SELECTIVE FORMATION OF ETHYLENE FROM CO_2 BY CATALYTIC ELECTROLYSIS AT A THREE-PHASE INTERFACE

Kotaro Ogura, Hiroshi Yano, and Takayasu Tanaka

Department of Applied Chemistry, Yamaguchi University, Tokiwadai, Ube 755-8611, Japan

Introduction

Chemical conversion of CO_2 to fuels or chemicals is a challenging subject for chemists in connection with the mitigation of greenhouse effect and the carbon resource after the exhaustion of petroleum. Several methods for chemically converting CO_2 have been proposed: e.g., hydrogenation over heterogeneous catalyst at high temperature or in supercritical conditions, electrochemical and photochemical reduction. CO_2 conversion should be achieved with the aid of low input energy and products be highly valuable so that the conversion process may be feasible without accompanying the secondary generation of CO_2. Hence, the most desirable process is an artificial photosynthesis in which CO_2 is convertible to valuable substances with a solar cell as the energy source at room temperature. To attain such a process, we have developed the catalytic electrolysis process in which CO_2 is converted selectively to ethylene at room temperature.[1-4] The conversion reaction takes place at the three-phase (gas/liquid/solid) interface on a Cu(I) halide-confined Cu-mesh electrode.

Experimental

The electrolysis cell used is described elsewhere.[1] The three-phase interface was constructed on a pure copper-mesh (purity 99.99%, 50 mesh, Nilaco Co.) which was fixed along with a glass filter (average pore size, 20 μm) at the bottom of a cathode compartment. The electrolytic solution was prevented from dropping by the glass filter. The solution surface was forced up by the pressure of CO_2 blown up from the lower part, and the electrolyte meniscus was extended on the copper mesh. Thus, the three-phase zone consisting of gas, liquid and solid was built, and electrochemical reactions took place predominantly in this zone. The copper-mesh put on the glass filter was bound to a Teflon cylinder tightened with a Teflon cap. The cylinder with the copper-mesh was attached to the cathode compartment via an O-ring, which was separated from an anode compartment by a cation-exchange membrane (Selemion CMV 10, Asahi Glass Co.). The purified CO_2 gas was circulated via the cathode compartment with a circulating pump. The three-phase provided on the Cu-mesh electrode was sustained during the electrolysis by adjusting the rate of CO_2. The net surface area of the Cu-mesh was 10.2 cm^2.

Copper-mesh electrode was modified by CuCl, CuBr and CuI. Before this work, the Cu-mesh electrode was immersed in a concentrated HCl solution to remove Cu oxide, and washed with doubly distilled water. The modification of copper(I) halides was done by the application of electric charge of 220C at a constant potential of +0.4V vs Ag/AgCl in a 0.1M HCl and a 0.5M KBr solution (pH 3) or by passing the electric charge of 20C at +0.2V in a 0.5M KI solution of pH 3. The thickness of CuCl, CuBr and CuI films thus obtained were 7.8, 9.5 and 7.5μm, respectively. The film thickness was measured with a field emission scanning electron microscope (FE-SEM, Horiba EMAX-7000). The electrolysis of CO_2 was performed by the galvanostatic method. Various amounts of electric charge were applied with a constant current (usually 250mA) by changing the electrolysis time. Platinum or copper gauze with a large surface area and an Ag/AgCl/saturated KCl electrode were used as the anode and reference electrodes, respectively. The electrolytes mainly used were 3M or 4M KCl, KBr and KI solutions of pH 3. The change in pH of catholyte during the electrolysis was monitored with a pH controller (NPH-660NDE, Nissin Co.). The electrolyte in the anode compartment was a 0.5M $KHSO_4$ solution of pH 0. In some experiments, a concentrated solution of sulfuric acid was added to the anode compartment between times during the electrolysis in order to indirectly lower the pH of the catholyte.

A Shimadzu GC-8AIT and a GC-8AIF gas chromatograph with a Porapak N column and an active carbon or alumina column were used for the determination of gaseous samples. Aqueous samples were analyzed with a Shimadzu organic analyzer (LS-10AD type) and a Shimadzu GC-MS spectrometer. The electrochemically deposited copper halides were characterized with an X-ray diffractometer (Shimadzu XD-D1), and the XRD patterns were recorded with X-ray line of Cu-Kα (30kV, 30mA).

Results and Discussion

The electrolysis of CO_2 was performed at the three-phase interface on a copper(I) halides-confined Cu-mesh electrode in a potassium halide solution. In **Figure 1**, the conversion percentage of CO_2 obtained with a CuBr-confined Cu-mesh electrode in a KBr solution of pH 3 is shown versus the applied amount of electric charge. The CO_2 conversion increases with increasing the amount of electric charge until about 4500C, but beyond this amount the conversion percentage approximates a constant value of 68%. As seen from this figure, however, the conversion continues to increase when the pH of the catholyte was lowered by adding a concentrated solution of sulfuric acid to the anolyte between times during the electrolysis, and the conversion percentage reached 88% at the electric charge of 8928C. Hence, it is suggested that the approach of the conversion percentage to the constant value in the electrolysis charged with more than 4500C is attributed to the deficiency of proton concentration for the CO_2 reduction, which is discussed below.

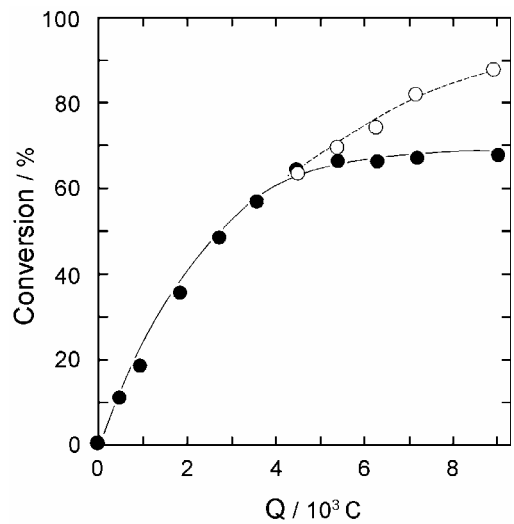

Figure 1. Plot of the conversion percentage of CO_2 versus the applied amount of electric charge in a 4 M KBr solution. The reduction of CO_2 was performed with a CuBr-confined Cu-mesh electrode at a constant current of 250 mA. The pH of the catholyte was lowered by adding a H_2SO_4 solution between times to the anolyte: ---○---, and such a pH-controlling was not given: —●—. The area of a copper-mesh substrate, 10.2 cm^2; initial volume of CO_2, 577 cm^3.

Table 1 Current efficiencies for the products obtained with a CuBr-confined Cu-mesh electrode in the galvanostatic reduction of CO_2[a)]

Run	Q [b)]	Potential [c)]	pH [d)]	Current efficiency / %									Conv. [e)]	Selec. [f)]	η [g)]
	C	V	−	Ethylene	Methane	CO	Ethane	Ethanol	Formic [h)]	Acetic [i)]	Lactic [j)]	H_2	%	%	%
1	453	−2.08 ~ −1.98	2.93	72.4	6.2	5.9	0.6	2.1	1.8	1.7	0.3	15.9	11.5	68.6	107
2	903	−2.10 ~ −1.93	2.69	62.5	5.9	4.6	0.6	1.1	1.3	1.2	0.1	21.0	19.0	71.0	98
3	2699	−2.10 ~ −1.92	2.75	48.2	2.2	5.2	0.5	1.0	2.0	1.1	0.2	13.4	48.9	64.3	74
4	4483	−2.08 ~ −1.89	3.78	39.2	1.0	4.0	0.4	0.6	2.9	0.3	0.0	10.6	66.3	63.2	59
4 [k)]	4500	−2.12 ~ −1.87	2.09	40.7	1.2	2.7	0.3	0.3	2.8	0.3	0.0	10.6	63.3	68.8	59
5	7157	−2.18 ~ −1.89	5.01	25.9	0.8	1.9	0.2	0.3	2.3	0.3	0.0	7.3	67.9	64.1	39
5 [k)]	7160	−2.13 ~ −1.89	2.32	33.3	0.9	2.8	0.2	0.3	2.1	0.4	0.0	7.1	81.9	69.1	47
6	8981	−2.15 ~ −1.88	6.14	21.0	0.4	1.5	0.6	0.2	1.7	0.2	0.0	9.9	68.6	65.6	36
6 [k)]	8928	−2.12 ~ −1.91	2.17	30.4	0.7	1.5	0.3	0.3	1.5	0.5	0.0	6.1	87.7	74.0	41

a) Electrolyte, 4M KBr, initial pH, 3.0; the apparent area of a copper-mesh surface, 10.2 cm^2; the thickness of confined CuBr film, 7.9 μm; applied current, 250 mA; initial volume of CO_2, 577 cm^3; catholyte, 232 cm^3; Anode, copper net; anolyte, a 0.5M $KHSO_4$ solution of pH 0. Cathode and anode compartments were separated by a cation-exchange membrane.
b) Amount of the electric charge applied in the electrolysis. This value was varied by changing the electrolysis time under the galvanostatic condition. C: coulomb (=ampere×sec)
c) Change in electrode potential (vs. Ag/AgCl) during the galvanostatic reduction.
d) Final pH of the catholyte. e) Conversion percentage of CO_2.
f) Selectivity for the formation of ethylene on the basis of carbon content.
g) Total current efficiency in the reduction. h) formic acid. i) acetic acid. j) lactic acid.
k) A concentrated solution of sulfuric acid was added to the $KHSO_4$ solution in the anode compartment between times during the electrolysis in order to indirectly lower the pH of the catholyte.

The major gases generated in the electroreduction of CO_2 were C_2H_4, CO and H_2, and their current efficiencies are plotted versus the applied amount of electric charge in **Figure 2**. The current efficiency for C_2H_4 decreases with an increase of amount of electric charge, but it still maintains more than 20% even at the electric care of 8900C. This current efficiency was risen to be 30% at the same electric charge when the pH of the catholyte was lowered by controlling the pH of the anolyte.

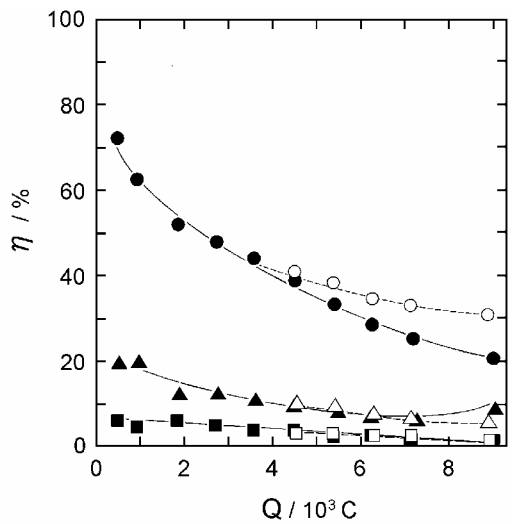

Figure 2. Plot of the current efficiencies for C_2H_4 (○, ●), CO (□, ■), and H_2 (△, ▲) versus the applied amount of electric charge. A H_2SO_4 solution was added to the anolyte: ---○---, ---△---, ---□---, and not: —●—, —▲—, —■—. The experimental conditions were the same as those given in Figure 1.

The detailed distribution of the products is exhibited in **Table 1**. The electrolysis was performed for a given period of time by applying a constant current of 250mA, and the electrode potential was −2.1V~−1.9V vs Ag/AgCl. The major gaseous products were C_2H_4 and CO, the formation of CH_4 was negligible, and the current efficiencies of liquid products were very low except that of formic acid in the prolonged electrolysis. In the electrolysis of Run 1~6 without adjusting the pH of the catholyte, the pH rose as the amount of electric charge was increased, and it became 6.14 after the electrolysis charged with 8981C (Run 6). On the other hand, in Run 4^k~6^k, the pH of the catholyte was adjusted to around 2.2 by adding a H_2SO_4 solution to the anolyte. As compared with the former results, the conversion percentage of CO_2 and the current efficiency for C_2H_4 were always enhanced, i.e., compare between the results of Run 4 and 4^k, 5 and 5^k, and 6 and 6^k. This means obviously that the concentration of protons in the catholyte is insufficient for the efficient reduction of CO_2 in the former case. It is noted that such a high current efficiency and a conversion percentage were brought about by adjusting the pH of the catholyte not directly but through the proton transport from the anode compartment. The current efficiency and conversion percentage were both considerably decreased when the pH of the catholyte was directly controlled by adding strong acid. This is probably caused by the transformation of an interfacial structure of the three-phase zone including adsorbed intermediates. Interestingly, the current efficiency for hydrogen evolution was smaller in the catholyte of which pH was suppressed low compared to that in the catholyte without pH-controlling. The selectivity for the formation of C_2H_4 estimated on the basis of carbon content was 74% at the applied electric charge of 8928C. The selective conversion of CO_2 to C_2H_4 is attributed to the immobilized CuX which operates as a heterogeneous catalyst by offering adsorption sites for reduction intermediates such as CO and methylene radicals.[3] A part of CuX is reduced to Cu ($CuX + e^- \rightarrow Cu + X^-$) simultaneously with the reduction of CO_2, but new copper(I) halide is always formed on the Cu-mesh electrode by the reduction ($Cu^{2+} + X^- + e^- \rightarrow CuX$) of Cu^{2+} ions which are afforded through the cation-exchange membrane from the anode compartment. Therefore, the electrochemical conversion of CO_2 continue to proceed via the catalysis reactions involving CuX.

References

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