Electrochemical Reduction of Carbon Dioxide to Hydrocarbons with High Faradaic Efficiency in LiOH/Methanol

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The electrochemical reduction of CO_2 with a Cu electrode in LiOH/methanol-based electrolyte was investigated. A divided H-type cell was employed, the supporting electrolytes were 80 mmol dm^{-3} lithium 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 of 78%, 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 in the range from 2.2 to 4.3. In LiOH/methanol, the efficiency of hydrogen formation, a competing reaction of CO_2 reduction, was depressed to below 2% at relatively negative potentials. On the basis of this work, the high efficiency electrochemical CO_2 to hydrocarbon conversion method appears to be achieved. Future work to advance this technology may include the use of solar energy as the electric energy source. This research can contribute to the large-scale manufacturing of fuel gases from readily available and inexpensive raw materials, CO_2-saturated methanol from industrial absorbers (the Rectisol process).

Introduction

The chemical fixation of carbon dioxide (CO_2), by radiochemical, chemical, thermochemical, photochemical, electrochemical, and biochemical procedures, has been of significant interest form both fundamental and practical viewpoints.[1,2] The electrochemical method appears to be a very suitable method for the conversion and reduction of CO_2.[2,3]

In the electrochemical reduction of CO_2, in water, at most metal electrodes the major reaction products were carbon monoxide and formic acid.[4,5] However, only copper has proven a suitable electrode for the formation of hydrocarbons such as methane and ethylene, which can be used as fuel gases.[5−10] Azuma et al.[5] 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. Murata et al.[6] reported 32.2% Faradaic efficiency for methane and 5.2% for ethylene in the electrochemical reduction of CO_2 on Cu electrode, in 100 mmol dm^{-3} aqueous $LiHCO_3$ solution. Kyriacou et al.[7] described the formation efficiencies in the electrochemical reduction of CO_2 on Cu, in 500 mmol dm^{-3} $LiHCO_3$ solution, at 298 K, as follows: 26% for methane; 4% for ethylene; etc.

Recently, many investigators have actively studied the electrochemical reduction of CO_2 using various metal electrodes in organic solvents, given that organic aprotic solvents dissolve much more CO_2 than water.[11−13] Reduced products containing carbon monoxide, oxalic acid, and formic acid were produced by the electroreduction of CO_2 in dimethyl sulfoxide, *N*,*N*-dimethylformamide, propylene carbonate, and acetonitrile. However, even at a copper electrode, no hydrocarbons were obtained in these organic solvents.[13]

Methanol is a better solvent of CO_2 than water, particularly at low temperature. The solubility of CO_2 in methanol is approximately 5 times that in water, at ambient temperature, and 8−15 times that in water, at temperatures below 273 K.[14−16] Therefore, methanol has been industrially used as a physical absorbent of CO_2 in the Rectisol method, at 243−263 K.[16] Currently, over 70 large-scale plants apply the Rectisol process. In addition, compared to water, methanol is a poor solvent of acidic gases such as SO_x and NO_x. Due to these two properties of methanol, the direct electrochemical reduction of CO_2 in methanol-based electrolyte is an advantageous choice. Thus, we have investigated the electrochemical reduction of CO_2 on copper electrodes by using methanol as the solvent, at 243 K.[17−21] In methanol-based catholyte, the formation of methane and ethylene was observed. The maximum current efficiency for hydrocarbons was of 43%, with benzalkonium chloride salt.[17] However, the achieved efficiency was inadequate for applying the process on the industrial scale.

This study deals mainly with the electrochemical reduction of CO_2 to hydrocarbons, at copper electrodes, in LiOH/methanol-based electrolyte, a process that can be performed with high Faradaic efficiency.

Experimental Section

The apparatus and experimental conditions for the electrochemical reduction of CO_2 are shown in Table 1. The electrochemical reduction of CO_2 was performed in a homemade, 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.

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TABLE 1: Apparatus and Experimental Conditions

	Electrochemical Reduction
cell	H-type cell
potentiostat/galvanostat	Hokuto HA-105
coulometer	Integrator 1109 (Fusou Seisakujyo, Inc., Japan)
potential sweep	Hokuto HB-111 function generator
XY recorder	Graphtec WX1100
thermostat	NES Lab., Instruments, Inc., 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)
electrolyte	
catholyte	80 mmol dm^{-3} LiOH in methanol
anolyte	300 mmol dm^{-3} KOH in methanol
carbon dioxide	99.9999% purity
potential	−2.0 to −5.0 V vs Ag/AgCl sat. KCl
temperature	243 ± 0.5 K
	Product Analysis
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

Methanol (99%, Nacalai Tesque, Inc., Japan) was purified by double distillation from metallic magnesium. Water content in the pure methanol was less than 1 ppm (confirmed by the Karl Fischer test). Lithium hydroxide (95%, Nacalai Tesque, Inc.) was used as the ionophore in the methanol-based catholyte. The pH of catholyte was measured with a glass electrode for nonaqueous solvent (Horiba, 6377-10D), calibrated in water. Other details for the pH measurement were described elsewhere.[22,23] The pH scale for the methanol was in the range of 1.8 to 17.2.[24] The pH of 80 mmol dm^{-3} LiOH/methanol was ∼14 and after the saturation of the electrolyte with CO_2 the pH was 6.2. 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, 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 −2.0 to −5.0 V vs Ag/AgCl, sat. KCl. The catholyte was stirred magnetically. The Faradaic efficiency of the main products was calculated assuming that a total of 50 coulombs of charge passed through the cell. Gaseous products obtained during 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 Discussion

The solubility of CO_2 in a solution of 80 mmol dm^{-3} LiOH/methanol, at 243 K, was 18 cm^3 cm^{-3} (∼800 μmol CO_2/cm^3 methanol). Literature data[14,15] for the solubilities of CO_2 in pure methanol and water, at 288 K, were of 4.6 and 0.821 cm^3 cm^{-3}, respectively. Although $LiHCO_3$ may be formed in the methanol while bubbling CO_2 through the solution for several minutes, the amount of hydrogen carbonate is assumed to be negligible, since 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.

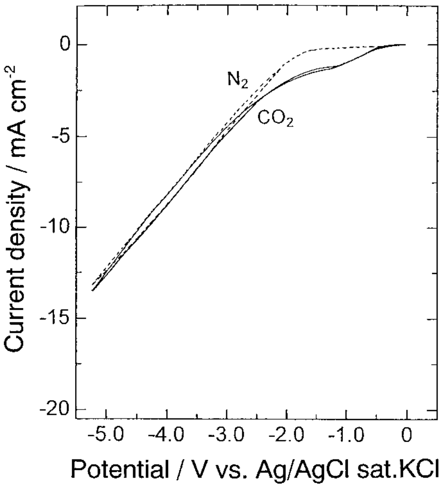


Figure 1. Cyclic voltammograms on Cu electrode in methanol at 243 K. Solid line, CO_2 atmosphere; broken line, N_2 atmosphere. Catholyte, 80 mmol dm^{-3} LiOH/methanol; anolyte, 300 mmol dm^{-3} KOH/methanol.

The electrolysis was performed at 243 K because temperature in the Rectisol process is customarily in the range of 243 to 263 K.[16]

Cyclic Voltammetry. First, cyclic voltammograms (CV) at the Cu electrode in LiOH/methanol-based catholyte were recorded at 243 K. The potential was scanned at a sweep rate of 50 mV s^{-1}. Figure 1 shows the current−potential curves with the Cu electrode in CO_2-saturated methanol and in N_2-purged methanol. CO_2 reduction is evident on the voltammogram recorded 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. Under nitrogen atmosphere, hydrogen formation efficiency was approximately 98% in the electrolysis, with no CO_2 being reduced. Hence, we conclude that the cathodic currents can be attributed solely to the reduction of residual water, present slightly in the methanol catholyte. The onset (starting) potential of the cathodic current, i.e., those potential value at which a current density of 0.1 mA cm^{-2} is observed, in CO_2-saturated methanol was around −0.5 V. From this potential value, scanning in the negative direction, the current density gradually increased until reaching the potential of −2.0 V in which the current abruptly increased. At cathodic polarizations below −2.0 V, the current density recorded in CO_2-saturated electrolyte appears to be similar to that in N_2-purged electrolyte. The current−potential characteristics can be attributed to a number of processes such as kinetics, adsorption, desorption, and diffusion. Ortiz et al.[25] have reported a cyclic voltammogram with Cu electrode in CO_2-saturated $NaClO_4$/methanol electrolyte, at room temperature. In the voltammetric measurements, the onset potential was about −0.6 V vs Ag/Ag^+ and the polarization curve slowly dropped scanning at values more negative than −0.6 up to −1.3 V. More negative than this latter value, the polarization curve significantly diminished. Thus, the shape of our CVs in LiOH/MeOH was nearly the same as that reported for $NaClO_4$/MeOH. In LiOH/methanol-based electrolyte, the onset potential recorded in N_2-purged methanol was shifted to more negative potential values relative to the onset

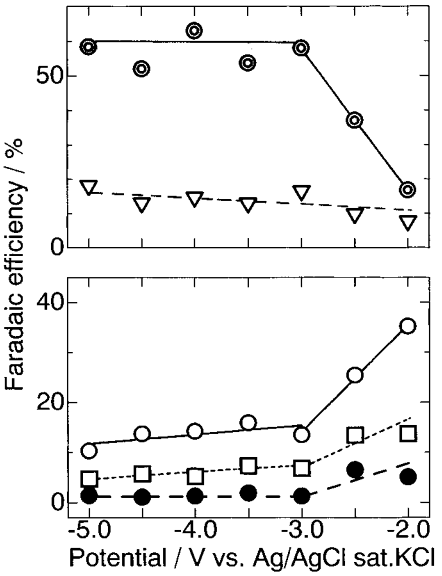


Figure 2. Effect of potential on Faradaic efficiencies for the products by electrochemical reduction of CO_2 at Cu electrode in methanol at 243 K: CH_4 (⊙); C_2H_4 (▽), CO (○), HCOOH (□), H_2 (●). Catholyte, 80 mmol dm^{-3} LiOH/methanol; anolyte, 300 mmol dm^{-3} KOH/methanol.

potential recorded in CO_2-saturated methanol. The pH of catholyte after saturation with CO_2 was 6.2 and the pH of N_2-purged methanol was ~14. Both the reduction and onset potentials may be affected by the pH of catholyte. These effects are still being examined.

Once the onset potentials were determined from polarization experiments, we attempted to investigate the effect of potential on the Faradaic efficiency of the products.

Effect of Potential of 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 Cu in LiOH/methanol at 243 K are illustrated in Figure 2. Methane, ethylene, CO, and formic acid were detected as reduction products from CO_2.

The current efficiency of methane increased from 20% to 60% from −2.0 to −3.0 V. At potentials more negative −3.0 V, the high efficiency was maintained. The current efficiency of ethylene gradually increased to 18%, as the potential was lowered. The current efficiency of methane was larger than those of ethylene in the entire investigated potential range. A maximum Faradaic efficiency for hydrocarbons (methane and ethlene, 78%) was observed at −4.0 V. The formation efficiency curves of CO and formic acid gradually increased with the positive direction at less than −3.0 V. At the polarizations above −3.0 V, both curves rose abruptly. In LiOH/methanol electrolyte, ethane was not produced but the efficiency of methane was much better than those obtained in water (24.7%, 32.2%, and 26%)[5−7] and the methanol containing benzalkonium chloride (43%).[17]

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 LiOH/methanol-based electrolyte, the Faradaic efficiency for hydrogen formation on the Cu electrode, at 243 K, was suppressed to less than 2%, at polarizations below −3.0 V. In the electrochemical reduction of CO_2 on Cu in water,[5−7] the hydrogen formation efficiencies were 60.5% and 68% in 100 and 500 mmol dm^{-3} $LiHCO_3$ solution, respectively, and 52.0% in 50 mmol dm^{-3} $KHCO_3$ solution. It has been reported that low temperature was effective for the depression of hydrogen formation in the methanol electrolyte.[17−21] 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.

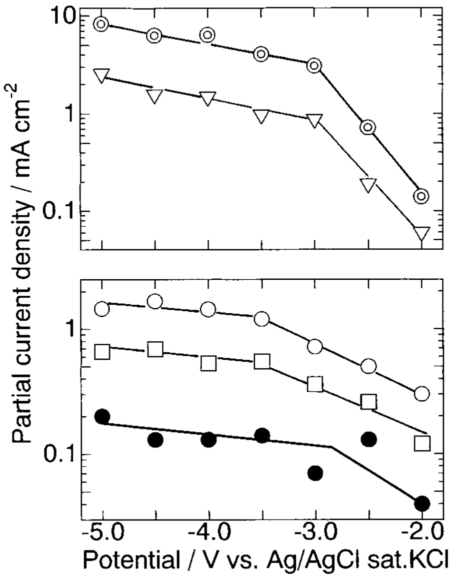
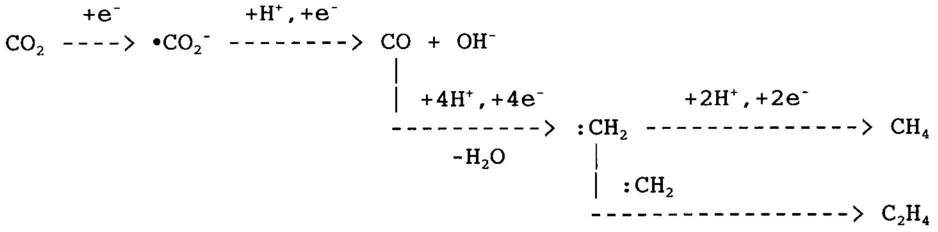


Figure 3. Tafel plots of the products by electrochemical reduction of CO_2 at Cu electrode in methanol at 243 K. CH_4 formation (⊙); C_2H_4 formation (▽); CO formation (○); HCOOH formation (□); H_2 evolution (●). Catholyte, 80 mmol dm^{-3} LiOH/methanol; anolyte, 300 mmol dm^{-3} KOH/methanol.

Tafel Plots. The effect of the potential on partial current densities for CO_2 reduction and hydrogen evolution at Cu electrode in LiOH/methanol-based catholyte was evaluated. The Tafel plots are shown in Figure 3. Methane and ethylene formations and hydrogen evolution became diffusion-controlled at around −3.0 V. A maximum partial current density for hydrocarbons was about 10 mA cm^{-2} at −5.0 V. At approximately −3.5 V, CO and formic acid formations became diffusion-controlled. Again, the reaction rate on the electrode is governed by various processes such as kinetics, adsorption, desorption, and diffusion. By considering this Tafel plot study, a limitation of CO_2 diffusion to the electrode may be a dominant process for the rate-determining step. The partial current density ratio of CO_2 reduction and hydrogen evolution, $i(CO_2)/i(H_2)$, was >47 at potentials more nagative than −3.0 V.

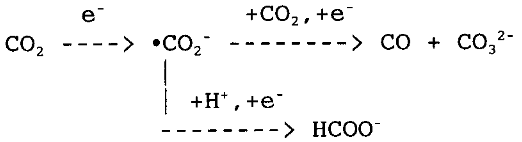
Mechanism of the Electrochemical Reduction of CO_2. The mechanism of the electrochemical reduction of CO_2 in LiOH/methanol-based electrolyte was investigated for a copper electrode. A GC−MS study with deuterated methanol catholyte demonstrated that no reduction product was produced from methanol.[26] When the electrolysis was conducted under nitrogen atmosphere, electrolysis yielded exclusively hydrogen. Consequently, the targeted products were produced by the electrochemical reduction of CO_2. These experimental data and literature reports[7,17−21,26] suggest the pathway by which methane, ethylene, carbon monoxide, and formic acid are formed.

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



The adsorbed $^{\bullet}CO_2^-$ 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.

For the formation of formic acid and CO, we assume the usual pathway, which involves a one-electron reduction followed by a second electronation/protonation to yield formic acid, and by the disproportionation of $^{\bullet}CO_2^-$ radical anions to neutral CO molecules and dinegative carbonate ions.



In the electrochemical reduction of CO_2, at a copper electrode in $LiHCO_3$ aqueous solution,[6,7] the ratios of the current efficiency of methane and ethylene, $r_f(CH_4)/r_f(C_2H_4)$, were 6.2 and 6.5. In LiOH/methanol-based electrolyte, the ratio was in the range 2.2−4.3. On the other hand, the ratio was relatively low (0.13 to 0.34) in CsOH/methanol catholyte.[21] Several researchers[6,7] have presented that the methane/ethylene Faradaic efficiency ratio increased as the radius of the cation increased, i.e., $Li^+ < Na^+ < K^+ < Cs^+$, in the electrochemical reduction of CO_2 on Cu in water. Hence, a similar tendency may be obtained in the electrochemical reduction of CO_2 at Cu electrode in methanol. Small cations such as Li^+ and Na^+ were not adsorbed at the electrode surface, due to their strong hydration. In addition, small cations carry to the cathode a large number of water molecules and thus supply protons for the electroreduction. The conversion of intermediate $Cu{=}CH_2$ to methane requires the presence of adsorbed hydrogen. Thus, this reaction may be favored at larger surface hydrogen coverage, as is the case of Li^+.

Saeki et al.[27] have reported the electrochemical reduction of CO_2 with Cu electrode, in methanol, under high pressure. In the electrochemical reduction of high-pressure CO_2, the reduction of CO_2 was suppressed in the presence of lithium ion because of the stability of the ion pair of one-electron reduced species with the cation of the supporting salt, $\{Li^+{-}^{\bullet}CO_2^-\}$. The formation of $\{Li^+{-}^{\bullet}CO_2^-\}$ will be greater under a high pressure of CO_2, but is hardly reduced further. Generally, the $^{\bullet}CO_2^-$ species may be stabilized by being adsorbed on the cathode and/or by forming the ion pair with a cation of the supporting electrolyte. Therefore, due to a number of adsorbed $^{\bullet}CO_2^-$ species which were formed under ambient pressure, the CO_2 reduction seems to proceed in this system.

In recent years, several investigators[8−10] have described that the poisoning of the electrode reaction occurred during the electrocatalysis and the formation of a black deposit on the Cu electrode surface was observed. Hence, it was proposed that the major route to loss of electrode activity is via the formation of formic acid which is then reduced to graphitic carbon.[9] In the present study, the Faradaic efficiency for formic acid was relatively low (less than 13%) and the black deposit on the surface of cathode was not formed during the electrolysis. Therefore, the deactivating process may not become appreciable in the electrochemical reduction of CO_2 on Cu in LiOH/methanol-based electrolyte until 50 coulombs.

Conclusion

The electrochemical reduction of CO_2 with Cu electrode in LiOH/methanol-based electrolyte at low temperature (243 K) was studied. The best current efficiency for methane was 63% 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 2% at relatively negative potentials. Since methanol is widely used in industry as a CO_2 absorbent at 243 to 263 K in the Rectisol process,[16] this research may contribute to applications in the conversion of CO_2-saturated methanol into 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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