SHORT COMMUNICATION

Selective ethylene formation by pulse-mode electrochemical reduction of carbon dioxide using copper and copper-oxide electrodes

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Abstract Although the electrochemical reduction of carbon dioxide (CO_2) with a copper electrode produces hydrocarbons, the activity toward the conversion of CO_2 is lost for several 10 min by the deposition of poisoning species on the electrode. To solve the poisoning species problem, the electrochemical reduction of CO_2 was carried out using a copper electrode with a pulse electrolysis mode with anodic as well as cathodic polarization. The anodic polarization intervals suppressed the deposition of poisoning species on the electrode, and the amount of two hydrocarbons, CH_4 and C_2H_4, barely decreased even after an hour. By choosing appropriate anodic potential and time duration, the selectivity for the C_2H_4 formation was greatly 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 made with the copper-oxide electrode. The highest efficiency of about 28% is obtained at −3.15 V.

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

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Introduction

Carbon dioxide (CO_2) is a serious pollutant to warm the earth by the greenhouse effect [1]. Besides, very recently, it was found out that CO_2 is causing the ecological destruction of the sea by acidification of seawater [2]. These environmental problems could be solved if CO_2 was reduced and recycled as fuels or organic compounds. Electrochemical reduction is one of the most potential reduction methods of CO_2, which was already reported in 1914 [3], because it barely needs high temperature and pressure.

The electrode substrates play very significant roles in the electrochemical reduction of CO_2. The obtained reduced organic products depend strongly on the electrode substrates. According to Hori and his coworkers, among the various electrode substrate metals, copper is the only one that yields hydrocarbons and alcohols as major products [4–8]. The faradaic efficiencies of the major products are listed in Table 1 [8]. Unfortunately, however, all the faradaic efficiencies drop suddenly about several 10 min after the start of the electrochemical reduction, and the copper electrode loses its high catalytic activity toward the conversion of CO_2 [9, 10]. The loss of the activity is due to the deposition of poisoning species onto the electrode [10–15]. To solve the poisoning species problem, potential modulation methods are known to be effective [9, 13–15]. In this letter, we attempt to do the electrochemical reduction of CO_2 using a pulse electrolysis mode with anodic as well as cathodic polarization. The anodic polarization intervals probably suppress the deposition of poisoning species on the electrode. Besides, another but more important purpose in this letter is to enhance the selectivity for the C_2H_4 formation by changing the electrolytic conditions such as the anodic and cathodic potentials.

Table 1 Faradaic efficiencies of the various reduced products from the electrochemical reduction of CO_2 using a copper electrode

CH_4	C_2H_4	C_2H_5OH	C_3H_7OH	CO	$HCOO^-$	H_2
33.3	25.5	5.7	3.0	1.3	9.4	20.5

No loss of the activity toward the conversion of CO_2 was observed during the pulse electrolysis. By choosing appropriate anodic potential and time duration, the selectivity for the C_2H_4 formation was greatly 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 made with the copper-oxide electrode.

Experimental details

The electrochemical reduction was performed by a Hokuto Denko HABF-501 potentiostat with a Hokuto Denko HB-104 function generator. The electrolysis cell used in this study was a simple two-compartment cell made of acrylic resin. 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. A high-purity copper plate (purity higher than 99.9%, Nirako, 4N4%) was used after electropolishing as a copper electrode. The counter electrode was a Pt plate, and the reference electrode was a commercial Ag/AgCl electrode with the Luggin capillary tip (Toa Denpa, model HS-205C). High purity CO_2 (purity 99.99%) 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 CO_2 inside the cell was maintained at 1 atm.

All chemicals were of reagent grade and used without further purification. The electrolyte was 0.1 M (1 M=1 mol dm^{-3}) aqueous $KHCO_3$ solution. The copper-oxide plate electrode was prepared by heating the copper plate until the surface colored reddish brown. The formation of the copper oxide was confirmed by the X-ray diffraction (XRD) analysis (Rigaku).

The effluent CO_2 was introduced into gas chromatographs (Shimadzu, models GC-14A FID and GC-8A TCD), and the gaseous products contained in the effluent CO_2 were analyzed. The concentration of the gaseous products kept almost constant in the effluent CO_2 gas during the electrochemical reduction.

Results and discussions

Figure 1 shows the relationship between the cathodic polarization potential (E_c) and the faradaic efficiencies of the major gaseous products, C_2H_4, CH_4, CO, and H_2, during the electrochemical reduction of CO_2, where the potential pulse was applied continuously (see Fig. 1 bottom). As can be seen in Fig. 1, the two hydrocarbons, C_2H_4 and CH_4, are predominantly formed within the limited cathodic polarization potential range between −1.8 and −3.2 V, where the formation of both CO and H_2 is suppressed. Within the potential range, there is the same tendency for the faradaic efficiency of the CH_4 formation to outnumber that of the C_2H_4 formation as shown in Table 1. The definitely different point was that no faradaic efficiencies of the CH_4 and C_2H_4 formation decreased until at least 30 min after the start of the electrochemical reduction. Although neutral bicarbonate solutions have been mostly employed as the electrolytes because of their high solubility of CO_2, the poisoning reactions are accelerated at such a high pH [16]. The pulse mode electrolysis suppressed the poisoning reactions and enabled the copper electrode to maintain its high catalytic activity toward the conversion of CO_2.

With the intention of obtaining high selectivity for the C_2H_4 formation, two anodic polarization parameters, the anodic polarization potential (E_a) and duration time (t_a),
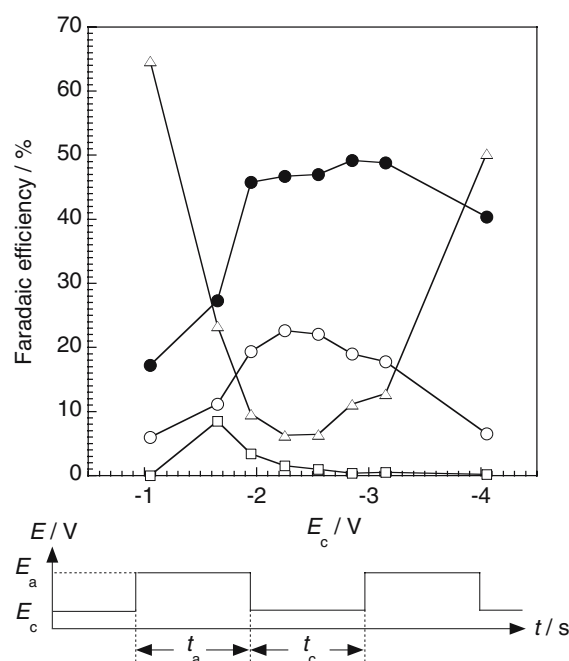

Fig. 1 Dependence of the faradaic efficiencies on the cathodic polarization potential (E_c) in the pulse-mode electrochemical reduction of CO_2 in 0.1 M (1 M=1 mol dm^{-3}) aqueous $KHCO_3$ solution using a copper electrode. CH_4 (•), C_2H_4 (○), H_2 (□), and CO (□). The *bottom* shows the applied waveform: E_a=+0.05 V and t_c=t_a=3 s
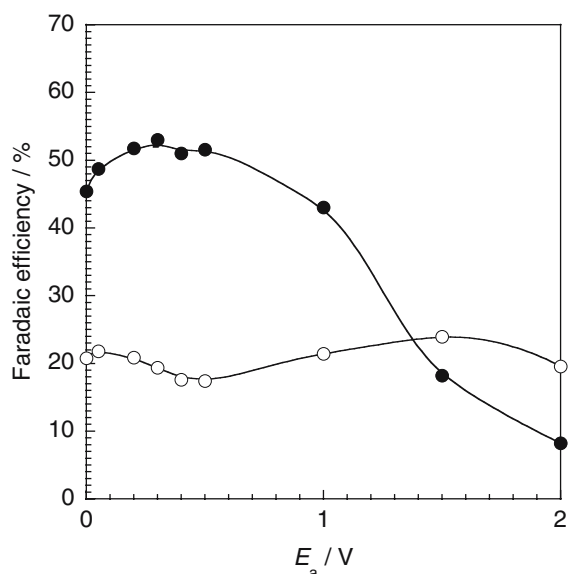
Fig. 2 Effect of the anodic polarization potential (E_a) on the faradaic efficiencies of CH_4 (•) and C_2H_4 (○)

were changed, and the electrochemical reduction was carried out. Figures 2 and 3 indicate how the faradaic efficiencies of C_2H_4 and CH_4 are influenced by altering E_a and t_a of the electrochemical reduction. It is interesting to find that the anodic polarization is advantageous to the C_2H_4 formation rather than to the CH_4 formation. The faradaic efficiency of the C_2H_4 formation is higher than that of the CH_4 formation in $E_a > 1.4$ V (Fig. 2) and $t_a > 6$ s (Fig. 3).

The XRD patterns revealed that two kinds of copper oxides, Cu_2O and CuO, were formed on the surface of the electrodes which experienced the electrochemical reduction of CO_2 with the anodic polarization with $E_a \geq 0.5$ V. To
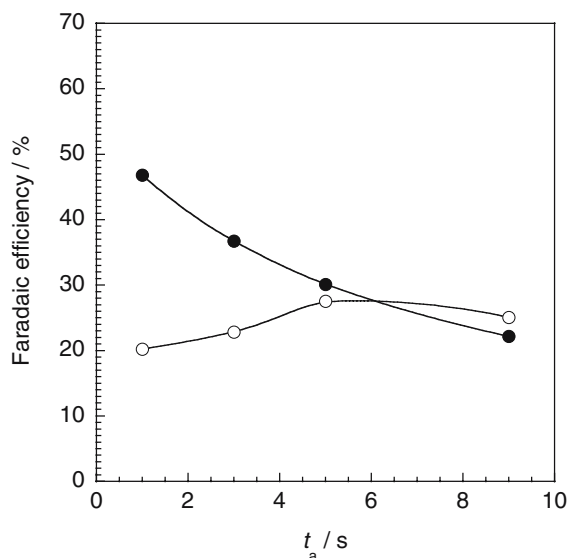

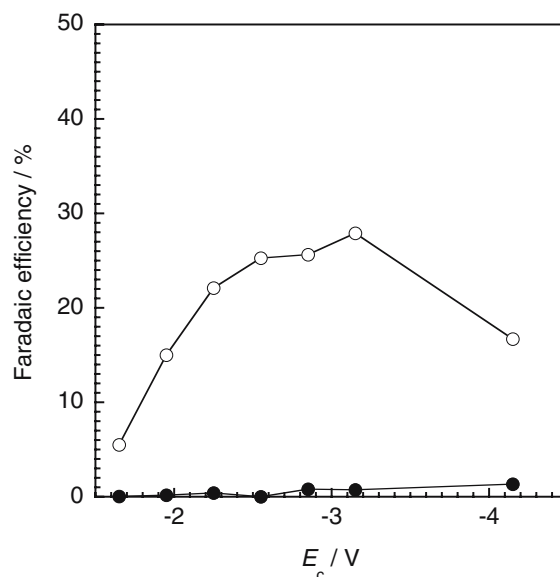Fig. 3 Effect of the anodic polarization time (t_a) on the faradaic efficiencies of CH_4 (•) and C_2H_4 (○)

Fig. 4 Dependence of the faradaic efficiencies on E_c in the electrochemical reduction of CO_2 in 0.1 M (1 M=1 mol dm^{-3}) aqueous $KHCO_3$ solution using a copper-oxide electrode. CH_4 (•) and C_2H_4 (○)

examine whether the copper oxides contributed to the predominant C_2H_4 formation, an oxide-rich copper electrode was used instead of the copper electrode, and the electrochemical reduction was performed. The electrode was prepared by heating the copper electrode in air. The existence of Cu_2O and CuO on the electrode surface was confirmed by the XRD patterns. Figure 4 illustrates how the faradaic efficiencies of the CH_4 and C_2H_4 formation are dependent on E_c. Similar dependence to Fig. 1 is evident for the C_2H_4 formation, while the faradaic efficiency of the CH_4 formation is extremely low within the whole E_c range. In other words, the high selectivity for the C_2H_4 formation is achieved by using the copper-oxide electrode. In addition, the highest efficiency of about 28% is obtained at −3.15 V.
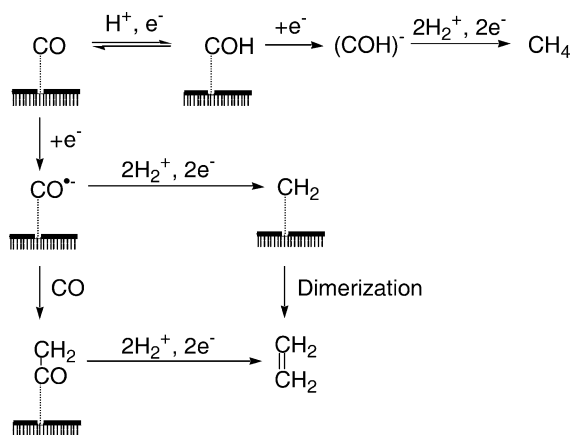

Fig. 5 Reaction pathway diagram of the electrochemical reduction of the adsorbed CO

In the electrochemical reduction of CO_2 on the copper electrode, $CO_2 \cdot^-$ generated by the reduction adsorbs on the electrode surface, and then adsorbed $CO_2 \cdot^-$ is changed to CO [8]. The reaction pathways toward the CH_4 and C_2H_4 formation from the adsorbed CO are shown in Fig. 5 [8, 17, 18]. The speculation for the predominance of the C_2H_4 formation is that the copper oxides prevent the adsorbed CO from being protonated (equilibrium reaction in Fig. 5). The interaction between the copper oxides and the adsorbed CO has been examined to obtain the direct evidence.

The electrochemical reduction of CO_2 using the pulse electrolysis mode not only suppresses the deposition of poisoning species on the copper electrode but also enhances the selectivity for the C_2H_4 formation by changing the electrolytic conditions. The selectivity was further improved when the electrochemical reduction is made with the copper-oxide electrode. Recently, the selective C_2H_4 formation was confirmed in the constant potential electroreduction of CO_2 at the three-phase (gas/liquid/solid) interface containing Cu^{2+} [19]. Compared with the method, our method is more practical because it needs no such special apparatus and no heavy metal ions such as Cu^{2+}.

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