Electrochemical Reduction of High Pressure Carbon Dioxide on Metal Electrodes and Gas Diffusion Electrodes

Kohjiro Hara and Tadayoshi Sakata

Department of Electronic Chemistry, Interdisciplinary Graduate School of

Science and Engineering, Tokyo Institute of Technology, 4259 Nagatsuta,

Midori-ku, Yokohama 226, Japan

(Received August 22,1995)

Abstract : Electrochemical reduction of carbon dioxide under high pressure on Fe electrodes and a gas diffusion electrode containing Pt catalyst (Pt–GDE) had been investigated. Formic acid was formed on Fe electrode with a faradaic efficiency of 60% at a current density of 120 mA cm^{-2} under 30 atm of CO_2. Hydrocarbons such as CH_4, C_2H_6, C_3H_6, 1-C_4H_8, and n-C_5H_{12} are also formed. The distribution of hydrocarbons followed well the Schultz-Flory distribution. CH_4 was formed efficiently as the main reduction product on Pt–GDE.

Keywords : High pressure carbon dioxide, Electrochemical reduction, Gas diffusion electrode

1. Introduction

The electrochemical reduction of CO_2 on various metal electrodes has been studied extensively by many workers, and it has been found that the reduction products depend strongly on the electrode material[1-10]. For example, formic acid is the predominant reduction product on Hg, Pb, In, and Sn electrodes under 1atm CO_2 in aqueous solutions, but the main reduction product on Ag, Au, Zu, and Pd electrodes is carbon monoxide. Methane, ethylene, and ethanol are formed mainly on Cu electrode and in

case of 8–10 metals (Fe, Ni, Co, and, Pt), the predominant reduction product is hydrogen via the reduction of water. However, one of the problems in the electrochemical reduction of CO_2 is the low solubility of CO_2 in water (0.033 mol dm^{-3} at 25°C under 1 atm[11]) which leads to mass transfer limitations for large current density (reaction rate) electrolyses.

Recently, the authors have investigated the electrochemical reduction of CO_2 under high pressure (< 60 atm) on various metal electrodes in order to increase the concentration of CO_2 in aqueous solution and the current density for CO_2 reduction[12–16]. From these results, the current density for CO_2 reduction on many electrodes increased remarkably with increasing the CO_2 pressure. Interestingly, carbon monoxide and/or formic acid which were produced in very small quantities under 1 atm CO_2, were formed with high Faradaic efficiencies under high CO_2 pressure on 8–10 metals electrodes. Moreover, hydrocarbons such as methane, ethane, ethylene, propane, and butane were formed on Fe, Co, and Ni electrodes under high pressure. In this paper, we report the formation of hydrocarbons on the electrochemical reduction of CO_2 under high pressure on Fe electrodes in aqueous solution.

On the other hand, it seems advantageous to carry out the electrochemical reduction of gaseous CO_2 on gas diffusion electrodes containing electrocatalysts which have been developed for the fuel cells in order to increase the current density for

CO_2 reduction. Some investigations of the electrochemical reduction of 1atm of CO_2 on gas diffusion electrodes containing various metal and metal compound electrocatalysts have been reported[17]. In this paper, we report the electrochemical reduction of gaseous CO_2 under high pressure on gas diffusion electrodes containing Pt.

2. Experimental

The electrolyses under high pressure were carried out using a three compartments glass cell in a stainless autoclave, as shown in a previous article[16]. The catholyte compartment was separated from the anolyte one by a cation exchange membrane (Nafion 417). In the case of the electrolyses using gas diffusion electrodes, the catholyte compartment was filled with gaseous CO_2, and the anolyte one was filled with the aqueous electrolyte. The electrolyte were 0.1 mol dm^{-3} $KClO_4$ and 0.5 mol dm^{-3} $KHCO_3$ aqueous solutions, prepared from reagent grade chemicals and distilled water (Wako Pure Chemical Industries, LTD). $KClO_4$ was recrystallized by distilled water for purification. Moreover, the electrolyte was purified by pre-electrolysis with a Pt black cathode to eliminate heavy metal impurities before electrolyses.

Fe wires (ϕ 0.5 mm; apparent surface area, 0.16 cm^2), which were electropolished in $HClO_4+(CH_3CO)O+H_2O$ (18–75–7) solution for

Table 1 Effect of current density on the electrochemical reduction of CO_2 under 30 atm on Fe electrodes

Current density / mA cm^{-2}	E^a / V	faradaic efficiency / %								
		CH$_4$	C$_2$H$_6$	C$_2$H$_4$	C$_3$H$_8$	C$_3$H$_6$	CO	HCOO$^-$	H$_2$	Total
30	−1.37	1.89	0.46	0.21	0.39	0.27	trace	15.7	62.6	81.7
60	−1.53	1.24	0.43	0.22	0.40	0.25	4.5	59.5	23.1	89.8
120	−1.61	1.19	0.28	0.12	0.20	0.13	5.4	59.6	23.5	90.5
200	−1.63	1.42	0.41	0.19	0.34	0.20	10.0	34.6	40.1	87.5
300	−1.72	1.42	0.19	0.09	0.10	0.06	3.2	46.0	37.5	88.6
400	−1.73	1.66	0.35	0.17	0.21	0.14	2.0	22.2	58.2	85.0

Working electrode, Fe wire (99.5%, 0.16 cm^2); electrolyte, 0.1 mol dm^{-3} KClO$_4$; passed charge, 300 C.

^{a} The potential were corrected with an *IR* compensation instrument (vs. Ag/AgCl)

30 s and were rinsed with distilled water before electrolyses, were employed as the working electrode. A gas diffusion electrode containing Pt catalyst (Pt–GDE, the amount of incorporated Pt, 0.56 mg cm^{-2}; apparent surface area, 1 cm^2) which were purchased from Tanaka Noble Metal, Ctd., were also employed as the working electrode. The Pt catalyst layer was directed toward the CO_2 gas phase while the gas diffusion layer faced the aqueous electrolyte. The following is the cell configuration.

Gaseous CO_2 / Pt catalyst layer / gas diffusion layer

/ electrolyte / Pt

A Pt wire was employed as an anode, and a reference electrode was Ag / AgCl / saturated KCl. CO_2 of 99.99% purity was introduced directly into the autoclave without purification.

The electrolyses were carried out galvanostatically at 25°C using a potentiostat /

galvanostat (Hokuto, HA–501) connected in series with a coulometer (Hokuto, HF–201). The electrode potential was corrected with an *IR* compensation instrument (Hokuto, HI–203). Reduction products such as hydrocarbons, carbon monoxide, ethanol, and hydrogen were quantitatively analyzed by a gas chromatograph, and formic acid was determined by an HPLC as had been described in detail in a previous article [16].

3. Results and Discussion

3.1. Fe electrode

The faradaic efficiencies of the reduction products on the electrochemical reduction of CO_2 under 30 atm on Fe electrodes in KClO$_4$ aqueous solution at current density of 30–400 mA cm^{-2} are shown in Table 1. Formic acid formed as a main CO_2

reduction product with a high faradaic efficiency of 60% (60–120 mA cm^{-2}). The maximum partial current density for formic acid formation reached 138 mA cm^{-2}. The reduction product was only hydrogen formed by reduction of water under 1 atm CO_2 at the constant current density of 5 mA cm^{-2} in 0.1 mol dm^{-3} $KHCO_3$ aqueous solution [18, 19]. It is interesting that CO_2 is efficiently reduced to formic acid even on Fe electrodes by the high pressure electrolyses. The faradaic efficiency of carbon monoxide was much less than that of formic acid at each current density (< 10%).

As shown in Table 1, hydrocarbons such as methane, ethane, ethylene, and propane formed at each current density condition. The maximum partial current density for methane and total hydrocarbon

Fig. 1. Schultz–Flory plot for hydrocarbons formed on the electrochemical reduction of CO_2 under 30 atm on a Fe electrode at 100 mA cm^{-2} in 0.1 mol dm^{-3} $KClO_4$.

formations were 6.6 and 10.4 mA cm^{-2} at the current density of 400 mA cm^{-2}. Moreover, the formation of longer chain hydrocarbons such as 1-butene, trans-2-butene, iso and normal pentanes was observed under 30 atm at the current density of 100 mA cm^{-2} (faradaic efficiencies: butene; 0.5%, pentane; 0.2%), in addition to methane, ethane, ethylene, and propane.

The dependence of the amounts of hydrocarbons on the passed charge under 30 atm on Fe electrodes at 60 mA cm^{-2} was investigated. Amounts of each hydrocarbon increased with increasing the passed charge at least until 1000 C. Electrolysis for control experiment was carried out under Ar (30 atm). No hydrocarbon was produced by this electrolysis. These results demonstrate that hydrocarbons were formed by the electrochemical reduction of CO_2 on Fe electrodes.

The distribution of the hydrocarbons formed by the Fisher–Tropsch (FT) reaction is known to follow the Schultz–Flory (SF) distribution. The SF distribution is expressed by the following equation

$$\ln (M_p / P) = \ln (\ln^2 \alpha) + P \ln \alpha$$

In this equation, M_p is the weight percent of the hydrocarbon whose carbon number is P, α represents the probability of chain growth. Cook showed that the hydrocarbon formation in the electrochemical reduction of CO_2 on Pd electrodes under 1 atm [9] followed the SF distribution, and suggested that the mechanism of hydrocarbon formation on Pd electrodes was similar to the FT reaction [20, 21].
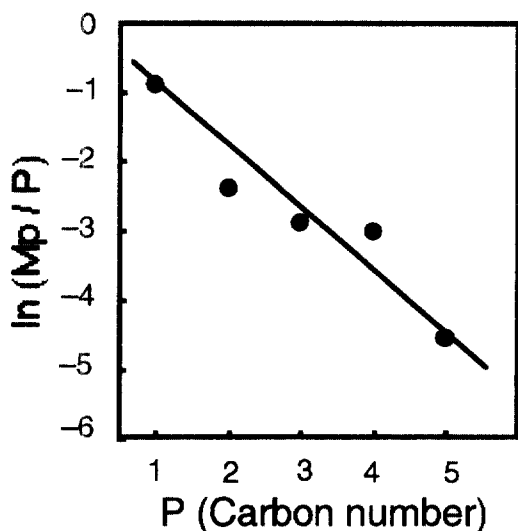
Moreover, under high pressure conditions, the formation of hydrocarbons on Ni electrode also followed the SF distribution[13, 14]. Fig. 1 shows the SF distribution analysis of hydrocarbons formed on a Fe electrode under CO_2 30 atm at the current density of 100 mA cm^{-2}. As can be seen in Fig. 1, linearity between ln (M_p / P) and P is observed. Thus, the hydrocarbon formation on Fe electrodes also follows the SF distribution. This observation suggests that hydrocarbons formed on Fe electrodes via the FT reaction path, i.e., polymerization of carbene species (CH_2) formed by the reaction of adsorbed carbon monoxide with adsorbed hydrogen on the electrode surface.

3.2. Gas diffusion electrode containing Pt catalyst (Pt–GDE)

Table 2 shows the current density dependence of the reduction products by the electrochemical reduction of CO_2 under 30 atm on the Pt–GDE. The CO_2 reduction products such as methane, ethane, ethylene, ethanol, carbon monoxide, and formic acid were produced. The faradaic efficiency for total CO_2 reduction reached 41–50% at each current density and a quite large partial current density of 415 mA cm^{-2} for CO_2 reduction was achieved. Methane formed as a main CO_2 reduction product at faradaic efficiencies of 17–35%. On the control experiment under Ar 30 atm instead of CO_2, only hydrogen was produced by the reduction of water. Moreover, no products of CO_2 reduction were produced by the electrolysis using the gas diffusion electrode without Pt catalyst. These results shows that the products such as methane, ethanol, carbon monoxide, and formic acid were produced by CO_2 reduction and Pt catalyst plays an important role for CO_2 reduction. Interestingly, when the Pt catalyst layer was directed toward the electrolyte (i.e., the gas diffusion layer facing the gaseous CO_2), methane was hardly produced, and the predominant reduction product was hydrogen even under high pressure CO_2. Thus, CO_2

Table 2 Effect of current density on CO_2 reduction on Pt–GDE under 30 atm of CO_2.

| Current density | E^a | faradaic efficiency / % | | | | | | | |
/mA cm^{-2}	/V	CH_4	C_2H_6	C_2H_4	C_2H_5OH	CO	$HCOO^-$	H_2	Total
100	−1.65	17.6	0.06	0.63	0.6	17.1	12.0	32.3	80.3
200	−1.73	31.3	0.10	0.59	1.2	6.4	9.5	30.5	79.6
400	−1.82	27.9	0.10	0.46	1.9	3.0	8.8	36.0	78.2
600	−1.93	33.4	0.08	0.67	2.3	3.3	10.5	28.8	79.1
900	−1.92	34.8	0.14	0.50	2.2	2.0	7.9	33.3	79.4

Working electrode, Pt–GDE; electrolyte, 0.5 mol dm^{-3} $KHCO_3$; passed charge, 150 C.

a The potential were corrected with an *IR* compensation instrument (vs. Ag/AgCl).

was efficiently reduced to methane only when the Pt catalyst layer was directed toward the gaseous CO_2.

As shown in Table 2, the faradaic efficiency for methane formation increased with increasing the current density, whereas that for carbon monoxide formation decreased. We have reported that carbon monoxide was formed as the main product at less negative potentials (−1.5 V vs. Ag/AgCl, i.e., low current density), and at more negative potentials (−1.7 V vs. Ag/AgCl, i.e., high current density), methane, ethylene, and ethanol were formed on a Cu electrode under 30 atm of CO_2 in aqueous electrolytes [22]. The tendency that methane formation increases and carbon monoxide formation decreases with increasing the current density on the Pt–GDE is similar to that on the Cu electrode. Faradaic efficiencies for formic acid and hydrogen were hardly

changed by increasing the current density (8–12% and 29–37%, respectively).

The CO_2 pressure dependence of methane and hydrogen by electrolyses at the constant current density of 600 mA cm^{-2} for 150 C is shown in Fig. 2. Because of the limitation of CO_2 transfer to electrocatalyst, hydrogen formed by the reduction of water was predominant under 1 atm of CO_2. The faradaic efficiency for methane formation increased remarkably with increasing CO_2 pressure. Thus, CO_2 pressure (i.e., concentration of CO_2) is important for the methane formation. In this experiment, the electrode potential was hardly changed with increasing CO_2 pressure. From this result, it is concluded that the change of the product selectivity from hydrogen to methane was caused by the change of the CO_2 pressure, and not by the change of the electrode potential.
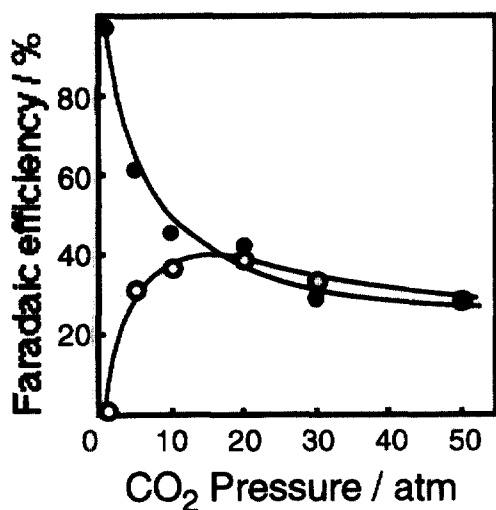
Fig. 2. The dependence of the faradaic efficiencies for CH_4 and H_2 on the CO_2 pressure at 600 mA cm^{-2} for 150 C: (○) CH_4; (●) H_2.

References

1. Y. Hori, K. Kikuchi and S. Suzuki, *Chem. Lett.*,

1695 (1985).

2. Y. Hori, A. Murata, K. Kikuchi and S. Suzuki,
   J. Chem. Soc., Chem. Commun., 728 (1987).

3. H. Noda, S. Ikeda, Y. Oda, K. Imai, M. Maeda
   and K. Ito, *Bull. Chem. Soc. Jpn.*, **63**, 2459
   (1990).

4. S. Ikeda, T. Takagi and K. Ito, *Bull Chem. Soc.
   Jpn.*, **60**, 2517 (1987).

5. D. P. Summers, S. Leach and J. K. W. Frese,
   J. Electroanal. Chem., **205**, 219 (1986).

6. D. P. Summers and J. K. W. Frese, *Langmuir*,
   4, 51 (1988).

7. J. K. W. Frese and S. Leach, *J. Electrochem. Soc.*,
   132, 259 (1985).

8. M. Azuma, K. Hashimoto, M. Hiramoto, M.
   Watanabe and T. Sakata, *J. Electrochem. Soc.*,
   137, 1772 (1990).

9. M. Azuma, K. Hashimoto, M. Watanabe and
   T. Sakata, *J. Electroanal. Chem.*, **294**, 299 (1990)

.10. I. Taniguchi in J. O'M. Bockris, R. E. White
   and B. E. Conway (Eds.), "Modern Aspects of
   Electrochemistry Vol. 20", Plenum Press, New
   York, 1989, p. 327.

11. D. R. Palmer and R. van Eldik, Chem. Rev., **83**,
   651 (1983).

12. S. Nakagawa, A. Kudo, M. Azuma and T. Sakata,
   J. Electroanal. Chem., **308**, 339
   (1991).

13. A. Kudo, S. Nakagawa, A. Tsuneto and T. Sakata,
   J. Electrochem. Soc., **140**, 1541 (1993).

14. K. Hara, A. Tsuneto, A. Kudo and T. Sakata,
   Shokubai (Catalyst), **35**, 513 (1993).

15. K. Hara, A. Kudo and T. Sakata, *J. Electroanal.
   Chem.*, **386**, 257 (1995).

16. K. Hara, A. Kudo and T. Sakata, *J. Electroanal.
   Chem.*, **391**, 141 (1995).

17. K. Hara, A. Kudo and T. Sakata and M.Watanabe,
   J. Electrochem. Soc., **142**, L57 (1995).

18. A. Murata and Y. Hori, *Denki Kagaku
   (Electrochemistry)*, **59**, 499 (1991).

19. Y. Hori, H. Wakebe, T. Tsukamoto and O. Koga,
   Electrochimica Acta, **39**, 1833 (1994).

20. R. L. Cook, R. C. MacDuff and A. F. Sammells,
   in Proceeding of International Symposium on
   Chemical Fixation of Carbon Dioxide, Nagoya,
   1991 p. 39.

21. A. F. Sammells and R. L. Cook in, B. P. Sullivan,
   K. Krist and H. E. Guard (eds.), "Electrochemical
   and Electrocatalytic Reaction of Carbon Dioxide",
   Elsevier Sci. Pub., Amsterdam, 1993, p. 255.

22. K. Hara, A. Tsuneto, A. Kudo and T. Sakata,
   J. Electrochem. Soc., **141**, 2097 (1994).