Electrochemical reduction of high pressure carbon dioxide at a Cu electrode in cold methanol with CsOH supporting salt

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Abstract

The electrochemical reduction of high pressure CO_2 at a Cu electrode in cold methanol was investigated with cesium hydroxide supporting salt. A divided H-type glass cell, which was placed in a high-pressure stainless steel vessel, was employed. The main products from CO_2 by the electrochemical reduction were carbon monoxide, formic acid, methane and ethylene. The maximum current efficiency of CO was of 84% at −3.5 V. In the potential region more negative than −3.0 V, the efficiency of hydrogen formation, being a competitive reaction against CO_2 reduction, was depressed to less than 2%. The partial current density ratio of CO_2 reduction and hydrogen evolution, $i(CO_2)/i(H_2)$, was more than 42 at potentials more negative than −3.0 V. This reserch can contribute to the large-scale manufacturing of useful material from readily available and inexpensive raw materials, CO_2-saturated methanol from industrial absorbers (the Rectisol process).
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Keywords: Electrochemical reduction of high pressure CO_2; Cold methanol; Cesium hydroxide supporting salt; Cu electrode

1. Introduction

As natural oil reserves become depleted, attention will increasingly focus on alternative energy sources. Hydrogen is one of the most promising energy carriers for future energy systems, consisting of the fuel-cell vehicles and the fuel-cell power-generation technologies. In the production of hydrogen from hydrocarbons, which are included in all kinds of fossil fuels, biomass, organic wastes, etc., gas products from the hydrocarbon gasificaton with water primarily contain not only hydrogen, but also carbon monoxide and carbon dioxide (CO_2). Concerns that increases in atmospheric CO_2 may lead to serious global climate changes have led a number of investigators to suggest that CO_2 itself may be used as a source of carbon for the production of petroleum-like materials [1–3]. Therefore, the electrochemical method appears to become one of the very suitable methods for the conversion and reduction of CO_2 [1–3].

Recently, many researchers have actively studied the electrochemical reduction of CO_2 with a variety of metallic electrodes in organic solvents, because organic aprotic solvents dissolve much more CO_2 than water does [4–6]. It has been reported that low reduced products containing formic acid, carbon monoxide and oxalic acid were produced by the electrochemical reduction of CO_2 in acetonitrile, dimethyl sulfoxide (DMF), *N*,*N*-dimethyl formamide (DMSO) and propylene carbonate. However, even at a Cu electrode, few hydrocarbons have been obtained in these organic solvents [6].

Methanol is a better solvent of CO_2 than water, particularly at low temperature. The solubility of CO_2 in methanol is approximately four times that in water, at ambient temperature, and more than eight times that in water, at temperatures below 273 K [7–9]. Therefore, methanol has been industrially used as a physical absorbent of CO_2 in the Rectisol method, at low temperature [9,10]. 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. Since the first report of electrochemical reduction of CO_2 in methanol-based electrolyte in 1993 [11], many research groups have brought focus into its reduction system [11–28]. In our groups [11–21], the electrochemical reduction of CO_2 using various metal electrodes in the methanol-based catholyte has been actively investigated at low temperature. On the other hand, the electrochemical reduction of high pressure CO_2 in methanol

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at ambient temperature has been presented by Fujishima and co-workers [22–26] and Aydin and Koleli [27,28]. Metal electrodes were used in the former, and polyaniline and polypyrrole electrodes in the later. However, little information on the electrochemical reduction of high pressure CO_2 in cold methanol has been reported, although the operating conditions in the Rectisol process have required low temperature and high pressure [9,10].

In the previous paper [21], we have presented the electrochemical reduction of high pressure CO_2 at Cu electrode in cold methanol with LiCl supporting salt. In the system, the Faradaic efficiency of hydrogen was relatively high because of the hydrophilic environment at the electrode surface by Li ion. This study deals mainly with the electrochemical reduction of high pressure CO_2 at a Cu electrode in cold methanol with cesium hydroxide supporting salt.

2. Experimental

A home-made, divided H-type cell with an SUS-316 stainless steel high pressure vessel for the electrochemical reduction of high pressure CO_2 was similar to those reported in a previous paper [21]. The detailed experimental conditions for the electrochemical reduction of CO_2 are shown in Table 1. An Aldrich Nafion 117-type ion exchange membrane (0.18 mm thickness) was used as the diaphragm. A silver rod covered with epoxy, with only the end exposed, was used as a quasi-reference electrode (QRE)

The methanol (99%, Nacalai Tesque Inc., Japan) was purified by double distillation from metallic magnesium. Water content in the pure methanol was less than 0.1% (confirmed by the Karl Fischer test). Cesium hydroxide (95%, Nacalai Tesque Inc.)

Table 1
Apparatus and experimental conditions

Electrochemical reduction	
Cell	H-type cell (in stainless steel vessel)
Potentiostat/galvanostate	Hokuto HA-3001A
Coulometer	Integrator 1109 (Fusou Seisakujyo Inc., Japan)
Potential sweep	Hokuto HB-111 function generator
Working electrode	Cu foil (15 mm × 20 mm, 0.1 mm thickness, 99.98% purity)
Counter electrode	Pt foil (5 mm × 20 mm, 0.1 mm thickness, 99.98% purity)
Reference electrode	Ag rod quasi-reference electrode (Ø20 mm × 100 mm, 99.98% purity)
Electrolyte	500 mmol dm^{-3} CsOH in methanol
Carbon dioxide	99.9999% purity
Pressure	10 atm
Potential	−2.0 to −3.5 V vs. Ag QRE
Temperature	248 ± 0.5 K
Product analysis	
Gas products	Gas chromatography TCD (GL Sciences GC-320, Molecular Sieve 5A; 13X-S, Ar and He carrier gas) FID (GL Sciences GC-353B, Porapak Q, N$_2$ carrier gas)
Liquid products	HPLC with UV detector (Hitachi L4000) TCD and FID gas chromatography

was used as the ionophore in the methanol-based electrolyte. Mechanical processing of the Cu 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. Both electrodes were 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.

A discontinuous electroreduction procedure was used. First, the electrolyte solution was deaerated by the introduction of CO_2 to the controlled pressure followed by the flushing of the gas to atmospheric pressure. This procedure was repeated three times. Next, CO_2 gas was introduced into the pressure vessel and was allowed to equilibrate for 1 h at 10 atm. Then, the CO_2-saturated solution was reduced potentiostatically at cathodic polarizations in the range from −2.0 to −3.5 V versus Ag QRE. The catholyte was stirred magnetically. The Faradic efficiencies of formation for the main products were calculated from the total charge passed during batch electrolyses, which was set to 50 coulombs. In control experiments, 1 atm nitrogen gas was used. After the electrolysis, high-pressure gas was released into a larger volume vessel to reduce the system pressure. Gaseous products obtained in the vessel were analyzed by GC. Products soluble in the catholyte were analyzed by using HPLC and GC.

3. Results and discussion

Literature data [7–9] for the solubilities of CO_2 in pure methanol, at 243, 263 and 288 K, and in water, at 288 K, were of 15, 8, 4.6 and 1.07 cm^3 cm^{-3}, respectively. Moreover, it has been reported that the solubilities of CO_2 in high pressured cold-methanol at 243 and 263 K at 10 atm were of 270 and 100 cm^3 cm^{-3}, respectively [9]. Since it has been reported in the previous work [21] that low temperature was effective for the electrochemical reduction of high pressure CO_2, 248 K was selected in this work. Although $CsHCO_3$ may be formed in the methanol while introducing high pressed CO_2 into the solution for several minutes, the amount is assumed to be very small, since one cannot observe any precipitate through the window which was equipped on the side of stainless steel vessel. Therefore, 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. The electrolysis was performed at 10 atm because its pressure was customarily in the operating pressure conditions of the Rectisol process [9,10].

The effect of the potential on the product formation efficiencies in the electrochemical reduction of CO_2 at Cu electrode in CsOH/methanol at 248 K and 10 atm was evaluated (Fig. 1). The electrolysis was not performed at temperatures below 248 K, because CO_2 changes to the liquid conditions. Methane, ethylene, carbon monoxide and formic acid are the principal products identified by the analytical system used in this study. The reproducibility of the electrolysis (relative standard deviation; R.S.D. for Faradic efficiency of the reduction products) was better than R.S.D. 10% for five repeated measurements. The
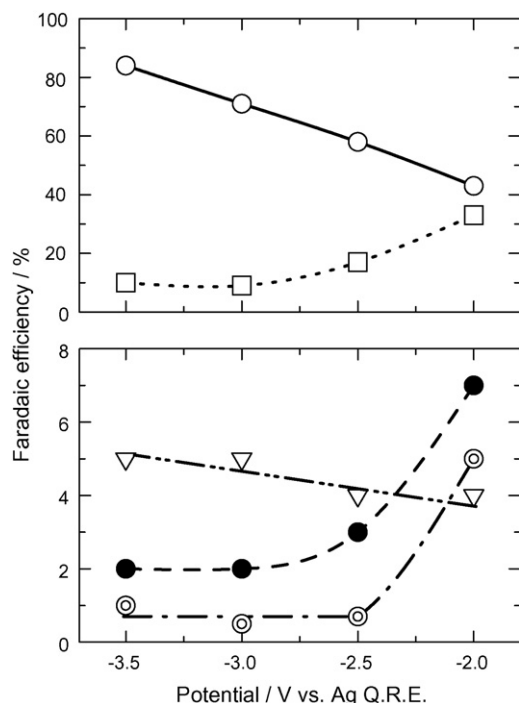
Fig. 1. Effect of potential on Faradaic efficiencies for the products by electrochemical reduction of high pressure CO_2 at Cu electrode in cold methanol. CH_4, ⊚; C_2H_4, ▽; CO, ○; HCOOH, □; H_2, ●. Catholyte, 500 mmol dm^{-3} CsOH/methanol; anolyte, 500 mmol dm^{-3} CsOH/methanol; pressure, 10 atm; temperature, 248 K.

Fig. 2. Polarization curves of CO_2 reduction and H_2 evolution by electrochemical reduction of high pressure CO_2 at Cu electrode in cold methanol. CO_2 reduction, ○; H_2 evolution, ●; catholyte, 500 mmol dm^{-3} CsOH/methanol; anolyte, 500 mmol dm^{-3} CsOH/methanol; pressure, 10 atm; temperature, 248 K.

current efficiency of carbon monoxide increased from 43% to 84% with increasing potential in the negative direction, and the same phenomena for ethylene were observed. On the contrary, the Faradaic efficiencies of methane, formic acid and hydrogen decreased with the more negative potential. Hence, the reduction products could be divided into the two groups: (1) CO and C_2H_4; (2) CH_4, HCOOH and H_2. The hydrophobic electrode surface is thought to allow hydrophobic cations such as Cs^+ to adsorb on the electrode surface, thus producing a hydrophobic environment. In the present study, Cs ion may provide a hydrophobic environment and hydrogen-poor conditions near the electrode surface during the cathodic polarization. The protonation reaction of CO_2 reduction intermediates for the formation of CH_4 and HCOOH and H_2 evolution reaction therefore seems to proceed less efficiently at relatively more negative potential (under high reaction rate) whereas the formation of CO may be favorable. Fujishima et al. [24] have investigated the electrochemical large pressure CO_2 reduction in methanol at ambient temperature, and in this system carbon monoxide formation was favorable in the hydrophobic atmosphere provided by tetrabutylammonium (TBA) cation whereas methyl formate formation [29] and H_2 evolution proceeded efficiency in the hydrophilic atmosphere provided by Li ion. It could be realized that our experimental results were basically consistent with those studied by Fujishima et al. The total formation efficiency for CO_2 reduction at comparatively more negative potential region was better compared to those obtained in the high pressure CO_2 reduction in cold methanol with LiCl supporting salt [21].
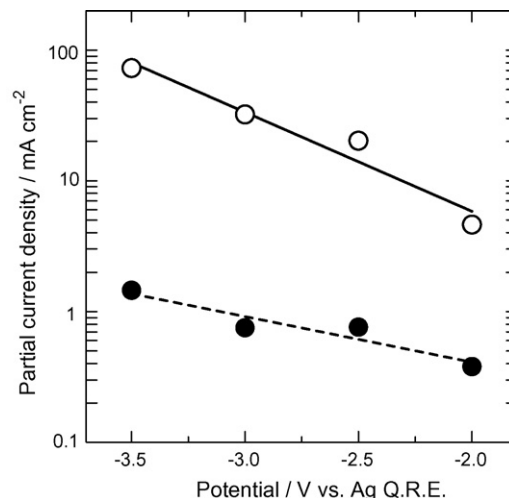
Generally, in the electrochemical reduction of CO_2 in water, hydrogen formation is simultaneous to CO_2 reduction. Therefore, the depression of hydrogen formation is very significant because the applied energy is wasted on hydrogen evolution instead of being used for the reduction of CO_2. In the electrochemical reduction of high pressure CO_2 at Cu electrode in cold methanol with CsOH supporting salt hydrogen formation was suppressed to less than 2%, in the polarization region more negative than -3.0 V. In cold methanol with LiCl supporting salt [21], hydrogen formation efficiency was 78% at -3.5 V versus Ag QRE. These effects may be due to the adsorbed hydrogen-poor conditions because of less hydrophilic environment near the cathode surface provided by Cs ion.

In order to discuss the influence of the potential on partial current densities (PCDs) for CO_2 reduction and hydrogen evolution, the polarization curves for the electrochemical reduction of high pressure CO_2 in cold methanol with CsOH supporting salt were evaluated. The results are illustrated in Fig. 2. The log current densities for CO_2 reduction and hydrogen increase linearly, even in the more negative potential range. The results indicate the reduction of CO_2 is not limited by its mass transfer in this potential region. Therefore, adequate transport of CO_2 to the electrode may be achieved in this reduction system. The partial current density ratio of CO_2 reduction and hydrogen evolution, $i(CO_2)/i(H_2)$, was >42 at potentials more negative than -3.0 V.

The mechanism of the electrochemical reduction of high pressure CO_2 in cold methanol wish cesium hydroxide supporting salt was investigated for a copper electrode. A GC-MS study with deuterated methanol catholyte demonstrated that no reduction product was produced from methanol [11]. When the electrolysis was conducted as the control experiments under nitrogen atmosphere, electrolysis yielded exclusively hydrogen. Fujishima et al. have described that the reduction products were produced from CO_2 in the electrochemical reduction of high pressure CO_2 in methanol at ambient pressure [22–26].

Consequently, the targeted products were produced by the electrochemical reduction of CO_2, and these experimental data and literature reports [1–6,11–28] suggest that the pathway, by which methane, ethylene, carbon monoxide and formic acid are formed, appears to be identical to that estimated in the electrochemical reduction of CO_2 in methanol-based electrolyte at ambient temperature [16]. In the photoelectrochemical reduction of CO_2, Yoneyama et al. [30] reported that the difference in the hydrophilicities at the electrode surface determines the product selectivity. In the previous works [15,16,18], i.e. in the electrochemical reduction of CO_2 in cold methanol at ambient pressure, the lithium supporting salts were especially suitable for methane formation (for example, 71.8% for $LiClO_4$ supporting salts), whereas when Cs salts were used the formation of ethylene was favorable ($r_f = 32.3\%$ for CsOH supporting salts). In the high pressure CO_2 reduction in cold methanol with LiCl supporting salt [21], the reduction products were formed in the sequence of carbon monoxide, methane, formic acid and ethylene, and the current efficiency of methane, $r_f = 20\%$, was larger relative to those of ethylene (for instance, 2.3%). Conversely, the production of ethylene ($r_f = 5\%$) predominated compared to those of methane in the present study. Since large cations such as Cs^+ seem to be adsorbed on the electrode surface, the electrode vicinity may be more hydrophobic environments and hydrogen-poor conditions. Therefore, the dimerization of intermediate $Cu=CH_2$ to ethylene may be favored at lower surface hydrogen coverage in the case of Cs salt, because its reaction does not require the presence of adsorbed proton. The electrode reaction mechanism in the electrochemical reduction of CO_2 at Cu cathode in methanol at low temperature almost seems to be similar to the model reported by Fujishima et al. [24] and Yoneyama et al. [30].

4. Conclusion

The electrochemical reduction of high pressure CO_2 at Cu electrode in cold methanol was studied with cesium supporting salt. At comparatively more negative potential (-3.5 V), the Faradaic efficiency of carbon monoxide was $r_f = 84\%$, and the CO_2 electrochemical reduction proceeded more efficiently, compared with hydrogen evolution. In the potential region more negative than -3.0 V, hydrogen formation efficiency was suppressed to less than 2%. The reduction product distribution may be related with the hydrophobicity of the electrode surface supplied by supporting salts. Provided that the present reduction system combines with the solar cell, it can be considered as the storage system of solar energy by the conversion of CO_2 to useful products. Thus, the synthesis of useful material by the electrochemical reduction of CO_2 might be of practical interest in fuel production, storage of solar energy and the production of intermediate materials for the petrochemical industry.

Acknowledgments

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

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

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

[7] D.R. Lide (Ed.), Handbook of Chemistry and Physics, 85th ed., CRC Press, Boca Raton, FL, 2004, pp. 8–87.

[8] H. Chihara (Ed.), Kagaku binran-kiso (Handbook of Basic Chemistry, in Japanese), vol. II, 3rd ed., Maruzen, Tokyo, 1984, p. 158, 165.

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

[10] U. Koss, M. Meyer, Proceedings of Annual International Pittsburgh Coal Conference 20th, University of Pittsburgh, Pittsburgh, PA, 2003, p. 779.

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

[12] 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.

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

[14] S. Kaneco, K. Iiba, K. Ohta, T. Mizuno, A. Saji, J. Electroanal. Chem. 441 (1998) 215.

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

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

[17] S. Kaneco, K. Iiba, K. Ohta, T. Mizuno, J. Solid State Electrochem. 3 (1999) 424.

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

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

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

[21] S. Kaneco, K. Iiba, H. Katsumata, T. Suzuki, K. Ohta, Electrochim. Acta 51 (2006) 4880.

[22] T. Saeki, K. Hashimoto, Y. Noguchi, K. Omata, A. Fujishima, J. Electrochem. Soc. 141 (1994) L130.

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

[24] T. Saeki, K. Hashimoto, N. Kimura, K. Omata, A. Fujishima, J. Electroanal. Chem. 390 (1995) 77.

[25] T. Saeki, K. Hashimoto, N. Kimura, K. Omata, A. Fujishima, Chem. Lett. 24 (1995) 361.

[26] T. Saeki, K. Hashimoto, N. Kimura, K. Omata, A. Fujishima, J. Electroanal. Chem. 404 (1996) 299.

[27] R. Aydin, F. Köleli, J. Electroanal. Chem. 535 (2002) 107.

[28] R. Aydin, F. Köleli, Synth. Met. 144 (2004) 75.

[29] In the electrochemical reduction of high pressure CO_2 in methanol at ambient temperature [23], the formation of methyl formate was confirmed by GC-MS analysis. Fujishima et al. have supposed that this methyl formate formation in the methanol corresponds to the formic acid production in the aqueous CO_2 reduction system. Formic acid can be partially converted to methyl formate in methanol, and it should be considered that methyl formate may be under the dissociation equilibrium of methanol and formic acid. In this study, these reduction products in the dissociation equilibrium have been simply expressed as formic acid. The formation efficiency takes account into both HCOOH and $HCOOCH_3$.

[30] H. Yoneyama, K. Sugimura, S. Kawabata, J. Electroanal. Chem. 249 (1998) 143.