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# Electrochemical reduction of $CO_2$ in copper particle-suspended methanol

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## Abstract

The electrochemical reduction of $CO_2$ in copper particle-suspended methanol was investigated with lead and zinc electrodes. Without copper particles, only formic acid and carbon monoxide were formed in the electrochemical reduction of $CO_2$, and the formation of hydrocarbons could not be observed. On the contrary, hydrocarbons were obtained in the copper particle-suspended electrolyte. The Faradaic efficiencies for methane and ethylene increased gradually with increasing the amounts of copper particles, however the current efficiencies of formic acid and CO decreased. The maximum formation efficiencies of methane were of 6% and 12%, at Pb and Zn electrodes, respectively. It was found to be able to roughly change and control the reduction product distributions by the addition of metal particles into the catholyte in the electrochemical reduction of $CO_2$.

*Keywords:* Electrochemical reduction of $CO_2$; Copper particle suspension; Methanol; Methane; Pb and Zn electrodes

## 1. Introduction

Carbon dioxide ($CO_2$) represents a potential source of C1 feedstock for the production of chemicals and fuels in view of the vastness of its supply. Therefore, the interest in the development of the technologies that achieve multielectron reduction of $CO_2$ remains extremely high. The electrochemical reduction of $CO_2$, as well as the electrochemical modification of the substrates via simple procedures, has been proposed for the reduction and conversion of $CO_2$ [1–3].

Recently, many investigators have actively studied the electrochemical reduction of $CO_2$ using various metal electrodes in organic solvents, because organic aprotic solvents dissolve much more $CO_2$ than water does [4–7]. It has been described that low reduced products containing carbon monoxide, oxalic acid and formic acid were produced by the electroreduction of $CO_2$ in dimethyl sulfoxide, *N*,*N*-dimethyl formamide, propylene carbonate and acetonitrile. However, even at a copper electrode, few hydrocarbons such as methane and ethylene have been obtained in these organic solvents [7].

Methanol is a better solvent of $CO_2$ than water, particularly at low temperature. The solubility of $CO_2$ in methanol is approximately five times that in water, at ambient temperature, and more than seven times that in water, at temperatures below 273 K [8–10]. Therefore, methanol has been industrially used as a physical absorbent of $CO_2$ in the Rectisol method, at 243–263 K [10]. Currently, over 70 large-scale plants apply the Rectisol process. Therefore, the direct electrochemical reduction of $CO_2$ in methanol is an advantageous choice, especially when the process is performed under energetically efficient conditions.

Recently, many research groups (our group [11–24], Fijishima and co-workers [25], Koleli et al. [26], Schrebler et al. [27], Eggins et al. [28]) have brought focus into the electrochemical reduction of $CO_2$ in methanol-based electrolyte. In our groups, the electrochemical reduction of $CO_2$ with a copper electrode in the methanol-based electrolyte has been actively investigated at low temperature [11,12,16–21]. From these studies, it has been found that the methanol at low temperature was the best electrolyte to obtain hydrocarbons, compared to various organic solvents.

The photocatalytic reduction of $CO_2$ has been exclusively performed in the semiconductor suspension when the photocatalyst is the form of powder or particle [1–3]. However, in the electrochemical reduction of $CO_2$ in both aqueous and nonaqueous organic solutions, little information on the electrolysis in the suspension has been reported [29]. This study deals mainly with the electrochemical reduction of $CO_2$ at lead and zinc electrodes in metal particle-suspended methanol.

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## 2. Experimental

The apparatus and experimental conditions for the electrochemical reduction of $CO_2$ are shown in Table 1. Electrochemical reduction of $CO_2$ was performed in a laboratory-made, divided H-type cell. An Aldrich Nafion 117-type ion exchange membrane (0.18 mm thickness) was used as the diaphragm. The cathode potential was measured with respect to an Ag/AgCl saturated KCl electrode that was connected with the catholyte through the Luggin capillary (the agar salt bridge), in order to compensate for the ohmic potential drop due to solution resistance between the reference and working electrodes.

Methanol (99%, Nacalai Tesque, Inc., Japan) was used as received without further purification. Water content in the pure methanol was less than 0.1% (confirmed by the Karl Fischer test). Sodium hydroxide (96%, Nacalai Tesque, Inc.) was used as the ionophore in the methanol-based electrolyte. It was reported in a previous work [21] that pH of methanol with 80 mmol $dm^{-3}$ NaOH supporting salt at 243 K was approximately 14 and the pH after the saturation of the catholyte with $CO_2$ was about 5.3. Copper particles (CUE08PB, Kojundo Chemical Laboratory Co., Ltd.) were added into the catholyte for the metal particle suspension. Mechanical processing of the Pb, Zn and Pt electrodes required polishing each surface with successively finer grades of alumina powder (Baikalox emulsion, manufactured by Baikowski International Co.) down to 0.05 μm, followed by the removal of grease with acetone. The Pb electrode was chemically conditioned by immersion in 18 mol $dm^{-3}$ sulfuric acid for 20 s. The Pt anode was activated electrochemically at 500 mA for 100 s in 14.7 mol $dm^{-3}$ phosphoric acid. Following the above treatment, the electrodes were rinsed with both water and ethanol.

Table 1
Apparatus and experimental conditions

| | |
|---|---|
| Electrochemical reduction | |
| Cell | H-type cell |
| Potentiostat/galvanostate | Hokuto HA-301 |
| Coulometer | Integrator 1109 (Fusou Seisakujyo, Inc., Japan) |
| Potential sweep | Hokuto HB-111 function generator |
| XY recorder | Graphtec WX1100 |
| Working electrode | Pb foil (30 mm × 20 mm, 0.1 mm thickness, 99.98% purity)<br>Zn foil (30 mm × 20 mm, 0.2 mm thickness, 99.98% purity) |
| Counter electrode | Pt foil (30 mm × 20 mm, 0.1 mm thickness, 99.98% purity) |
| Reference electrode | Ag/AgCl saturated KCl (Horiba, 2060A-10T) |
| Electolyte | |
| Catholyte | 80 mmol $dm^{-3}$ NaOH in methanol (Cu particle added [Ø 1 μm, 99.99% purity]) |
| Anolyte | 300 mmol $dm^{-3}$ KOH in methanol |
| Carbon dioxide | 99.9999% purity |
| Potential | −2.3 to −2.9 V vs. Ag/AgCl saturated KCl |
| Temperature | 243 ± 0.5 K |
| Product analysis | |
| Gas products | Gas chromatography<br>TCD (GL Sciences GC-320, Molecular Sieve 5A; 13X-S, Ar and He carrier gas)<br>FID (GL Sciences GC-353B, Porapak Q, $N_2$ carrier gas) |
| Liquid products | HPLC with UV detector (Hitachi L4000)<br>TCD and FID gas chromatography |

A discontinuous electroreduction procedure was used. First, $CO_2$ gas was bubbled into the methanol catholyte for 1 h at a rate of 30 mL $min^{-1}$. Then, the $CO_2$-saturated solution was reduced electrolytically at cathodic polarizations in the range from −2.3 to −2.9 V versus Ag/AgCl, saturated KCl. The catholyte was magnetically stirred for maintaining the suspension conditions. The Faradic efficiencies of formation for the main products were calculated from the total charge passed during batch electrolyses, which was set to 50 C. Gaseous products obtained during the electroreduction were collected in a gas collector and were analyzed by GC. Products soluble in the catholyte were analyzed by using HPLC and GC. In control experiment, nitrogen gas was used.

## 3. Results and discussion

Literature data [8,9] for the solubility of $CO_2$ in pure methanol and water, at 288 K, were of 4.6 and 1.07 $cm^3\ cm^{-3}$, respectively. It has been presented in a previous study [21] that the solubility of $CO_2$ in a solution of 80 mmol $dm^{-3}$ NaOH/methanol, at 243 K, was approximately 15 $cm^3\ cm^{-3}$ (about 670 μmol $CO_2/cm^3$ methanol). Although $NaHCO_3$ may be formed in the methanol while bubbling $CO_2$ through the solution for several minutes, the amount is assumed to be very small or negligible, since one cannot observe any precipitate. Therefore, a large proportion of $CO_2$ can be considered to be physically dissolved, i.e., under intact form in the methanol catholyte. The increased solubility of carbon dioxide in our system relative to water appears to be very advantageous. In the electrochemical reduction of $CO_2$ at lead and zinc wire electrodes in methanol-based electrolyte, the predominant formations of formic acid and carbon monoxide were observed, respectively [13,22], and the current efficiency of methane was less than 0.4%. On the other hand, it has been found in previous works [11,12,16–21] that copper electrode was very effective for the formation of hydrocarbon in the electrochemical $CO_2$ reduction in methanol-based catholyte. Hence, lead and zinc cathodes in combination with the copper particle suspension were evaluated in the present work. The electrolysis was performed at 243 K because temperature in the Rectisol process is customarily in the range of 243–263 K [10].

### 3.1. Effect of addition of copper particles

The influence of the addition of copper particles on the electrochemical reduction of $CO_2$ at Pb and Zn electrodes in methanol is illustrated in Figs. 1 and 2. The reproducibility of the electrolysis (relative standard deviation for faradic efficiency of the reduction products) was better than R.S.D. 10% for five repeated measurements. The current densities increased gradu-

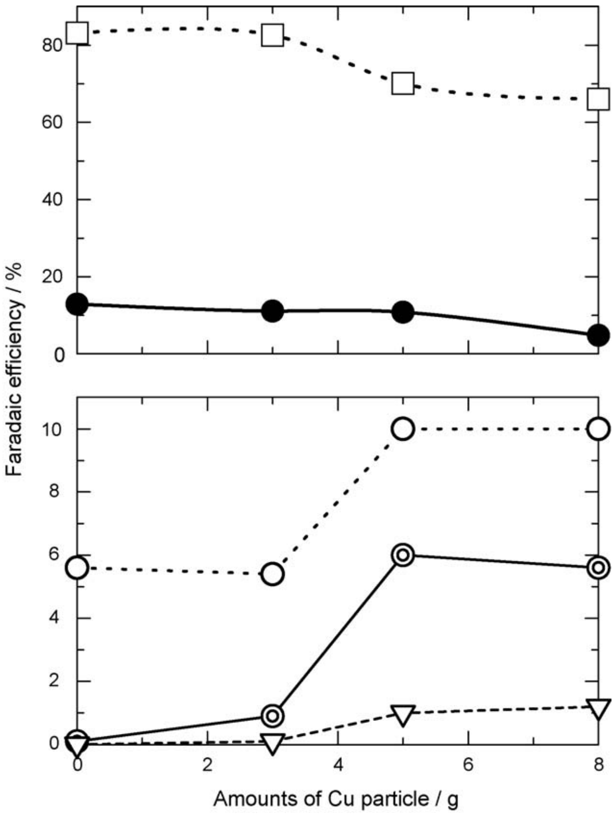

Fig. 1. Effect of amounts of metal particles on Faradaic efficiencies for the products by electrochemical reduction of $CO_2$ at lead electrode in copper particle-suspended methanol. ◎, $CH_4$; ▽, $C_2H_4$; ○, CO; □, HCOOH; ●, $H_2$; potential, −2.5 V; temperature, 243 K.

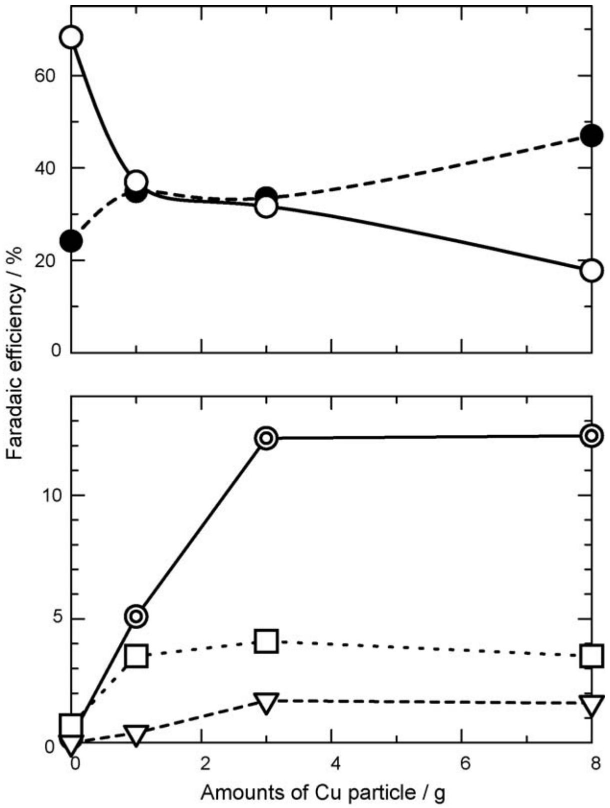

Fig. 2. Effect of amounts of metal particles on Faradaic efficiencies for the products by electrochemical reduction of $CO_2$ at zinc electrode in copper particle-suspended methanol. ◎, $CH_4$; ▽, $C_2H_4$; ○, CO; □, HCOOH; ●, $H_2$; potential, −2.5 V; temperature, 243 K.

ally as the copper particle amounts increased in the electrolyte. In the normal electrochemical reduction of $CO_2$ at Pb and Zn foil electrodes (without Cu particles), the distributions of the reduction products were nearly the same as those obtained with the wire electrodes [13,22], except for much higher Faradaic efficiency of hydrogen. The reason for higher formation efficiency of hydrogen compared to that at the wire electrodes may be due to the difference of the electrode shape. On Pb electrode, the formation efficiencies of methane, ethylene and CO tended to increase with increasing the amounts of copper particles in the methanol catholyte. The maximum efficiencies of methane and ethylene were of 6.0% and 1.2% with 5 and 8 g of copper particles, respectively. The maximum total hydrocarbon efficiency was obtained with 5 g of Cu particles (7.0%). On the other hand, the current efficiencies of formic acid and hydrogen decreased gradually with an increase in the particle amounts. With Zn electrode, the Faradaic efficiencies of methane, ethylene, formic acid and hydrogen roughly increased with the amounts of copper particles. After the addition of more than 3 g of Cu particles, the formation efficiencies of methane and ethylene were almost constant. Only the current efficiency for CO decreased sharply with increasing the copper powder amounts. In the electrochemical $CO_2$ reduction at Cu electrode in NaOH/methanol-based electrolyte, the Faradaic efficiency of methane was extremely high (for example, 63.0% at −4.0 V [21]). Although the formation efficiency for methane in this work was worse than that obtained with Cu electrode, it was found that hydrocarbons such as methane and ethylene could be formed on metal electrodes besides copper in the electrochemical reduction of $CO_2$ in copper particle-suspended methanol. For the subsequent experiments, 5 and 3 g of copper particles were added into the methanol-based catholyte with lead and zinc electrodes, respectively.

### 3.2. *Current–potential curves*

The current–potential curves at the Pb and Zn electrodes in Cu particle-suspended methanol were recorded at 243 K. The potential was scanned at a sweep rate of 50 mV $s^{-1}$. The typical current–potential curves are illustrated in Fig. 3. The onset (starting) potentials of the cathodic current, i.e. those potential values at which a current density of 0.1 mA $cm^{-2}$ is observed, in $CO_2$-saturated methanol were approximately −1.9 and −0.9 V on Pb and Zn cathodes, respectively. No voltammetric peak was observed in the potential range down to −3.0 V because further $CO_2$ reduction may proceed with increasingly negative potentials. Once the onset potentials were determined from polarization experiments, we attempted to investigate the effect of potential on the electrochemical reduction of $CO_2$ in Cu particle-suspended methanol.

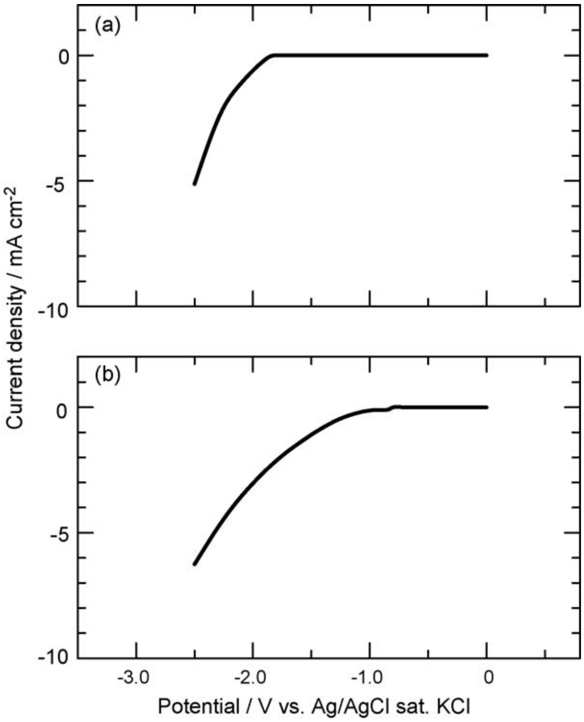

Fig. 3. Current–potential curves for lead and zinc electrodes in $CO_2$-saturated methanol at 243 K. (a) Pb electrodes. Copper particles, 5 g. (b) Zn electrodes. Copper particles, 3 g.

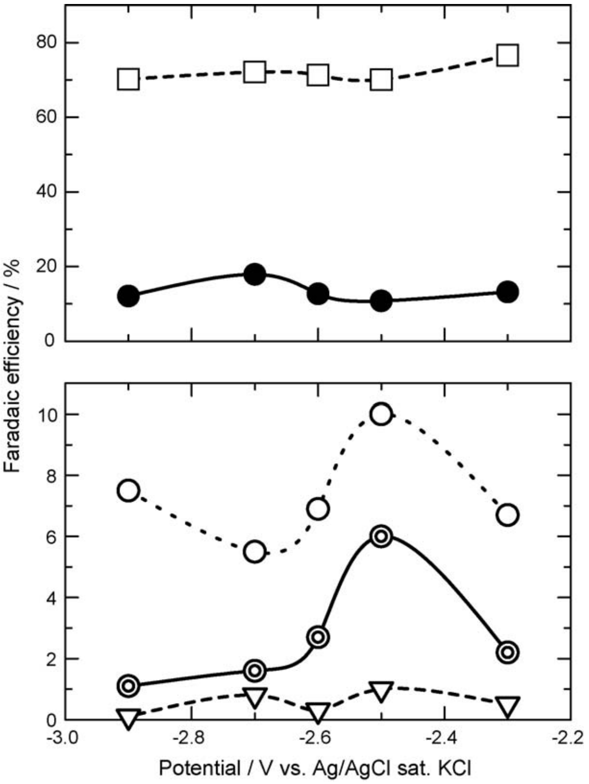

Fig. 4. Effect of potential on Faradaic efficiencies for the products by electrochemical reduction of $CO_2$ at Pb electrode in copper particle-suspended methanol. ⊚, $CH_4$; ▽, $C_2H_4$; ○, CO; □, HCOOH; ●, $H_2$; temperature, 243 K; copper particles, 5 g.

### 3.3. Effect of potential on the product Faradaic efficiency

The results dealing with the effect of the potential on the current efficiencies for the products by the electrochemical reduction of $CO_2$ on Pb and Zn in copper particle-suspended methanol at 243 K are shown in Figs. 4 and 5. On Pb electrode, the predominant formation of formic acid was observed in the potential range of −2.3 to −2.9 V. The current efficiency curves for methane and carbon monoxide has a convex pattern, and both maximum efficiencies were obtained at the same potential (−2.5 V). Ethylene formation was less than 1% at all potentials studied. On Zn cathode, the formation of carbon monoxide dominated in the potential from −2.4 to −2.9 V. The Faradaic efficiency of formic acid roughly tended to increase with decreasing the potential. At only potential of −2.5 V, the formation efficiency of methane was extraordinary in the electrochemical reduction of $CO_2$ at zinc electrode in copper particle-suspended methanol. Even after repeated measurements, the results were the same and the reason could not be made clear. The maximum current efficiency of ethylene, 1.7%, was obtained at the same potential (−2.5 V).

Generally, in the electrochemical reduction of $CO_2$ in water, hydrogen formation is simultaneous to $CO_2$ reduction. Therefore, the suppression of hydrogen formation is very important because the applied energy is wasted on hydrogen evolution instead of being used for the reduction of $CO_2$. In the electrochemical reduction of $CO_2$ at Pb electrode in copper particle-suspended methanol, the Faradaic efficiency for hydrogen formation, at 243 K, was less than 17.9%. In the electrochemical reduction of $CO_2$ on Pb in water [30], hydrogen formation efficiencies were 93.3% and 82.9% in 50 mmol dm$^{-3}$ $KHCO_3$ solution at 293 and 273 K, respectively. Although the hydrogen formation efficiency in the suspension was higher than that obtained with the lead wire electrode in methanol [13], the efficiency was smaller than that observed during the electrolysis in water. On Zn electrode, hydrogen formation efficiency in the copper suspension was below 42%, at polarizations above −2.7 V. In the electrochemical reduction of $CO_2$ at Zn electrode in aqueous solution, the current efficiency of hydrogen was 68.1% [30]. It has been reported that low temperature was effective for the depression of hydrogen formation in the methanol electrolyte [11–24]. Therefore, we were able to confirm that methanol based catholyte, at low temperature, was suitable to suppress hydrogen formation.

### 3.4. Reaction mechanism

The mechanism for the electrochemical reduction of $CO_2$ in copper particle-suspended methanol was investigated for lead and zinc electrodes. The previous GC-MS study with deuterated methanol catholyte demonstrated that no reduction product was produced from the decomposition of methanol [12]. When the electrolysis in the suspension was conducted under a nitrogen atmosphere as the control experiment, electrolysis yielded exclusively hydrogen. Many researchers [25–28] stated that the reduction products were produced from $CO_2$ in the $CO_2$ electrochemical reduction in methanol. Consequently, the needed

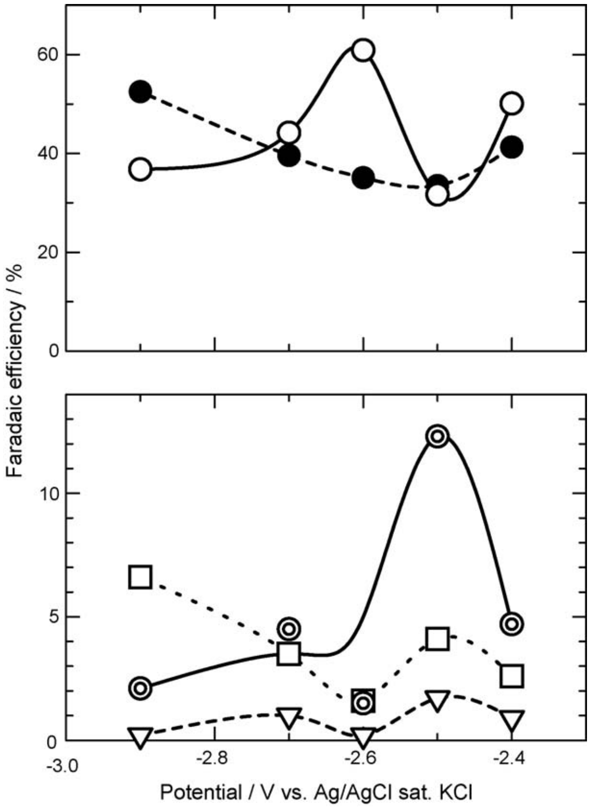

Fig. 5. Effect of potential on Faradaic efficiencies for the products by electrochemical reduction of $CO_2$ at Zn electrode in copper particle-suspended methanol. ◎, $CH_4$; ▽, $C_2H_4$; ○, CO; □, HCOOH; ●, $H_2$; temperature, 243 K; copper particles, 3 g.

products were produced by the electrochemical reduction of $CO_2$.

The experimental data in this work and literature reports [1–7,11–30] suggest that the pathways by which methane, ethylene, carbon monoxide and formic acid are formed on Pb and Zn electrodes are those shown in Fig. 6. Furthermore, the schematic cross-sections of the chemical reaction site on the electrode are shown in Fig. 7. In the electrochemical reduction of $CO_2$ in copper particle-suspended methanol, three adsorption/reaction sites on the electrode surface can be supposed for the electrochemical reduction reaction: (A) the cathode surface site, (B) the corner site surrounded between the cathode surface and the copper particle and (C) the surface site of copper particle. On the adsorption/reaction site (B), the chemical species, $CO_2$, can undergo a number of electronation processes from both the electrode surface and the copper particle. As shown in the right side of reaction pathways in Fig. 6, formic acid and carbon monoxide may be almost produced on the adsorption site (A). On the other hand, hydrocarbons such as methane and ethylene seem to be formed on the adsorption sites (B) and (C), owing to the catalytic property of copper metal. The formation efficiency of methane at Zn electrode was better than that obtained with Pb electrode. The reason cannot be clarified. It may be suggested that zinc electrode are favorable to produce the reaction intermediate CO for the formation of methane. So far, in order to control the distribution of reduction products in the electrochemical reduction of $CO_2$, a variety of factors such as the metal type of cathode, the supporting salts, temperature and pressure have been reported [1–3]. On the basis of this work, it may be possible to roughly change and control the reduction product distributions in the electrochemical reduction of $CO_2$ by the addition of metal particles into the electrolyte.

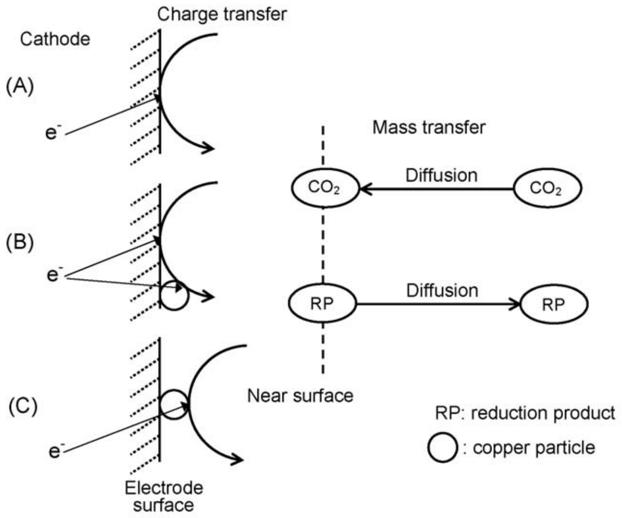

Fig. 7. Schematic cross-sections of the adsorption/reaction site on the cathode.

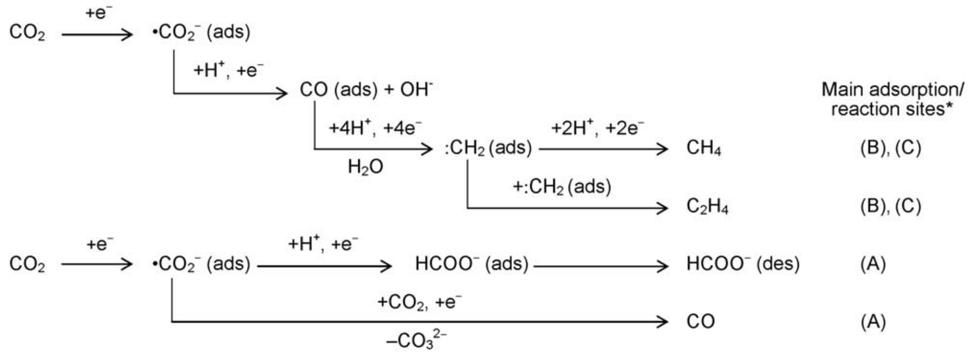

Fig. 6. Reaction mechanism of the electrochemical reduction of $CO_2$ at lead and zinc electrodes in copper particle-suspended methanol. *The adsorption sites (A), (B) and (C) correspond to those in Fig. 7.

## 4. Conclusion

The electrochemical reduction of $CO_2$ in copper particle-suspended methanol was investigated at lead and zinc foil electrodes. Without the copper particle suspension, formic acid and carbon monoxide were formed in the electrochemical reduction of $CO_2$, and the formation of methane and ethylene could not be observed. On the contrary, the formation of hydrocarbons on the copper particle-suspended electrolyte was obtained with both cathodes. The Faradaic efficiencies of methane and ethylene increased gradually with an increase in the amounts of copper powders, and on the other hand the formation efficiencies of formic acid and carbon monoxide decreased. In the electrochemical reduction of $CO_2$, it may become possible to roughly control the distribution of reduction product formations by the addition of metal particles. Because methanol is widely used industrially as a $CO_2$-absorbent at low temperature in the Rectisol process [10], this research may contribute to applications in the conversion of $CO_2$-saturated methanol into useful products. Thus, the synthesis of hydrocarbons by the electrochemical reduction of $CO_2$ might be of practical interest in fuel production, storage of solar energy and production of intermediate materials for the petrochemical industry

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## References

[1] M.M. Halmann, M. Steinberg, Greenhouse Gas Carbon Dioxide Mitigation: Science and Technology, Lewis Publishers, Boca Raton, FL, 1999.

[2] M.A. Scibioh, B. Viswanathan, in: S. Kaneco (Ed.), Photo/Electrochemistry and Photobiology in the Environment, Energy and Fuel, Research Signpost, Kerala, 2002, pp. 1–46.

[3] G.R. Dey, K. Kishore, in: S. Kaneco (Ed.), Photo/Electrochemistry and Photobiology in the Environment, Energy and Fuel, Research Signpost, Kerala, 2005, pp. 357–388.

[4] C. Amatore, J.M. Savéant, J. Am. Chem. Soc. 103 (1981) 5021.

[5] K. Ito, S. Ikeda, T. Iida, A. Nomura, Denki Kagaku 50 (1982) 463.

[6] K. Ito, S. Ikeda, N. Yamauchi, T. Iida, T. Takagi, Bull. Chem. Soc. Jpn. 58 (1985) 3027.

[7] S. Ikeda, T. Takagi, K. Ito, Bull. Chem. Soc. Jpn. 60 (1987) 2517.

[8] D.R. Lide (Ed.), Handbook of Chemistry and Physics, 85th ed., CRC Press, Boca Raton, FL, 2004, pp. 8–88.

[9] H. Chihara (Ed.), Kagaku binran-kiso (Handbook of Basic Chemistry, in Japanese), vol. II, third ed., Maruzen, Tokyo, 1984, pp. 158–165.

[10] G. Hochgesand, Ind. Eng. Chem. 62 (1970) 37.

[11] S. Kaneco, H. Katsumata, T. Suzuki, K. Ohta, in: C. Liu, R.G. Mallinson, M. Aresta (Eds.), Utilization of Greenhouse Gases, ACS Symposium Series 852, American Chemical Society, Washington, DC, 2003, pp. 169–182.

[12] A. Naitoh, K. Ohta, T. Mizuno, H. Yoshida, M. Sakai, H. Noda, Electrochim. Acta 38 (1993) 2177.

[13] S. Kaneco, R. Iwao, K. Iiba, K. Ohta, T. Mizuno, Energy 12 (1998) 1107.

[14] S. Kaneco, K. Iiba, K. Ohta, T. Mizuno, A. Saji, Electrochim. Acta 44 (1998) 573.

[15] S. Kaneco, K. Iiba, K. Ohta, T. Mizuno, A. Saji, J. Electroanal. Chem. 441 (1998).

[16] S. Kaneco, K. Iiba, K. Ohta, T. Mizuno, Energy Source 21 (1999) 643.

[17] S. Kaneco, K. Iiba, S. Suzuki, K. Ohta, T. Mizuno, J. Phys. Chem. B 103 (1999) 7456.

[18] S. Kaneco, K. Iiba, H. Hiei, K. Ohta, T. Mizuno, T. Suzuki, Electrochim. Acta 44 (1999) 4701.

[19] S. Kaneco, K. Iiba, M. Yabuuchi, N. Nisho, H. Ohnishi, H. Katsumata, T. Suzuki, K. Ohta, Ind. Eng. Chem. Res. 41 (2002) 5165.

[20] S. Kaneco, H. Yamauchi, H. Katsumata, T. Suzuki, K. Ohta, in: S.E. Park, J.S. Chang, K.W. Lee (Eds.), Carbon Dioxide Utilization for Global Sustainability. Studies in Surface Science and Catalysis, Elsevier Science, Amsterdam, 2004, pp. 277–282.

[21] S. Kaneco, H. Katsumata, T. Suzuki, K. Ohta, J. Solid State Electrochem., submitted for publication.

[22] S. Kaneco, R. Iwao, K. Iiba, K. Ohta, T. Mizuno, ITE Lett. Batt. New Technol. Med. 2 (2001) 640.

[23] S. Kaneco, R. Iwao, H. Katsumata, T. Suzuki, K. Ohta, Photo/Electrochem. Photobiol. Environ. Energy Fuel 1 (2002) 69, SciFinder 2004:281054.

[24] S. Kaneco, R. Iwao, H. Katsumata, T. Suzuki, K. Ohta, Photo/Electrochem. Photobiol. Environ. Energy Fuel 2 (2003) 181, SciFinder 2004:276792.

[25] T. Saeki, K. Hashimoto, A. Fujishima, N. Kimura, K. Omata, J. Phys. Chem. 99 (1995) 8440.

[26] F. Koleli, T. Ropke, C.H. Hamann, Electrochim. Acta 48 (2003) 1595.

[27] R. Schrebler, P. Cury, C. Suarez, E. Munoz, H. Gomez, R. Cordova, J. Electroanal. Chem. 533 (2002) 167.

[28] B.R. Eggins, C. Ennis, R. McConnell, M. Spence, J. Appl. Electrochem. 27 (1997) 706.

[29] K. Ohta, Y. Ohuguchi, S. Kaneco, T. Mizuno, Energy Source 21 (1999) 467.

[30] M. Azuma, K. Hashimoto, M. Hiramoto, M. Watanabe, T. Sakata, J. Electrochem. Soc. 137 (1990) 1772.