Large Current Density CO_2 Reduction under High Pressure Using Gas Diffusion Electrodes

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Electrochemical reduction of CO_2 was studied under high pressure on Co, Rh, Ni, Pd, Pt, Ag, and Cu electrocatalysts supported in the gas diffusion electrode (GDE). CO was produced on Pd and Ag catalysts at faradaic efficiencies of 58 and 86%, respectively, at 300 mA cm^{-2} under CO_2 20 atm. In the case of Cu-GDE, CO and formic acid were produced as the main reduction products. Hydrogen was the predominant reduction product in the electrolyses using other GDEs. Effects of the CO_2 pressure, the current density, and the passed charge in the electrochemical reduction of CO_2 using Pd and Ag-GDEs were investigated in detail. The maximum partial current density of CO formed on the Pd-GDE under CO_2 20 atm was 450 mA cm^{-2}. A very large partial current density of CO formation of 3.05 A cm^{-2} was achieved in the electrolysis under 30 atm on the Ag-GDE.

We have been investigating the electrochemical reduction of CO_2 under high pressure on various metal electrodes in aqueous electrolytes.[1—7] The effect of the CO_2 pressure on the electrochemical CO_2 reduction on metal electrodes was studied. The CO_2 reduction at large current density (i.e. high rate) could be achieved by the high pressure electrolysis due to high concentration of CO_2 in the aqueous electrolyte.

By using the gas diffusion electrode (GDE) which has been developed and employed for fuel cells, a large current density electrolysis can be also achieved. The electrochemical CO_2 reductions on various metals and metal compounds loaded in the GDE under 1 atm were conducted by several workers. They have reported the achievement of larger current density for CO_2 reduction, compared to the electrolysis in aqueous electrolyte using metal electrodes.[8—18] Recently, we began to investigate the electrochemical reduction of high pressure CO_2 using Pt-GDE, which is on the market.[19,20] In the case of the reverse arrangement, at which the Pt catalyst layer was directed toward the CO_2 gas phase while the gas diffusion layer faced the aqueous electrolyte, methane was produced as the predominant reduction product and the maximum partial current density of methane under 30 atm was 338 mA cm^{-2}. It was shown that the product selectivity depended strongly on the electrode arrangement, CO_2 pressure, current density, passed charge, and temperature. In order to clarify the effect of the metal catalyst, we prepared GDEs loaded with Co, Rh, Ni, Pd, Pt, Ag, and Cu electrocatalyst. The electrochemical CO_2 reduction was investigated under high pressure. In this publication, these results are reported.

Experimental

Preparation of GDEs.   The gas diffusion electrode without electrocatalyst which has a structure of the gas diffusion layer and the catalyst layer, (purchased from Tanaka Noble Metal, Industries,

Ltd.), was employed as the base GDE. These are the reagents employed for preparation of the electrocatalyst: special grade reagents of $Co(NO_3)_2 \cdot 6H_2O$, $Ni(NO_3)_2 \cdot 6H_2O$, $AgNO_3$, $Cu(NO_3)_2 \cdot 3H_2O$, (Kanto Chemical CO., Inc.), and $RhCl_3$, $PdCl_2$, H_2PtCl_6, (special grade reagent, Nippon Engellhard, Ltd.). A fixed amount of methanol or ethanol solutions of these metal compounds (concentration: 2 mmol dm^{-3}—0.3 mol dm^{-3}, containing a small amount of H_2O), were dropped on the surface of the catalyst layer of the base GDE (4 cm^2), and they then penetrated inside. After the desiccation in the air at ambient temperature for over 1 h, the hydrogen treatment of the GDE was conducted in hydrogen atmosphere at 220 °C for 1 h in order to reduce metal ions. Amounts of metal catalysts supported in the GDE calculated from amounts of the solutions are the following: Co 4.9 μmol cm^{-2}, Ni 16 μmol cm^{-2}, Rh 0.4 μmol cm^{-2}, Pd 0.6 μmol cm^{-2}, Pt 1.3 μmol cm^{-2}, and Cu 2.3 μmol cm^{-2}.

Electrolyses.   Electrolyses under high pressure were conducted in a glass cell equipped within a stainless steel autoclave (content of inner gas phase: 624 mL), as described in the previous paper.[20] The GDEs containing the electrocatalysts (apparent surface area: 1 cm^2) were employed in the arrangement in which the catalyst layer was directed toward the aqueous electrolyte (normal arrangement). Effect of the electrode arrangement on the selectivity of the reduction products was already shown for the Pt-GDE in previous papers.[19,20] In this experiment, GDEs were mainly used in the normal arrangement. The aqueous electrolyte was 0.5 mol dm^{-3} KHCO$_3$ and 2.0 mol dm^{-3} KOH aqueous solution, which was prepared from reagent grade chemicals and distilled water (Wako Pure Chemical Industries, Ltd.). The electrolyte was purified by the pre-electrolysis with a Pt black cathode at a constant current density of 0.25 mA cm^{-2} under Ar atmosphere for 15 h to eliminate heavy metal impurities. A magnetic stirrer was used for agitation of the electrolyte and the gas phase. The reference electrode Ag/AgCl/sat. KCl and Pt wire (apparent surface area: about 20 cm^2) was employed as a counter electrode.

After the bubbling of CO_2 for 20 min to exchange the atmosphere, a known pressure of CO_2 was introduced into the autoclave. The electrolysis under 1 atm CO_2 was conducted using the autoclave

with 1 atm of CO_2 and 9 atm of Ar balance. The electrolyses were conducted galvanostatically (passage of 150 C) at 25 °C with a potentiostat-galvanostat (Hokuto, HA-305 and 501) and a coulomb meter (Hokuto, HF-201). The electrode potential of the cathode was measured and corrected with an IR compensation instrument (Hokuto, HI-203). Large current density electrolyses were conducted by 2 electrode electrolyses without any reference electrode.

Analysis of the Reduction Products. The autoclave was left for about 30 min after each electrolysis in order to attain the equilibrium of the gaseous reduction products in the autoclave. The sampling capillary gas outlet is located in the upper part of the autoclave. In order to substitute the gas phase in the capillary gas outlet, the emission of the inner gas was conducted before the sampling of the gas phase. Quantitative analysis of the electrolysis products contained in the gas phase were conducted using the following instruments. A gas chromatograph (Ohkura GC-802) equipped with a MS-13X column (4 mm×2 m) and a thermal conduction detector (TCD) for CO, and with an active carbon column (4 mm×2 m) and a TCD for hydrogen and a gas chromatograph (Ohkura GC-202) equipped with a VZ-10 column (4 mm×2 m) and flame ionization detector (FID) for hydrocarbons, were used. Formic acid was analyzed by a high pressure liquid chromatograph (HPLC, Shimadzu LC-4A equipped with a column (Shodex-Ionpack KC-811, 8 mm×300 mm) with a UV detector (220 nm)).

Results and Discussion

Electrocatalytic Activity of Various Metals. Faradaic efficiencies of the reduction products produced at the electrochemical reduction of CO_2 under 20 atm using GDEs containing various metal catalysts, are shown in Table 1. In the case of the electrolysis using GDE without metal catalyst, hydrogen formed by the reduction of water was the predominant product (faradaic efficiency of 84%), although formic acid was produced at a faradaic efficiency of 2.1%. Hydrogen was also the main reduction product in cases of Co, Ni, Rh, and Pt-GDEs, as shown in Table 1. Faradaic efficiencies of CO produced on Ni, Rh, and Pt catalysts were only 2.4, 9.8, and 7.9%, respectively. The authors previously reported that CO and formic acid were produced at high faradaic efficiencies on the electrochemical CO_2 reduction under high pressure using metal electrodes such as Fe, Co, Ni, Rh, and Pt.[1—3,5,6] However, a product selectivity different from that on these electrodes was observed on the GDEs with these

metal catalysts, as shown in Table 1, i.e., almost no CO_2 reduction products were produced and hydrogen was the predominant product even under CO_2 high pressure. The number of the reaction sites of adsorbed hydrogen formation on these metal electrocatalyst supported in GDE would be larger than that of metal wire and plate electrode, due to the large surface area of the electrocatalyst in GDE. By increase in the reaction sites for formation of adsorbed hydrogen, the reaction rate of hydrogen formation by the combination of two adsorbed hydrogen (i.e. Tafel reaction) would increase remarkably. Hence, hydrogen might be the predominant reduction product in cases of Co, Ni, Rh, and Pt catalysts, due to the remarkable increase in the reaction rate of hydrogen formation.

In the cases of Pd and Ag-GDEs, on the other hand, CO was produced at faradaic efficiencies of 58 and 86%, respectively, at a current density of 300 mA cm^{-2}, as shown in Table 1. The fact that CO was not produced in the case of GDE without any metal catalyst, as shown in Table 1, suggests that CO is produced on Pd and Ag catalysts. It is well-known that CO is the main reduction product for the electrochemical CO_2 reduction on Pd and Ag electrode in aqueous electrolytes.[21—23] No change in the product selectivity was observed between the electrolyses using Pd and Ag-GDEs, and those using Pd and Ag metal wire electrodes.

In the case of Cu-GDE, as shown in Table 1, CO and formic acid were produced at faradaic efficiencies of 31 and 28%, respectively, at a current density of 900 mA cm^{-2}. In this electrolysis condition, faradaic efficiencies of methane and ethylene which are known as the main products of CO_2 reduction using Cu electrode, were only 0.5 and 0.2%, respectively, as shown in Table 1. Cook et al. conducted an electrochemical CO_2 reduction using the Cu-GDE in 1 mol dm^{-3} KOH aqueous electrolyte.[14] Methane and ethylene were produced at 9 and 69%, respectively, in the electrolysis of 400 mA cm^{-2}. Furuya et al. studied the dependence of the electrode potential on the faradaic efficiencies of reduction products in the electrochemical CO_2 reduction using the Cu-GDE. In their results, hydrogen was the main reduction product and faradaic efficiencies of CO and formic acid were 30 and 15%, respectively, at −1.6 V vs. Ag/AgCl.[12]

Table 1. Electrochemical Reduction of CO_2 under High Pressure on GDEs at the Normal Arrangement

Catalyst[a]	Current density mA cm^{-2}	E[b] V	Faradaic efficiency / %						
			CH$_4$	C$_2$H$_6$	C$_2$H$_4$	CO	HCOO$^-$	H$_2$	Total
—	600	−2.12	0.16	0.03	Trace	N	2.1	84.4	86.7
Co	300	−1.56	0.20	0.14	N	N	0.6	92.3	93.2
Rh	300	−1.34	0.09	Trace	N	9.8	3.6	82.0	95.5
Ni	600	−1.88	0.76	0.21	0.40	2.4	0.9	91.0	96.1
Pd	300	−1.33	0.03	0.02	N	57.5	2.3	26.5	86.7
Pt	300	−1.38	0.27	0.05	Trace	7.9	0.2	65.8	74.2
Cu	900	−1.27	0.5	0.02	0.2	31.0	27.8	45.4	104.9
Ag	300	−1.22	N	N	N	86.0	1.8	2.0	89.8

Electrolysis condition: CO_2 pressure, 20 atm; charge passed, 150 C; electrolyte, 45 mL of 0.5 mol dm^{-3} KHCO$_3$.   a) The catalysts were supported with the impregnation method.   b) Electrode potential were corrected with an IR compensation instrument (vs. Ag/AgCl).

The faradaic efficiency of methane was only less than 1%. Ikeda et al. also conducted the electrochemical CO_2 reduction using Cu-GDE.[17,18] The faradaic efficiencies of methane and ethylene reached 21% at -1.6 V vs. Ag/AgCl and 22% at -1.5 V, respectively. These results indicate that the selectivity of reduction products depends remarkably on the property of Cu catalyst (such as purity and particle size) and on the preparation method of the GDE, in addition to the electrolysis conditions such as the electrode potential (current density). We investigated the electrochemical reduction of CO_2 under high pressure using a Cu electrode in an aqueous electrolyte. As a result, predominant reduction products were not hydrocarbons but CO and formic acid under the electrolysis condition at which a large amount of CO_2 is supplied to the electrode.[4] This result suggests that preferential formation of CO and formic acid in the present experiment is caused by an efficient supply of CO_2 to the Cu-GDE.

The drastic effect of the electrode arrangement observed for the Pt-GDE[19,20] was not observed in the cases of Ni, Rh, Pt, and Pd-GDEs prepared in this experiment. This might be caused by a difference in nature of the electrocatalyst due to different details of preparation, e.g. amount, particle size, or distribution.

Current-Potential Curve. The current-potential curves obtained using Ag, Ni, and Pd-GDEs in 0.5 $mol\,dm^{-3}$ $KHCO_3$ aqueous solution, are shown in Figs. 1, 2, and 3, respectively. The current–potential curves were measured in the Ar and CO_2 atmosphere. In the case of Ag-GDE, the current–potential curve obtained under CO_2 1 atm was shifted toward anodic direction, compared to that under Ar 1 atm, as shown in Fig. 1. Moreover, a remarkable anodic shift was observed under CO_2 50 atm. A similar anodic shift of the current was observed in the electrochemical CO_2 reduction
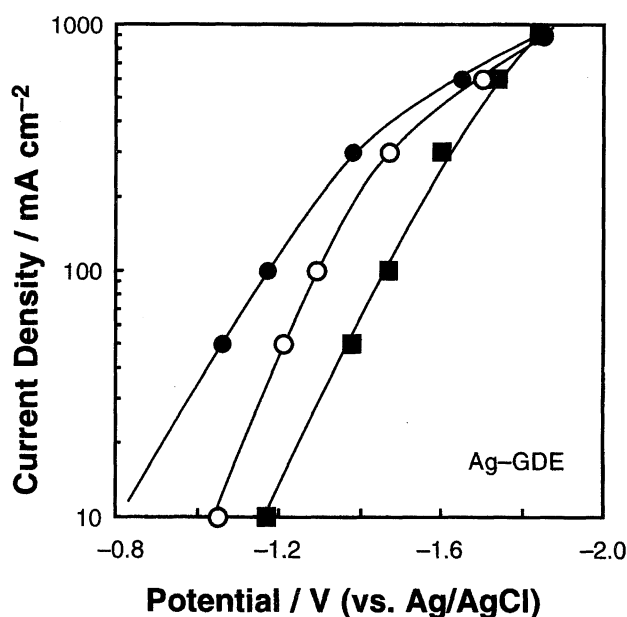
Fig. 1.   Tafel plots of total current density obtained on a Ag-GDE in 0.5 $mol\,dm^{-3}$ $KHCO_3$: (■) Ar 1 atm, (○) CO_2 1 atm, (●) CO_2 50 atm.
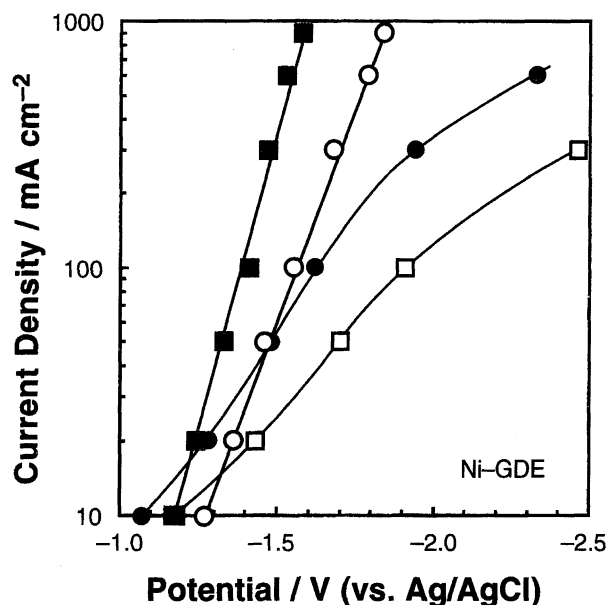
Fig. 2.   Tafel plots of total current density obtained on a Ni-GDE in 0.5 $mol\,dm^{-3}$ $KHCO_3$: (■) Ar 1 atm, (○) CO_2 1 atm, (●) CO_2 10 atm, (□) CO_2 50 atm.
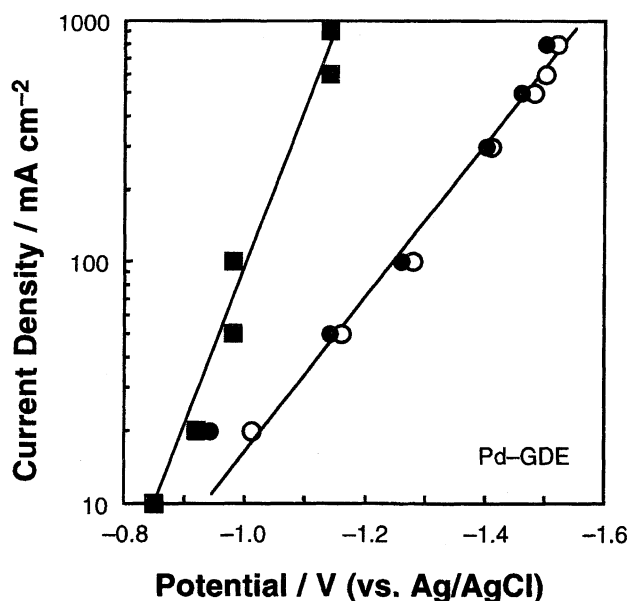
Fig. 3.   Tafel plots of total current density obtained on Pd-GDE in 0.5 $mol\,dm^{-3}$ $KHCO_3$: (■) Ar 1 atm, (○) CO_2 1 atm, (●) CO_2 50 atm.

on Ag metal electrode with increasing the CO_2 pressure in an aqueous electrolyte.[6] Ito et al. reported a similar anodic shift of the current-potential curve under CO_2 atmosphere, compared to that under N_2 atmosphere in the case of In and Pb electrodes in aqueous and non-aqueous electrolytes.[24—26] They supposed that the anodic shift under CO_2 atmosphere was due to the increase in the current of CO_2 reduction with increasing the concentration of CO_2 in the electrolyte.

On the other hand, in the case of Ni-GDE, the current-potential curve under CO_2 1 atm was shifted toward the cathodic direction, compared to that under Ar 1 atm, as shown

in Fig. 2. This indicates the suppression of the electrode reaction under CO_2 atmosphere. This negative shift increases with increasing the CO_2 pressure, as shown in Fig. 2. Hori et al. reported the negative potential shift under 1 atm of CO_2, compared to under Ar atmosphere, in the electrochemical CO_2 reduction on Ni electrode in the aqueous electrolyte.[27] They concluded that the negative potential shift is caused by adsorbed CO formed by the reduction of CO_2 on the electrode surface, which prevents hydrogen formation. Taking into consideration these previous studies, we suggest that adsorbed CO was formed on Ni catalyst by the CO_2 reduction and suppresses the CO_2 reduction, resulting in the predominant formation of hydrogen in the electrochemical CO_2 reduction using the Ni-GDE, as shown in Table 1. The result in Fig. 2, that the negative shift increased with increasing the CO_2 pressure in a high current density region, indicates an increase in the amount of adsorbed CO (and/or adsorbed CO_2) on the Ni catalyst with increasing the CO_2 pressure. The adsorbed CO might suppress hydrogen formation. The negative potential shift was also observed in the case of Pd-GDE, as shown in Fig. 3. It indicates that adsorbed CO was also formed on the Pd catalyst in the same way as on the Ni catalyst. Interestingly, the negative shift observed for the Pd-GDE hardly depends at all on the CO_2 pressure, being different from Ni-GDE.

In the case of Ni-GDE, the positive potential shift under CO_2 20 atm, compared to Ar 1 atm were observed at low current density (about 10 $mA\,cm^{-2}$), as shown in Fig. 2. This might be caused by an increase in the current of CO_2 reduction with increasing CO_2 pressure.

CO_2 Reduction Using Pd-GDE.   The Pd catalyst has high electrocatalytic activity for CO_2 reduction to CO, as shown in Table 1. We investigated in detail the electrochemical CO_2 reduction under high pressure using the Pd-GDE. Figure 4 shows the dependence of the faradaic efficiencies of CO and hydrogen formation on the current density for the electrochemical CO_2 reduction under 20 atm in 0.5 mol dm^{-3} $KHCO_3$ solution. As shown in this figure, CO was produced at maximum faradaic efficiency of 77% at 80 $mA\,cm^{-2}$. The faradaic eifficiency of CO formation decreased with increasing the current density, while that of hydrogen increased. Figure 5 shows the relationship between the current density and the partial current density of CO formation. The partial current density of CO formation increased with increasing the current density, and the limiting current density of CO formation under CO_2 20 atm reaches 450 $mA\,cm^{-2}$, as shown in Fig. 5. Figure 6 shows the relationship between the yield of CO and the passed charge in the electrochemical CO_2 reduction on Pd-GDE under 20 atm in 0.5 mol dm^{-3} $KHCO_3$ solution. As shown in this figure, the yield of CO increases in proportion to the passed charge until 900 C. This indicates that CO is produced by the electrochemical reduction of CO_2 on Pd catalyst and the electrocatalytic activity of CO formation is hardly changed until 900 C.

As shown in Figs. 4 and 5, CO was produced by CO_2 reduction at a high faradaic eifficiency (max 77% at 80 $mA\,cm^{-2}$) and a large current density (max 450 $mA\,cm^{-2}$ under 20
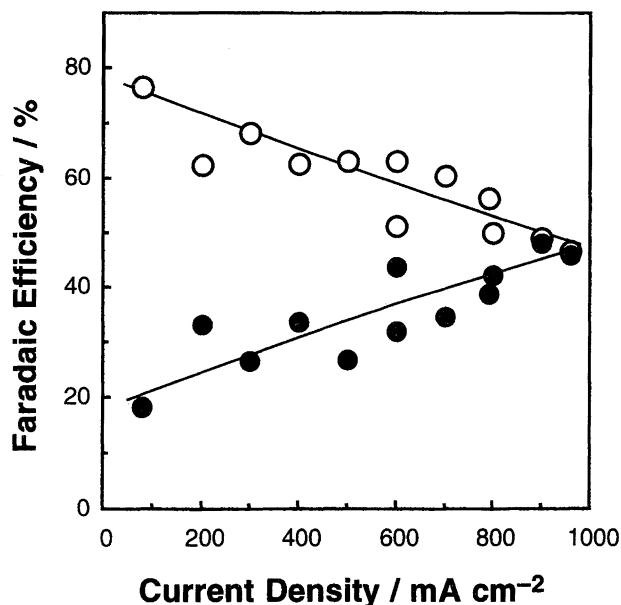

Fig. 4.   The dependence of the faradaic efficiencies of reduction products on the current density in the electrochemical reduction of CO_2 under 20 atm on a Pd-GDE: (○) CO, (●) H_2.
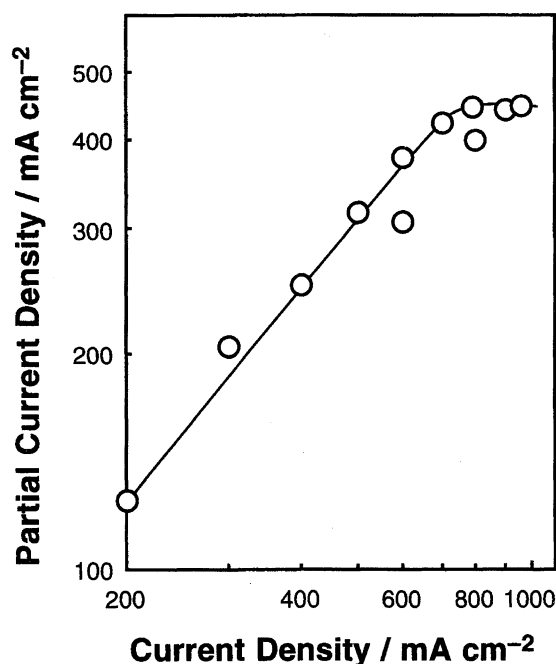

Fig. 5.   Relationship between the current density and the partial current density for CO formation in the electrochemical reduction of CO_2 under 20 atm on a Pd-GDE.

atm). Moreover, no deactivation of catalytic CO formation was observed until 900 C, as shown in Fig. 6. These results show that the Pd-GDE prepared in the present study has a high electrocatalytic activity for CO formation. However, few hydrocarbons were produced in the CO_2 reduction using Pd-GDE, as shown in Table 1. In order to clarify the possibility of hydrocarbon formation by further reduction of CO on Pd catalyst, the electrochemical reduction of CO instead of
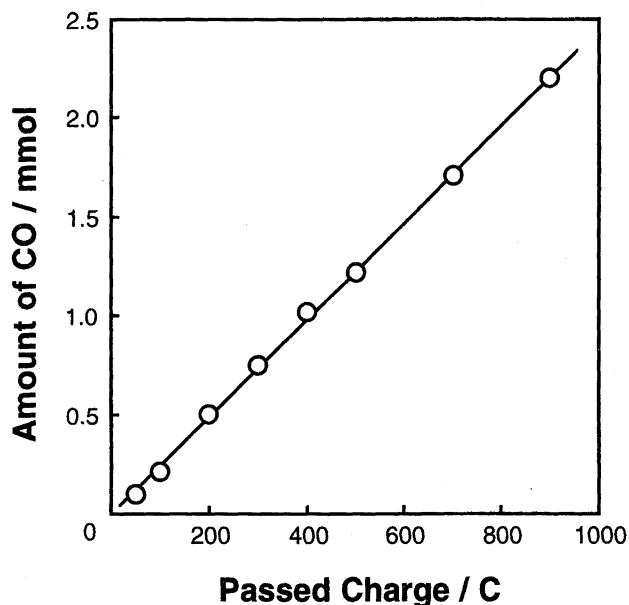
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Fig. 6. The dependence of the yield of CO on the passed charge in the electrochemical reduction of CO_2 under 20 atm on a Pd-GDE at 600 mA cm^{-2}.

Fig. 7. The dependence of the faradaic efficiencies of reduction products on the CO_2 pressure in the electrochemical reduction of CO_2 on a Ag-GDE at 300 mA cm^{-2} in 0.5 mol dm^{-3} KHCO$_3$: (○) CO, (□) HCOO$^-$, (●) H$_2$.

CO_2 using Pd-GDE under 20 atm at a constant current density of 200 mA cm^{-2}, was conducted. But, no hydrocarbon formation was observed and the reduction product was only hydrogen. This result suggests that the Pd-GDE dose not have the electrocatalytic activity of hydrocarbon formation from CO but has that of CO_2 reduction to CO.

CO_2 Reduction Using Ag-GDE. Electrochemical CO_2 reduction under high pressure using the Ag-GDE, which has shown high electrocatalytic activity for the CO_2 reduction in ways similar to Pd-GDE, was also investigated in detail. Figure 7 shows the dependence of the faradaic efficiencies of CO, formic acid, and hydrogen formation on the CO_2 pressure for the electrochemical CO_2 reduction using a Ag-GDE at 300 mA cm^{-2} in 0.5 mol dm^{-3} KHCO$_3$ solution. The faradaic efficiency of CO formation was 44% at 1 atm of CO_2 and increased with increasing the CO_2 pressure. It reached 86% at 20 atm, as shown in Fig. 7. The faradaic efficiency of hydrogen decreased with increasing the CO_2 pressure. Hydrogen formation on the Ag catalyst might be suppressed by increase in the rate of CO formation with increasing the CO_2 pressure. The faradaic efficiency of formic acid formation was lower than that of CO at each electrolysis condition, and decreased with increasing the CO_2 pressure while that of CO increased. This suggests that formic acid formation was also prevented by the CO formation, in ways similar to hydrogen formation. The result that the CO_2 pressure dependence of formic acid formation is similar to that of hydrogen suggests that hydrogen species, such as adsorbed H and proton, would take part in the formation of formic acid.

As shown in Table 1, the Ag-GDE prepared in the present study shows high electrocatalytic activity of CO formation from CO_2. CO was produced at high faradaic efficiency of 86% under 20 atm, even at a large current density of 300
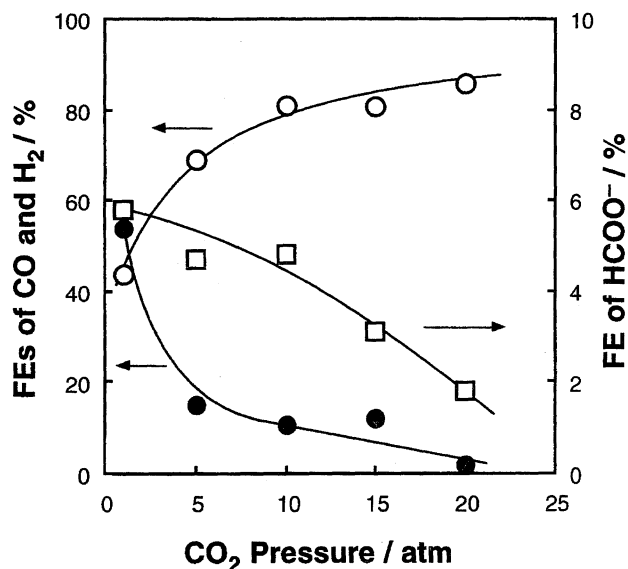
mA cm^{-2}. This indicates that the supply of CO_2 to Ag catalyst is not the rate-determining step under this current density condition. In order to achieve the high rate CO_2 reduction, large current density CO_2 reduction was conducted using the Ag-GDE (current density of < 4.3 A cm^{-2}). Figure 8 shows the relationship between the current density and the partial current densities of CO and formic acid formed in the CO_2 reduction using a Ag-GDE under 30 atm in 2.0 mol dm^{-3}
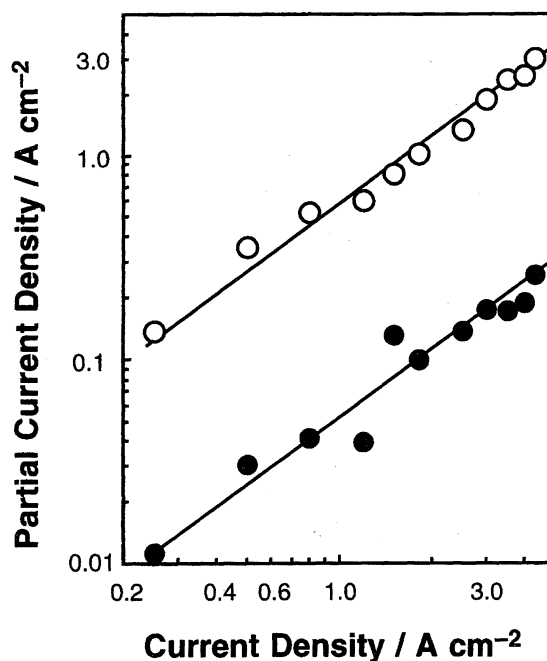

Fig. 8. Relationship between the current density and the partial current densities of reduction products formed in the electrochemical reduction of CO_2 under 30 atm on a Ag-GDE; (○) CO, (●) HCOO$^-$.

KOH aqueous solution. As shown in Fig. 8, partial current densities of CO and formic acid increased up to 4.3 A cm^{-2}, with increasing the current density. This indicates that the rate-determining step of the electrode reaction is not the mass transfer of CO_2 to the Ag catalyst but the electron transfer process, even at such a large current density condition. Several studies of large current density CO_2 reduction under high pressure or using GDEs were reported. For example, Fujishima et al. reported a successful CO_2 reduction with a partial current density of 420 mA cm^{-2} on a Cu electrode under 40 atm in methanol solution.[28] Formic acid was produced by CO_2 reduction with a current density of 560 mA cm^{-2} at In electrode under 60 atm of CO_2 in 0.5 mol dm^{-3} KHCO$_3$ aqueous solution.[7] Moreover, Cook et al. showed that methane and ethylene were produced at faradaic efficiencies of 9 and 69%, respectively, at Cu-GDE at a large current density of 400 mA cm^{-2} under 1 atm.[14] In the present experiment, it is surprising that the maximum partial current density of CO formation reached 3.05 A cm^{-2}. It is for the first time that such a high rate over 1 A cm^{-2}, for CO_2 reduction on the electrocatalyst was achieved. This is due to the efficient supply of CO_2 to the electrocatalyst in the electrolysis using the GDE under high pressure.

As shown above, CO_2 can be reduced to CO at high faradaic efficiency and at very large current density by the electrochemical reduction of CO_2 under high pressure using the Ag-GDE.

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