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## High-efficiency electrochemical CO<sub>2</sub>-to-methane reduction method using aqueous KHCO<sub>3</sub> media at less than 273 K

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**Abstract** The electrochemical reduction of CO<sub>2</sub> with a Cu electrode in a KHCO<sub>3</sub> aqueous solution was investigated at low temperature. A divided H-type cell was employed; the electrolyte was a 1.1 mol dm<sup>-3</sup> KHCO<sub>3</sub> aqueous solution. The temperature during the electrolysis of CO<sub>2</sub> was reduced to 269 K. Methane, ethylene, and formic acid were obtained from CO<sub>2</sub> as the main products. The maximum faradaic efficiency of methane was 44% at a relatively negative potential and 269 K. The efficiency of hydrogen formation, as the competition against CO<sub>2</sub> reduction, significantly decreased with lowering the temperature. On the basis of this work, the high-efficiency electrochemical CO<sub>2</sub> to methane conversion method appears to be achieved.

**Keywords** Electrochemical reduction · Carbon dioxide · Copper electrode · Methane · Low temperature

### Introduction

The chemical fixation of carbon dioxide (CO<sub>2</sub>) by a variety of methods, such as radiochemical, chemical, thermochemical, photochemical, electrochemical, and biochemical procedures, has been a worldwide attractive topic from both fundamental and practical viewpoints [1, 2]. The electrochemical method appears to be very

promising for the conversion and reduction of CO<sub>2</sub> [2, 3].

With most flat metallic electrodes, carbon monoxide and formic acid were mainly produced by the electrochemical reduction of CO<sub>2</sub> in aqueous solution [4, 5]. However, it has been proven that only copper was a suitable electrode for the formation of hydrocarbons such as methane and ethylene, which can be used as fuel gases [4, 5, 6, 7, 8, 9, 10, 11, 12, 13]. Kyriacou et al. [6] reported the following formation efficiencies for the electrochemical reduction of CO<sub>2</sub> on Cu in a 500 mmol dm<sup>-3</sup> KHCO<sub>3</sub> solution at 298 K: 16% for methane, 14% for ethylene, etc. Azuma et al. [5] investigated the electrochemical reduction of CO<sub>2</sub> at a Cu electrode in a 50 mmol dm<sup>-3</sup> KHCO<sub>3</sub> aqueous solution at 293 K and obtained methane, ethylene, and ethane with faradaic efficiencies of 17.8%, 12.7%, and 0.039%, respectively. Moreover, they attempted to lower the temperature to 273 K and could obtain current efficiencies for methane, ethylene, and ethane of 24.7%, 6.5%, and 0.015%, respectively. The solubility of CO<sub>2</sub> in water increases with decreasing temperature. However, few reports have dealt with the electrochemical reduction of CO<sub>2</sub> in an aqueous solution at less than 273 K, owing to the freezing point of water [13].

With a high concentration of solutes, the aqueous solution cannot freeze at less than 273 K, because of freezing point lowering. In this study, we report that methane can be obtained with high faradaic efficiency in the electrochemical reduction of CO<sub>2</sub> in a KHCO<sub>3</sub> aqueous solution at less than 273 K.

### Experimental

The apparatus and experimental conditions for the electrochemical reduction of CO<sub>2</sub> are described in Table 1. Electrochemical reduction of CO<sub>2</sub> was performed in a laboratory-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 to 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-310
Coulometer	Integrator 1109 (Fusou Seisakujo, Japan)
Potential sweep	Hokuto HB-111 function generator
XY recorder	Graphtec WX1100
Thermostat	EYELA, Tokyo Rikakikai, ESC-50
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	1.1 mol dm <sup>-3</sup> KHCO <sub>3</sub> (70 cm <sup>3</sup> )
Anolyte	1.1 mol dm <sup>-3</sup> KHCO <sub>3</sub> (70 cm <sup>3</sup> )
Carbon dioxide	99.9999% purity
Potential	-1.6 to -2.2 V vs. Ag/AgCl sat. KCl
Temperature	269 to 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 <sub>2</sub> and H <sub>2</sub> carrier gas)
Liquid products	HPLC with UV detector (Hitachi L4000) TCD and FID gas chromatography

Potassium bicarbonate (Nacalai tesque, Kyoto, Japan) was used as the ionsphere in the electrolyte. After saturation of the 500 mmol dm<sup>-3</sup> KHCO<sub>3</sub> aqueous solution with CO<sub>2</sub>, the pH of the catholyte was 7.5. Mechanical processing of the Cu and Pt electrodes required polishing each surface with successively finer grades of alumina powder (Baikalox emulsion, Baikowski International, 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<sup>-3</sup> phosphoric acid. After the above treatment, the electrodes were rinsed with both water and methanol.

A discontinuous electroreduction procedure was used. After CO<sub>2</sub> gas was bubbled into the catholyte for 1 h at a rate of 30 mL min<sup>-1</sup>, the CO<sub>2</sub>-saturated KHCO<sub>3</sub> aqueous solution was electrolytically reduced at a cathodic polarization in the range from -1.6 to -2.2 V vs. Ag/AgCl sat. KCl. Agitation of the electrolyte was provided by a magnetic bar. The faradaic efficiencies for the formation of 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 gas chromatography. Products soluble in the catholyte were analyzed using high-performance liquid chromatography and gas chromatography.

## Results and discussion

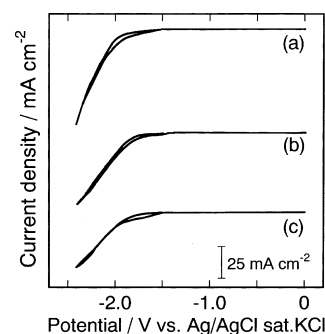
Following the research results of Hori et al. [4], copper was chosen as the cathode in this study because of its excellent character for the formation of hydrocarbons. Generally, the freezing point of an aqueous solution decreases with an increase in the concentration of the dissolved substances. Hence, the optimum concentration of the supporting salt was checked. At 268 K,

1.1 mol dm<sup>-3</sup> KHCO<sub>3</sub> aqueous solution could freeze or a precipitation of the supporting salt was observed. At this temperature, 1.2 mol dm<sup>-3</sup> KHCO<sub>3</sub> did not completely dissolve. Consequently, the electroreduction of CO<sub>2</sub> was tested in a 1.1 mol dm<sup>-3</sup> KHCO<sub>3</sub> aqueous solution at 269 K. In order to confirm a higher solubility of CO<sub>2</sub> at low temperature, we investigated CO<sub>2</sub> solubility in a 1.1 mol dm<sup>-3</sup> KHCO<sub>3</sub> solution. The solubility of CO<sub>2</sub> at 269, 278, and 288 K was 1.3, 1.0, and 0.64 cm<sup>3</sup> cm<sup>-3</sup> (~58, 45, and 29 μmol CO<sub>2</sub>/cm<sup>3</sup> solution). Literature data for the solubility of CO<sub>2</sub> in water at 288 K was 0.821 cm<sup>3</sup> cm<sup>-3</sup> [14]. Therefore, the increased solubility of carbon dioxide at low temperature in our system relative to ambient temperature conditions appears to be very advantageous.

## Cyclic voltammetry

Cyclic voltammograms (CVs) at the Cu electrode in the 1.1 mol dm<sup>-3</sup> KHCO<sub>3</sub> aqueous solution were measured at 269–288 K. The potential was scanned at a sweep rate of 50 mV s<sup>-1</sup>. Figure 1 shows the current-potential curves of the Cu electrode in the CO<sub>2</sub>-saturated KHCO<sub>3</sub> solution. The onset (starting) potentials of the cathodic current, i.e. the potential values at which a current density of 0.1 mA cm<sup>-2</sup> are observed, were almost -1.50 V at all the temperatures tested. In the N<sub>2</sub>-purged KHCO<sub>3</sub> solution, also, the current-potential curves were checked and the onset potentials were almost independent of the temperature (about -1.55 V). In the electrochemical reduction of CO<sub>2</sub> in aqueous LiClO<sub>4</sub> solution [13], the onset potentials of the cathodic current decreased with decreasing the temperature. Hori et al. [15] reported that the onset potentials obtained in the CO<sub>2</sub>-saturated, 0.1 mol dm<sup>-3</sup> KHCO<sub>3</sub> aqueous solution and N<sub>2</sub>-purged, 0.1 mol dm<sup>-3</sup> phosphate buffer solution were approximately -0.95 and -0.90 V vs. SCE. The onset potentials may be affected by the pH of the catholyte and the type and concentration of the supporting electrolytes. These effects are still being examined.

In general, the slope of the cathodic current (current density) in CO<sub>2</sub>-saturated solution was half as much as

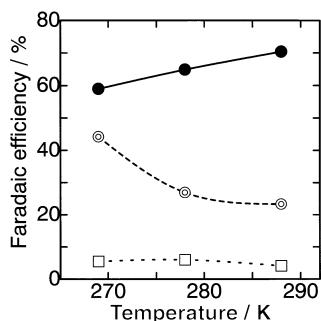


**Fig. 1** Cyclic voltammograms of a Cu electrode in a KHCO<sub>3</sub> aqueous solution: (a) 288 K; (b) 278 K; (c) 269 K. Electrolyte: 1.1 mol dm<sup>-3</sup> KHCO<sub>3</sub>

that in  $N_2$ -purged solution. Hence,  $CO_2$  reduction was evident owing to the difference of voltammogram shapes. The current densities increased with temperature owing to the  $iR$  potential drop decline. However, at 269 K and  $-2.2$  V, the cathodic current density (approximately  $30 \text{ mA cm}^{-2}$ ) was large enough to evaluate the electrochemical  $CO_2$  reduction process. No voltammetric peak could be observed in the potential range down to  $-2.2$  V 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  $KHCO_3$  aqueous solution at a cathodic polarization exceeding the onset potential. Therefore, the potentials for the Cu electrode were set in the range  $-1.6$  to  $-2.2$  V vs. Ag/AgCl sat. KCl.

### Effect of low temperature

Figure 2 presents the effect of the low temperature on the faradaic efficiencies for the products from the electrochemical reduction of  $CO_2$  on Cu in the  $KHCO_3$  aqueous solution at  $-2.0$  V. Methane, ethylene, and formic acid were detected as the reduction products of  $CO_2$ . The faradaic efficiency of methane increased up to 44% on decreasing the temperature to 269 K. Formic acid formation, the efficiency of which was approximately 5%, was almost independent of the temperature. Ethylene formation efficiency was less than 0.3% under the experimental conditions studied. In the electrochemical reduction of  $CO_2$  with the copper electrode in water [5, 6], the faradaic efficiencies of methane were 16% and 17.8% at 293 K and 273 K in  $50 \text{ mmol dm}^{-3}$  aqueous  $KHCO_3$  solution, respectively, and 16% in  $500 \text{ mmol dm}^{-3}$   $KHCO_3$  solution. Since the total faradaic efficiency at 269 K was more than 100%, the analytical errors for the reduction products need to be taken into account. However, even though the analytical errors for methane formation efficiency were taken into consideration, it could be regarded that the



**Fig. 2** Effect of temperature on faradaic efficiencies for the products from the electrochemical reduction of  $CO_2$  at a Cu electrode in  $KHCO_3$  aqueous solution at  $-2.0$  V. Double circles:  $CH_4$ ; open squares:  $HCOOH$ ; filled circles:  $H_2$ . Electrolyte:  $1.1 \text{ mol dm}^{-3}$   $KHCO_3$

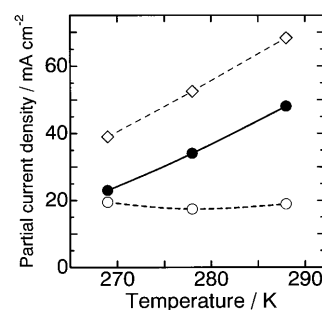
low temperature below 273 K was very efficient for the increase in the selective formation of methane in the electrochemical reduction of  $CO_2$ .

Generally, in the electrochemical reduction of  $CO_2$  in water, hydrogen formation is simultaneous with  $CO_2$  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 this work, the formation efficiency of hydrogen decreased down to 59% with lowering the temperature to 269 K. Consequently, it was found that low temperature was effective for the depression of hydrogen formation.

The effect of temperature on partial current densities (PCDs) for  $CO_2$  reduction,  $H_2$  evolution, and total current density at the Cu electrode was investigated at  $-2.0$  V. The results are illustrated in Fig. 3. First, the total current density rose as the temperature increased. This phenomenon is reasonable, judging from the cyclic voltammograms obtained. Here we define the selectivity of  $CO_2$  reduction over hydrogen evolution as the PCD ratio of  $CO_2$  reduction to hydrogen evolution,  $i(CO_2)/i(H_2)$ . The PCD for  $H_2$  evolution decreased in a similar way as the total current density, although the curve for  $CO_2$  reduction was nearly flat. As a result, the selectivity increased enormously with the decrease in temperature. The selectivity,  $i(CO_2)/i(H_2)$ , at 269 K was 0.85. Hence, the low temperature seems to play a significant role in the improvement of the selectivity of  $CO_2$  reduction over  $H_2$  evolution.

### Effect of potential

Since it was found that the electrochemical  $CO_2$  reduction process proceeded in water at 269 K and at that temperature the faradaic efficiency for methane was extraordinary, the effect of the potential on current efficiencies for the products from  $CO_2$  electrochemical reduction with a Cu electrode in  $KHCO_3$  aqueous solution was investigated at 269 K. As shown in Fig. 4, the



**Fig. 3** Effect of temperature on the partial current densities (PCDs) for  $CO_2$  reduction and  $H_2$  evolution by electrochemical reduction of  $CO_2$  at a Cu electrode in  $KHCO_3$  aqueous solution at  $-2.0$  V. Diamonds: total current density; open circles: PCDs for  $CO_2$  reduction; filled circles: PCD for  $H_2$  evolution. Electrolyte:  $1.1 \text{ mol dm}^{-3}$   $KHCO_3$



source. This research may be able to contribute to the large-scale manufacture of fuel gases.

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