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Electrochemical reduction of carbon dioxide on copper in methanol with various potassium supporting electrolytes at low temperature

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Abstract The electrochemical reduction of CO₂ at a Cu electrode was investigated in a methanol-based electrolyte using such potassium supporting salts as CH₃COOK, KBr, KI and KSCN at extremely low temperature (–30 °C). The main products obtained from CO₂ by the electrochemical reduction were methane, ethylene, ethane, carbon monoxide and formic acid. The maximum Faradaic efficiency of ethylene was 19.9% in KI/methanol-based catholyte at –3.0 V vs. Ag/AgCl saturated KCl. The best methane formation (27.0%) was obtained in CH₃COOK/methanol electrolyte at –3.0 V. In the system containing a potassium halide, the efficiency of hydrogen formation, being a competitive reaction against CO₂ reduction, was suppressed to less than 8.1%. The product selectivity of the electrochemical reduction of CO₂ in methanol was greatly affected by the anionic species. This research can contribute to the large-scale manufacturing of useful organic products from readily available and cheap raw materials: CO₂-saturated methanol from industrial absorbers (the Rectisol process).

Key words Electrochemical reduction · Carbon dioxide · Copper electrode · Methanol · Potassium supporting electrolytes

Introduction

The electrochemical reduction of carbon dioxide (CO₂) has attracted considerable attention as a possible source

of carbon for the synthesis of useful organic products and as a possible means of energy storage [1, 2].

Recently, many investigators have actively studied the electrochemical reduction of CO₂ using various metal electrodes in organic solvents, because organic aprotic solvents dissolve much more CO₂ than water [3–5]. It has been described that low reduced products containing carbon monoxide, oxalic acid and formic acid were produced by the electroreduction of CO₂ in dimethyl sulfoxide, *N,N*-dimethylformamide, propylene carbonate and acetonitrile. However, even at a copper electrode, few hydrocarbons have been obtained in these organic solvents.

Methanol, also, is a better solvent of CO₂ than water, particular at low temperature, because the solubility of CO₂ in methanol is approximately five times that in water at ambient temperature and 8–15 times that in water at temperature less than 0 °C [6–8]. Therefore, methanol has been industrially used as a physical absorbent of CO₂ in the Rectisol method at –10 to –30 °C [8]. Until now, more than 70 large-scale plants for the Rectisol process have been established. Moreover, compared to water, methanol is a poor solvent of acidic gases such as SO_x and NO_x. Owing to these two properties, the direct electrochemical reduction of CO₂ in a methanol-based electrolyte is an advantageous choice. Thus, we have studied the electrochemical reduction of CO₂ on Cu in a methanol-based catholyte with such supporting salts as potassium hydroxide, benzalkonium chloride and tetraethylammonium perchlorate at –30 °C [9–12]. 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.

Thus far, various potassium supporting salts containing KHCO₃, KCl, KClO₄, K₂SO₄, K₂HPO₄ and KOH were examined in the electrochemical reduction of CO₂ on Cu in a water [13]. However, there are few reports concerning the anionic species effect on the electrochemical reduction of CO₂ on Cu in a K⁺/methanol-based electrolyte. In this study, the electrochemical

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reduction of CO₂ at a copper electrode in methanol with various potassium supporting salts has been investigated. Moreover, the effect of the anionic species on the reduction reaction on the electrode surface has been discussed.

Experimental

The apparatus and experimental conditions for the electrochemical reduction of CO₂ are shown in Table 1. Electrochemical reduction of CO₂ was performed in a custom-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 sat. KCl electrode that was connected with the catholyte through an agar salt bridge.

The methanol (99%, Nacalai Tesque, Japan) was purified by double distillation from metallic magnesium. Potassium acetate, bromide, iodide and thiocyanate (Nacalai Tesque) were used as the supporting salt in the methanol-based catholyte. The pH of the catholyte was measured with a glass electrode for nonaqueous solvents (Horiba, 6377-10D), calibrated in water. 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. The electrodes were activated by anodic polarization at 500 mA for 100 s in 14.7 mol dm⁻³ phosphoric acid. Finally, both electrodes were rinsed with water and ethanol.

A discontinuous electroreduction procedure was used: first, CO₂ gas was bubbled into the methanol catholyte for 1 h at a rate of 30 ml min⁻¹, then the CO₂-saturated solution was reduced electrolytically at cathodic polarizations in the range from -3.0 to -7.0 V vs. Ag/AgCl sat. KCl. Stirring of the catholyte was provided by a magnetic bar. The Faradaic efficiencies of formation for the main products were calculated assuming that a total of 50 C of charge passed through the cell. Gaseous products obtained during electroreduction were collected in a gas collector and were analyzed by gas chromatography. Products soluble in the catholyte were analyzed by using high-performance liquid chromatography and gas chromatography.

Results and discussion

A suitable potassium supporting electrolyte was explored for the electrochemical reduction of CO₂ in methanol. Therefore, the solubility in methanol at -30 °C was studied for various potassium salts such as KNO₃, KHCO₃, K₂HPO₄, KCl, KHSO₄, K₂SO₄, KBr, KI, CH₃COOK and KSCN. Consequently, these compounds could be classified into three groups according to the solubility: (1) insoluble: KNO₃, KHCO₃, K₂HPO₄, KCl, KHSO₄ and K₂SO₄; (2) soluble: (~100 mmol dm⁻³) KBr; (3) very soluble (>500 mmol dm⁻³): KI, CH₃COOK and KSCN. Therefore, potassium acetate, bromide, iodide and thiocyanate were selected as the supporting electrolyte and the concentrations for each supporting salt were determined as shown in Table 1.

The solubility of CO₂ in methanol and the pH of methanol after CO₂ saturation were investigated for the potassium supporting salts at -30 °C. Table 2 shows the results compared with literature values in water. In each case the solubility of CO₂ in the system studied was much larger than that in water.

The electrolysis was performed at -30 °C because the temperature in the Rectisol process was in the range of -10 to -30 °C [8].

Onset potential

The effect of the anionic species on the electrochemical reduction of CO₂ on Cu in K⁺/methanol electrolyte was evaluated using the onset potentials of the cathodic current. The onset potentials were obtained by cyclic voltammetric measurements at a scanning rate 50 mV s⁻¹

Table 1 Apparatus and experimental conditions

<i>Electrochemical reduction</i>	
Cell	H-type cell
Potentiostat/galvanostat	Hokuto HA-105
Coulometer	Integrator 1109 (Fusou Seisakujyo, Japan)
Potential sweep	Hokuto HB-111 function generator
XY recorder	Graphtec WX1100
Thermostat	NES Lab. Instruments, RTE-110
Working electrode	Cu foil (30 mm × 20 mm, 0.1 mm thickness, 99.98% purity)
Counter electrode	Pt foil (30 mm × 20 mm, 0.1 mm thickness, 99.98% purity)
Reference electrode	Ag/AgCl sat. KCl (Horiba, 2060A-10T)
<i>Electrolyte</i>	
Catholyte	50 mmol dm ⁻³ CH ₃ COOK, 500 mmol dm ⁻³ CH ₃ COOK, 50 mmol dm ⁻³ KBr, 50 mmol dm ⁻³ KI, 500 mmol dm ⁻³ KI, 50 mmol dm ⁻³ KSCN and 500 mmol dm ⁻³ KSCN in methanol
Anolyte	300 mmol dm ⁻³ KOH in methanol
Carbon dioxide	99.9999% purity
Potential	-3.0 to -7.0 V vs. Ag/AgCl sat. KCl
Temperature	-30 ± 0.5 °C
<i>Product analysis</i>	
Gas products	Gas chromatography TCD (GL Science GC-320, molecular sieve 5A; 13X-S, Ar and He carrier gas) FID (Shimadzu GC-14B, Porapak Q, N ₂ and H ₂ carrier gas)
Liquid products	HPLC with UV detector (Hitachi L4000) TCD and FID gas chromatography

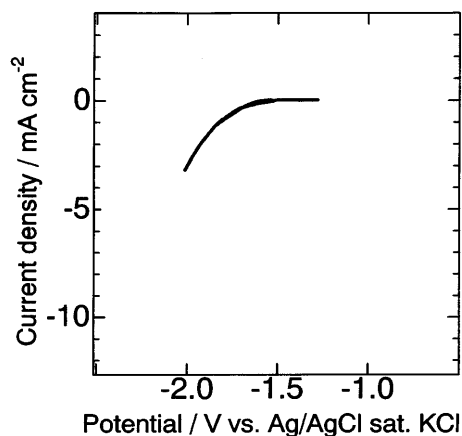
Table 2 pH after CO₂ saturation and solubility of CO₂ in methanol at -30 °C

Supporting salt (mmol dm ⁻³)	pH	Solubility of CO ₂ (cm ³ cm ⁻³)
CH ₃ COOK (50)	6.8	20.0
CH ₃ COOK (500)	7.4	20.1
KBr (50)	4.7	20.1
KI (50)	4.6	18.5
KI (500)	4.6	16.7
KSCN (50)	4.2	19.8
KSCN (500)	4.6	16.6
KOH ^a (100)	8.5	16.0
Water ^b		0.821

^a Ref. [14]^b Ref. [6]; solubility of CO₂ at 15 °C

in CO₂-saturated methanol. A typical cyclic voltammogram is illustrated in Fig. 1. CO₂ reduction is evident on the voltammograms recorded in CO₂-saturated methanol. With any supporting salts, no voltammetric peak was obtained in the potential range studied. The onset (appearance) potentials for the cathodic current, i.e. those potential values at which a current density of 0.1 mA cm⁻² is observed, were approximately -1.3, -1.3, -1.4, -1.5, -1.5 and -1.6 V in 50 and 500 mmol dm⁻³ CH₃COOK, 50 mmol dm⁻³ KBr, 50 and 500 mmol dm⁻³ KI, 50 and 500 mmol dm⁻³ KSCN/methanol-based electrolyte, respectively. In these methanol-based catholytes, the onset potentials were nearly similar. It has been reported that the onset potential at a Cu electrode in CO₂-saturated TEAP/methanol-based catholyte at -30 °C was about -1.1 V vs. SCE [11]. Ortiz et al. [15] have stated that the onset potential recorded with a Cu electrode in NaClO₄/methanol electrolyte at room temperature was -0.6 V vs. Ag/Ag⁺. The onset potentials may be affected by the pH of catholyte; these effect are still being examined.

Once the onset potentials were determined from polarization experiments, we attempted to investigate the electrochemical reduction of CO₂ in CO₂-saturated

**Fig. 1** Cyclic voltammogram on a Cu electrode in CO₂-saturated methanol at 243 K. Catholyte: 500 mmol dm⁻³ KI/methanol. Anolyte: 300 mmol dm⁻³ KOH/methanol

methanol at cathodic polarizations exceeding the onset potential. Therefore, the potentials were set in the range of -3.0 to -7.0 V vs. Ag/AgCl sat. KCl.

Faradaic efficiency of the products

Table 3 shows the current efficiencies of the products by electrochemical reduction of CO₂ in a methanol-based catholyte using various K salts at -30 °C. The reduction products from CO₂ were methane, ethylene, ethane, CO and formic acid. A maximum Faradaic efficiency of methane (27.0%) was observed in 500 mmol dm⁻³ CH₃COOK/methanol electrolyte. The best ethylene formation efficiency (19.9%) was obtained in 50 mmol dm⁻³ KI/methanol-based catholyte. Ethane formation efficiency was less than 0.34% under the experimental conditions studied. The total current efficiency for hydrocarbons may roughly be independent of the supporting salts. In KOH/methanol-based electrolyte [10], the total efficiency of hydrocarbons was relatively low (2.0%). The reason for the differences in the efficiency of the hydrocarbons is not clear. It may be attributable to the cathode potential, the pH of catholyte or the shape of the electrode. In a 50 mmol dm⁻³ KHCO₃ solution [16], CO₂ was reduced at a copper electrode to methane, ethylene, ethane, CO and formic acid with Faradaic efficiencies of 17.8%, 12.7%, 0.039%, 5.4% and 10.2%, respectively. Therefore, the total Faradaic efficiency for hydrocarbons was similar to or better than those obtained in 50 mmol dm⁻³ KHCO₃ aqueous solution. The efficiency of CO formation in CH₃COOK/methanol-based catholyte was worse than those in methanol in the presence of other salts.

Generally, for the electrochemical reduction of CO₂ in water, hydrogen formation competes with the CO₂ reduction reaction. Therefore, the depression of hydrogen formation is very important because the applied energy is wasted on hydrogen evolution instead of being used for the reduction of CO₂. In K⁺/methanol-based electrolyte, the Faradaic efficiency for hydrogen formation on the Cu electrode at -30 °C was suppressed to less than 15.3% except for that in the case of acetate. Especially, the efficiency was below 8.1% when potassium halide salts were used as the supporting electrolytes. Only in CH₃COOK/methanol electrolyte was hydrogen formation efficiency relatively high (53.9% and 32.5%) at -3.0 V and decreased with the negative potential. Hydrogen evolution may be affected by the anionic species. Generally, the methanol-based electrolyte with potassium supporting salts at low temperature was suitable to suppression of hydrogen formation in the electrochemical reduction of CO₂.

Reaction mechanism

The mechanism of the electrochemical reduction of CO₂ with a copper electrode in methanol was studied for

Table 3 Faradaic efficiencies of the products by electrochemical reduction of CO₂ on Cu in methanol-based catholyte with various potassium supporting salts

Salt (mmol dm ⁻³)	Potential (V vs. Ag/AgCl)	Current density (mA cm ⁻²)	Faradaic efficiency (%)							
			CH ₄	C ₂ H ₄	C ₂ H ₆	CO	HCOOH	H ₂	Total	HC ^a
CH ₃ COOK (50)	-3.0	3.4	8.6	3.2	-	5.4	13.1	53.9	84.2	11.8
	-5.0	8.7	18.4	11.4	0.01	19.4	12.7	8.7	70.6	29.8
CH ₃ COOK (500)	-3.0	12.9	27.0	7.1	0.02	6.5	13.0	32.5	86.1	34.1
	-4.0	25.0	16.1	14.6	0.01	4.2	13.7	18.0	66.6	30.7
KBr (50)	-3.0	3.2	6.4	9.8	-	35.0	17.4	3.6	72.2	16.2
	-5.0	11.8	19.1	18.2	0.13	12.0	12.0	4.6	66.0	37.4
KI (50)	-3.0	4.2	15.8	19.9	0.17	15.2	- ^b	3.5	54.6	35.9
	-6.0	13.4	6.8	12.5	0.13	16.8	- ^b	4.0	40.2	19.4
	-7.0	17.8	19.4	10.5	0.01	21.0	- ^b	1.2	52.1	29.9
KI (500)	-3.0	24.7	7.0	14.9	-	14.1	- ^b	8.1	44.1	21.9
	-3.0	2.6	22.4	12.6	0.23	21.0	- ^b	15.3	71.5	35.2
KSCN (50)	-6.0	13.4	22.5	9.5	0.01	27.1	- ^b	2.6	61.7	32.0
	-3.0	15.3	16.7	16.5	0.34	11.1	- ^b	8.1	52.7	33.5
KSCN (500)	-4.0	50.2	11.8	16.0	0.01	5.5	- ^b	9.7	43.0	27.8
	-1.8 ^d	- ^b	1.0	1.0	-	30.0	26.0	1.4	58.0	2.0
Water ^e	-2.2 ^d	- ^b	17.8	12.7	0.039	5.4	10.2	52.0	98.0	30.5

^a Total Faradaic efficiency for hydrocarbons (methane, ethylene and ethane)

^b Not measured

^c Ref. [10]

^d vs. SCE

^e Ref. [16]

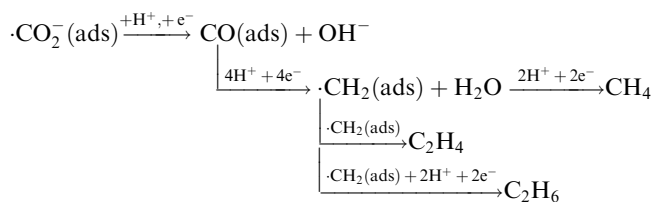
various potassium supporting electrolytes. A GC-MS study with deuterated methanol catholyte demonstrated that no reduction product was produced from methanol [17]. When the electrolysis was conducted under a nitrogen atmosphere, with any potassium supporting salts, exclusively hydrogen was evolved, no CO₂ being reduced. Consequently, the needed products were not formed from the decomposition of methanol and supporting salts at the cathode and were produced by the electrochemical reduction of CO₂, and the reaction path of the reduction products seems to be identical for all supporting salts used. The electroreduction of CO₂ is, apparently, a very complex process whose mechanism is not yet fully understood [18–20]. From these experimental data and literature reports [9–14, 21–24], the pathway by which methane, ethylene, ethane, carbon monoxide and formic acid on Cu electrode are formed can be estimated.

Most studies have indicated that the first steps in the reduction of CO₂ at high hydrogen overpotential cathodes are [21–23] as follows:



The presence of adsorbed ·CO₂⁻ and HCOO⁻ anion radicals at Hg electrodes was ascertained by electrochemical and spectroscopic techniques [23, 24]. For the reduction of CO₂ at a Cu electrode there are no data suggesting adsorption of ·CO₂⁻ and HCOO⁻ anion radicals, but some workers [13] propose reaction (1) as the first step.

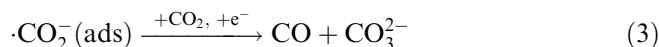
Hydrocarbons are yielded by a series of simultaneous or consecutive electronation/protonation steps, according to the following simplified scheme:



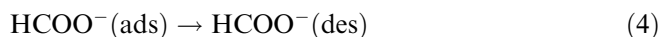
Scheme 1

The adsorbed ·CO₂⁻ radical anion formed in the first electronation step undergoes a second electronation/protonation to yield adsorbed CO as the key intermediate. By a succession of four electronation/protonation steps an adsorbed reactive methylene group forms, and this may either stabilize as a methane molecule by a subsequent double electronation/protonation sequence or dimerize to form ethylene and ethane.

For the formation of CO, we assume the usual pathway, which involves a one-electron reduction followed by the disproportionation of ·CO₂⁻ radical anions to neutral CO molecules and dinegative carbonate ions:



Although adsorbed ·CO₂⁻ anion radicals seem to be predominantly formed at the first step, a part of the ·CO₂⁻ radicals may convert to adsorbed HCOO⁻ anions. Therefore, formic acid will be generated from the desorption of these adsorbates:



Saeki et al. [25] have reported the electrochemical reduction of CO₂ at a Cu electrode in methanol under high pressure. In the electrochemical reduction of high pressure CO₂ in methanol, the cationic species had a large

effect on the reaction. In contrast, the effect of the anionic species was small. However, in the present system, the product selectivity was greatly affected by the anionic species. Hydrogen formation tends to increase in the order of halide < thiocyanate < acetate. On the other hand, CO formation efficiencies were relatively high when halide and thiocyanate were used as the supporting electrolyte and those were relatively low in the presence of acetate. The Faradaic efficiency for hydrocarbons may be independent of the supporting salts used. Therefore, in the electrochemical reduction of CO₂ at a Cu electrode in methanol at low temperature, the anionic species may affect the competition between small-number electron reduction reactions (CO and hydrogen formations).

Conclusion

The electrochemical reduction of CO₂ with a Cu electrode in methanol was studied for various potassium supporting salts. The selectivity of the electrochemical reduction products of CO₂ on Cu in methanol depended remarkably on the anionic species. The best current efficiency for ethylene (19.9%) was obtained in KI/methanol-based electrolyte at -3.0 V. A maximum efficiency for methane formation was 27.0% in CH₃COOK/methanol catholyte at -3.0 V. In the system with a potassium halide as supporting electrolytes, the formation efficiency for hydrogen was depressed to below 8.1%. Since methanol is widely used industrially as a CO₂ absorbent at -10 to -30 °C in the Rectisol process [8], this research may contribute to applications in the conversion of CO₂-saturated methanol into useful products. Thus, the synthesis of hydrocarbons by the electrochemical reduction of CO₂ might be of practical interest in fuel production, storage of solar energy or the production of intermediate materials for the petrochemical industry.

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