

# PULSED ELECTROREDUCTION OF CARBON DIOXIDE ON GLASSY CARBON ELECTRODE

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## Introduction

It is important to convert CO<sub>2</sub> to valuable organic substances from the point of view of CO<sub>2</sub> recycling. Electroreduction of CO<sub>2</sub> is one of important methods for the conversion. Numerous papers have been published with regard to this subject.<sup>1-6)</sup> Few of papers have dealt with the reduction of CO<sub>2</sub> at glassy carbon electrode.<sup>7-10)</sup> It appears to be inadequate for the evaluation of carbon electrode for the electroreduction of CO<sub>2</sub>. We have been studying the comparison between glassy carbon electrode and metallic electrodes such as copper or copper-modified silver electrode for the production of hydrocarbons (CH<sub>4</sub> and C<sub>2</sub>H<sub>4</sub>) by pulsed electroreduction, and also we are studying the microstructural effect of carbon on the productivity of hydrocarbons.

In this work, the pulsed electroreduction of CO<sub>2</sub> on glassy carbon electrode was investigated, especially, the selectivity of CH<sub>4</sub> and C<sub>2</sub>H<sub>4</sub> studied.

## Experimental

Pulsed electroreduction was carried out in a CO<sub>2</sub> saturated solution using a conventional H-type gas-tight plastic cell divided by an ion exchange membrane (Nafion N-350). The working electrode was a 0.3 cm<sup>2</sup> glassy carbon rod from Tokai Instruments. The electrolyte solutions were 0.1 mole dm<sup>-3</sup> KHCO<sub>3</sub> and K<sub>2</sub>SO<sub>4</sub> containing 4.1-18 x 10<sup>-4</sup> mole dm<sup>-3</sup> CuSO<sub>4</sub>. Before the electrolysis, CO<sub>2</sub> gas was bubbled into the solution to maintain a CO<sub>2</sub>-saturated solution. Gaseous products were analyzed by FID and TCD detectors after the reduction experiments. A potentiostat used was a Hokuto Denko HA-301. The glassy carbon electrode was polished with a 0.3 mm alumina powder (Buehler) and cleaned in an ultrasonic bath and then washed by purified water. Pulsed electroreductions were carried out at 30 °C and Tc = Ta = 1 sec (Tc and Ta represent time intervals during which the cathodic and anodic bias were applied). The electroreductions were carried out during 1 h.

## Results and Discussion

Faradaic efficiencies of hydrocarbons (CH<sub>4</sub> and C<sub>2</sub>H<sub>4</sub>) for the pulsed electroreduction of CO<sub>2</sub> on glassy carbon electrode were of a few percentages. The pulsed electroreductions were performed in the presence of copper(II) ions using KHCO<sub>3</sub>, K<sub>2</sub>SO<sub>4</sub>, KCl and NH<sub>4</sub>Cl as a supporting electrolyte. Table 1 resumes the faradaic efficiencies of CO<sub>2</sub> to the hydrocarbons (CH<sub>4</sub> and C<sub>2</sub>H<sub>4</sub>). Modification of glassy carbon electrode surface caused the increases of faradaic efficiencies. Faradaic efficiencies of the hydrocarbons were found to increase at the supporting electrolytes, KHCO<sub>3</sub> and K<sub>2</sub>SO<sub>4</sub>. The relationship between the supporting electrolytes and the nature of the products is remarkable. The highest faradaic efficiencies of hydrocarbons were obtained in KHCO<sub>3</sub>. C<sub>2</sub>H<sub>4</sub> is the main product in K<sub>2</sub>SO<sub>4</sub>. The pulsed electroreduction was performed using KHCO<sub>3</sub> and K<sub>2</sub>SO<sub>4</sub> from above these results.

Figs. 1 and 2 show the dependence of faradaic efficiencies on the concentration of copper(II) ions. The faradaic efficiency is a peak at 1.2 x 10<sup>-4</sup> mol dm<sup>-3</sup> at KHCO<sub>3</sub> and K<sub>2</sub>SO<sub>4</sub>.

Fig. 3 shows the dependence of faradaic efficiencies on the on the cathodic bias V<sub>C</sub> at constant anodic bias, V<sub>A</sub> = 0.7 V at [Cu(II)] = 1.2 x 10<sup>-4</sup> mol dm<sup>-3</sup>. It is apparent that the optimum conditions are E<sub>c</sub> = -2.0, E<sub>a</sub> = 0.7 V for the CH<sub>4</sub> formation and E<sub>c</sub> = -1.7, E<sub>a</sub> = 0.7 V vs. Ag/AgCl for C<sub>2</sub>H<sub>4</sub> formation. The maximum total faradaic efficiency for the hydrocarbons (CH<sub>4</sub> and C<sub>2</sub>H<sub>4</sub>) was ca. 50 %.

Fig. 4 shows the dependence of faradaic efficiencies on the cathodic bias V<sub>B</sub> at constant anodic bias V<sub>A</sub> = -0.35 V vs. Ag/AgCl for copper electrode. The maximum total faradaic efficiency for the hydrocarbons was ca. 65 %. The selective production of CH<sub>4</sub> and C<sub>2</sub>H<sub>4</sub> was found at the pulsed electroreduction by glassy carbon electrode. The dependence of faradaic

efficiencies of the hydrocarbons on the cathodic potential at glassy carbon electrode was found to be very different to those at the copper electrode. This is ascribed to the difference in surface properties of the deposited copper on glassy carbon and a pure copper electrode. We will report the microstructural effects of glassy carbon on the productivity of CH<sub>4</sub> and C<sub>2</sub>H<sub>4</sub>. Fig. 5 shows the dependence of the values (C<sub>2</sub>H<sub>4</sub>/CH<sub>4</sub>) on the cathodic bias. The values of C<sub>2</sub>H<sub>4</sub>/CH<sub>4</sub> at glassy carbon electrode were found to be larger than those at the copper electrode.

### Conclusions

The pulsed electroreductions on glassy carbon electrode were performed in the presence of copper(II) ions using KHCO<sub>3</sub> and K<sub>2</sub>SO<sub>4</sub> as supporting electrolytes. The optimum conditions are found to be E<sub>c</sub> = -2.0, E<sub>a</sub> = 0.7 V for CH<sub>4</sub> formation and E<sub>c</sub> = -1.7, E<sub>a</sub> = 0.7 V vs. Ag/AgCl for C<sub>2</sub>H<sub>4</sub> formation. The maximum total faradaic efficiency for the hydrocarbons(CH<sub>4</sub> and C<sub>2</sub>H<sub>4</sub>) was ca. 50 %. The selective production of CH<sub>4</sub> and C<sub>2</sub>H<sub>4</sub> was found at the pulsed electroreduction by glassy carbon electrode.

### References

1. S. Kaneco, K. Iiba, S-k. Suzuki, K. Ohta, and T. Mizuno, *J. Phys. Chem.B*, 103, 7456(2000)
2. H. Noda S, Ikeda Y. Oda, K. Iwai. M. Maeda, and K. Ito, *Bull. Chem. Soc. Jpn.*, **63**, 2459 ( 1990).
3. Y.Hori, A. Murata, and R. Takahashi, *J.Chem. Soc.,Farady Trans. 1*,85,2309(1989).
4. R. Shratsuichi, Y. Aikoh, and G. Nogami, *J. Electrochem. Soc.*,140,3479(1993).
5. G. Nogami, H. Itagaki, and R. Shratsuichi, *J. Electrochem. Soc.*,141,1138(1994).
6. R. Shratsuichi and G. Nogami, *J. Electrochem. Soc.*,143,582(1996).
7. .R.L. Cook, R.C. MacDuff, and A. F. Sammells, *J. Electrochem. Soc.*, 135, 1320 (1988).
8. R. M. Hernandez, J,Marquez, O.P. Marquez, M. Choy, C. Ovalles, J. j. Gacia, and B. Scharifker, *J. Electro. Chem. Soc.*,146, 4131(1999).
9. K. Hara ,A. Kudo, and T. Sakata, *J. Electroanal. Chem.*, **421**,1 (1997).
- 10.K. Hara ,A. Kudo, and T. Sakata, *J. Electroanal. Chem*, **421**, 14 (1997).

Table 1. Faradaic efficiencies of hydrocarbons at glassy carbon electrode.

Electrolyte	E <sub>c</sub> =-2.0, E <sub>a</sub> =0.7 V vs.Ag/AgCl			E <sub>c</sub> =-1.7, E <sub>a</sub> =0.7 V vs.Ag/AgCl		
	CH <sub>4</sub> %	C <sub>2</sub> H <sub>4</sub> %	total %	CH <sub>4</sub> %	C <sub>2</sub> H <sub>4</sub> %	total %
KHCO <sub>3</sub>	37.8	10.6	48.4	10.8	23.6	33.9
K <sub>2</sub> SO <sub>4</sub>	28.9	3.4	32.3	7.3	23.6	31
KCl	23.5	3.1	26.6	5.1	14.5	19.6
NH <sub>4</sub> Cl	2.1	0	2.1	12.6	0	12.6

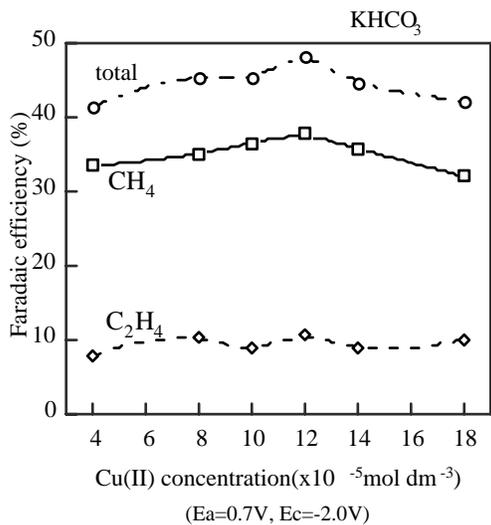


Fig.1. The dependence of the faradaic efficiencies on Cu(II) concentration.

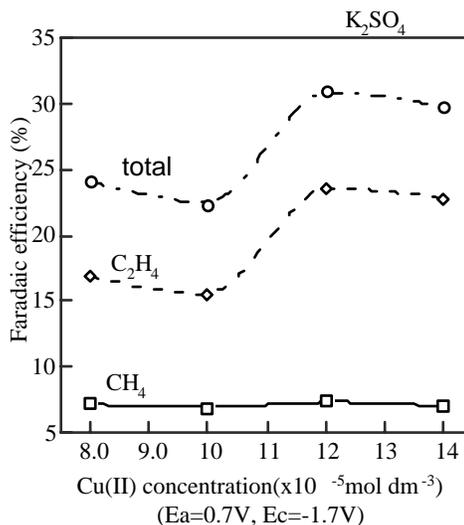


Fig.2. The dependence of the faradaic efficiencies on Cu(II) concentration.

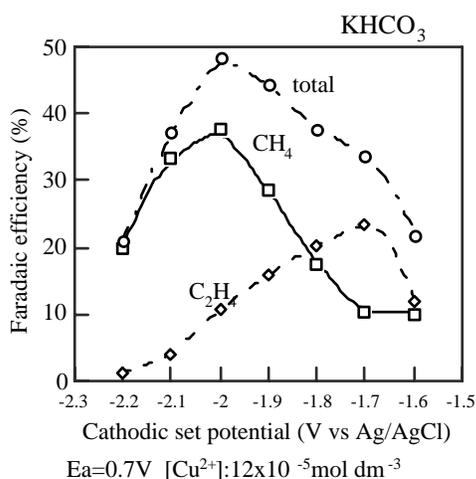


Fig.3. The dependence of the faradaic efficiencies on the cathodic bias  $V_c$ .

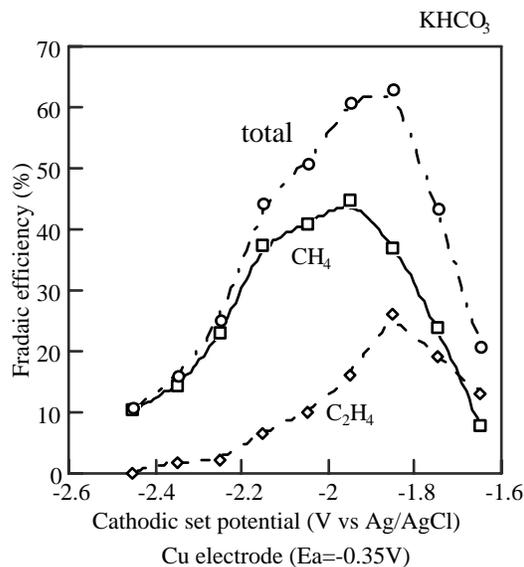


Fig.4. The dependence of the faradaic efficiencies on the cathodic bias  $V_c$ .

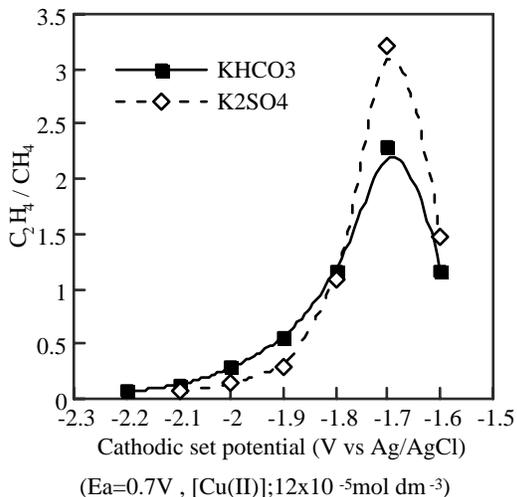


Fig.5. The dependence of the values for  $\text{C}_2\text{H}_4 / \text{CH}_4$  on the cathodic bias  $V_c$ .