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# Reduction of Carbon Dioxide in 3-Dimensional Gas Diffusion Electrodes

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**Abstract**–Experiments on the electrochemical reduction of $CO_2$ were carried out by using a Cu/PTFE-bonded gas diffusion electrode (GDE) to investigate the effect of solvents, Cu/C ratio and electrolyte concentration on the characteristics of reduction products. The experimental conditions were a voltage range from −2.0 to −3.5 V vs. saturated calomel electrode (SCE) and electrolyte concentration from 0.1 M to 0.5 M. Significant performance differences were found between water and organic solvent (isobutanol+EtOH). The GDE was more active with water than that with organic solvent. And then, in the case of the Cu/PTFE-bonded gas diffusion electrode using organic solvent, the maximum faradaic efficiencies of reduction products were achieved in a Cu/C ratio of 0.5. The faradaic efficiency of $C_2H_4$ among the reduction products decreased as the Cu/C ratio increased; whereas, those of CO and alcohol increased. Since the difference in pH at the electrode influences the variation of product selectivity, the faradaic efficiency of $C_2H_4$ might increase due to the pH increase caused by electrolyte concentration difference.

Key words: Carbon Dioxide, Electrochemical Reduction, Gas Diffusion Electrode, Cu/PTFE

## INTRODUCTION

In the last decade, many workers have extensively studied the electrochemical and electrocatalytic reduction of $CO_2$ using various metal electrodes in aqueous electrolytes. As a result, it has been determined that the electrocatalytic activity of the electrode depends strongly on the metal used [Hori et al., 1989, 1994; Azuma et al., 1990]. For example, on Hg, Pb, In and Sn, which have large overpotentials for hydrogen formation, formic acid is predominantly formed. Methane, ethylene and ethanol are preferential reduction products formed on a Cu electrode. However, one of the problems associated with electrochemical reduction of $CO_2$ in water is the low solubility of $CO_2$ (0.033 mol $dm^3$ at 25 °C under ambient pressure) which leads to a mass transfer limitation for electrolysis at high current density. In order to increase the current density for $CO_2$ reduction, the electrochemical reduction of $CO_2$ under 1 atm using a gas diffusion electrode (GDE) has also been studied.

In order to increase the effective population of electrolyte/electrocatalyst/$CO_2$ interfacial sites for promoting gas phase $CO_2$ reduction, many research groups have applied the technology developed for $H_2$ fuel cell electrodes into electrochemical $CO_2$ reduction. Mahmood et al. [1987] investigated the electrochemical reduction of gaseous $CO_2$ using GDEs incorporating metal phthalocyanines, Pb, In, and Sn at ambient pressure. They reported the formation of formic acid on a Pb-GDE with 100 % faradaic efficiency and a current density of 115 mA/$cm^2$. Furuya et al. [1988] also reported $CO_2$ reduction using a GDE containing various metals such as Pb, Zn, Au, Ag, and Cu. Cook et al. [1990] and Schwarz et al. [1994] reported the electrochemical reduction of $CO_2$ on GDEs containing Cu and Cu alloys such as Cu-Ag, Cu-Pb, Cu-Zn, and Cu-Cd at 1 atm. Moreover, they showed that ethanol was formed with a faradaic efficiency of 31% and a current density of 180 mA/$cm^2$ on a GDE containing $La_{1.8}Sr_{0.2}CuO_4$. These results show successful of $CO_2$ reduction at a large current density under the condition of gas-phase. Since the electrodes of pure copper had been shown to favor the production of hydrocarbons in the electrochemical reduction of $CO_2$ in aqueous solutions, an effort was made to optimize the performance of GDE loaded with copper. From a comparison with other electrode systems, GDE seems to offer the most practical approach for efficient $CO_2$ reduction, because high current densities can be achieved. An essential further target with the GDE will be to lower the overpotential required and preferably to achieve direct $CO_2$ reduction to hydrocarbons.

The objective of the present study is to establish the optimum method to fabricate the gas diffusion electrode (GDEs) used for the reduction of carbon dioxide. In the electrode fabrication process, carbon/PTFE (polytetrafluroethylene)/catalyst composition, sintering condition and solvent are the main parameters. Therefore, we investigated the influence of reduction products in accordance with the composition of carbon/PTFE/catalyst, solvents (isobutanol+EtOH and water) and electrolyte concentration.

## EXPERIMENTAL

### 1. Electrodes

The Cu/PTFE-bonded GDE was made using the rolling method. The Cu/PTFE-bonded GDE containing 45 wt% PTFE was

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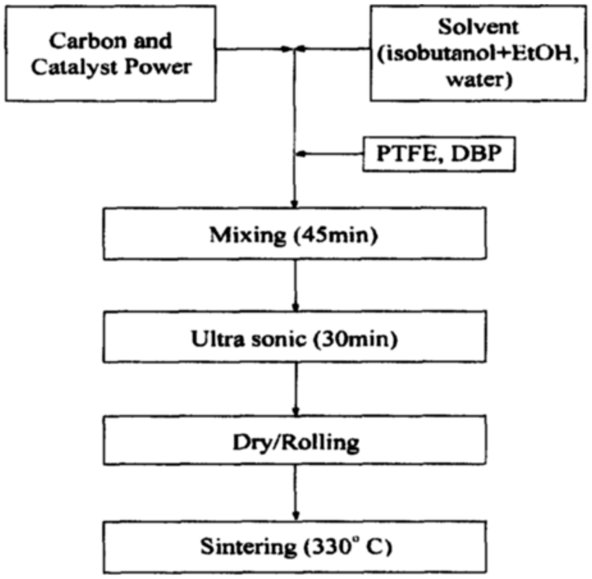

**Fig. 1. Fabrication procedure of Cu/PTFE-bonded gas diffusion electrode.**

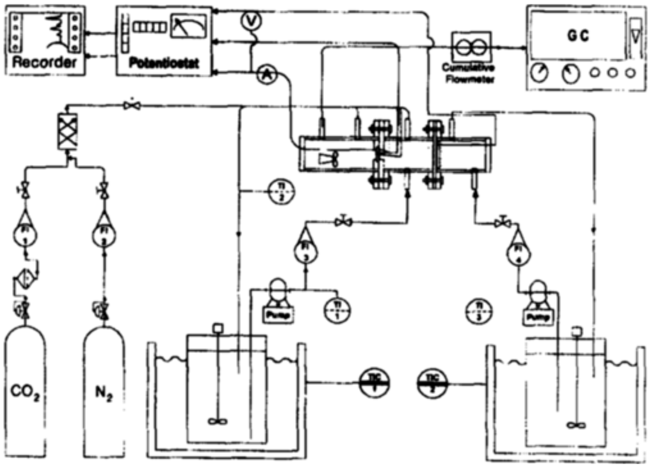

**Fig. 2. Schematic diagram of Cu/PTFE-bonded gas diffusion electrode.**

1. Catholyte compartment
2. Anolyte compartment
3. Working electrode (cathode)
4. Reference electrode (SCE)
5. Counter electrode (anode)
6. Constant temperature bath
7. CO gas filter
8. Gas mixer

FI: Flow meter (indicator)
TI: Temperature indicator
TIC: Temperature indicator and controller

prepared as shown in Fig. 1. Mixed carbon powders (40 g, Lonza KS-44) were used as supporting conductors and Cu as the catalyst and isobutanol/ethanol or water as a solvent. Then the additives DBP (Dibutyle phtalate) and PTFE (38 g, Dupont J-30) were added. The resulting mixture was stirred for 45 min. And it was uniformed using an ultra sonic for 30 min, and then dried after rolling process. Sintering at 330 °C after cold pressing made electrodes. The Cu-loaded gas diffusion electrode had an apparent working area of 2.89 cm$^2$ (1.7×1.7 cm).

### 2. Cell and Electrolyte

The electrochemical reduction of carbon dioxide was potentiostatically conducted using an all-acrylic electrolytic reactor with a Cu/PTFE-bonded GDE in a KHCO$_3$ electrolyte. Fig. 2 shows the schematic diagram of the electrochemical CO$_2$ reduction cell containing the 3-dimensional GDEs. In order to minimize the hydrocarbon oxidation, the catholyte compartment was separated from the anolyte compartment by a cation exchange membrane (Nafion, 417). A gas phase mixer was used for the agitation of the gas phase in the gas chamber. Cu/PTFE-bonded GDE was chosen as working electrode (cathode). CO$_2$ was provided from the cathode gas chamber before the experiment. The distance between anode and cathode was 4 cm. KHCO$_3$ aqueous solution was used as electrolyte. The aqueous electrolyte was 200 ml of KHCO$_3$ aqueous solution prepared from reagent grade chemicals and distilled water (Kanto Chemical Co, Inc.).

### 3. Electrolysis

The electrode potential was measured by SCE. The platinized Ti was used as a counter electrode (anode). A controlled potential electrolysis was carried out at the Cu/PTFE-bonded GDE under ambient pressure and temperature. The cathode gas chamber was filled with carbon dioxide gas before electrolysis. The electrolysis was conducted potentiostatically at 20 °C using Potentiostat/Galvanostat (EG&G PARC 362). Quantitative analysis of electrolysis products contained in the gas phase was conducted using the following instrument: a gas chromatograph (HP 5890 series II) equipped with a carbosieve-SII column (6 feet and 1/8 inches), a TCD (thermal conductivity detector) for H$_2$ and CO, and a FID (flame ionization detector) for hydrocarbons were used.

## RESULT AND DISCUSSION

### 1. Effect of Potential

The faradaic efficiencies were calculated on the basis of the number of electrons required for the formation of one molecule of the products from CO$_2$ and H$_2$O; 8 for CH$_4$, 12 for C$_2$H$_4$, 2 for CO, 2 for H$_2$. The faradaic efficiencies of the products produced by the electrochemical reduction of CO$_2$ using the GDE$_{(o)}$ (Cu/PTFE bonded GDEs using organic solvent [isobutanol+EtOH)] were measured at various Cu/C ratio.

In the case of Cu/C ratio and 0.1 M KHCO$_3$ electrolyte, H$_2$ was produced in the faradaic efficiency range 47.6% to 71.6%, at the potential of −2.0 V, as shown in Table 1. CO was produced in the faradaic efficiency range 3.5% to 22.5% at the same experimental conditions. CO was not produced in the case of the GDE without any metal catalyst [Hara et al., 1997]. It is well known that CO is the main reduction product for the electrochemical CO$_2$ reduction on Ag, Au, and Pb electrodes in aqueous electrolytes [Hori et al., 1985, 1994; Ito et al., 1990]. In this paper, CH$_4$ has the highest faradaic efficiency of 14.2% at the potential of −2.0 V on a Cu/C ratio of 0.5 in 0.1 M KHCO$_3$. Meanwhile, C$_2$H$_4$ has the highest faradaic efficiency of 22.1% at −2.5 V under the same conditions. Cook et al. [1990] conducted the electrochemical CO$_2$ reduction using the Cu-GDE in 1 M KOH. According to their result, CH$_4$ and C$_2$H$_4$ were produced at 9 and 69% faradaic efficiencies, respectively, in the electrolysis of 400 mA/cm$^2$. Furuya et al. [1988] studied

**Table 1. Product of electrochemical reduction of $CO_2$ in Cu/PTFE-bonded GDE used organic solvent (isobutanol+EtOH) as solvent at Cu/C ratio (0.3 to 0.7) in 0.1 M $KHCO_3$**

| Cu/C ratio | Conc. | Potential (V vs. SCE) | Faradaic efficiency (%) | | | | | | |
|---|---|---|---|---|---|---|---|---|---|
| | | | | Hydrocarbons | | | | | |
| | | | $H_2$ | CO | $CH_4$ | $C_2H_4$ | $C_2H_5OH$ | Total | Total |
| 0.30 | 0.1 M | −2.0 | 71.6 | 3.5 | 1.5 | 6.9 | 0.0 | 11.9 | 83.5 |
| | | −2.5 | 69.9 | 3.2 | 5.0 | 6.8 | 0.0 | 15.0 | 84.9 |
| | | −3.0 | 69.0 | 6.5 | 2.8 | 4.4 | 0.0 | 13.7 | 82.7 |
| | | −3.5 | 73.6 | 2.9 | 0.9 | 5.3 | 0.0 | 9.1 | 82.7 |
| 0.35 | 0.1 M | −2.0 | 50.2 | 22.9 | 1.2 | 8.5 | 0.0 | 32.6 | 82.8 |
| | | −2.5 | 52.0 | 19.4 | 2.0 | 15.7 | 0.0 | 37.1 | 89.1 |
| | | −3.0 | 70.9 | 5.7 | 0.5 | 15.0 | 0.0 | 21.2 | 92.1 |
| | | −3.5 | 73.3 | 5.5 | 0.2 | 6.6 | 0.0 | 12.3 | 85.6 |
| 0.40 | 0.1 M | −2.0 | 70.4 | 11.5 | 0.8 | 6.3 | 0.0 | 18.6 | 89.0 |
| | | −2.5 | 61.6 | 12.2 | 1.1 | 14.5 | 0.0 | 27.8 | 89.4 |
| | | −3.0 | 64.9 | 5.0 | 0.5 | 10.5 | 0.0 | 15.9 | 80.8 |
| | | −3.5 | 70.7 | 4.2 | 0.2 | 6.3 | 0.0 | 10.7 | 81.4 |
| 0.45 | 0.1 M | −2.0 | 64.7 | 10.8 | 1.3 | 5.9 | 0.0 | 18.0 | 82.7 |
| | | −2.5 | 63.4 | 10.2 | 0.5 | 15.8 | 0.0 | 26.5 | 89.9 |
| | | −3.0 | 72.4 | 4.3 | 0.2 | 10.4 | 0.0 | 14.9 | 87.3 |
| | | −3.5 | 55.6 | 3.4 | 0.3 | 10.7 | 12.8 | 27.2 | 82.8 |
| 0.50 | 0.1 M | −2.0 | 47.6 | 22.5 | 14.2 | 14.6 | 0.0 | 51.3 | 98.9 |
| | | −2.5 | 57.9 | 18.1 | 1.7 | 22.1 | 0.0 | 41.9 | 99.8 |
| | | −3.0 | 58.0 | 6.1 | 0.5 | 14.7 | 0.0 | 21.2 | 79.2 |
| | | −3.5 | 56.3 | 5.2 | 0.7 | 14.6 | 12.5 | 32.9 | 89.3 |
| 0.60 | 0.1 M | −2.0 | 52.3 | 26.4 | 1.1 | 10.2 | 0.0 | 37.7 | 90.0 |
| | | −2.5 | 49.9 | 13.6 | 0.6 | 17.2 | 0.0 | 31.4 | 81.3 |
| 0.70 | 0.1 M | −2.0 | 71.6 | 9.6 | 1.1 | 1.9 | 0.0 | 12.6 | 84.2 |
| | | −2.5 | 67.7 | 17.1 | 0.7 | 3.3 | 0.0 | 21.1 | 88.8 |
| 0.50 | 0.3 M | −2.0 | 60.0 | 11.2 | 1.0 | 27.5 | 0.0 | 39.7 | 99.7 |
| | | −2.5 | 75.4 | 7.0 | 3.6 | 11.9 | 0.0 | 22.5 | 97.9 |
| 0.60 | 0.3 M | −2.0 | 57.1 | 9.7 | 0.5 | 19.6 | 0.0 | 29.8 | 86.9 |
| | | −2.5 | 41.5 | 5.6 | 0.6 | 27.4 | 0.0 | 33.6 | 75.1 |
| 0.70 | 0.3 M | −2.0 | 48.6 | 14.8 | 0.8 | 8.8 | 0.0 | 24.4 | 73.0 |
| | | −2.5 | 48.7 | 13.2 | 0.2 | 16.9 | 0.0 | 30.3 | 79.0 |
| 0.50 | 0.5 M | −2.0 | 49.1 | 9.6 | 0.9 | 18.8 | 0.0 | 29.3 | 78.4 |
| | | −2.5 | 54.0 | 6.4 | 1.7 | 18.9 | 0.0 | 27.0 | 81.0 |
| 0.60 | 0.5 M | −2.0 | 61.4 | 9.2 | 1.3 | 25.3 | 0.0 | 35.8 | 97.2 |
| | | −2.5 | 57.5 | 5.6 | 5.9 | 21.0 | 0.0 | 32.6 | 90.1 |
| 0.70 | 0.5 M | −2.0 | 53.0 | 18.3 | 0.4 | 18.3 | 0.0 | 37.0 | 90.0 |
| | | −2.5 | 58.9 | 8.4 | 0.2 | 24.8 | 0.0 | 33.4 | 92.3 |

the dependence of the electrode potential on the faradaic efficiencies of the products in the electrochemical reduction of $CO_2$ using Cu-GDE. In their results, $H_2$ was the main reduction product and the faradaic efficiencies of CO and formic acid were 30 and 15%, respectively, at −1.6 V vs Ag/AgCl .

As illustrated in Table 1, CO was decreased according to an increasing potential. But $C_2H_4$ was maximum at −2.5 V, and then decreased over −2.5 V. It could be found that this tendency of $C_2H_4$ was due to the influence of CO. And then, CO was decreased from 22.5% to 18.1% for the faradaic efficiency change of $C_2H_4$, so it could be determined that CO contributed to the formation of $C_2H_4$. Some workers reported that CO contributed to the formation of hydrocarbon products, and this will be mentioned from the following reaction pass result.

The effect of the electrode potential on the products formed on the $GDE_{(w)}$ (Cu/PTFE-bonded GDE by using water as solvent) was shown in Fig. 3. As for the effect of the electrode potential on faradaic efficiency in Fig. 3, $H_2$ and CO were decreased with negative potentials, from 66.9% to 40.1% and from 9.8% to 7.3%, respectively. However, $C_2H_4$ formation was increased with negative potential, from 13.3 % to 37.6%.

These results show that the main products were CO and $C_2H_4$. Since the faradaic efficiencies of $CH_4$ are known, the main product in $CO_2$ reduction using a Cu electrode was lower

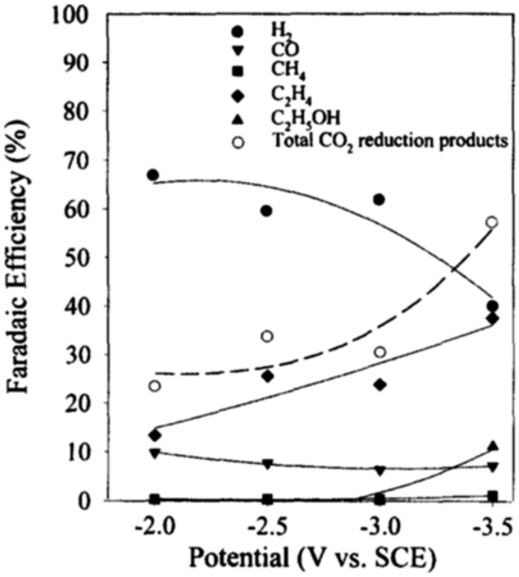

**Fig. 3. Faradaic efficiency of $CO_2$ reduction products according to electrode potential on the $GDE_{(w)}$ at the Cu/C ratio of 0.5 in 0.3 M $KHCO_3$.**

than that of $C_2H_4$. On the basis of other studies, the reaction mechanisms that CO converts to $CH_4$ and $C_2H_4$ differ, respectively, in these results [Hori et al., 1995; Sullivan, 1993]. Then, the faradaic efficiencies of the $CO_2$ reduction products at the $GDE_{(o)}$ were high at the potential of −2.0 V and −2.5 V. In the case of the $GDE_{(w)}$, the total faradaic efficiency of $CO_2$, the reduction product was increased with negative potential.

## 2. Reaction Path

The mechanism of the $CO_2$ reduction has not been established yet. The reaction step via a copper carbon was proposed by Wasmus et al. [1990]. They proposed that the $CO_2$ molecule was adsorbed on the electrode surface by the nucleophilic attack on the partially positive reduced copper surface. The desorbed $CO_2$ molecules were converted to the carbene compound. This carbene either got further protonated to form a $CH_4$ molecule or recombined with another carbene to $C_2H_4$.

According to Table 1, when the Cu/C ratio was incrementally increased until 0.5, the faradaic efficiency of hydrocarbons increased continuously, and that of $C_2H_4$ reached a maximum at this condition. This result can be explained by the reaction mechanism of Terunuma et al. [1997]. The reaction mechanism is summarized as follows: Hydrogen is produced on the surface of rich Cu oxide, while CO is produced on the surface of pure Cu metal. $CH_4$ is produced on the surface of both Cu oxide and metallic Cu, having a high affinity for adsorbed oxygen. $C_2H_4$ is also produced on the surface of a high active $CH_4$. The hydrocarbon productions may be interpreted as follows; atomic hydrogen is produced largely by the reduction of protons from water at a $Cu_2O$ site. The Cu metal site is formed by the electrochemical reduction of the surface oxide film. The Cu metal site has weaker activity for the reduction of protons than the $Cu_2O$ site. Therefore, it is preferable to the physical adsorption of $CO_2$. CO is relatively easily formed and chemically adsorbed at the first step to reduce $CO_2$. Hydrocarbons are produced by the interaction between adsorbed CO and atomic hydrogen at the reaction site, where $Cu_2O$ and metallic Cu are present side by side or close enough to suppress the CO and that of $H_2$ generation. Such sites provide a large amount of atomic hydrogen. It is known that the adsorption heat of CO on $Cu_2O$ is larger than that on metallic Cu, and this adsorption character may be similar to that under the electrolytic conditions. Then, since CO prefers the $Cu_2O$ site to the Cu site, hydrocarbons may be produced on the $Cu_2O$ site in the neighborhood of the Cu site. If the donation of atomic hydrogen to the adsorbed CO is insufficient due to the decrease in the number of the $Cu_2O$ sites, CO is produced without further reduction to hydrocarbons. Thus, there is a possibility that the $Cu_2O$ site is necessary to produce the hydrocarbons.

Therefore, the results of this study also proved that $H_2$ and CO increased with increasing $C_2H_4$. It could be noted that the structure of the GDE was distributed uniformly in catalyst compounds of Cu and Cu oxide. $C_2H_4$ was formed by carbene polymerization. It could be noted that the reason the faradaic efficiency of $C_2H_4$ was higher than that of $CH_4$, was that the polymerization between carbene was effective to faradaic efficiency of $C_2H_4$. Moreover, the dimerization of carbene occurred when $H_2$ was insufficient under the reaction condition of carbene.

## 3. Effect of Electrolyte Concentration

The selectivity of the reduction products depended remarkably on electrolysis conditions such as current density, $CO_2$ pressure, electrolyte concentration, and temperature. The effect of electrolyte concentration on the selectivity of reduction products was reported in this result. Table 1 shows that for faradaic efficiencies of the products at the $GDE_{(o)}$ in various concentrations of $KHCO_3$ solution, the Cu/C ratio ranged from 0.3 to 0.7 in the $GDE_{(o)}$. In the result of the Cu/C ratio of 0.5 to 0.7, the faradaic efficiencies of the $CO_2$ reduction products were in the 12.6% to 51.3% range at 0.1 M $KHCO_3$, 22.5% to 39.7% at 0.3 M $KHCO_3$ and 27% to 37% at 0.5 M $KHCO_3$.

As stated in Table 1, the faradaic efficiencies results of products were high at the potential of −2.0 V and −2.5 V in Cu/C ratio range from 0.3 to 0.5, at 0.1 M $KHCO_3$. As a result, in a comparison to the faradaic efficiencies of the Cu/C ratio of 0.5 and 0.7 and the concentration, the faradaic efficiencies of the $CO_2$ reduction products were high at a Cu/C ratio of 0.5. Moreover, those were higher at −2.0 V than at −2.5 V. Among the reduction products, CO was formed at the 0.1 M, CO and $C_2H_4$ was formed at the 0.3 M and $C_2H_4$ was formed at the 0.5 M as the major product.

Table 2 shows the faradaic efficiencies of products at the $GDE_{(w)}$ in $KHCO_3$ solution of various concentrations at the Cu/C ratio of 0.5. The results of the faradaic efficiencies of reduction product, excepting $H_2$, were in the 44.5% to 58.9% range at 0.1 M, 23.4% to 57.3% at 0.3 M and 44.5% to 65.0% at 0.5 M $KHCO_3$. When the main products are compared from Tables 1 and 2, the result is that the major product at the $GDE_{(w)}$ had a similar tendency to the $GDE_{(o)}$, but it was observed that $C_2H_4$ was the major product in 0.3 M and 0.5 M excepting 0.1 M $KHCO_3$ from Table 2.

These results are similar to those of Murata and Hori [1991].

**Table 2. Products of electrochemical reduction of $CO_2$ in Cu/PTFE-bonded GDE used water solvent at Cu/C ratio 0.5 and in various concentrations**

| Cu/C ratio | Conc. | Potential (V vs. SCE) | Faradaic efficiency (%) | | | | |
|---|---|---|---|---|---|---|---|
| | | | CO | $CH_4$ | $C_2H_4$ | $C_2H_5OH$ | Total |
| 0.50 | 0.1 M | −2.0 | 47.9 | 1.7 | 1.8 | 7.6 | 58.9 |
| | | −2.5 | 39.1 | 0.9 | 1.5 | 3.0 | 44.5 |
| | | −3.0 | 42.6 | 1.0 | 2.2 | 4.0 | 49.7 |
| | | −3.5 | 47.3 | 0.8 | 4.9 | 3.8 | 56.8 |
| 0.50 | 0.3 M | −2.0 | 9.8 | 0.3 | 13.3 | 0.0 | 23.4 |
| | | −2.5 | 7.8 | 0.4 | 25.6 | 0.0 | 33.8 |
| | | −3.0 | 6.4 | 0.3 | 23.8 | 0.0 | 30.5 |
| | | −3.5 | 7.3 | 1.2 | 37.6 | 11.2 | 57.3 |
| 0.50 | 0.5 M | −2.0 | 9.5 | 0.4 | 23.5 | 19.7 | 53.2 |
| | | −2.5 | 8.7 | 0.5 | 37.9 | 17.9 | 65.0 |
| | | −3.0 | 7.0 | 0.4 | 34.2 | 15.7 | 57.2 |
| | | −3.5 | 7.2 | 1.9 | 27.7 | 7.7 | 44.5 |

**Table 3. The change of electrolyte pH, before and after experiment (Cu/C ratio: 0.5)**

| Concentration | Potential (V. vs SCE) | pH | |
|---|---|---|---|
| | | Before | After |
| 0.1 M | −2.0 | 8.6 | 8.0 |
| | −2.5 | 8.6 | 7.9 |
| | −3.0 | 8.7 | 7.9 |
| | −3.5 | 8.7 | 7.9 |
| 0.3 M | −2.0 | 8.6 | 8.6 |
| | −2.5 | 8.6 | 8.7 |
| | −3.0 | 8.6 | 8.8 |
| | −3.5 | 8.6 | 8.9 |
| 0.5 M | −2.0 | 8.5 | 8.4 |
| | −2.5 | 8.6 | 8.6 |
| | −3.0 | 8.7 | 8.9 |
| | −3.5 | 8.6 | 8.8 |

They reported that $C_2H_4$ formation was relatively increased with the pH of the bulk solution in CO electrochemical reduction. Thus, in this study, it is reasonable that the $C_1/C_2$ ratio tends to have a smaller value in a higher concentration of hydrogen carbonate solution when pH becomes higher on the electrode. Table 3 shows the pH change of electrolyte. The pH before experiment was constantly in the 8.5 to 8.7 range without regard to concentration. The pH after that was decreased from 7.8 to 8.0 in 0.1 M $KHCO_3$, but, the pH increased slightly at 0.3 M and 0.5 M conditions. In a low concentration condition, it seemed that a decreasing pH might be due to the low buffer capacity of electrolyte.

### 4. Effect of Cu/C Ratio

The catalyst site provides the reaction layer for the electrochemical reduction of $CO_2$ and then the element of a catalyst is a major parameter for the reduction of $CO_2$. Fig. 4 shows the relationship between the Cu content and the reduction product at the $GDE_{(o)}$. The faradaic efficiencies of the $CO_2$ reduction products increased with the increase in the Cu/C ratio until it reached 0.5 and then decreased with further increase in Cu content. Therefore, it can be noted that a Cu/C ratio of 0.5 was optimum. In this condition, the faradaic efficiency of reduction product was 51.3% and that of $H_2$ was 47.6%.

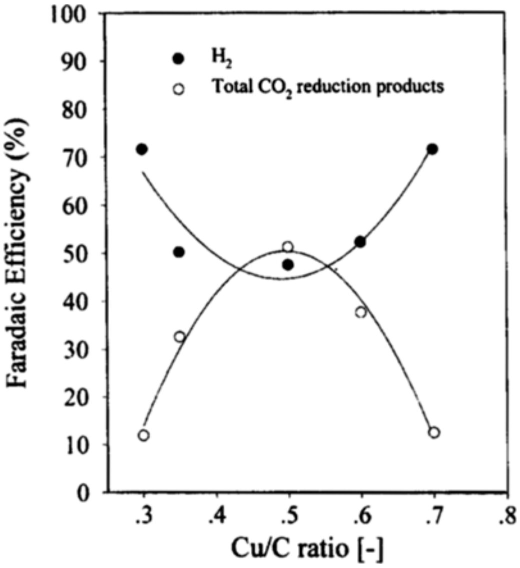

**Fig. 4. Faradaic efficiency of $CO_2$ electrochemical reduction products according to Cu/C ratio on the $GDE_{(o)}$ at −2.0 V in 0.1 M $KHCO_3$.**

Figs. 5 and 6 show the faradaic efficiencies of the reduction products as Cu content in 0.3 M $KHCO_3$ at −3.5 V and in 0.5 M $KHCO_3$ at −2.0 V. These results show that CO and alcohol increased with the Cu/C ratio, while $C_2H_4$ decreased. And then the faradaic efficiencies of total hydrocarbons were observed to be constant as the Cu/C ratio changed. Even though the optimum performance of 0.5 was observed in Fig. 4, it was not observed in Figs. 5 and 6. It could be thought that solvent change used for fabricating electrode influenced to the results.

Moreover, in the results of the electrode analysis presented in Fig. 7 and Table 4, there were large differences with respect to specific surface area and micro pore size with kinds of elec-

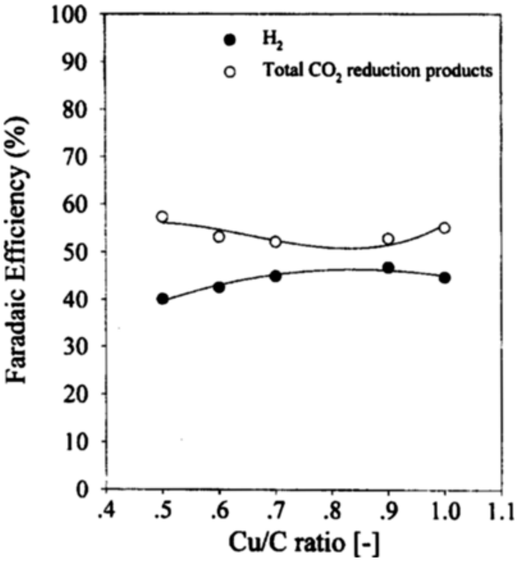

**Fig. 5. Faradaic efficiency of $CO_2$ electrochemical reduction products according to Cu/C ratio on the $GDE_{(w)}$ at −3.5 V in 0.3 M $KHCO_3$.**

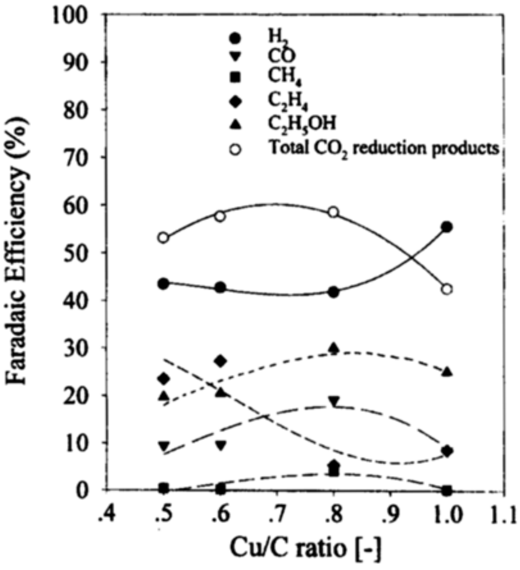

**Fig. 6. Faradaic efficiency of $CO_2$ electrochemical reduction products according to Cu/C ratio on the $GDE_{(w)}$ at −2.0 V in 0.5 M $KHCO_3$.**

trolyte. It has been reported that increasing the specific surface area and micro pore size in a GDE would improve the reaction rate of electrode. Therefore, it could be that the reason the optimum point was widely observed, from 0.5 to 0.8 in $CO_2$ reduction reaction using the $GDE_{(w)}$, was because of the differences of specific surface area and micro pore size.

Therefore it was found that Cu/C ratio control is necessary from the viewpoint of reaction rate and product selectivity.

## 5. Effect of Fabrication Method of Cu-PTFE Bonded GDE

Fig. 8 shows the reduction products at a Cu/C ratio of 0.5 in 0.1 M $KHCO_3$. In this figure, hydrogen evolution was 50% of the reduction products, while total hydrocarbon was less than 50%. Fig. 9 shows the results of $GDE_{(w)}$ under the same conditions. In Fig. 8, CO is increased with electrode potential except at −2.0 V. The faradaic efficiency of CO is greater than 40%, while the others are less than 10%.

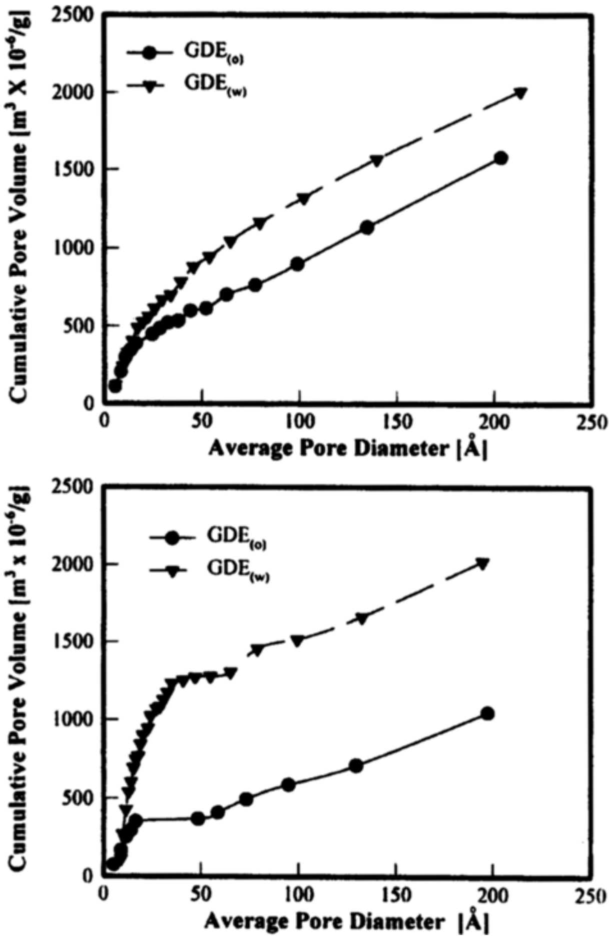

**Fig. 7. Cumulative pore volume according to average pore diameter of the GDEs at Cu/C ratio 0.7.**

**Table 4. BET surface area of $GDE_{(o)}$ and $GDE_{(w)}$ at Cu/C ratio 0.5 and 0.7** [$m^2$/g]

| Solvent | 0.5 | 0.7 |
|---|---|---|
| $GDE_{(o)}$ | 0.8945 | 1.8198 |
| $GDE_{(w)}$ | 1.4383 | 2.5129 |

There were some differences with the two kinds of electrodes with respect to the reduction products. For the $GDE_{(o)}$, the faradaic efficiencies of $H_2$, CO and others were 47.6%, 22.5% and 28.8%, respectively. For the $GDEs_{(w)}$, the faradaic efficiencies of $H_2$ and CO were 44%, 47.9%, respectively. The reduction efficiencies at the $GDE_{(w)}$ are better than those in the electrochemical reduction of $CO_2$ on the $GDE_{(o)}$.

Table 5 shows the faradaic efficiency of the $CO_2$ reduction product according to the kinds of GDEs. In these results with respect to the faradaic efficiencies of the $CO_2$ reduction products, the $GDE_{(w)}$ was more efficient than those of organic solvents (isobutanol+EtOH). Also, the results of electrolyte concentration were similar to those of organic solvents.

The $GDEs_{(w)}$ had higher reduction rates than the $GDEs_{(o)}$. It

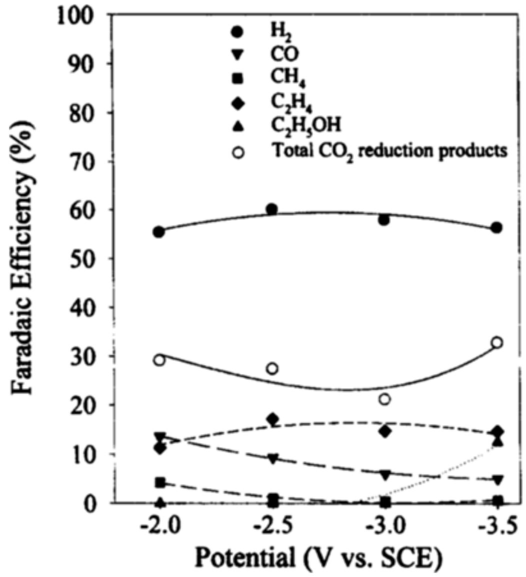

**Fig. 8. Faradaic efficiency of $CO_2$ electrochemical reduction products according to electrode potential on the $GDE_{(o)}$ at Cu/C ratio of 0.5 in 0.1 M $KHCO_3$.**

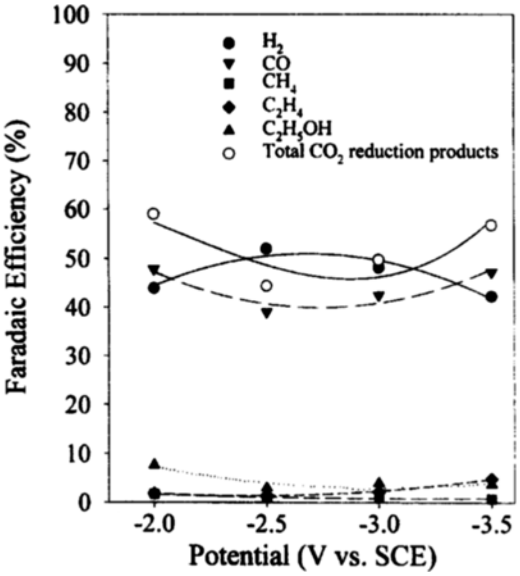

**Fig. 9. Faradaic efficiency of $CO_2$ electrochemical reduction products according to electrode potential on the $GDE_{(w)}$ at Cu/C ratio of 0.5 in 0.1 M $KHCO_3$.**

**Table 5. $CO_2$ reduction product according to kinds of GDE**

| Concentration | Cu/C ratio | −2.0 V (vs. SCE) | | −2.5 V (vs. SCE) | |
|---|---|---|---|---|---|
| | | Isobutanol+EtOH | Water | Isobutanol+EtOH | Water |
| 0.1 M | 0.5 | 51.3 | 58.9 | 41.9 | 44.5 |
| | 0.6 | 37.7 | 49.0 | 31.4 | 63.4 |
| | 0.7 | 12.6 | 35.9 | 12.6 | 36.6 |
| 0.3 M | 0.5 | 39.7 | 23.4 | 22.5 | 33.8 |
| | 0.6 | 29.8 | 34.2 | 33.6 | 34.0 |
| | 0.7 | 24.4 | 30.1 | 30.3 | 40.0 |
| 0.5 M | 0.5 | 29.3 | 53.2 | 27.0 | 65.0 |
| | 0.6 | 35.8 | 57.2 | 32.6 | 51.3 |
| | 0.7 | 37.0 | 38.2 | 33.4 | 43.9 |

was found that the rate of reaction step from carbon monoxide to $C_2H_4$ was much faster than that from CO to methane.

## CONCLUSION

The aim of this study was to investigate the influence of the structure of GDEs on $CO_2$ reduction. Carbon/PTFE/Catalyst composition and solvent selection were major factors. According to the concentration of electrolyte, the electrochemical reduction of $CO_2$ was investigated and the conclusions obtained are summarized below.

1. With the reduction of $CO_2$ according to the operational potential at the GDE involving Cu as a catalyst, CO was the main product according to the electrolyte concentration. The faradaic efficiency of ethylene increased with electrolyte concentration. But the faradaic efficiency of $CH_4$ was relatively less than that of CO and that of $C_2H_4$ was almost constant. It was found that the reaction path of $CH_4$ was different from that of $C_2H_4$.

2. From the effect of electrolyte concentration on carbon dioxide reduction, when the electrolyte concentration was increased, the faradaic efficiency of ethylene and pH was increased. Thus, it seemed that ethylene was significantly influenced by pH.

3. From the result of the faradaic efficiency of the $CO_2$ reduction products, a Cu/C ratio of 0.5 reveals an optimum performance with organic solvent. At the $GDE_{(w)}$, however, the faradaic efficiencies of hydrocarbons were almost constant according to the Cu/C ratio. By using the $GDEs_{(w)}$, it was estimated that the selectivity for a specific product was improved by copper content.

4. From the result of $CO_2$ reduction efficiency, the $GDE_{(w)}$ was better than the $GDE_{(o)}$, and the $GDE_{(w)}$ had a higher rate of $CO_2$ reduction than that of the $GDE_{(o)}$. It was also noted that the CO to $C_2H_4$ reaction rate was much faster than the CO to $CH_4$.

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## NOMENCLATURE

$GDE_{(o)}$ : Cu/PTFE bonded GDEs using organic solvent (isobutanol + EtOH)
$GDE_{(w)}$ : Cu/PTFE bonded GDEs using water as solvent

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