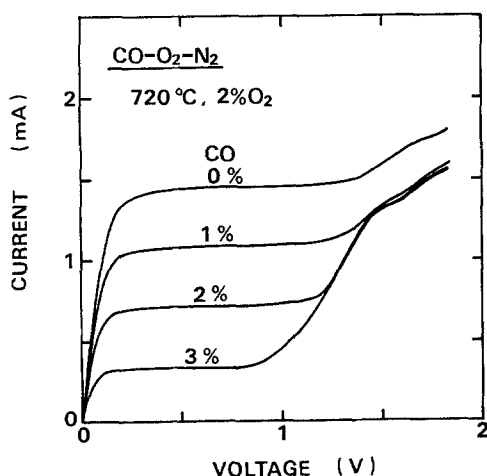


Fig. 8. Effect of CO in CO-2% O<sub>2</sub>-N<sub>2</sub> mixtures on the current-voltage characteristics of the sensor at 720°C.

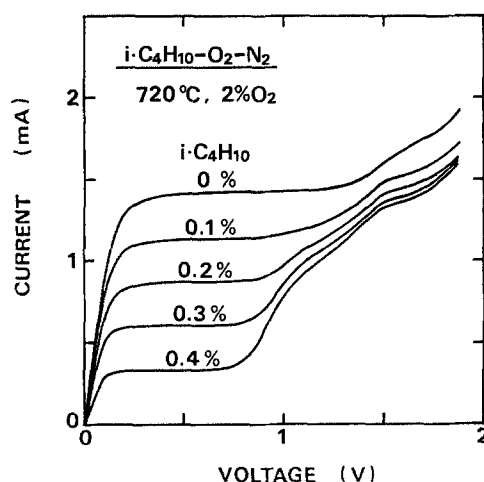


Fig. 9. Effect of i-C<sub>4</sub>H<sub>10</sub> in i-C<sub>4</sub>H<sub>10</sub>-2% O<sub>2</sub>-N<sub>2</sub> mixtures on the current-voltage characteristics of the sensor at 720°C.

and

$$J_x = \frac{D_x S}{l} C_x \quad (7)$$

where  $J_{O_2}$  and  $J_x$  are the diffusion rates of O<sub>2</sub> and the combustible gas, respectively, and  $D_x$  is the diffusion coefficient of the combustible gas in the porous coating. On the assumption that the transferred O<sub>2</sub> flux  $J_{O_2}$  is consumed by the combustible gas flux  $J_x$ , the limiting current is expressed as

$$\begin{aligned} I_l &= 4F(J_{O_2} - nJ_x) \\ &= \frac{4FD_{O_2}S}{l} \left( C_{O_2} - \frac{nD_x}{D_{O_2}} C_x \right) \end{aligned} \quad (8)$$

This equation indicates that the decrease in the limiting current is  $D_x/D_{O_2}$  times as much as that for case I. Accordingly, we introduce normalized current reduction,  $\gamma$ , which is defined as the ratio of the decrease in limiting current to that in case I. Then,

$$\gamma = D_x/D_{O_2} \quad (9)$$

In Equation 9, the value of  $\gamma$  is estimated to be 4 for H<sub>2</sub>, 1.07 for CO and 0.74 for i-C<sub>4</sub>H<sub>10</sub>, for the case of Knudsen diffusion in the porous coating.

The predicted current reduction is compared with the experimental results in terms of  $\gamma_{exp}$ , which is the ratio of the experimental current reduction normalized with that for case I. The temperature variation of  $\gamma_{exp}$  is shown in Fig. 10. This figure shows that the value of  $\gamma_{exp}$  for i-C<sub>4</sub>H<sub>10</sub> is in good agreement with case II. However,  $\gamma_{exp}$  for H<sub>2</sub> has a value intermediate between the two cases, and varies with temperature. This indicates that the reaction of H<sub>2</sub> with O<sub>2</sub> occurs both in the cathode and in the gas mixture before reaching the sensor surface. The value of  $\gamma_{exp}$  for CO is slightly larger than 1 and, therefore, case II would be plausible.

## 5. Conclusions

In gas mixtures containing H<sub>2</sub>O or CO<sub>2</sub>, in addition to O<sub>2</sub> and N<sub>2</sub>, the limiting current-type oxygen sensor

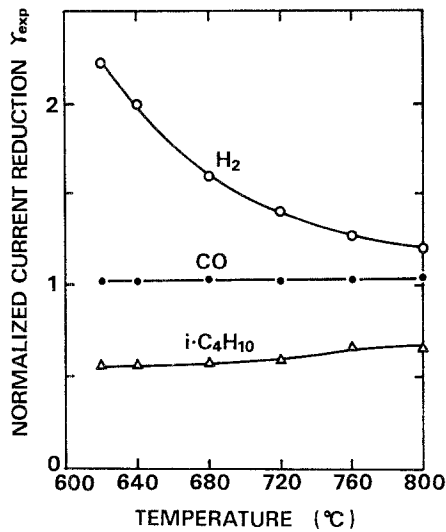


Fig. 10. Variation of normalized current reduction with temperature.

shows a two-stage current plateau. The magnitude of the sensor current in the first stage corresponds to oxygen concentration in the gas mixture, and is practically independent of the presence of H<sub>2</sub>O and CO<sub>2</sub>. The sensor current in the second stage increases with increasing H<sub>2</sub>O or CO<sub>2</sub> concentration. The second stage characteristics are considered to originate from the diffusion of these gases as a rate-limiting step in the porous coating.

For gas mixtures containing combustible gas and O<sub>2</sub>, the limiting current corresponding to O<sub>2</sub> concentration decreases linearly with increase in combustible gas concentration. The decrease in limiting current is predicted by a model including both the reaction of these gases at the cathode and in the gas mixtures before reaching the sensor surface. In the model, the diffusion of the combustible gas in the porous coating is rate limiting.

## References

- [1] S. Matsushita, T. Inoue, K. Nakanishi, K. Kato and N. Kobayashi, SAE Paper 850044, SAE International Congress and Exposition, Detroit, Michigan, 25 Feb.–1 March 1985.
- [2] Y. Kimbara, K. Shinoda, H. Koide and N. Kobayashi, SAE Paper 851210, SAE Government/Industry Meeting and Exposition, Washington, DC, 20–23 May 1985.
- [3] H. Dietz, *Solid State Ionics* 6 (1982) 175.
- [4] K. Saji, H. Takahashi, H. Kondo, T. Takeuchi and I. Igarashi, 'Proceedings of the 4th Sensor Symposium', Institute of Electrical Engineers of Japan, Tokyo (1984) p. 147.
- [5] K. Saji, *J. Electrochem. Soc.* 134 (1987) 2430.
- [6] K. Saji, H. Kondo, H. Takahashi, T. Takeuchi and I. Igarashi, 'Digest of Technical Papers' Presented at the 3rd International Conference on Solid-State Sensors and Actuators, Philadelphia, Pennsylvania, 11–14 June (1985) p. 336.
- [7] H. Takahashi, K. Saji, H. Kondo, T. Takeuchi and I. Igarashi, 'Proceedings of the 5th Sensor Symposium', Institute of Electrical Engineers of Japan, Tokyo (1985) p. 133.
- [8] T. Usui, A. Asada and Y. Isono, 'Proceedings of the 6th Sensor Symposium', Institute of Electrical Engineers of Japan, Tokyo (1986) p. 279.
- [9] S. Pizzini, M. Bianchi, P. Colombo and S. Torchio, *J. Appl. Electrochem.* 3 (1973) 153.

## Appendix

The sensor current,  $I$ , is considered as the sum of current components caused by O<sub>2</sub> molecules and dissociated oxygen from H<sub>2</sub>O and CO<sub>2</sub>. These components,  $I_{O_2}$ ,  $I_{H_2O}$  and  $I_{CO_2}$ , in the sensor current are related to the diffusion rates of O<sub>2</sub>, H<sub>2</sub>O and CO<sub>2</sub>, respectively. For H<sub>2</sub>O–O<sub>2</sub>–N<sub>2</sub> mixtures, the relations are given by

$$I = I_{O_2} + I_{H_2O} \quad (A1)$$

$$I_{O_2} = 4FJ_{O_2} \quad (A2)$$

$$I_{H_2O} = 2FJ_{H_2O} \quad (A3)$$

where  $J_{O_2}$  and  $J_{H_2O}$  are the diffusion rates of O<sub>2</sub> and H<sub>2</sub>O in the porous coating, respectively. The diffusion rates are represented by

$$J_{O_2} = -D_{O_2}S \left( \frac{C_{O_2,c} - C_{O_2}}{l} \right) \quad (A4)$$

$$J_{H_2O} = -D_{H_2O}S \left( \frac{C_{H_2O,c} - C_{H_2O}}{l} \right) \quad (A5)$$

where  $C_{H_2O,c}$  is H<sub>2</sub>O concentration at the cathode. Since the zirconia electrolyte can be assumed to be impervious, therefore,

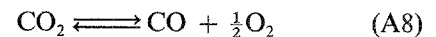
$$J_{H_2O} + J_{H_2} = 0 \quad (A6)$$

Here,  $J_{H_2}$  is the diffusion rate of H<sub>2</sub> in the porous coating, and represented by

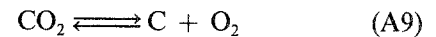
$$J_{H_2} = -D_{H_2}S \left( \frac{C_{H_2,c} - C_{H_2}}{l} \right) \quad (A7)$$

where  $D_{H_2}$  is the diffusion coefficient of H<sub>2</sub>, and  $C_{H_2,c}$  and  $C_{H_2}$  are H<sub>2</sub> concentrations at the cathode and in the ambient gas, respectively.

For CO<sub>2</sub>–O<sub>2</sub>–N<sub>2</sub> mixtures, CO<sub>2</sub> dissociates by either



or



Therefore, for the gas mixtures, equations corresponding to A1, A3 and A6 are given by

$$I = I_{O_2} + I_{CO_2} \quad (A10)$$

$$I_{CO_2} = 4F(J_{CO_2} + J_{CO}/2) \quad (A11)$$

$$J_{CO_2} + J_{CO} = J_{cd} \quad (A12)$$

where  $J_{CO_2}$  and  $J_{CO}$  are the diffusion rates of CO<sub>2</sub> and CO in the porous coating, respectively, and  $J_{cd}$  denotes the deposition rate of carbon at the cathode. These diffusion rates are similarly related to the gas concentrations.

On the other hand, it is hypothesized that gas composition at the cathode is chemically equilibrated due to the catalytic activity of the cathode, since platinum usually has high catalytic activity for the reaction of O<sub>2</sub> with H<sub>2</sub> and CO, in H<sub>2</sub>–O<sub>2</sub>–H<sub>2</sub>O and CO–O<sub>2</sub>–CO<sub>2</sub> systems. The gas composition of the equilibrated atmosphere can be calculated in terms of the equi-

librium constants of these reactions. Based on this hypothesis and the above equations, the gas composition at the cathode can be numerically calculated.

The calculated concentration of  $O_2$  at the cathode gives the relationship between sensor voltage and sensor current, as expressed by Equation 3. In the calculation for  $CO_2-O_2-N_2$  mixtures, the magnitude of the limiting current due to the decomposition of  $CO_2$  by

Reaction A9 is expected to be twice the magnitude expressed by Equation 4. However, experimental results indicated considerably smaller magnitude of the sensor current than that yielded by Reaction A9 and even Reaction A8 also. Therefore, the calculated current-voltage curves in which only Reaction A8 is assumed to occur, are shown in Fig. 6.