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Effect of sodium cation on the electrochemical reduction of CO_2 at a copper electrode in methanol

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Abstract The electrochemical reduction of CO_2 with a Cu electrode in methanol was investigated with sodium hydroxide supporting salt. A divided H-type cell was employed; the supporting electrolytes were 80 mmol dm^{-3} sodium hydroxide in methanol (catholyte) and 300 mmol dm^{-3} potassium hydroxide in methanol (anolyte). The main products from CO_2 were methane, ethylene, carbon monoxide, and formic acid. The maximum current efficiency for hydrocarbons (methane and ethylene) was 80.6%, at −4.0 V vs Ag/AgCl, saturated KCl. The ratio of current efficiency for methane/ethylene, $r_f(CH_4)/r_f(C_2H_4)$, was similar to those obtained in LiOH/methanol-based electrolyte and larger relative to those in methanol using KOH, RbOH, and CsOH supporting salts. In NaOH/methanol-based electrolyte, the efficiency of hydrogen formation, a competing reaction of CO_2 reduction, was suppressed to below 4%. The electrochemical CO_2 reduction to methane may be able to proceed efficiently in a hydrophilic environment near the electrode surface provided by sodium cation.

Keywords Electrochemical reduction of CO_2 · Methanol · NaOH supporting salt · Methane · Sequestration of CO_2

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Introduction

Carbon dioxide (CO_2) is the ultimate by-product of processes involving the oxidation of carbon compounds. From the viewpoint of the vastness of the CO_2 supply, it represents a possible potential source for carbon in the manufacturing of chemicals. Many methods have been proposed for the conversion of CO_2 into valuable chemicals involving homogeneous and heterogeneous systems. The electrochemical method appears to become one of the very suitable methods for the conversion and reduction of CO_2 [1–3]. A great number of studies dealing with electrochemical fixation of CO_2 are both of fundamental and of preparative interest [1–3].

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 seven times that in water, at temperatures below 273 K [4–6]. Therefore, methanol has been industrially used as a physical absorbent of CO_2 in the Rectisol method, at 243–263 K [7, 8]. Currently, over 70 large-scale plants apply the Rectisol process all over the world. Therefore, the direct electrochemical reduction of CO_2 in methanol is an advantageous choice, especially when the process is performed under energetically efficient conditions. Many research groups (our groups [8–18], Fujishima et al. [19], Köleli et al. [20], and Schrebler et al. [21]) have brought focus into the electrochemical reduction of CO_2 in methanol-based electrolyte. In our groups, the electrochemical reduction of CO_2 in the methanol-based electrolyte has been actively investigated with a copper electrode [9–14, 17, 18]. From these studies, it was found that the methanol at low temperature was the best electrolyte to obtain hydrocarbons, such as

methane and ethylene, compared to various organic solvents. To control the product selectivity in the electrochemical CO_2 reduction with Cu electrode in methanol, the influence of supporting salts on the product distribution has been systematically evaluated. The lithium hydroxide supporting electrolyte was especially suitable for methane formation [10]. On the other hand, when KOH, RbOH, and CsOH were used as the supporting electrolytes, predominate formation of ethylene was observed [11, 18]. However, little information on the influence of sodium cation on the electrochemical reduction of CO_2 in methanol has been presented with the detailed reaction mechanism.

This study deals mainly with the electrochemical reduction of CO_2 at a copper electrode in methanol with sodium hydroxide supporting salt. Moreover, the detailed reaction mechanism on the cationic effect on the reduction reaction has been discussed from the viewpoint of hydrophilicity at the electrode.

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 home-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) to lower the ohmic potential drop due to solution resistance between the reference and working electrodes. However, in the present reduction system, the IR drop between the Luggin capillary tip and the working electrode could not be completely compensated, owing to the large solution resistance of catholyte.

The methanol (99%, Nacalai Tesque, 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). Sodium hydroxide (96%, Nacalai Tesque) was used as the supporting salt in the methanol-based catholyte. The pH of catholyte was measured with a glass electrode for nonaqueous solvent (Horiba, 6377-10D), which was calibrated in water. The pH of methanol with 80 mmol dm^{-3} NaOH supporting salt was approximately 14, and the pH after the saturation of the catholyte with CO_2 was 5.3. 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) 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. After the above treatment, the electrodes were rinsed with both water and ethanol.
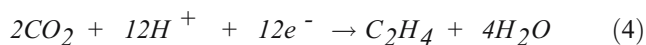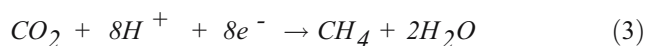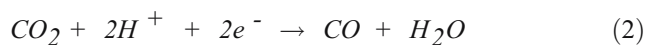
A discontinuous electroreduction procedure was used. First, CO_2 gas was bubbled into the methanol catholyte for 1 h at a rate of 30 ml min^{-1}. Then, the CO_2-saturated

Table 1 Apparatus and experimental conditions

Electrochemical reduction	Characteristic
Cell	H-type cell
Potentiostat/galvanostate	Hokuto HA-3001A
Coulometer	Integrator 1109 (Fusou Seisakujyo, Japan)
Potential sweep	Hokuto HB-111 function generator
XY recorder	Graphtec WX1100
Working electrode	Cu foil (30×20 mm, 0.1 mm thickness, 99.98% purity)
Counter electrode	Pt foil (30×20 mm, 0.1 mm thickness, 99.98% purity)
Reference electrode	Ag/AgCl saturated KCl (Horiba, 2060A-10T)
Electrolyte	
Catholyte	80 mmol dm^{-3} NaOH in methanol (60 ml)
Anolyte	300 mmol dm^{-3} KOH in methanol (60 ml)
Carbon dioxide	99.9999% purity
Potential	−2.0 to −5.0 V vs Ag/AgCl saturated KCl
Temperature	243±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

solution was reduced electrolytically at cathodic polarizations in the range from −2.0 to −5.0 V vs Ag/AgCl, saturated KCl. The catholyte was stirred magnetically. The temperature of electrolytes was set to 243 K by using the cooling device (ESC-50, EYELA, Tokyo, Japan).

The faradaic efficiencies of formation for the main products were calculated from the total charge passed during batch electrolyses, which was set to 50 C. The reactions of the main products for the calculation of faradaic efficiency were as follows:

$$CO_2 + H^+ + 2e^- \rightarrow HCOO^- \qquad (1)$$

$$CO_2 + 2H^+ + 2e^- \rightarrow CO + H_2O \qquad (2)$$

$$CO_2 + 8H^+ + 8e^- \rightarrow CH_4 + 2H_2O \qquad (3)$$

$$2CO_2 + 12H^+ + 12e^- \rightarrow C_2H_4 + 4H_2O \qquad (4)$$

The current densities were in the range of 2.1 to 12.9 mA cm^{-2}. In control experiments, nitrogen gas was used. 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.

Results and discussions

The solubility of CO_2 in NaOH–methanol was investigated at 243 K. The solubility of CO_2 in a solution of 80 mmol dm^{-3} NaOH/methanol, at 243 K, was about 15 cm^3 cm^{-3} (about 670 μmol CO_2 per cubic centimeter methanol). Literature data [4, 5] for the solubilities of CO_2 in pure methanol and water, at 288 K, were of 4.6 and 1.07 cm^3 cm^{-3}, respectively. 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 because one cannot observe any precipitate. 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 243 K because temperature in the Rectisol process is customarily in the range of 243 to 263 K [6, 7].

First, current–potential curves at the Cu electrode in NaOH/methanol-based electrolyte were recorded at 243 K. The potential was scanned at a sweep rate of 50 mV s^{-1}. Figure 1 depicts the current–potential curves with the Cu
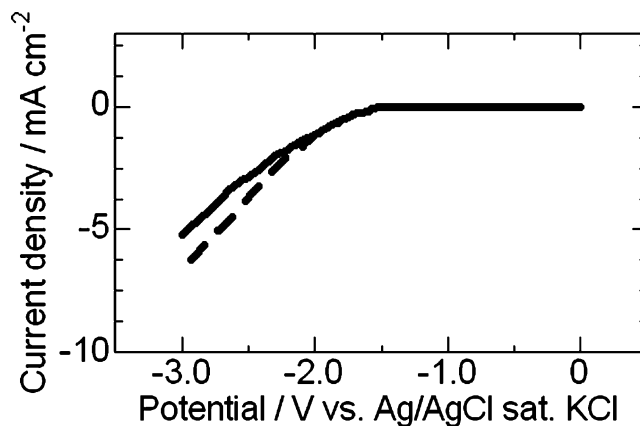

Fig. 1 Current–potential curves for Cu electrode in methanol at 243 K. *Solid line* CO_2 atmosphere, *Broken line* N_2 atmosphere, *catholyte* 80 mmol dm^{-3} NaOH/methanol, *anolyte* 300 mmol dm^{-3} KOH/methanol

electrode in CO_2-saturated methanol and in N_2-purged methanol. CO_2 reduction is evident because of the difference in voltammograms recorded in their methanols. Under nitrogen atmosphere, hydrogen formation efficiency was approximately 98% in the electrolysis, with no other product being produced. Hence, we conclude that the cathodic currents can be attributed solely to the reduction of residual water, which was present slightly in the methanol catholyte. The onset (starting) potential 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 NaOH/methanol-based catholyte was around −1.5 V. In the current–potential curves using LiOH, KOH, RbOH, and CsOH supporting electrolytes under essentially the same conditions, the onset potentials were about −0.5, −1.4, −1.3, and −1.5 V, respectively [10, 11, 18]. The onset potential recorded in N_2-purged methanol was almost the same as that obtained in CO_2-saturated methanol. No voltammetric peak was observed in the potential range down to −5.2 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 faradaic efficiency of the products.

The results dealing with the effect of the potential on the current efficiencies for the products by the electrochemical reduction of CO_2 at Cu electrode in NaOH/methanol at 243 K are illustrated in Fig. 2. Methane, ethylene, CO, and formic acid were detected as reduction products from CO_2. The current efficiency of ethylene gradually increased to 20% as the potential decreased. The current efficiency of methane increased from 47 to 62% from −2.0 to −3.0 V. At potentials more negative than −3.0 V, the high efficiency was maintained. The current efficiency of methane was higher than those of ethylene in the entire investigated
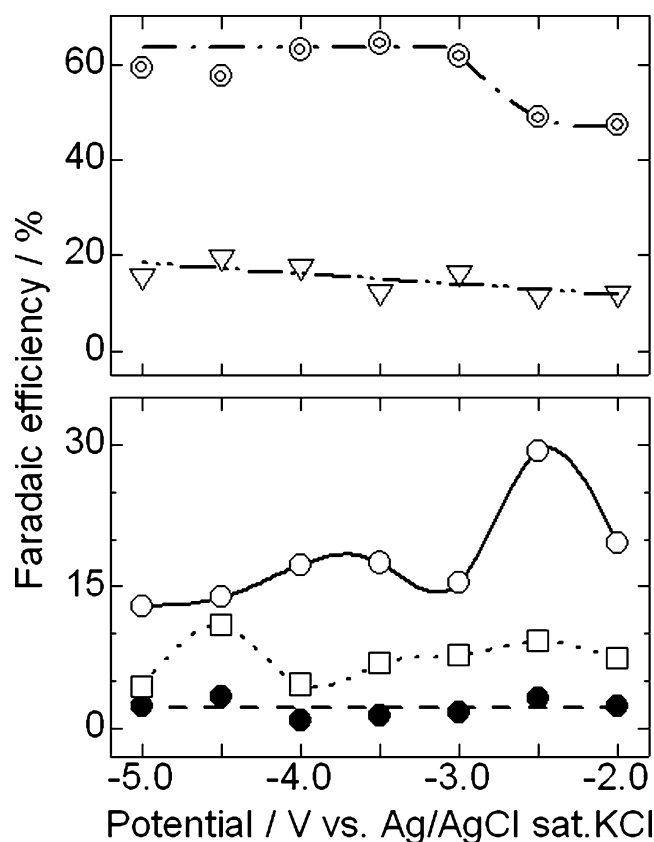
Fig. 2 Effect of potential on faradaic efficiencies for the products by electrochemical reduction of CO_2 at Cu electrode in NaOH/methanol-based electrolyte. CH_4 (◎), C_2H_4 (▽), CO (○), HCOOH (□), H_2 (●), *catholyte* 80 mmol dm^{-3} NaOH/methanol, *anolyte* 300 mmol dm^{-3} KOH/methanol

potential range. A maximum faradaic efficiency for hydrocarbons (methane and ethylene, 80.6%) was observed at −4.0 V. The formation efficiency curve of CO roughly rose as the potential became more positive, and the maximum efficiency was 29% at −2.5 V. The optimum potential of formic acid formation was observed at −4.5 V (11%). Azuma et al. [22] investigated the

electrochemical reduction of CO_2 at a Cu electrode in 50 mmol dm^{-3} $KHCO_3$ aqueous solution, at 293 K, and obtained methane, ethylene, and ethane with faradaic efficiencies of 17.8, 12.7, and 0.039%, respectively. Moreover, at 273 K, the current efficiency was 24.7% for methane, 6.5% for ethylene, and 0.015% for ethane. Kyriacou and Anagnostopoulos [23] described the formation efficiencies in the electrochemical reduction of CO_2 on Cu, in 500 mmol dm^{-3} $NaHCO_3$ solution, at 298 K, as follows: 19% for methane, 11% for ethylene, etc. These data are the general and average ones in the electrochemical reduction of CO_2 at Cu electrode in the aqueous solution. In NaOH/methanol electrolyte, ethane was not produced, but the efficiency of methane was much better than those obtained in water and was similar to those in the methanol containing LiOH supporting salt [10].

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 NaOH/methanol-based electrolyte, the faradaic efficiency for hydrogen formation on the Cu electrode, at 243 K, was suppressed to less than 3.3%. In the electrochemical reduction of CO_2 on Cu in water [22, 23], hydrogen formation efficiencies were 52 and 59% in 50 and 500 mmol dm^{-3} $KHCO_3$ solution, respectively. It has been reported that low temperature was effective for the depression of hydrogen formation in the methanol electrolyte [8–18]. These effects may be due to the poor electroactivity for hydrogen evolution reaction at low temperature because of the stabilization of adsorbed hydrogen on the electrode. Therefore, we were able to confirm that methanol-based catholyte, at low temperature, was suitable to suppress hydrogen formation.

The mechanism for the electrochemical reduction of CO_2 in methanol-based electrolyte with NaOH supporting salt was investigated for a copper electrode. A GC-MS study

Table 2 Ratios of typical faradaic efficiency of methane and ethylene in the electrochemical reduction of CO_2 at Cu electrode

Cation of supporting salts[a]	Faradaic efficiency (%)							
	Methanol[b]				Water[c]			
	CH_4	C_2H_4	Total	Ratio	CH_4	C_2H_4	Total	Ratio
Li (−503, −100.8)	63.0	14.7	77.7	4.3	26	4	30	6.5
Na (−404, −69)	63.0	17.6	80.6	3.6	19	11	30	1.7
K (−320, −34)	16.0	37.5	53.5	0.43	16	14	30	1.1
Rb (−290, −22)	4.6	31.0	35.6	0.15	–	–	–	–
Cs (−259, −18)	4.1	32.7	36.8	0.13	15	13	28	1.2

[a] *Parenthesis* Hydration enthalpy (kilojoules per mole) and hydration entropy (kilojoules per mole) at room temperature
[b] *Supporting salts* NaOH (this work), LiOH ([10]), KOH and RbOH ([18]), and CsOH ([11])
[c] *Supporting salts* Hydrogen carbonates ([23])

with deuterated methanol catholyte demonstrated that no reduction product was produced from methanol [9]. When the electrolysis was conducted under a nitrogen atmosphere, electrolysis yielded exclusively hydrogen. Many researchers [19–21] have concluded that the reduction products were produced from CO_2 in the CO_2 electrochemical reduction in methanol. Consequently, the needed products were not formed from the decomposition of methanol and were produced by the electrochemical reduction of CO_2, and the experimental data and literature reports [1–3, 8–25] suggest that the reaction path, by which methane, ethylene, ethane, carbon monoxide, and formic acid on Cu electrode are formed, seems to be identical to that estimated in the electrochemical CO_2 reduction in methanol with other supporting salts [10, 11, 18]. In the electrochemical reduction of CO_2 in water at comparatively large overvoltage, hydrogen evolution generally becomes predominant because the electrode potential is more negative than hydrogen overpotential [22]. On the other hand, it is interesting to note that methane formation efficiency was extremely higher compared with that of hydrogen in the electrochemical reduction of CO_2 in NaOH/methanol-based electrolyte at relatively more negative potential region (−3.0 to −5.0 V). The reason is not clear. Maybe, it is attributed that the diffusion of CO_2 to the cathode in methanol-based electrolyte is more effective than those in the aqueous solution, owing to the large solubility of CO_2 in methanol at 243 K. Furthermore, adsorbed hydrogen atoms, formed in the reduction of proton, may play a very important role in the formation of methane.

Table 2 summarizes the ratios of the current efficiency of methane and ethylene, $r_f(CH_4)/r_f(C_2H_4)$, to discuss the effect of the cationic species on the reduction reaction. In the photoelectrochemical reduction of CO_2, Yoneyama et al. [24] reported that the difference in the hydrophilicities at the electrode surface determines the product selectivity. Our experimental results may be explained similarly. Actually, one of the major differences between alkaline metals is their hydrophilicity. The hydration enthalpy and hydration entropy at room temperature are presented in Table 2, which are intimately related with the hydrophilicity and the hydrophobicity. A hydrophobic surface is thought to allow hydrophobic cations such as Cs^+ and Rb^+ to adsorb on the cathode surface, thus producing a hydrophobic environment. Because small cations such as Li^+ and Na^+ seem to less adsorb on the electrode surface due to their strong hydration, the electrode vicinity may have more hydrophilic conditions. Therefore, methane formation, whose reaction requires a number of adsorbed protons, can be expected to proceed more efficiently in the hydrophilic atmosphere compared to ethylene formation. 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 obtained in the aqueous solutions [23, 24] and in the electroreduction of high-pressure CO_2 [19].

Conclusion

The electrochemical reduction of CO_2 with Cu electrode in methanol with sodium hydroxide supporting salt at low temperature (243 K) was studied. The maximum current efficiency for hydrocarbons was 80.6% at −4.0 V vs Ag/AgCl. A predominant formation of methane was observed in the potential range of −2.5 to −5.0 V vs Ag/AgCl. The formation efficiency for hydrogen was suppressed to less than 4%. The cost of industrial sodium hydroxide is much lower relative to that of lithium hydroxide. Because methanol is widely used in the industry as a CO_2 absorbent in the Rectisol process [6, 7], this research may contribute to the applications in the conversion of CO_2-saturated methanol into fuel products. 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 fuel 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 the production of intermediate materials for the petrochemical industry.

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