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# Selective formation of ethylene from $CO_2$ by catalytic electrolysis at a three-phase interface

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## Abstract

A new electrolysis system has been developed for the selective conversion of $CO_2$ to ethylene in which the electrochemical reduction takes place at the three-phase (gas/liquid/solid) interface on a Cu-mesh electrode mediated with copper(I) halide in an aqueous solution of potassium halide. The conversion percentage of $CO_2$ (initial volume: 577 $cm^3$) reaches about 90% by the electrolysis with the electric charge of 8.9 kC, and the selectivity for $C_2H_4$ formation is about 75%. The selective conversion of $CO_2$ to $C_2H_4$ is attributed to the immobilized copper(I) halide which operates as a heterogeneous catalyst by offering adsorption sites for reduction intermediates such as CO and carbene.

*Keywords:* $CO_2$; Copper(I) halide; Ethylene; Three-phase interface

## 1. 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. In the conversion of $CO_2$, a matter of significance is that a required energy in the reaction should be as low as possible, the reaction rate high, and products valuable. The use of fossil fuel to obtain the required energy is not permitted, because the secondary generation of $CO_2$ is feared. The conversion products, which have been reported so far, are mostly $C_1$ compounds such as CO, $CH_4$, $CH_3OH$ and HCOOH [1,2]. From a viewpoint of utilization of $CO_2$, it is obvious that a compound with C–C bond is much more useful than $C_1$ species. So, the most desirable process is an artificial photosynthesis in which $CO_2$ is convertible to valuable compounds with a solar cell as the energy source at room temperature. To put this process to practical use, however, the rate of artificial photosynthesis is required to be much higher than that of natural photosynthesis. For this purpose, we have developed the electrolysis process with a copper(I) halide-mediated Cu-mesh electrode in which $CO_2$ is selectively converted to ethylene [3–6]. This reaction is a room temperature catalysis taking place at the three-phase (gas/solid/liquid) interface. In the process, the required energy is not severe, and a solar cell can be used as the energy source. Furthermore, ethylene, the most abundant product obtained in such an electrolysis process, is useful as a raw material in chemical industry. Hence, the conversion process of $CO_2$ developed by us may make a contribution not only to the mitigation of global warming but also to the security of carbon resource after the exhaustion of petroleum.

In the present study, the galvanostatic reduction of $CO_2$ was performed with a CuBr-mediated Cu-mesh electrode at the three-phase interface in a KBr solution, and the conversion percentage of $CO_2$ was found to reach about 90%.

## 2. Experimental

The electrolysis cell used is described elsewhere [3]. 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

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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 reaction gas blown up from the lower part, and the electrolyte meniscus was extended on the copper mesh. Thus, the three-phase zone consisting of gas, solid and liquid was built, and electrochemical reactions took place predominantly in this zone. Three-phase interface thus obtained is schematically represented in Fig. 1. 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 electrochemically active area of the Cu-mesh electrode was 10.2 $cm^2$.

A pure and a CuBr-modified Cu-mesh electrode were used as the cathode electrode. Before the modifying process, the Cu-mesh electrode was immersed in a concentrated HCl solution to remove Cu oxide, and washed with doubly distilled water. Copper(I) bromide was deposited onto a Cu-mesh substrate by the galvanostatic oxidation with a current density of 7.1 mA $cm^{-2}$ in a 0.5 M KBr solution of pH 3. In this experiment, the electric charge of 240 C was always applied, and the film thickness was 7.6 μm. The thickness was measured with a field emission scanning electron microscope (FE-SEM, Horiba EMAX-7000). The electrolysis of $CO_2$ with a pure or a CuBr-confined Cu-mesh electrode thus prepared was carried out under a constant current (usually 250 mA), and various amounts of electric charge were applied by changing the electrolysis time. A platinum or copper mesh with a large surface area and an Ag/AgCl/saturated KCl electrode were used as the anode and reference electrodes, respectively. The electrolyte mainly used was a 4 M KBr solution of pH 3. The change in pH of the catholyte during the electrolysis was monitored with a pH controller (NPH-660NDE, Nissin Co.). The electrolyte in the anode compartment was a 0.5 M $KHSO_4$ solution of pH 0. In some experiments, a concentrated solution of $H_2SO_4$ was added to the anode compartment between times during the electrolysis in order to indirectly lower the pH of the catholyte.

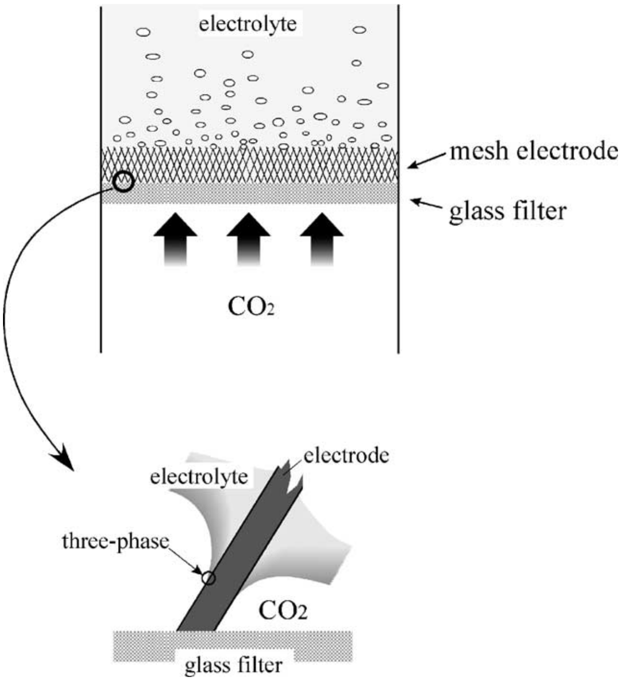


Fig. 1. Schematic representation of three-phase (gas/liquid/solution) interface.

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 CuBr was characterized with an X-ray diffractometer (Shimadzu XD-D1), and the XRD pattern was recorded with X-ray line of Cu Kα (30 kV, 30 mA).

## 3. Results

The electrolysis of $CO_2$ was first performed at the three-phase interface on a pure Cu-mesh electrode in a potassium bromide solution. The current efficiencies of major reduction products are plotted versus the amount of electric charge in Fig. 2. As seen from this figure, the current efficiency of each product is dependent on the kind of counter electrode, and the most abundant compound is $C_2H_4$ and the other major products are CO, $CH_4$ and $H_2$. Each current efficiency decreased with an increase in amount of electric charge, but the diminution rate of current efficiency of $C_2H_4$ was smaller in the electrolysis with Cu anode than with Pt. Correspondingly, the conversion percentage of $CO_2$ was larger in the former electrolysis than the latter (Fig. 3). In both cases, the conversion efficiency approached a constant value in the electrolysis with the electric charge beyond 4 kC: 57% (with Cu anode); 44% (with Pt anode).

The results obtained with a pure Cu-mesh electrode are shown more in detail in Table 1. The electrolysis was performed for a given period of time by applying a constant current of 250 mA, and the electrode potential ranged between −2.0 and −1.8 V versus Ag/AgCl. In addition to major four products, ethane, ethanol, formic, acetic and lactic acids were slightly observed. In Table 1, the pH of the catholyte was measured after each run. The final pHs in the electrolysis with Cu anode were always higher than those with Pt anode when compared with the comparable amounts of applied electric charge. Conversion percentage of $CO_2$ and the current efficiency of $C_2H_4$ were much higher in the electrolysis with Cu anode. These results indicate that Cu

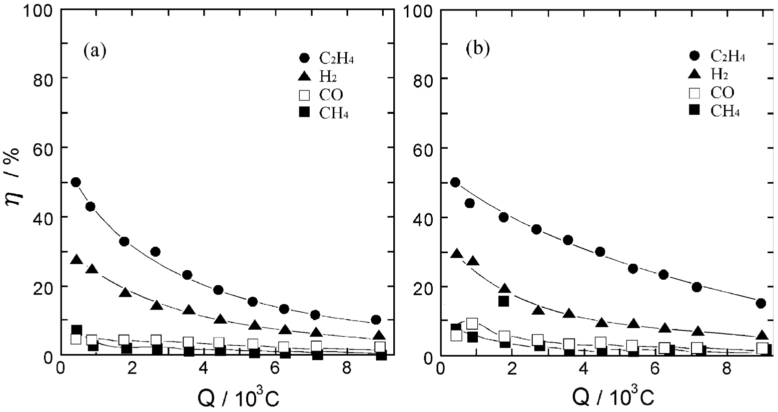


Fig. 2. Current efficiencies vs. the amount of electric charge passed in the electrolysis with a pure Cu-mesh cathode and a Pt (a) or a Cu (b) anode.

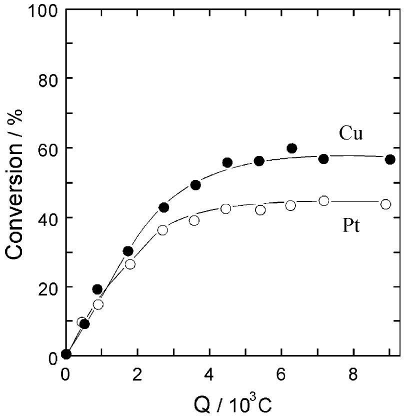


Fig. 3. Conversion percentage of $CO_2$ vs. the amount of electric charge passed in the electrolysis with the same electrodes as those used in Fig. 2.

ions are more abundantly transported than protons are from the anode compartment to the catholyte via the membrane in the electrolysis with Cu anode, because the concentration of Cu ions dissolved from the Cu anode is built up in the prolonged electrolysis. Further, that a good supply of copper ions to the catholyte is necessary for the efficient reduction of $CO_2$ to $C_2H_4$. As described later, an appropriate movement of protons from the anode compartment to the catholyte is also required for the favorable conversion of $CO_2$.

The electrochemical reduction of $CO_2$ was then performed with a CuBr-confined Cu-mesh electrode at the three-phase interface. The fixation of CuBr onto a Cu-mesh substrate was conducted by the anodic deposition at a constant current in a 0.5 M KBr solution. XRD pattern of the confined copper bromide is shown in Fig. 4(a), confirming

Table 1

Current efficiencies for the products obtained with a pure Cu-mesh electrode in the galvanotatic reduction of $CO_2$[a]

| Run | Counter electrode[b] | $Q$[c] (C) | Potential[d] (V) | pH[e] | Current efficiency (%) | | | | | | | | | Conversion[f] (%) | Selectivity[g] (%) | $\eta$[h] (%) |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| | | | | | Ethylene | Methane | CO | Ethane | Ethanol | Formic[i] | Acetic[j] | Lactic[k] | $H_2$ | | | |
| 1 | Pt | 472 | −1.99 to −1.98 | 3.29 | 49.9 | 8.0 | 4.9 | 0.8 | 1.3 | 2.7 | 2.0 | 0.2 | 28.1 | 9.5 | 59.4 | 98 |
| 2 | Pt | 2704 | −2.03 to −1.99 | 2.85 | 30.9 | 2.8 | 4.2 | 0.3 | 0.4 | 2.5 | 1.9 | 0.1 | 15.1 | 36.6 | 54.4 | 58 |
| 3 | Pt | 4451 | −2.02 to −1.98 | 3.33 | 18.7 | 2.3 | 3.4 | 0.3 | 0.3 | 1.8 | 2.3 | 0.0 | 11.0 | 42.7 | 46.4 | 40 |
| 4 | Pt | 6256 | −2.02 to −1.98 | 3.57 | 13.6 | 1.2 | 2.3 | 0.1 | 0.3 | 1.5 | 1.4 | 0.0 | 8.3 | 43.2 | 47.8 | 29 |
| 5 | Pt | 8927 | −2.02 to −1.91 | 4.28 | 10.1 | 0.8 | 1.7 | 0.2 | 0.3 | 1.2 | 0.6 | 0.0 | 6.3 | 44.0 | 48.9 | 21 |
| 6 | Cu | 454 | −1.98 to −1.96 | 3.37 | 49.7 | 7.6 | 5.9 | 0.6 | 2.0 | 2.8 | 1.8 | 0.3 | 29.3 | 9.5 | 57.0 | 100 |
| 7 | Cu | 2722 | −2.00 to −1.97 | 4.19 | 36.2 | 3.7 | 4.4 | 0.6 | 1.0 | 3.3 | 1.9 | 0.1 | 13.3 | 43.3 | 54.4 | 65 |
| 8 | Cu | 4473 | −2.01 to −1.85 | 5.00 | 29.9 | 1.3 | 3.6 | 0.4 | 0.8 | 2.5 | 1.1 | 0.0 | 9.8 | 56.1 | 57.1 | 49 |
| 9 | Cu | 6247 | −2.00 to −1.88 | 5.91 | 23.2 | 1.2 | 2.6 | 0.3 | 0.7 | 2.4 | 0.9 | 0.0 | 8.2 | 61.4 | 56.0 | 40 |
| 10 | Cu | 8962 | −1.98 to −1.81 | 6.71 | 14.7 | 0.6 | 2.1 | 0.2 | 0.6 | 1.4 | 0.2 | 0.0 | 6.0 | 56.9 | 55.0 | 26 |

[a] Electrolyte, 4 M KBr; initial pH, 3.0; the apparent area of a Cu-mesh surface, 10.2 cm; applied current, 250 mA; initial volume of $CO_2$, 577 $cm^3$; catholyte, 232 $cm^3$.

[b] Counter electrode, Pt or Cu mesh; anolyte, a 0.5 M $KHSO_4$ solution of pH 0.

[c] 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 × second).

[d] Change in electrode potential (vs. Ag/AgCl).

[e] Final pH of the catholyte.

[f] Conversion percentage of $CO_2$.

[g] Selectivity for the formation of ethylene on the basis of carbon content.

[h] Total current efficiency in the reduction.

[i] Formic acid.

[j] Acetic acid.

[k] Lactic acid.

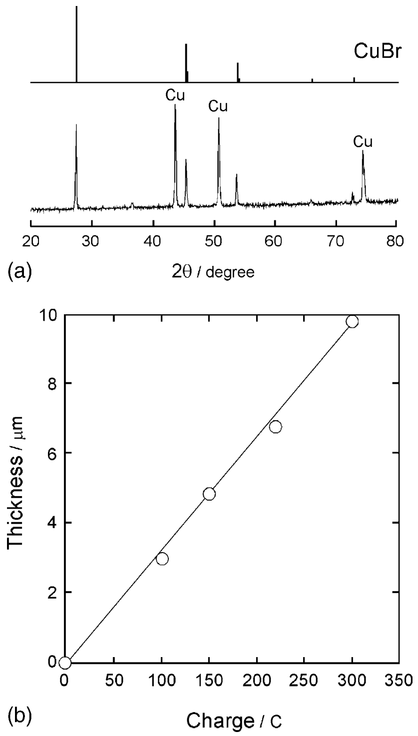


Fig. 4. (a) XRD pattern of CuBr deposited on a Cu-mesh electrode. The pattern is compared with its authentic one. (b) Thickness of CuBr deposited on a Cu-mesh electrode vs. the electric charge passed during the galvanostatic oxidation in a 0.5 M KBr solution of pH 3.

that the deposit is CuBr in comparison with the authentic one. As shown in Fig. 4(b), the thickness of the deposited CuBr is linearly related with the applied electric charge at least within 10 μm. In the present study, the thickness of CuBr was always 7.6 μm.

The main products obtained with a CuBr-confined Cu-mesh electrode were $C_2H_4$, CO, $CH_4$ and $H_2$ in the same manner as the case with a pure Cu mesh. The current efficiencies of these substances versus the amount of electric charge are shown in Fig. 5, where Pt and Cu meshes were used as the counter electrode in parts (a) and (b), respectively. Compared with Fig. 2, it is seen that the fixation of CuBr always enhances the current efficiency of $C_2H_4$ while that of $H_2$ is decreased. Furthermore, a comparison between Fig. 5(a) and (b) indicates that higher current efficiency of $C_2H_4$ is maintained in the prolonged electrolysis with Cu anode than with Pt anode, which is the same trend as that observed in the electrolysis with the pure Cu-mesh electrode (Fig. 2). On the other hand, the pH regulation of the catholyte was found to be very important to keep the yield of $C_2H_4$ high in the long-term electrolysis. As seen from Fig. 5(b), the current efficiency of $C_2H_4$ was increased from about 20 to 30% at the electric charge of 8.9 kC when the pH of the catholyte was lowered by adding a concentrated solution of sulfuric acid to the anode compartment between times during the electrolysis. By this way, the pH of the catholyte was kept around 3 during the electrolysis.

In Fig. 6, the conversion percentage of $CO_2$ obtained with a CuBr-confined Cu-mesh electrode in a KBr solution of pH 3 is shown as a function of the amount of electric charge, indicating again the superior characteristics of copper as the

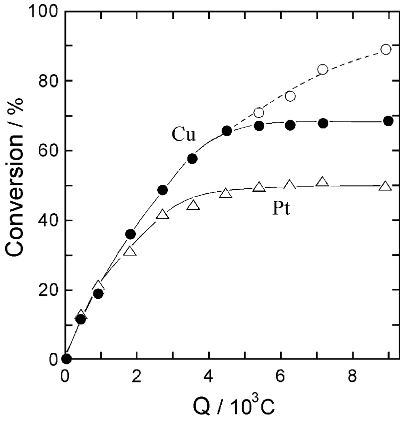


Fig. 6. Conversion percentage of $CO_2$ vs. the amount of electric charge passed in the electrolysis with the same electrodes as those used in Fig. 5. (- - -) The pH of the catholyte was regulated by the same way as that noted in Fig. 5.

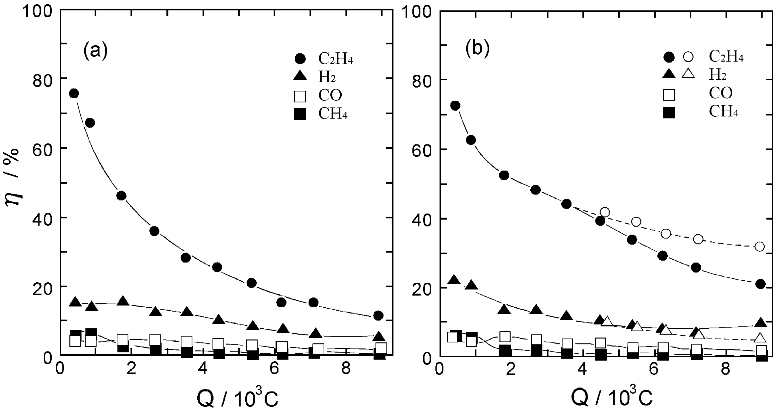


Fig. 5. Current efficiencies vs. the amount of electric charge passed in the electrolysis with a CuBr-confined Cu-mesh cathode and a Pt (a) or a Cu (b) anode. (- - -) The pH of the catholyte was regulated by adding $H_2SO_4$ to the anode compartment.

counter electrode. The indirect regulation of the pH of the catholyte achieved by the same way as that noted in Fig. 5 enhanced considerably the conversion percentage of $CO_2$ in the long-term electrolysis, i.e., about 90% of the initial volume of $CO_2$ was converted at the electric charge of 8.9 kC.

The detailed distribution of the products obtained with a CuBr-confined Cu-mesh electrode is exhibited in Table 2. The current efficiencies of liquid products were very low except that of formic acid. In the electrolysis with Cu anode (Runs 5, 7 and 9) without adjusting the pH of the catholyte, the pH was found to rise as the amount of electric charge was increased, which was the same tendency as that observed with the pure Cu-mesh electrode (Table 1). On the other hand, in Runs 6, 8 and 10, the pH of the catholyte was adjusted to around 3 by adding a concentrated solution of $H_2SO_4$ to the anode compartment. Compared with the former results (Runs 5, 7 and 9), the current efficiency of $C_2H_4$ and the conversion percentage of $CO_2$ were both always enhanced. This means obviously that the concentration of protons in the catholyte is insufficient for the efficient reduction of $CO_2$ in the former case. The selectivity for the formation of $C_2H_4$ on the basis of carbon content became 74% at the electric charge of 8.9 kC when the pH of the catholyte was thus regulated.

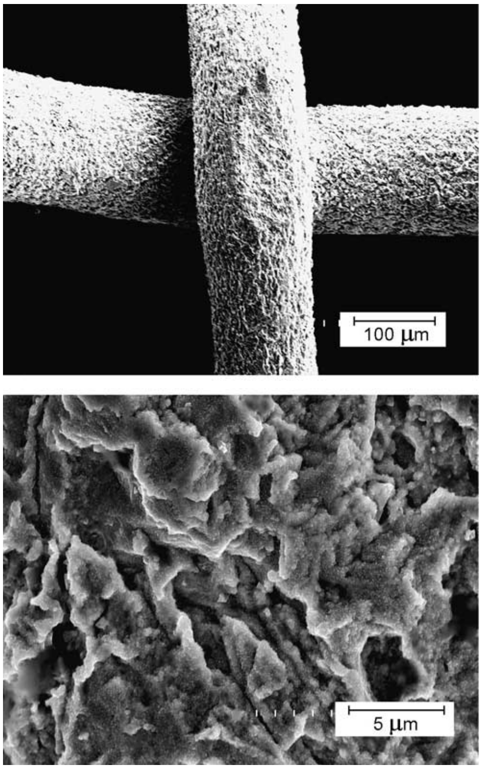


Fig. 7. FE-SEM image of a pure Cu-mesh electrode used as the cathode for the 10-h electrolysis of $CO_2$ with a constant current density of 24.5 mA $cm^{-2}$. Anode: Pt.

The FE-SEM images of pure and CuBr-confined Cu-mesh electrodes which were used for 10-h electrolysis of $CO_2$ with a constant current density of 24.5 mA $cm^{-2}$ are exhibited in Figs. 7 and 8, respectively. The electrode surface of the pure Cu mesh became blackish and rough (Fig. 7), which is considered to be related with the formation of poisoning species such as copper oxide [7,8] or graphitic carbon [9]. That is, it is known that the generation of a poisoning species on a Cu foil electrode results in a considerable decline of catalytic activity of copper electrode. In fact, the conversion of $CO_2$ was found to be much lower also in our electrolysis at the three-phase interface with a pure Cu-mesh electrode than with a modified Cu-mesh electrode (compare Figs. 3 and 6). On the other hand, the electrode surface of the CuBr-confined Cu-mesh electrode was bright and a dendritic growth of copper was observed after the 10-h electrolysis of $CO_2$ (Fig. 8). Such a growth of Cu is attributed to the result of the partial reduction of confined CuBr. However, this halide can be regenerated on the cathode surface if a copper electrode is used as the anode, i.e., $Cu^{2+}$ ions transferred from the anode compartment react with $Br^-$ ions to form

Table 2
Current efficiencies for the products obtained with a CuBr-confined Cu-mesh electrode in the galvanotatic reduction of $CO_2$[a]

| Run | Counter electrode | $Q$ (C) | Potential (V) | pH | Current efficiency (%) | | | | | | | | | Conversion (%) | Selectivity (%) | $\eta$ (%) |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| | | | | | Ethylene | Methane | CO | Ethane | Ethanol | Formic | Acetic | Lactic | $H_2$ | | | |
| 1 | Pt | 449 | −2.08 to −1.99 | 3.62 | 65.6 | 6.1 | 5.5 | 0.9 | 1.5 | 2.2 | 1.4 | 0.2 | 16.1 | 11.6 | 70.1 | 100 |
| 2 | Pt | 4459 | −2.10 to −1.99 | 4.30 | 25.4 | 0.9 | 3.4 | 0.2 | 0.3 | 2.2 | 0.5 | 0.0 | 10.9 | 47.2 | 57.7 | 44 |
| 3 | Pt | 7152 | −2.09 to −1.97 | 4.52 | 15.4 | 0.8 | 1.8 | 0.2 | 0.5 | 2.0 | 1.0 | 0.0 | 7.1 | 50.9 | 52.0 | 29 |
| 4 | Pt | 8924 | −2.10 to −1.92 | 4.77 | 11.5 | 0.6 | 1.7 | 0.2 | 0.3 | 1.8 | 0.3 | 0.0 | 6.1 | 49.4 | 49.5 | 23 |
| 5 | Cu | 4483 | −2.08 to −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 |
| 6[b] | Cu | 4500 | −2.12 to −1.87 | 2.92 | 40.7 | 1.2 | 2.7 | 0.3 | 0.3 | 2.8 | 0.3 | 0.0 | 10.6 | 63.3 | 68.8 | 59 |
| 7 | Cu | 7157 | −2.18 to −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 |
| 8[b] | Cu | 7160 | −2.13 to −1.89 | 2,96 | 33.3 | 0.9 | 2.8 | 0.2 | 0.3 | 2.1 | 0.4 | 0.0 | 7.1 | 81.9 | 69.1 | 47 |
| 9 | Cu | 8981 | −2.15 to −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 |
| 10[b] | Cu | 8928 | −2.12 to −1.91 | 3.01 | 30.4 | 0.7 | 1.5 | 0.3 | 0.3 | 1.5 | 0.5 | 0.0 | 6.9 | 87.7 | 74.0 | 41 |

[a] The thickness of confined CuBr film, 7.9 µm. The other conditions are the same as those given in Table 1.

[b] A concentrated solution of $H_2SO_4$ 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.

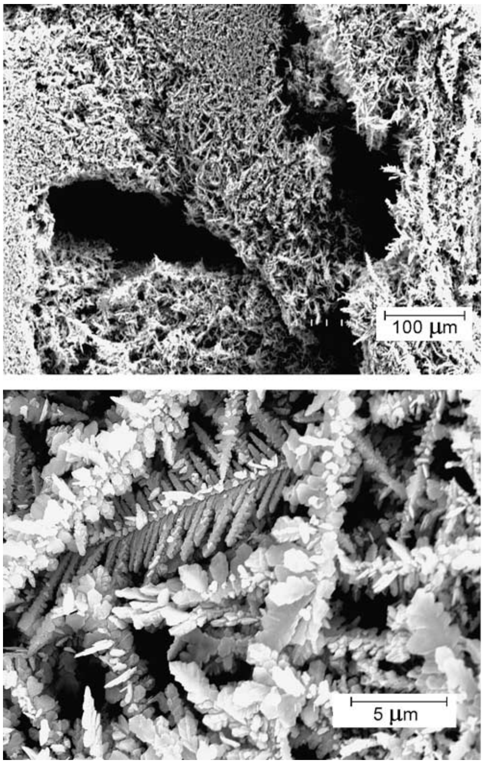


Fig. 8. FE-SEM image of a CuBr-confined Cu-mesh electrode used as the cathode for the 10-h electrolysis of $CO_2$ with a constant current density of 24.5 mA $cm^{-2}$. Anode: Pt.

the copper(II) bromide which are then electroreduced to CuBr.

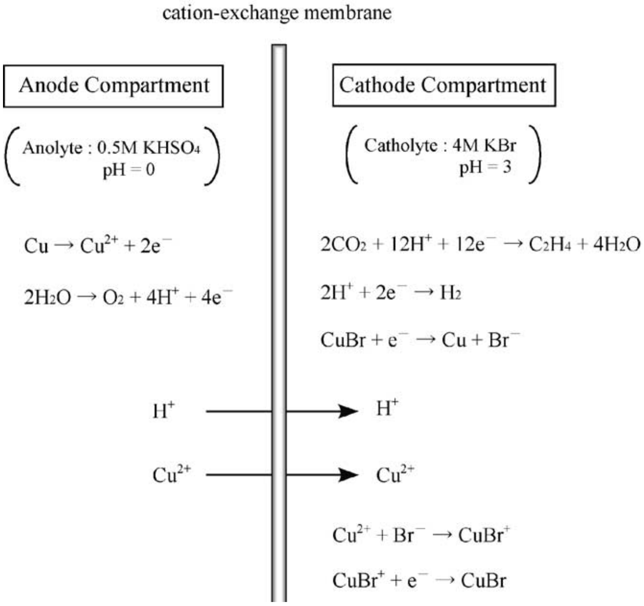
## 4. Discussion

As described above, the electrochemical reduction of $CO_2$ at the three-phase interface on a CuBr-confined Cu-mesh electrode leads to the selective formation of $C_2H_4$. The conversion percentage of $CO_2$ and the yield of $C_2H_4$ were considerably enhanced in the prolonged electrolysis when copper ions and protons were transferred from the anode compartment to the catholyte through the cation-exchange membrane. This is attributed to the regeneration of CuBr working as a heterogeneous catalyst and to the supplementation of protons consumed in the reduction. The electrode reactions taking place on the anode should be the dissolution of copper and the oxygen evolution. The latter reaction is accompanied by the formation of protons, but this concentration is not so sufficient as protons can diffuse efficiently to the cathode compartment via the membrane. So, the addition of strong acid to the anode compartment was necessary to indirectly lower the pH of the catholyte. It is noted that such high current efficiency and high conversion percentage were brought about by regulating the pH of the catholyte not directly but through the proton transport from the anode compartment via the membrane. When the pH of the catholyte was directly regulated by adding strong acid, the current efficiency and conversion percentage were both considerably decreased. This is probably caused by the presence of counter ions (sulfate) of strong acid ($H_2SO_4$) because the electrochemical reduction of $CO_2$ to $C_2H_4$ is hardly observed in an acidic solution containing sulfate ions [5]. It is therefore considered that reaction intermediates are expelled from the adsorption sites by the invasion of sulfate ions. The cathode and anode reactions are shown along with the ion transport during the electrolysis in Scheme 1.

Copper ions transferred from the anode compartment react with bromide ions to form $Cu(II)Br^+$ in the catholyte. This bromide is further reduced to Cu(I)Br to be deposited due to the extremely low solubility onto the electrode surface. Thus, new CuBr is always formed and works as the heterogeneous catalyst on the Cu-mesh electrode. The main total reaction consists of the reduction of $CO_2$ to $C_2H_4$ at the cathode and the oxidation of $H_2O$ to $O_2$ at the anode and is given by the following reaction:

$$2CO_2 + 2H_2O \rightarrow C_2H_4 + 3O_2 \quad (1)$$

Interestingly, the current efficiency of hydrogen evolution was smaller in the catholyte of which pH was regulated lower compared to that in the catholyte without pH controlling (compare Runs 9 and 10 in Table 2). This indicates that the fixation of CuBr onto a Cu-mesh electrode has a tendency to raise the hydrogen overpotential, while the $CO_2$ reduction is naturally favorable at lower pH. The cause for a favorable effect of CuBr is attributed to the ability of copper(I) halide to combine reversibly with CO and $C_2H_4$ [10–12]. Although it is known that Cu itself is capable of adsorbing CO in the linear form in the highly negative potential range −1.5 to −1.0 V versus SCE [13], the adsorbing ability of CuBr is considered to be much larger



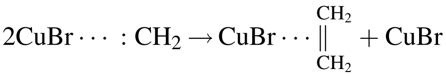
Scheme 1.

than that of Cu. At the three-phase interface, $CO_2$ (g) is first reduced electrochemically to CO (g). This gas is ready to adsorb to CuBr with its π-bond perpendicular to the surface and the CO is subjected to electron injection from the electrode to be reduced to carbene. The coupling of carbenes results in the formation of ethylene which may be stabilized by adsorbing to CuBr, but the attach of new $CO_2$ molecules onto the CuBr may detach $C_2H_4$ from the adsorption sites towards the gas phase. This scheme can be given by the following reactions:

$$CO_2(g) + 2H + 2e^- \rightarrow CO(g) + H_2O \quad (2)$$

$$CuBr + CO(g) \rightarrow CuBr\cdots CO \quad (3)$$

$$CuBr\cdots CO + 4H^+ + 4e^- \rightarrow CuBr\cdots : CH_2 + H_2O \quad (4)$$



$$2CuBr\cdots : CH_2 \rightarrow CuBr\cdots \overset{CH_2}{\underset{CH_2}{\|}} + CuBr \quad (5)$$

Thus, the electrochemical conversion of $CO_2$ may continue to proceed via the catalytic reactions involving CuBr.

## 5. Conclusions

Selective conversion of $CO_2$ to ethylene was achieved in the electrolysis at the three-phase interface on a CuBr-confined Cu-mesh electrode. The conversion percentage of $CO_2$ and the yield of $C_2H_4$ were considerably enhanced in the prolonged electrolysis when copper ions and protons were transferred from the anode compartment to the catholyte through the cation-exchange membrane. This was attributed to the regeneration of CuBr working as a heterogeneous catalyst and to the supplementation of protons consumed in the reduction.

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