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CO and CO₂ Sensing Properties of Electrochemical Gas Sensors Using an Anion-conducting Polymer as an Electrolyte

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Abstract

CO₂ and CO sensing properties of an electrochemical gas sensor employing an anion-conducting polymer (ACP) membrane as an electrolyte and Pt only, Pt mixed with ACP or 10 wt% Pt-loaded carbon black (Pt/CB) mixed with ACP as an electrode material, which were denoted as an EC(Pt), EC(Pt-ACP) or EC(Pt/CB-ACP) sensor, respectively, have been investigated in this study. All sensors showed positive Nernstian response to 400~20,000 ppm CO₂ in humid air at 30°C, and the EC(Pt-ACP) sensor showed large CO₂ response in comparison with those of EC(Pt) and EC(Pt-CB/ACP) sensors. These CO₂-sensing properties were largely dependent on humidity in sample and reference gases and CO₂ concentration in the reference gas. In addition, the electromotive force (EMF) of the sensors also varied with a change in O₂ concentration in a CO₂-free sample gas, when CO₂-free air was used also as a reference gas. However, the EMF was little dependent on the O₂ concentration in the sample gas containing CO₂. From these results, a 2-electron O₂-free redox reaction of CO₂ may determine the potential of the sensing electrode under atmosphere containing CO₂. On the other hand, EC(Pt-ACP) and EC(Pt/CB-ACP) sensors showed slow and negative response to CO in humid air at 21°C, and the magnitude of CO response of these sensors was almost proportional to the logarithm of CO concentration. In addition, the EMF was largely dependent on the O₂ concentration in the sample gas containing CO. The O₂ response behavior and current-voltage characteristics in N₂ containing 1000 ppm CO or 20% O₂ confirmed that the mixed potential consisting of CO oxidation and O₂ reduction is the most important factor to determine the magnitude of CO response.

Keywords: Gas sensor, Anion-conducting polymer, Carbon dioxide, Carbon monoxide
1. Introduction

Different kinds of electrolytes, namely liquid electrolytes such as sulfonic acid and general buffer aqueous solutions [1-4] and inorganic solid electrolytes such as lanthanum fluoride and antimonial acid [5-7], have been recently studied as an electrolyte for electrochemical gas sensors operable at low temperatures. Polymer electrolytes are also one of attractive materials for electrochemical gas sensors. Especially, proton-conducting polymers such as Nafion [8-11] have large proton conductivity and relatively excellent long-term stability. Therefore, many researchers have studied electrochemical gas sensors by using the proton-conducting polymers as an electrolyte, after the pioneering work on the H₂ and CO sensors using the Nafion by Miura et al. in the 1980's [8, 9]. On the other hand, anion-conducting polymers (ACP) with large OH⁻ conductivity and improved long-term stability have been also developed for various power devices by various researchers and companies in the past decades. Especially, polymer electrolyte fuel cells (PEFC) fabricated with ACP as an electrolyte are very promising because they showed high current density as well as high power density with relatively-low overpotential and their performance was quite comparable to those of PEFC employing proton-conducting polymers in the preliminary research stage [12-17]. Gas sensor applications of the ACP with large OH⁻ conductivity have also been performed by Manoukian et al. [18].

In this study, therefore, electrochemical gas sensors have been fabricated by employing an ACP membrane as an electrolyte and Pt-loaded carbon black or Pt mixed with ACP as an electrode material, and their CO₂ and CO sensing properties and mechanism have been investigated.

2. Experimental

2.1 Fabrication of electrochemical gas sensors

10 wt% Pt-loaded carbon black powder as an electrode material was prepared by an impregnation method. An appropriate amount of carbon black (CB; Sigma Aldrich Co. LLC., A7455) was added into a H₂PtCl₆ aqueous solution of 1.48 x 10⁻² M, and then it was ultrasonicated for 60 min. After the suspension obtained was dried on a hot plate and subsequently heat-treated under H₂ stream at 350°C for 1 h, 10 wt% Pt-loaded carbon black (Pt/CB) powder was obtained.

The Pt/CB powder was then added in an ACP solution (Tokuyama Corp., AS-4), which is an iso-propanol containing a 5 wt% hydrocarbon-type ionic polymer with quaternary ammonium salts (ion-exchange capacity: 1.3 mmol g⁻¹ and ion conductivity: ca. 13 mS cm⁻¹)
The weight ratio was Pt/CB : ACP = 1 : 1. The paste obtained (Pt/CB-ACP) was applied on the surface of each side of an ACP membrane (Tokuyama Corp., A201, 20 x 20 mm² in area and ca. 30 μm in thickness, ion-exchange capacity: 1.7 mmol g⁻¹ and OH⁻ conductivity: ca. 42 mS cm⁻¹), a polyolefin polymer which consists of hydrocarbon main chain and quaternary ammonium salts [14], as sensing and counter electrodes (the electrode area: 6 x 6 mm²). After drying at 70°C for 3 h, the electrochemical gas sensor was obtained as shown in Fig. 1. The electrochemical sensor was denoted as EC(Pt/CB-ACP).

In addition, we fabricated other two types of electrochemical sensors equipped with electrodes without carbon black. Namely, the mixture of Pt paste (Tanaka Kikinzoku Kogyo K. K., TR-7905) and the ACP solution (Pt-ACP, Pt : ACP = 3 : 97 at weight ratio) or the as-supplied Pt paste only was also applied on the surface of the each side of the ACP membrane as sensing and counter electrodes and it was subsequently treated in the same manner as that for EC(Pt/CB-ACP). Each sensor fabricated with the mixture or the Pt paste was denoted as EC(Pt-ACP) or EC(Pt), respectively.

2.2 Characterization of gas-sensing materials

Morphology and composition of electrode materials were observed with a scanning electron microscope (SEM; JEOL Ltd., JSM-7500F) equipped with an electron dispersive spectrooscope (EDS; JEOL Ltd., JED-2300). The pore size distribution and specific surface area were measured by general Barrett-Joyner-Halenda (BJH) and Brunauer-Emmett-Teller (BET) methods using N₂ adsorption-desorption isotherms (Micromeritics Inst. Corp., Tristar3000), respectively. Crystal phase was characterized by X-ray diffraction analysis (XRD; Rigaku Corp., RINT2200) using CuKα radiation (40 kV, 40 mA), and crystallite size was calculated by using Scherrer equation.

2.3 Measurement of CO₂ and CO sensing properties of electrochemical gas sensors

Gas-sensing properties of EC(Pt/CB-ACP), EC(Pt-ACP) and EC(Pt) to 400~20,000 ppm CO₂ and 100~1000 ppm CO in 0~80% O₂ balanced with N₂ in a sensing-electrode compartment were evaluated by measuring the electromotive force (EMF) at 30°C (CO₂) or 21°C (CO), when air containing 395 ppm CO₂ or CO₂-free air (synthetic air) was used as a reference gas in a counter-electrode compartment and RH in both the electrode compartments was controlled to be 0~80%. The magnitude of sensor response (ΔE = EMFₛ - EMFₐ) was defined as the difference between EMF under sample gas flowing (EMFₛ) and that under base gas flowing in a sensing-electrode compartment (EMFₐ). The magnitude of sensitivity (S)
was defined as a slope of the straight relationship between $\Delta E$ and CO$_2$ concentration.

3. Results and Discussions

3.1 Characterizations of gas-sensing materials

Figure 2 shows an XRD pattern of Pt/CB powder. The relatively-sharp XRD peaks of Pt with face-centered cubic structure [19] are observed, and the crystallite size (CS) of Pt nanoparticles, which was calculated from the (111) peak by using Scherrer equation, was ca. 15.4 nm. This CS value is quite reasonable in the view of relatively-high heat-treatment at 350°C under H$_2$ stream, because the CS of Pt nanoparticles, which were loaded on conventional carbon black (Vulcan XC-72 supplied by Cabot Corp.) by the impregnation and subsequent heat-treatment at 100°C under H$_2$ stream, was ca. 7.5 nm [19]. On the other hand, two broad peaks, "CB (002)" and "CB (100) and (101)", originated from amorphous-like graphitic crystallites of CB appear, and the CS along the c-axis of the CB, which was calculated from the (002), was ca. 1.67 nm. The CS value of the CB was larger than those of typical carbon blacks with large surface area, KB(EC600JD) (AkzoNobel N.V., 1.04 nm) and BP-2000 (Cabot Corp., 0.79 nm), but smaller than that of corrosion-proof acetylene black, AB-7 (Denki Kagaku Kogyo, 3.94 nm), and comparable with that of Vulcan XC-72 (1.53 nm) [20]. Figure 3 shows N$_2$ adsorption-desorption isotherms and a pore size distribution of Pt/CB powder, together with those of as-supplied CB powder. The N$_2$ adsorption-desorption isotherms of CB belong to "Type IV" according to the BET classification, because of abrupt and quite small increase in volume of adsorbed N$_2$ at low P/P$_0$ ($\leq$ 0.2), small positive slope of quasi-plateau at medium P/P$_0$ (0.2~0.8) and the abrupt and large increase in volume of adsorbed N$_2$ and hysteresis at high P/P$_0$ values ($\geq$ 0.8). In addition, the pore size distributions show that the CB has a relatively-large amount of well-developed mesopores as well as macropores. Namely, the CB has large pore volumes at the pore diameter of both 2~3 nm and several ten nanometers. In addition, the specific surface area (SSA) of CB (101.3 m$^2$ g$^{-1}$) was much smaller than those of Vulcan XC-72R (254 m$^2$ g$^{-1}$), KB(EC600JD) (1270 m$^2$ g$^{-1}$), BP-2000 (1475 m$^2$ g$^{-1}$), but much larger than that of AB-7 (49 m$^2$ g$^{-1}$) [20]. The medium CS (see Fig. 2) and SSA of the CB used in the present study, in comparison with those of other carbon blacks, predict relatively-excellent stability in an alkaline condition electrochemically [20]. It is obvious that the Pt loading to CB resulted in little effects on both CS and SSA. Figure 4 shows a SEM photograph of Pt/CB powder. The agglomerate size of Pt/CB (100~250 nm in diameter) is much larger than the sizes of Pt and CB crystallites. The EDS measurement showed that the amount of Pt in 10Pt/CB was
9.9 wt%, which is almost the same as the originally-loading amount of Pt to CB (10 wt%).

**Figure 5** shows SEM photographs of sensing electrodes of EC(Pt), EC(Pt-ACP) and EC(Pt/CB-ACP) sensors. Surface of the Pt electrode of the EC(Pt) sensor was quite rough with submicron-sized Pt particles and large pores, while that of the Pt-ACP electrode of the EC(Pt-ACP) sensor was relatively smooth, because the Pt particles was coated with ACP. Thickness of the Pt electrode of the EC(Pt) sensor and the Pt-ACP electrode of the EC(Pt-ACP) sensor was thicker than 150 μm and 100 μm, respectively. Here, as for the EC(Pt) and EC(Pt-ACP) sensors, partial exfoliation of the electrode materials from the ACP membrane was observed. Such exfoliation was likely occurred during the preparation of cross-sections of the sensors, due to a flexible nature of the ACP membrane. Surface of the Pt/CB-ACP electrode of the EC(Pt/CB-ACP) sensor was also smooth due to the coating with ACP on the surface of the large Pt/CB agglomerates (see Fig. 5 (c)(ii)), and the composite morphology indicating the mixture of ACP and Pt/CB agglomerates was conformed in some places (see Fig. 5 (c)(i)).

### 3.2 CO₂-sensing properties

**Figure 6** shows response transients of EC(Pt), EC(Pt-ACP) and EC(Pt/CB-ACP) sensors to 20,000 ppm CO₂ in air at 30°C, when air containing 395 ppm CO₂ (compressed air) was used as a reference gas in the counter-electrode compartment and RH in both the electrode compartments was 57%. All sensors showed clear and reversible CO₂ responses at all CO₂ concentration values, but the magnitude of CO₂ response and response-recovery speeds are slightly different among three sensors. The EC(Pt/CB-ACP) sensor showed the fastest response speed among them, while its recovery speed was comparable with those of the other two sensors. **Figure 7** shows the relationship between the magnitude of CO₂ response, ΔE, and CO₂ concentration. All sensors showed Nernstian response, and the magnitude of the response to 20,000 ppm CO₂ (ΔE = 63 mV) as well as CO₂ sensitivity (S = 37.9 mV/decade) of the EC(Pt-ACP) sensor are larger than those of the other two sensors (EC(Pt/CB-ACP): ΔE = 52 mV and S = 29.5 mV/decade, EC(Pt): ΔE = 42 mV and S = 29.3 mV/decade). The number of electron transferred per a CO₂ molecule (n) of the EC(Pt-ACP) sensor, 1.59, is a little bit smaller than those of the other two sensors (EC(Pt/CB-ACP): 2.04, EC(Pt): 2.05), but these results imply the progress of almost the same redox reaction on the electrodes of all sensors.

The effect of the existence of CO₂ gas in the reference gas on the magnitude of CO₂ response was investigated. **Figure 8** shows the relationship between the magnitude of CO₂
response and CO₂ concentration of the EC(Pt-ACP) sensor, when air containing 395 ppm CO₂ (compressed air) or CO₂-free air (synthetic air) was used as a reference gas. The flowing of CO₂-free air in place of air containing CO₂ as a reference gas increased the magnitude of CO₂ response by about +33 mV. This means that the EC(Pt-ACP) sensor is a CO₂ concentration cell. The CO₂ sensitivity under the CO₂-free air flowing (42.36 mV/decade) was comparable to that under the flowing of air containing CO₂ (37.89 mV/decade).

Figure 9(a) shows response transients of the EC(Pt-ACP) sensor to 20,000 ppm CO₂ under CO₂-free reference air flowing at 30°C when the RH values were 0~80% in both the electrode compartments. The RH dependence of the magnitude of 20,000 ppm CO₂ response of the sensor is plotted in Fig. 9(b). The EC(Pt-ACP) sensor showed extremely-slow response and recovery speeds as well as poor signal/noise (S/N) ratio in dry condition, due to very low anion-conductivity of the ACP electrolyte induced by the decrease in the water content in the electrolyte. On the other hand, the magnitude of CO₂ response in dry condition was higher than those in wet conditions, probably due to a large number of active sites without water molecules adsorbed. The magnitude of CO₂ response linearly decreased with an increase in RH, and the introduction of water vapor largely improved the S/N ratio and the response and recovery speeds, probably because of the increase in the amounts of water molecules in the ACP membrane and thus the large improvement in the anion-conductivity.

Effects of O₂ concentration in the sample gas on the EMF of the EC(Pt-ACP) sensor were investigated under CO₂-free gas flowing in both the electrode compartments. Figure 10 shows the response transients to 5~100% O₂ under CO₂-free reference air flowing and the O₂ concentration dependence of logarithmic \( P_1/P_2 \) at 30°C (RH in both electrode compartments: 57%), where \( P_1 \) and \( P_2 \) stand for oxygen partial pressure in the sensing and counter compartments, respectively. It is obvious that an increase in O₂ concentration resulted in a shift of the EMF positively, but the slope of the linear relationship (29.5 mV/decade) was too large in comparison with that estimated from 4-electron O₂ reduction pathway (15.0 mV/decade) and the number of electron transferred per an O₂ molecule calculated from this experimental slope was about 2.06. This probably means that other reactions such as 2-electron reduction pathway of O₂ to H₂O₂ control the EMF of the sensor under CO₂-free gas flowing.

Figure 11 shows response transients to O₂ of the EC(Pt-ACP) sensor under the flowing of N₂ containing 2% CO₂ as a sample gas at 30°C, when air containing 395 ppm CO₂ was used as a reference gas (RH in both electrode compartments: 57%). The O₂ concentration hardly contributes to the EMF, when CO₂ exists in the sample gas. It is very clear that the CO₂
concentration is the most important factor to determine the EMF of the sensor under the present conditions. Additionally, the EMF of this sensor negatively shifted slowly when CO was injected to the sample gas, as shown in the next section, and the direction of CO response is opposite to that of CO₂ response (positive shift). On the basis of experimental results obtained so far in this study, we propose that the reaction (1) determines the potential of both electrodes.

\[
\text{CO}_2 + \text{H}_2\text{O} + 2\text{e}^- \rightleftharpoons \text{CO} + \text{OH}^-
\]

(1)

Considering the electrode reaction, the Nernst equation is expressed as shown below.

\[
\text{EMF} = \frac{RT}{2F} \ln \frac{P_{\text{CO}_2\text{(SE)}} P_{\text{H}_2\text{O}\text{(SE)}} P_{\text{CO}\text{(CE)}}}{P_{\text{CO}_2\text{(CE)}} P_{\text{H}_2\text{O}\text{(CE)}} P_{\text{CO}\text{(SE)}}}
\]

(2)

Here, \(P_{x(y)}\) is partial pressure (\(x\): gas species, \(y\): the kind of electrode compartment (SE: sensing electrode, CE: counter electrode)), \(T\) is the absolute temperature, \(R\) is the gas constant, and \(F\) is the Faraday constant. If the partial pressure of CO₂ in the sensing electrode-compartment (\(P_{\text{CO}_2\text{(SE)}}\)) independently changes without influence on the other factors, we can explain every behavior of the electrochemical CO₂ sensors in this study by using the equation (2). However, the value of other components, especially \(P_{\text{CO}_{(y)}}\), also must vary gradually as the reaction (1) goes toward equilibrium, while \(P_{\text{H}_2\text{O}_{(y)}}\) is hardly expected to change because the humidity in both the electrode components is controlled. Therefore, it is impossible to fully explain the variation in the EMF with the CO₂ concentration in this study at present. On the other hand, some papers suggested different CO₂-sensing mechanisms. For example, Ishiji et al. showed that pH-dependent reduction of PtO-species on the surface of Pt electrode is the most important factor for CO₂ monitoring after CO₂ dissolution to KCl aqueous solution, for amperometric CO₂ sensors using the KCl aqueous solution as an electrolyte [1]. Manoukian et al. also discussed the CO₂-sensing properties of an amperometric sensors using ACP as an electrolyte, on the basis of the mechanism suggested by Ishiji et al [18]. Actually, CO₂ molecules seem to dissolve to the polymers with primary amino groups, to form carbamate- and bicarbonate-species [21-23]. Mayo et al. developed a CO₂ sensor employing a Cu sensing electrode and an ACP electrolyte on the basis of the high CO₂-reduction activity of Cu [24]. Thus, we have to collect more detailed experimental data in various gaseous conditions, to clarify the CO₂-sensing mechanism completely in near future.

3.3 Sensing behavior to CO
Figure 12 shows response transients of EC(Pt-ACP) and EC(Pt/C-ACP) sensors to 1000 ppm CO in synthetic air (CO$_2$-free air) and dependence of the magnitude of their CO response on the CO concentration at 21°C, when synthetic air was used also as a reference gas (RH in both electrode compartments: 50%). These sensors showed negative response to CO, and the magnitude of CO response of the EC(Pt/C-ACP) sensor (ΔE = -77 mV) is larger than that of the EC(Pt-ACP) sensor (ΔE = -47 mV). In addition, the magnitude of CO response of these sensors was almost proportional to the logarithm of CO concentration, and the sensitivity of the EC(Pt/C-ACP) sensor ($S = -38.3$ mV/decade) was almost comparable with that of the EC(Pt-ACP) sensor ($S = -35.2$ mV/decade). The response and recovery speeds of the EC(Pt/C-ACP) sensor are much faster than those of the EC(Pt-ACP) sensor. However, the response and recovery times of CO response are unusually longer than those of CO$_2$ response.

Effects of O$_2$ concentration on the EMF of the EC(Pt/C-ACP) sensor were investigated under the flowing of N$_2$ containing 1000 ppm CO in the sensing-electrode compartment and synthetic air in the counter-electrode compartment. Figure 13 shows variation in EMF of the EC(Pt/C-ACP) sensor with a change in O$_2$ concentration in 400 or 1000 ppm CO balanced with synthetic air at 21°C and the relationship between the EMF and the O$_2$ concentration (RH in both electrode compartments: 50%). The EMF nonlinearly increased with an increase in O$_2$ concentration in sample gas containing CO, irrespective of the CO concentration, and this behavior is completely different from that in synthetic gas containing CO$_2$ (see Fig. 11). The results indicate that redox reactions involving both CO and O$_2$ molecules determine the sensing-electrode potential. Miura et al. has already reported that the magnitude of CO response of an electrochemical CO sensor using Nafion as an electrolyte is largely dependent on the mixed potential between CO reduction and O$_2$ oxidation in 1980's [8, 9]. The CO sensing mechanism has been supported by other papers [25, 26]. Therefore, the current-voltage characteristics of the EC(Pt-ACP) sensor in N$_2$ containing 1000 ppm CO or 20% O$_2$ were investigated as shown in Fig. 14. In this experiment, a reference Pt electrode was fabricated on the side of the counter electrode with a Pt paste, in order to control the sensing electrode potential exactly. The rest potential of the sensing electrode in CO-free synthetic air was +9 mV vs. the reference Pt-ACP electrode, and the cathodic current was observed by the cathode polarization, according to the following O$_2$ reduction.

$$O_2 + H_2O + 4e^- \rightarrow 4OH^-$$ (3)

On the other hand, the rest potential of the sensing electrode in 1000 ppm CO balanced with
N$_2$ was -66 mV vs. the reference Pt-ACP electrode, and the anodic current was observed by anode polarization, according to the following CO oxidation.

$$\text{CO} + 4\text{OH}^- \rightarrow \text{CO}_2 + \text{H}_2\text{O} + 2\text{e}^- \quad (4)$$

The electrode potential intersected by these two polarization curves, namely mixed potential, was about -36 mV. As the difference between the rest potential in CO-free synthetic air and the mixed potential (-45 mV) is almost equal to the magnitude of CO response (-47 mV), it is confirmed that the mixed potential is the most important factor to determine the magnitude of CO response of this sensor. At present, CO-sensing properties of the electrochemical gas sensors in this study, especially the response and recovery speeds, were extremely low as shown in Fig. 12. Further improvement of CO sensing properties is now under investigation by the meso- and macro-structural optimization of electrode materials as well as boundaries between electrodes and ACP membrane on the basis of the possible CO-sensing mechanism described above.

4. Conclusion

Three kinds of electrochemical gas sensors, EC(Pt), EC(Pt-ACP) and EC(Pt/CB-ACP), were fabricated and their CO$_2$ and CO sensing properties and mechanism were investigated in this study. All sensors showed clear and reversible responses to 400~20,000 ppm CO$_2$ in air at 30°C (RH: 57%), and the EC(Pt-ACP) and EC(Pt/CB-ACP) sensors showed the largest response and the fastest response speed, respectively. All sensors showed Nernstian response, and the number of electron transferred per a CO$_2$ molecule of all sensors was 1.59~2.05. The CO$_2$-sensing properties were largely dependent on humidity in sample and reference gases, and the response speed in dry air was especially slow. Variation in O$_2$ concentration under CO$_2$-free atmosphere largely changed the EMF of the sensors, but that under atmosphere containing CO$_2$ hardly contributes to the EMF. These results may imply that a 2-electron O$_2$-free redox reaction of CO$_2$ determines the potential of the sensing electrode under the atmosphere containing CO$_2$. On the other hand, EC(Pt-ACP) and EC(Pt/CB-ACP) sensors showed extremely slow and negative response to CO, and the magnitude of CO response of the EC(Pt/C-ACP) sensor is larger than that of the EC(Pt-ACP) sensor. In addition, the EMF nonlinearly increased with an increase in O$_2$ concentration under the atmosphere containing CO. The O$_2$ response behavior and current-voltage characteristics in N$_2$ containing 1000 ppm CO or 20% O$_2$ confirmed that the mixed potential consisting of CO oxidation and O$_2$ reduction is the most important factor to determine the
magnitude of CO response.
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**Figure Captions**

Fig. 1. Schematic drawing of a typical electrochemical sensor.

Fig. 2. XRD pattern of Pt/CB powder.

Fig. 3. N$_2$ adsorption-desorption isotherms and pore size distributions of Pt/CB and CB powders.

Fig. 4. SEM photograph of Pt/CB powder.

Fig. 5. SEM photographs of sensing electrodes of EC(Pt), EC(Pt-ACP) and EC(Pt/CB-ACP) sensors.

Fig. 6. Response transients of EC(Pt), EC(Pt-ACP) and EC(Pt/CB-ACP) sensors to 20,000 ppm CO$_2$ in air at 30°C (reference gas: air containing 395 ppm CO$_2$, RH in both the electrode compartments: 57%). LM and HM mean low and high magnifications, respectively.

Fig. 7. Relationship between $\Delta E$ and CO$_2$ concentration in air at 30°C (reference gas: air containing 395 ppm CO$_2$, RH in both the electrode compartments: 57%).

Fig. 8. Relationship between $\Delta E$ and CO$_2$ concentration of the EC(Pt-ACP) sensor in air at 30°C (RH: 58%). Reference gas is (a) air containing 395 ppm CO$_2$ (compressed air) or (b) CO$_2$-free air (synthetic air).

Fig. 9. (a) Response transients to 20,000 ppm CO$_2$ at different RH (0~80%) and (b) RH dependence of the magnitude of 20,000 ppm CO$_2$ response of the EC(Pt-ACP) sensor under CO$_2$-free air flowing at 30°C (▲: gas in, ▼: gas out).

Fig. 10. Response transients to 5~100% O$_2$ of the EC(Pt-ACP) sensor under CO$_2$-free N$_2$ flowing and the O$_2$ concentration dependence of log($P_1/P_2$) at 30°C (reference gas: CO$_2$-free air, RH in both electrode compartments: 57%). $P_1$ and $P_2$ stand for oxygen partial pressure in the sensing and counter compartments, respectively.

Fig. 11. Response transients to O$_2$ of the EC(Pt-ACP) sensor under the flowing of N$_2$ containing 2% CO$_2$ as a sample gas at 30°C (reference gas: air containing 395 ppm
CO₂, RH in both electrode compartments: 57%).

Fig. 12. Response transients to 1000 ppm CO and dependence of the magnitude of CO response on the CO concentration of EC(Pt-ACP) and EC(Pt/C-ACP) sensors at 21ºC in synthetic air (reference gas: synthetic air, RH in both electrode compartments: 50%).

Fig. 13. (a) Variation in EMF of the EC(Pt/C-ACP) sensor with a change in O₂ concentration in 400 or 1000 ppm CO balanced with synthetic air at 21ºC and (b) the relationship between the EMF and the O₂ concentration (reference gas: synthetic air, RH in both electrode compartments: 50%). Dotted line: 400 ppm CO and solid line: 1000 ppm CO.

Fig. 14. Current-voltage characteristics of the EC(Pt-ACP) sensor in N₂ containing 1000 ppm CO or 20% O₂ (reference gas: synthetic air, RH in both electrode compartments: 50%).
Fig. 1. Hyodo et al.
Fig. 2. Hyodo et al.
(a) CB
(i) N₂ adsorption-desorption isotherms
Specific surface area
101.3 m² g⁻¹

(ii) Pore size distributions
Pore volume /
10⁻³ cm³ g⁻¹ nm⁻¹
Pore diameter / nm

(b) 10Pt/CB
(i) N₂ adsorption-desorption isotherms
Specific surface area
96.5 m² g⁻¹

(ii) Pore size distributions
Pore volume /
10⁻³ cm³ g⁻¹ nm⁻¹
Pore diameter / nm

Fig. 3. Hyodo et al.
Fig. 4. Hyodo et al.
Fig. 5. Hyodo et al.
Fig. 6. Hyodo et al.
Fig. 7. Hyodo et al.
Fig. 8. Hyodo et al.
Fig. 9. Hyodo et al.
Fig. 10. Hyodo et al.
Fig. 11. Hyodo et al.
Fig. 12. Hyodo et al.
Fig. 13. Hyodo et al.
Fig. 14. Hyodo et al.