Electrochemical conversion of carbon dioxide to methane in aqueous NaHCO₃ solution at less than 273 K

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Abstract

The electrochemical reduction of CO_2 on a Cu electrode was investigated in aqueous $NaHCO_3$ solution, at low temperature. A divided H-type cell was employed, the catholyte was 0.65 mol dm^{-3} $NaHCO_3$ aqueous solution and the anolyte was 1.1 mol dm^{-3} $KHCO_3$ aqueous solution. The temperature during the electrolysis of CO_2 was decreased stepwise to 271 K. Methane and formic acid were obtained as the main products. The maximum Faradaic efficiency of methane was 46% at −2.0 V and 271 K. The efficiency of hydrogen formation, a competing reaction of CO_2 reduction, was significantly depressed with decreasing temperature. Based on the results of this work, the proposed electrochemical method appears to be a viable means for removing CO_2 from the atmosphere and converting it into more valuable chemicals. The synthesis of methane by the electrochemical method might be of practical interest for fuel production and the storage of solar energy.
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1. Introduction

The more and more scientists are interested in the chemical fixation of carbon dioxide (CO_2) from both fundamental and practical standpoints [1,2]. A variety of methods, such as radiochemical, chemical, thermochemical, photochemical, electrochemical, and biochemical procedures, have been developed. The electrochemical technique appears to be very promising for the conversion and reduction of CO_2 [2,3].

When used in the aqueous solution, most flat metallic electrodes yielded carbon monoxide and formic acid [4,5]. Only copper was a suitable electrode for the formation of hydrocarbons such as methane and ethylene, which can be used as fuel gases [4–15]. Moreover, several studies revealed that the hydration of the metal ions of supporting salts plays a key role in controlling the selectivity of CO_2 electroreduction [15].

When small cations, such as Li$^+$ and Na$^+$, were used as the supporting electrolytes, methane formation efficiency was larger than those for ethylene.

Kyriacou et al. [6] reported the following formation efficiencies for the electrochemical reduction of CO_2 on Cu in a 500 mmol dm^{-3} KHCO₃ solution at 298 K: 16% for methane and 14% for ethylene. Azuma et al. [5] investigated the electrochemical reduction of CO_2 at a Cu electrode in a 50 mmol dm^{-3} KHCO₃ aqueous solution at 293 K and obtained methane, ethylene, and ethane with Faradaic efficiencies of 17.8, 12.7, and 0.039%, respectively. Furthermore, they attempted to lower the temperature to 273 K and obtained different current efficiencies for methane, ethylene, and ethane: 24.7, 6.5, and 0.015%, respectively. The solubility of CO_2 in bicarbonate solution increases with decreasing temperature. However, there is little information on the electrochemical reduction of CO_2 in an aqueous solution at less than 273 K, due to the freezing point of water [13,14].

On the other hand, we have investigated the electrochemical reduction of CO_2 on Cu in methanol at low

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temperature of less than 273 K [8–14]. Although the high formation efficiency of methane was obtained in the methanol electrolyte, the potentials between the cathode and the anode in methanol were much larger than those in the aqueous solution. Hence, if the electrochemical reduction system of CO_2 to methane with high Faradaic efficiency in the aqueous solution is possbile, the conversion technologies using the water might receive more considerable attention from the viewpoint of the applied potentials.

In a high concentration of solute, the aqueous solution will not freeze at less than 273 K because of freezing point lowering. In this study, we report the electrochemical reduction of CO_2 to methane with high Faradaic efficiency (46%) in a $NaHCO_3$ aqueous solution at less than 273 K.

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 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, sat. KCl electrode

Table 1
Apparatus and experimental conditions

Electrochemical reduction	
Cell	H-type cell
Potentiostat/galvanostat	Hokuto-denko model HA-310 (Tokyo, Japan)
Coulometer	Integrator 1109 (Fusou Seisakujyo, Inc., Japan)
Potential sweep	Hokuto-denko HB-111 function generator
XY recorder	Graphtec WX1100
Thermostat	EYELA, Tokyo Rikakikai CO. LTD., ESC-50
Working electrode	Cu foil
	30×20 mm^2, 0.1 mm thickness, 99.98% purity (The Nilaco Corp., Tokyo, Japan)
Counter electrode	Pt foil
	30×20 mm^2, 0.1 mm thickness, 99.98% purity (The Nilaco Corp., Tokyo, Japan)
Reference electrode	Ag/AgCl, sat. KCl (Horiba, 2060A-10T)
Electrolyte	
Catholyte	0.65 mol dm^{-3} NaHCO$_3$ (70 cm^3)
Anolyte	1.1 mol dm^{-3} KHCO$_3$ (70 cm^3)
Carbon dioxide	99.9999% purity
Potential	-1.6 to -2.0 V vs. Ag/AgCl sat. KCl
Temperature	271–288 K
Product analysis	
Gas products	Gas chromatography
	TCD (GL Science GC-320, Molecular Sieve 5A; 13X-S, Ar and He carrier gas)
	FID (GL Science GC-353B, Porapak Q, N$_2$ carrier gas)
Liquid products	HPLC with UV detector (Hitachi L4000)
	Gas chromatography with TCD and FID

that was connected to the catholyte through an agar salt bridge. Sodium bicarbonate (Nacalai Tesque, Inc., Kyoto, Japan) was used as the ionosphere in the catholyte. In order to minimize the anolyte effect in the comparison with the electrolysis results in the literatures [4–6], potassium bicarbonate was selected as supporting salts in the anolyte because of its generality in the electrochemical CO_2 reduction in water. After saturation of the 650 mmol dm^{-3} NaHCO$_3$ aqueous solution with CO_2, the pH of the catholyte was 7.2. Mechanical processing of the Cu and Pt electrodes required polishing each surface with successively finer grades of alumina powder (Baikalox emulsion, Baikowski International Co., NC, USA) down to 0.05 μm, followed by the removal of any grease with acetone. Both electrodes were electrochemically activated at 500 mA for 45 s in 14.7 mol dm^{-3} phosphoric acid. Finally, the electrodes were rinsed with water and methanol.

A discontinuous electroreduction procedure was used. After CO_2 gas was bubbled into the catholyte for 1 h at a rate of 30 cm^3 min^{-1}, the CO_2-saturated aqueous solution was electrolytically reduced at a cathodic polarization in the range of -1.6 to -2.0 V vs. Ag/ AgCl, sat. KCl. The electrolyte was stirred magnetically. The Faradaic efficiencies for the formation for the main products were calculated assuming that a total of 50 coulombs of charge passed through the cell. Gaseous products obtained during the electroreduction were collected in a gas collector and analyzed by GC. Products soluble in the catholyte were analyzed using HPLC and GC.

3. Results and discussion

Based up on the research of Hori et al. [4], copper was chosen as the cathode for its unique property of allowing the formation of hydrocarbons. Generally, the freezing point of an aqueous solution decreases with the increase of solute concentration. Hence, the optimum concentration of the supporting electrolyte was determined. At 270 K, 0.65 mol dm^{-3} NaHCO$_3$ aqueous solution could freeze or a precipitation of the supporting salt was observed. At this temperature, 0.70 mol dm^{-3} NaHCO$_3$ did not dissolve completely. Consequently, the electroreduction of CO_2 was tested in a 0.65 mol dm^{-3} NaHCO$_3$ aqueous solution at 271 K. The solubility of CO_2 in a 0.65 mol dm^{-3} NaHCO$_3$ solution at 271, 278, and 288 K was of 1.2, 0.86, and 0.60 cm^3 cm^{-3}, respectively, corresponding to concentrations of approximately 54, 38, and 27 μmol CO_2 cm^{-3}. Literature data for the solubility of CO_2 in water at 288 K was 0.821 cm^3 cm^{-3} [16]. Therefore, the increased solubility of carbon dioxide at low temperature in our system relative to ambient temperature

conditions appears to be very advantageous for the electrochemical reduction of CO_2.

3.1. Cyclic voltammetry

Cyclic voltammograms (CVs) at the Cu electrode in the 0.65 mol dm^{-3} NaHCO$_3$ aqueous solution were recorded at 271–288 K. The sweep rate was 50 mV s^{-1}. Fig. 1 shows the current–potential curves of the Cu electrode in CO_2-saturated NaHCO$_3$ solution. The onset (starting) potentials of the cathodic current, i.e. the potential values at which a current density of 0.1 mA cm^{-2} is observed, at 271, 278, and 288 K were −1.36, −1.32, and −1.28 V, respectively. The onset potentials tends to decrease as the temperature is lowered. In the electrochemical reduction of CO_2 in aqueous LiClO$_4$ solution [13], the onset potentials of the cathodic current decreased with decreasing temperature. Hori et al. [17] reported that the onset potentials obtained in the CO_2-saturated, 0.1 mol dm^{-3} KHCO$_3$ aqueous solution was approximately −0.95 V vs. SCE. The current–potential characteristics including the onset potentials could be attributed to a number of processes such as the adsorption/desorption at the cathode surface. The pH of catholyte and the type and concentration of the supporting electrolyte may affect the processes. These effects are still being examined. The current densities increased with temperature since the IR potential drop decreased owing to the increase of diffusion efficiency. However, at 271 K and −2.0 V, the cathodic current density (approximately 25 mA cm^{-2}) was large enough to evaluate the electrochemical CO_2 reduction process. No voltammetric peak was observed in the range of 0– −2.0 V under the conditions given since further CO_2 electrochemical reduction may proceed with increasing negative potentials. Once the onset potentials were measured from polarization experiments, we attempted to investigate the electrochemical reduction of CO_2 in a NaHCO$_3$ aqueous solution at cathodic polarization
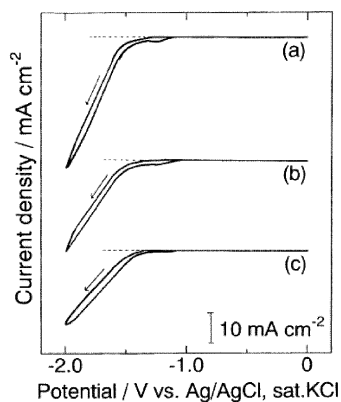
exceeding the onset potential. Therefore, the potential of the Cu electrode was set in the range of −1.6 to −2.0 V vs. Ag/AgCl, sat. KCl.

3.2. Effect of low temperature

The effect of the low temperature on the Faradaic efficiencies for the products of the electrochemical reduction of CO_2 on Cu in aqueous NaHCO$_3$ solution at −2.0 V is presented in Fig. 2. Methane, ethylene, and formic acid were detected as the reduction products of CO_2. The Faradaic efficiency of methane increased up to 46%, as the temperature was lowered to 271 K. The yield to formic acid slightly increased at lower temperatures. Ethylene formation efficiency was approximately 0.2% under these experimental conditions. In the electrochemical reduction of CO_2 with copper electrodes in water [5,6], the Faradaic efficiency of methane was 16 and 17.8% at 293 and 273 K, respectively, in 50 mmol dm^{-3} aqueous KHCO$_3$ solution, and 16% in 500 mmol dm^{-3} KHCO$_3$ solution at 298 K. Therefore, lowering temperature below 273 K was effective for the selective formation of methane in the electrochemical reduction of CO_2.

Generally, hydrogen evolution is a competing reaction of CO_2 reduction. Therefore, the suppression of hydrogen formation is very important, since it consumes the applied energy instead of the CO_2 reduction. In this work, the yield of hydrogen formation dropped to 51% at 271 K. Consequently, it appears that low temperature can effectively depress the hydrogen evolution.

The effect of temperature on partial current densities (PCDs) for CO_2 reduction, H$_2$ evolution, and the total current density at Cu electrode was examined at −2.0 V. Results are illustrated in Fig. 3. It is obvious that the total current density rose as the temperature increased. These phenomena were in agreement with the cyclic voltammograms obtained. Here, we define the selectivity of CO_2 reduction over hydrogen evolution as the PCD ratio of CO_2 reduction and hydrogen evolution, $i(CO_2)/i(H_2)$. The PCD for the H$_2$ evolution decreased by 60% as temperature dropped, while CO_2 reduction increased

Fig. 1. Cyclic voltammograms of Cu electrode in a NaHCO$_3$ aqueous solution: (a) 288; (b) 278; (c) 271 K. Catholyte, 0.65 mol dm^{-3} NaHCO$_3$; Anolyte, 1.1 mol dm^{-3} KHCO$_3$.
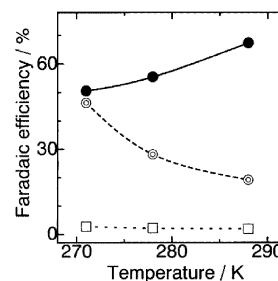

Fig. 2. Effect of temperature on Faradaic efficiencies for the products by electrochemical reduction of CO_2 at Cu electrode in NaHCO$_3$ aqueous solution at −2.0 V. CH$_4$, ⊚; HCOOH, □; H$_2$, ●. Catholyte, 0.65 mol dm^{-3} NaHCO$_3$; Anolyte, 1.1 mol dm^{-3} KHCO$_3$.

Fig. 3. Effect of temperature on PCDs for CO_2 reduction and H_2 evolution by electrochemical reduction of CO_2 at Cu electrode in $NaHCO_3$ aqueous solution at -2.0 V. Total current density, $\diamondsuit$; PCD for CO_2 reduction, $\bigcirc$; PCD for H_2 evolution, $\bullet$. Catholyte, 0.65 mol dm^{-3} $NaHCO_3$; Anolyte, 1.1 mol dm^{-3} $KHCO_3$.

by 25%. The selectivity increases enormously with decreasing temperature. The selectivity, $i(CO_2)/i(H_2)$, at 271 K was 0.97. Hence, low temperature seems to play a significant role in the improvement of the selectivity of CO_2 reduction over H_2 evolution.

3.3. Effect of potential

It was quite clear that the electrochemical CO_2 reduction process could proceed in a $NaHCO_3$ aqueous solution at 271 K and obtain a promising formation efficiency for methane. Therefore, the effect of the potential on current efficiencies for the electrochemical reduction products of CO_2 at 271 K was investigated. As shown in Fig. 4, the formation efficiency of methane increased from 24 to 46% with decreasing potential from -1.6 to -2.0 V, with a simultaneous decrease of the current efficiency to formic acid. Hydrogen Faradaic efficiency curve abruptly decreased from -1.6 to -1.7 V, then turned to gentle declining shape at potentials more negative -1.7 V. In the present electrochemical CO_2 reduction system, the methane formation efficiency was extremely high (more than 43%) at potentials more negative than -1.9 V.

The effect of the potential on PCDs for CO_2 reduction and hydrogen evolution was evaluated. The polarization curves are shown in Fig. 5. Methane formation and

Fig. 4. Effect of potential on Faradaic efficiencies for the products by electrochemical reduction of CO_2 at Cu electrode in $NaHCO_3$ aqueous solution at 271 K. CH_4, $\circledcirc$; HCOOH, $\square$; H_2, $\bullet$. Catholyte, 0.65 mol dm^{-3} $NaHCO_3$; Anolyte, 1.1 mol dm^{-3} $KHCO_3$.

Fig. 5. Polarization curves of H_2 evolution and the products by electrochemical reduction of CO_2 at Cu electrode in $NaHCO_3$ aqueous solution at 271 K. CH_4, $\circledcirc$; HCOOH, $\square$; H_2, $\bullet$. Catholyte, 0.65 mol dm^{-3} $NaHCO_3$; Anolyte, 1.1 mol dm^{-3} $KHCO_3$.

hydrogen evolution became diffusion-controlled at around -1.7 and -1.9 V, respectively. PCD of formic acid had a nearly flat pattern. The reaction rate on the electrode is governed by various processes, such as the kinetics of electron transfer, adsorption/desorption at the electrode surface, and diffusion of CO_2 to the Cu electrode. By considering this polarization curve study, a limitation of CO_2 diffusion to the electrode may be a dominant process for the rate-determining step. The maximum PCD ratio of CO_2 reduction and H_2 evolution, $i(CO_2)/i(H_2)$, was 0.97 at -2.0 V.

3.4. Reaction mechanism

The mechanism for the electrochemical reduction of CO_2 in a $NaHCO_3$ aqueous solution with a copper electrode was investigated. When the electrolysis was conducted under nitrogen atmosphere, electrolysis yielded exclusively hydrogen. Teeter and Van Rysselberghe [18] established that only dissolved CO_2 molecules take part in the reduction, and not bicarbonate HCO_3^- or carbonate CO_3^{2-} ions from solution and concluded that CO_2 and not HCO_3^- is the reducible species. Consequently, the targeted products were produced by the electrochemical reduction of the CO_2 substrate. Based on these experimental results and literature reports [4–15], the pathway by which methane, ethylene and formic acid on Cu electrode are formed can be estimated, as shown in Fig. 6. A possible scenario for the hydrocarbon formation at the Cu

Fig. 6. Reaction mechanism for the electrochemical reduction of CO_2 at a Cu electrode in a $NaHCO_3$ aqueous solution.

electrode surface may involve the following steps: the adsorbed HCO_2^- radical anion obtained by the first electronation step undergoes a second protonation/electronation to produce adsorbed CO as the key intermediate. By a succession of four protonation/electronation steps, an adsorbed reactive methylene group forms, and this may stabilize as either a methane molecule by a subsequent double protonation/electronation sequence or dimerize to ethylene. By lowering the temperature, this protonation/electronation reaction seems to proceed quickly. Therefore, the current efficiency of methane increases with lower temperature. However, the reason of the poor formation for ethylene is not clear. It may be owing that the high concentration of supporting electrolyte affected the dimerization of the adsorbed methylene group. For the formation of formic acid, we assume the usual pathway, which involves a one-electron reduction followed by a second electronation/protonation to yield formic acid [6].

4. Conclusion

The electrochemical reduction of CO_2 at a Cu electrode in a $NaHCO_3$ aqueous solution was studied at 271 K. The best current efficiency for methane was 46% at -2.0 V vs. Ag/AgCl, sat. KCl. With decreasing temperature, the hydrogen formation was significantly suppressed from 67% at 288 K to 51% at 271 K. Thus, the synthesis of hydrocarbons by the electrochemical reduction of CO_2 may become of practical interest in fuel production, the storage of solar energy, and the production of intermediate materials for the petrochemical industry. Since the present conversion efficiencies of single crystal, polycrystalline and amorphous silicon solar cells attainable in laboratory experiments are the respective levels of approximately 20, 15 and 12%, respectively, one possible system to industrially convert CO_2 to useful products may be a hybrid method of the solar cell and the CO_2 electrochemical reduction cell. Hence, future work to advance the present technology developed will include the use of solar energy as the electric energy source. Based on the circumstances, the present research may be able to contribute to the large-scale manufacturing of fuel gases.

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