

Pulse-mode electrochemical reduction of carbon dioxide using copper and copper oxide electrodes for selective ethylene formation

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Received: 2 July 2007 / Accepted: 10 June 2008 / Published online: 3 July 2008
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Abstract Although the electrochemical reduction of CO₂ at a copper electrode produces hydrocarbons, the activity for the conversion of CO₂ is significantly reduced after several tens of minutes by the deposition of poisoning species on the electrode. In order to solve the poisoning species problem, the electrochemical reduction of CO₂ was carried out using a copper electrode in the pulse electrolysis mode by anodic as well as cathodic polarization. The anodic polarization intervals suppressed the deposition of the poisoning species on the electrode, and the amount of two hydrocarbons produced, CH₄ and C₂H₆, decreased only slightly even after one hour. By choosing the appropriate anodic potential and time duration the selectivity for C₂H₆ formation was significantly enhanced. The enhancement was found to be due to the copper oxide formed on the copper electrode. The selectivity was further improved when the electrochemical reduction was carried out using a copper oxide electrode. The highest efficiency of about 28% was obtained at −3.15 V.

Keywords Electrochemical reduction · Carbon dioxide · Copper electrode · Copper oxide electrode · Pulse electrolysis · Ethylene

1 Introduction

It is widely accepted that the electrode substrates play very significant roles in the electrochemical reduction of CO₂.

The yield and type of the reduced organic products depend strongly on the electrode substrates. According to Hori and co-workers, the electrode substrate metals can be grouped in accordance with product selectivity [1]: (1) Cu; (2) Au, Ag, Zn, Pd and Ga; (3) Pb, Hg, In, Sn, Cd and Tl; (4) Ni, Fe, Pt and Ti. The Faradaic efficiencies for the major products are listed in Table 1 [1, 5]. Copper is the only metal that yields hydrocarbons and alcohols as major products, although the major products are CO, HCOO[−] and H₂ for the other metals [1–5]. From a practical point of view copper seems the most advantageous electrode substrate.

Unfortunately, however, all the Faradaic efficiencies suddenly drop after several tens of minutes from the start of the electrochemical reduction; this is caused by deposition of poisoning species on the electrode [6–9]. Once the poisoning species cover the surface, the electrode loses its high catalytic activity [6–9]. Potential modulation methods are known to remove poisoning species from the copper electrode [10–16]. In this study, to solve the poisoning species problem, we first attempted the electrochemical reduction of CO₂ using pulse electrolysis by both anodic as well as cathodic polarization [10–13]. Another, but more important purpose in this study is to enhance the selectivity for C₂H₄ formation by changing the electrolytic conditions such as the anodic and cathodic potentials. The anodic polarization intervals are expected not only to suppress the deposition of the poisoning species on the electrode but also to enhance the selectivity for C₂H₄ formation. Further, we carried out the same electrochemical reduction of CO₂ using copper oxide electrodes because copper oxide, which is formed on the surface of the copper electrode during anodic polarization, can contribute to selective C₂H₄ formation.

It turns out that (1) no activity loss during the conversion of CO₂ was observed during the pulse electrolysis, (2) by

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Table 1 Faradaic efficiencies (%) for various reduced products from the electrochemical reduction of CO₂ using several metal electrodes

Electrode	CH ₄	C ₂ H ₄	C ₂ H ₅ OH	C ₃ H ₇ OH	CO	HCOO ⁻	H ₂	Total
Cu	33.3	25.5	5.7	3.0	1.3	9.4	20.5	103.5
Au	0.0	0.0	0.0	0.0	87.1	0.7	10.2	98.0
Ag	0.0	0.0	0.0	0.0	81.5	0.8	12.4	94.6
Zn	0.0	0.0	0.0	0.0	79.4	6.1	9.9	95.4
Pd	2.9	0.0	0.0	0.0	28.3	2.8	26.2	60.2
Ga	0.0	0.0	0.0	0.0	23.2	0.0	79.0	102.0
Pb	0.0	0.0	0.0	0.0	0.0	97.4	5.0	102.4
Hg	0.0	0.0	0.0	0.0	0.0	99.5	0.0	99.5
In	0.0	0.0	0.0	0.0	2.1	94.9	3.3	100.3
Sn	0.0	0.0	0.0	0.0	7.1	88.4	4.6	100.1
Cd	1.3	0.0	0.0	0.0	13.9	78.4	9.4	103.0
Tl	0.0	0.0	0.0	0.0	0.0	95.1	6.2	101.3
Ni	1.8	0.1	0.0	0.0	0.0	1.4	88.9	92.4
Fe	0.0	0.0	0.0	0.0	0.0	0.0	94.8	94.8
Pt	0.0	0.0	0.0	0.0	0.0	0.1	95.7	95.8
Ti	0.0	0.0	0.0	0.0	0.0	0.0	99.7	99.7

choosing the appropriate anodic potential and reaction time, the selectivity for C₂H₄ formation was significantly enhanced, (3) this enhancement was found to be due to the copper oxide formed on the copper electrode, and (4) the selectivity was further improved when the electrochemical reduction was carried out using a copper oxide electrode.

2 Experimental part

The electrolysis cell was a simple two-compartment cell made of acrylic resin as shown in Fig. 1. The electrochemical reduction of CO₂ was carried out using a Hokuto Denko HABF-501 potentiostat with a Hokuto Denko HB-104 function generator. The catholyte of about 180 mL was separated by a cation exchange membrane (Nafion 117) from the anolyte. The cell was kept at 25 °C using a Yamato BL-22 water bath. To remove dissolved oxygen and to ensure comparable solution conditions, high purity CO₂ (purity 99.99%) was passed through the catholyte to achieve saturation before each experiment. High purity CO₂ was supplied at a constant flow rate into the electrolyte, which was vigorously stirred by a magnetic stirrer during the electrochemical reduction. The pressure of CO₂ inside the cell was maintained at 1 atm. A high purity copper plate (purity higher than 99.9%, Nirako Co., 4N4%) was used after electropolishing as the copper electrode. The counter electrode was a Pt plate, and the reference electrode was a commercial Ag/AgCl electrode with a Luggin capillary tip (Toa Denpa Co., model HS-205C).

All chemicals were of reagent grade and were used without further purification. The electrolyte was mainly a 0.1 M (1 M = 1 mol dm⁻³) aqueous KHCO₃ solution.

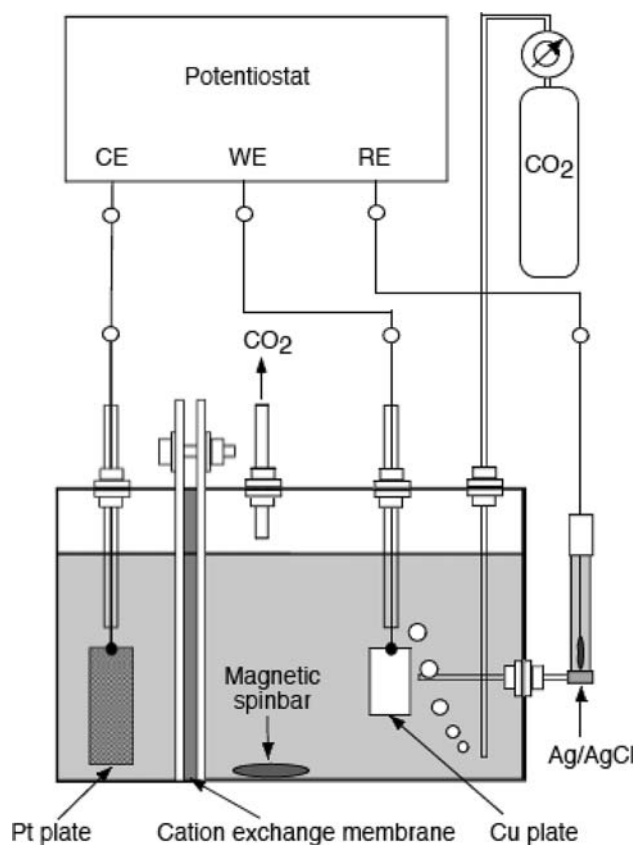


Fig. 1 Schematic diagram of cell for pulsed electrochemical reduction of CO₂

The copper oxide plate electrode was prepared by heating a copper plate until the surface was colored reddish brown [17]. The surface analysis of the copper and copper oxide was done using a Rigaku RINT 2000/PC X-ray

diffractometer (XRD), a Hitachi S-510 scanning electron microscope (SEM) and a JASCO V-570 spectrophotometer equipped with an ISN-470 integrating sphere.

The CO₂ effluent was introduced into the gas chromatographs (Shimadzu Co., model GC-14A FID and GC-8A TCD), and the gaseous products contained in the CO₂ effluent were analyzed. The concentration of the gaseous products remained almost constant in the CO₂ effluent gas during the electrochemical reduction.

3 Results and discussion

3.1 Faradaic efficiencies of the major gaseous products

Using the copper electrode, pulsed electroreduction of CO₂ was performed in three aqueous electrolyte solutions: 0.1 M K₂SO₄, 0.1 M Na₂SO₄ and 0.1 M M KHCO₃. Figure 2a–c show the relationship between the cathodic polarization potential (E_c) and the Faradaic efficiencies for the major gaseous products, C₂H₄, CH₄, CO and H₂, when the potential pulse was continuously applied (see Fig. 2 bottom). The two hydrocarbons, C₂H₄ and CH₄, are predominantly formed within the limited cathodic polarization potential range, where the Faradaic efficiencies for the formation of both CO and H₂ are greatly suppressed. Within the potential range, the same tendency of the Faradaic efficiency exists for CH₄ formation to be higher than that of C₂H₄ formation as shown in Table 1. The difference was that the Faradaic efficiencies for CH₄ and C₂H₄

formation did not decrease for at least 30 min after the start of electrochemical reduction.

Although neutral bicarbonate solutions have been mostly employed as the electrolytes because of their high CO₂ solubility, the poisoning reactions are accelerated at such a high pH [15]. Pulse mode electrolysis suppressed the poisoning reactions and allowed the copper electrode to maintain its high catalytic activity for the conversion of CO₂. In addition, the limited potential range, where C₂H₄ and CH₄ are predominantly formed varies with the type of electrolyte solution, and the widest potential range appears for 0.1 M KHCO₃ solution, ranging from –1.8 to –3.2 V. The widest potential range may be related to the highest solubility of CO₂ and the dissolution equilibrium. Because of its wide potential range, 0.1 M KHCO₃ solution was employed as electrolyte hereafter.

3.2 Effect of the anodic polarization on CH₄ and C₂H₄ formation

With the intention of obtaining high selectivity for C₂H₄ formation, two anodic polarization parameters, the anodic polarization potential (E_a) and reaction time (t_a), were changed and the electrochemical reduction was carried out. Figures 3 and 4 indicate how the Faradaic efficiencies for C₂H₄ and CH₄ are influenced by altering E_a and t_a . The Faradaic efficiency for C₂H₄ formation is higher than that for CH₄ formation at $E_a > 1.4$ V (Fig. 3) and $t_a > 6$ s (Fig. 4).

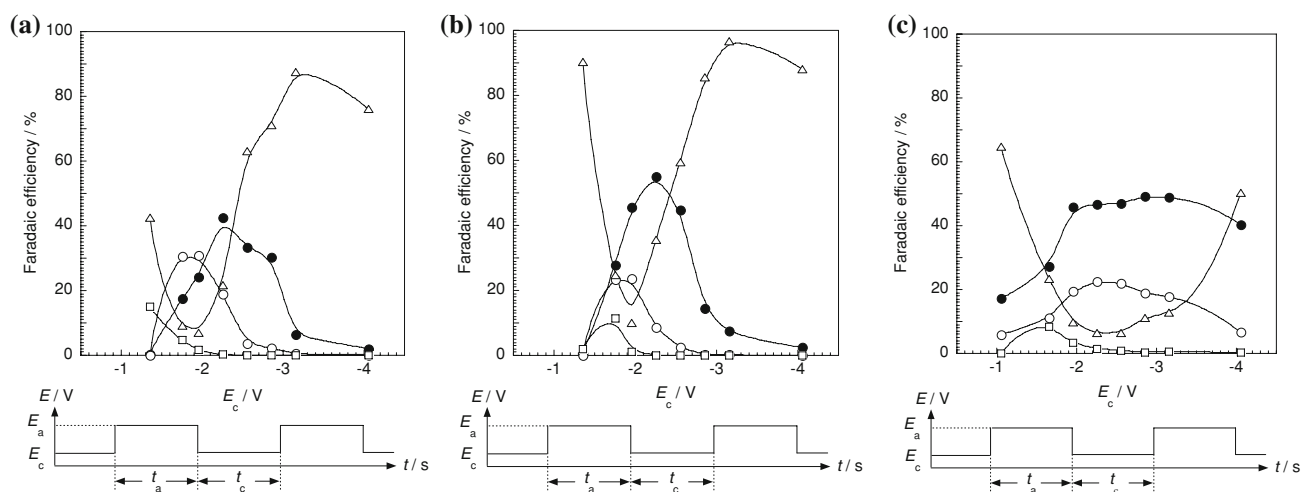


Fig. 2 (a) Dependence of Faradaic efficiencies on cathodic polarization potential (E_c) during pulse-mode electrochemical reduction of CO₂ in a 0.1 M (1 M = 1 mol dm⁻³) K₂SO₄ aqueous solution using a copper electrode. (●) CH₄, (○) C₂H₄, (△) H₂ and (□) CO. Bottom plot shows the applied waveform: $E_a = +0.05$ V and $t_c = t_a = 3$ s, (b) Dependence of Faradaic efficiencies on E_c during pulse-mode electrochemical reduction of CO₂ in 0.1 M Na₂SO₄ aqueous solution

using a copper electrode. (●) CH₄, (○) C₂H₄, (△) H₂ and (□) CO. Bottom plot shows the applied waveform: $E_a = +0.05$ V and $t_c = t_a = 3$ s. (c) Dependence of Faradaic efficiencies on E_c during pulse-mode electrochemical reduction of CO₂ in a 0.1 M KHCO₃ aqueous solution using a copper electrode. (●) CH₄, (○) C₂H₄, (△) H₂ and (□) CO. Bottom plot shows the applied waveform: $E_a = +0.05$ V and $t_c = t_a = 3$ s

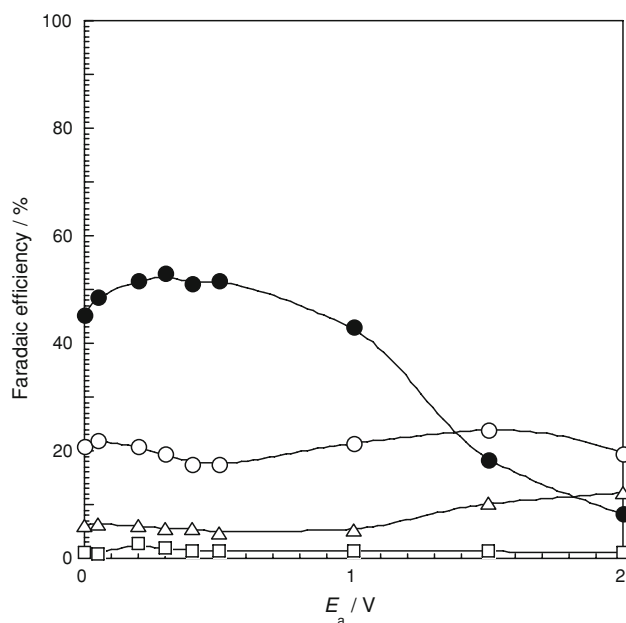


Fig. 3 Effect of anodic polarization potential (E_a) on Faradaic efficiencies for CH_4 (●), C_2H_4 (○), H_2 (△) and CO (□). Applied waveform: $E_c = -2.55$ V and $t_c = t_a = 3$ s

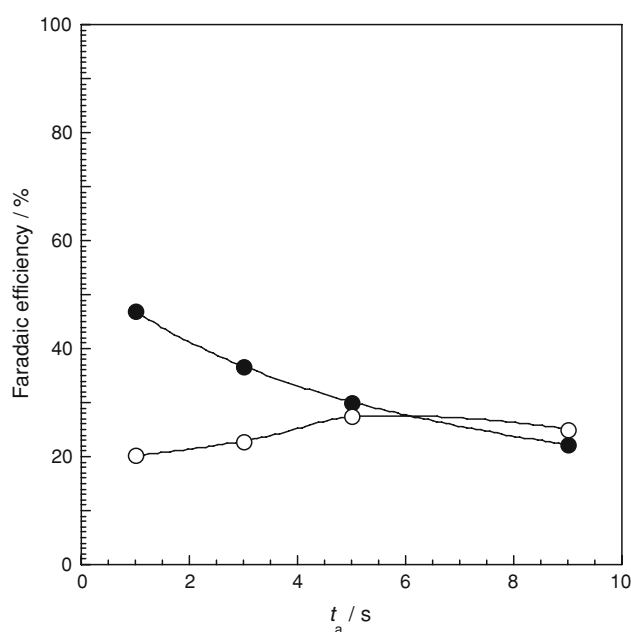


Fig. 4 Effect of anodic polarization time (t_a) on Faradaic efficiencies for CH_4 (●) and C_2H_4 (○). Applied waveform: $E_c = -2.85$ V, $E_a = +1.0$ V and $t_c = t_a = 3$ s

The electrode surface plays an important role in CH_4 and C_2H_4 formation because the formation reactions include dissociative adsorptions [18]. To examine what happens on the electrode surface, X-ray diffraction (XRD) patterns of the electrodes were examined after pulsed electroreduction (Fig. 5). There are three sharp peaks for

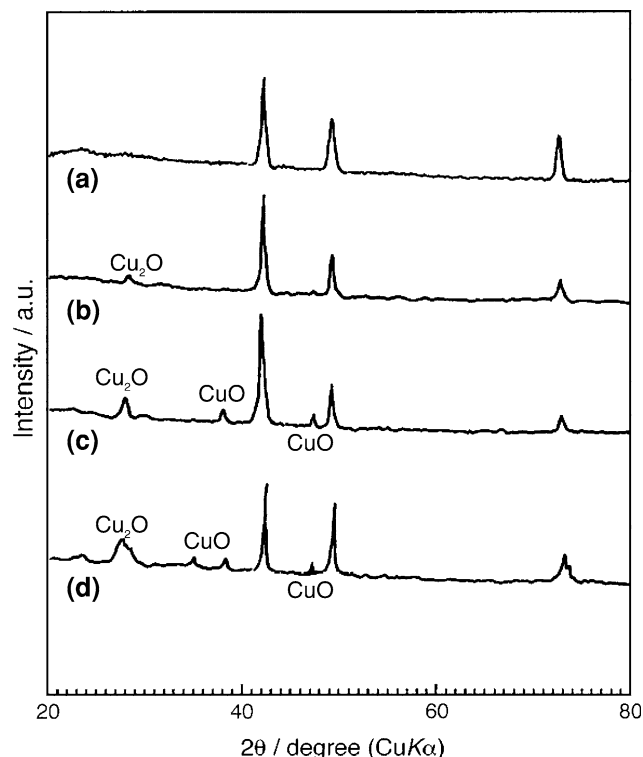


Fig. 5 XRD patterns of copper electrode surfaces after electrochemical reduction of CO_2 with applied waveform: $E_c = -2.55$ V, $t_c = t_a = 3$ s, $E_a = +0.05$ V (a), $E_a = +0.5$ V (b), $E_a = +0.9$ V (c) and $E_a = +1.2$ V (d)

$E_a = 0.05$ V (Fig. 5a) and they are all assigned to copper. Several new peaks are evident for $E_a \geq 0.05$ V (Fig. 5b–d) and they are ascribable to Cu_2O and CuO . According to Figs. 3 and 4, the greater the anodic polarization, the higher the Faradaic efficiency for C_2H_4 formation. Copper oxide is probably a favorable factor for C_2H_4 formation.

3.3 Pulsed electroreduction of CO_2 using copper oxide electrode

The XRD patterns revealed that copper oxide was formed on the electrode surface subjected to anodic polarization at $E_a \geq 0.5$ V. To examine whether the copper oxide contributed to the predominant formation of C_2H_4 , an oxide-rich copper electrode was used instead of the pure copper electrode and the electroreduction was repeated. The electrode was prepared by heating a copper electrode in air until the surface was colored reddish brown [17]. The existence of Cu_2O and CuO on the electrode surface was confirmed by XRD. Figure 6 illustrates how the Faradaic efficiencies for CH_4 and C_2H_4 formations are dependent on E_c . A similar dependence in Fig. 2 is evident for C_2H_4 formation, while the Faradaic efficiency for CH_4 formation is extremely low over the whole E_c range, which means that high selectivity for C_2H_4 formation is achieved using a copper oxide

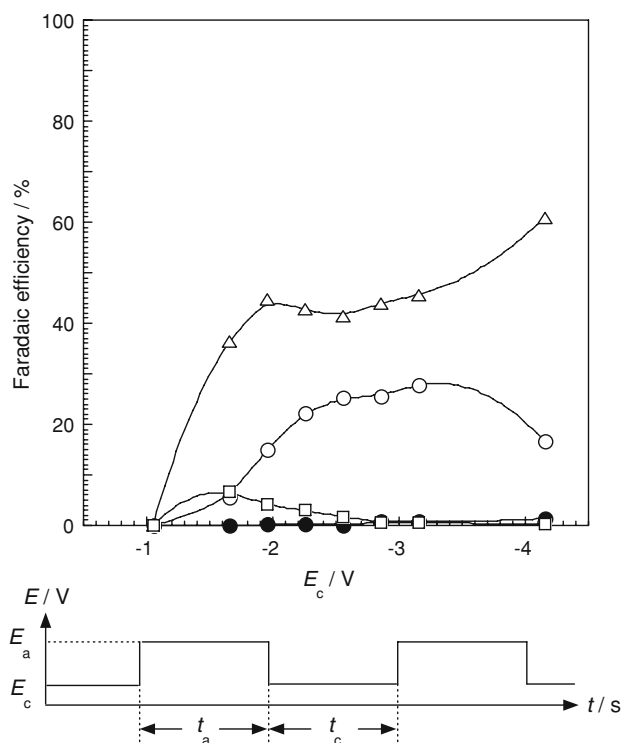


Fig. 6 Dependence of Faradaic efficiencies on E_c in the electrochemical reduction of CO_2 in 0.1 M KHCO_3 aqueous solution using copper oxide electrode. (●) CH_4 , (○) C_2H_4 , (△) H_2 and (□) CO . Bottom plot shows the applied waveform: $E_a = +0.05$ V and $t_c = t_a = 3$ s

electrode. In addition, the highest efficiency of about 28% is obtained at -3.15 V, this efficiency being 6% higher than that obtained with the copper electrode (see Fig. 2c).

Another interesting point in Fig. 6 is the much higher Faradaic efficiency for H_2 evolution than that in Fig. 2 within the potential range where C_2H_4 formation is predominant. This implies that active hydrogen is probably related to the catalytic reduction of C_2H_4 to C_2H_6 . In order to confirm this, palladium-catalyzed alumina particles (5 wt% Pd) were added to the cell, and the electroreduction of CO_2 was performed. The relationship between the Faradaic efficiencies and the added amount of the palladium-catalyzed alumina particles is shown in Fig. 7. As expected, as the catalyzed particles are added, the Faradaic efficiencies for C_2H_4 formation as well as H_2 evolution suddenly drop and C_2H_6 formation becomes predominant. Thus selective C_2H_4 formation may result in selective C_2H_6 formation because the particles could be used repeatedly.

3.4 Reaction pathways for the CH_4 and C_2H_4 formations

In the electrochemical reduction of CO_2 on copper, $\text{CO}_2^{\bullet-}$ generated by the reduction adsorbs on the electrode

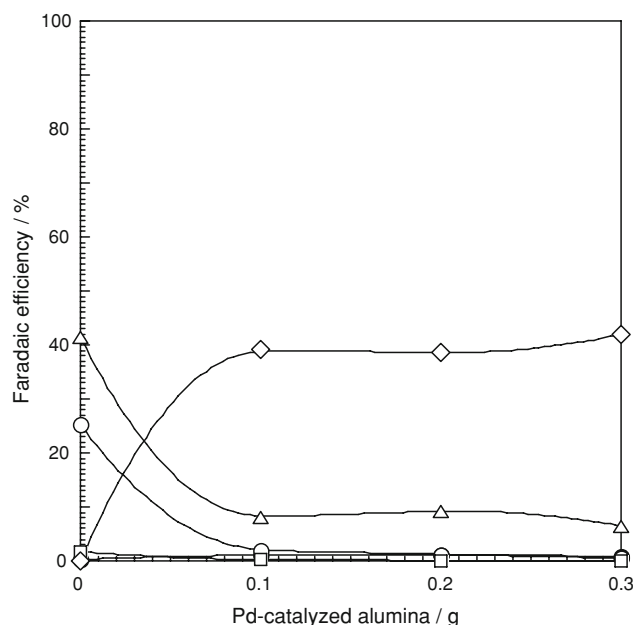


Fig. 7 Relationship between Faradaic efficiencies and added amount of palladium-catalyzed alumina particles in the electrochemical reduction of CO_2 in 0.1 M KHCO_3 aqueous solution on the copper oxide electrode. (◇) C_2H_6 , (○) C_2H_4 , (△) H_2 and (□) CO . Applied waveform: $E_a = +0.05$ V, $E_c = -2.55$ V and $t_c = t_a = 3$ s

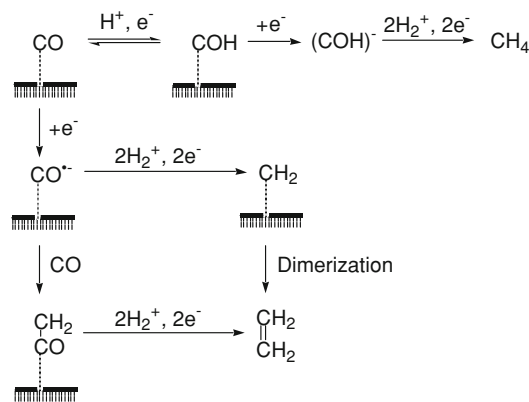


Fig. 8 Reaction pathway for electrochemical reduction of adsorbed CO

surface, and adsorbed $\text{CO}_2^{\bullet-}$ is converted to CO [5]. The reaction pathways toward CH_4 and C_2H_4 formation from adsorbed CO are shown in Fig. 8 [5, 19, 20]. Speculation regarding the predominance of the C_2H_4 formation is that the copper oxide prevents adsorbed CO from being protonated (equilibrium reaction in Fig. 8). This seems to be supported by the fact that CH_4 formation barely occurs when the electroreduction of CO_2 is carried out using copper oxide. The interaction between copper oxide and adsorbed CO has been examined to obtain direct evidence.

4 Conclusions

The electrochemical reduction of CO₂ using pulse electrolysis not only suppresses the deposition of poisoning species on the copper electrode but also enhances the selectivity for C₂H₄ formation by changing the electrolytic conditions. The selectivity is further improved when the electrochemical reduction is done using a copper oxide electrode. Furthermore, by adding palladium-catalyzed alumina particles in the cell, C₂H₄ is converted to C₂H₆ and selective C₂H₆ formation is achieved. Recently, selective C₂H₄ formation was confirmed by the constant potential electroreduction of CO₂ at a three-phase (gas/liquid/solid) interface containing Cu²⁺ [21]. Compared with that method, our method is more practical because it needs no such special equipment and no heavy metal ions such as Cu²⁺.

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