Electroreduction of CO$_2$ using modified boron-doped diamond electrode as the working electrode

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Abstract. Electroreduction of CO$_2$ becomes a popular study to resolve the problems due to the increase of CO$_2$ in atmosphere. In this work, electroreduction of CO$_2$ was studied using various working electrodes in 0.1 M NaCl solutions. A reduction peak potential around -1.5, -1.1 and -1.2 V, respectively, was observed at BDD, Cu, Cu-BDD, while Cu$_2$O-BDD with different deposition times showed typical peaks at around -1.3 V. Liquid chromatography analysis on the solutions after CO$_2$ electroreduction at the applied potential of -1.3 V (vs Ag/AgCl) showed that by using BDD and Cu electrodes only formic acid and formaldehyde could be produced. However, the use of various Cu$_2$O concentrations deposited on BDD electrodes can produce not only formic acid and formaldehyde, but also acetic acid and methanol with high selectivity of the products, indicating the electrode is promising to have more various products in the electrochemical reduction of CO$_2$.

Keywords: Electroreduction, CO$_2$, electrodeposition, BDD and Cu$_2$O

1. Introduction

The earth’s atmosphere contains enormous amount of carbon dioxide (CO$_2$) and it is known that the emission of CO$_2$ is dramatically increase every year [1, 2]. This phenomenon has attracted great attention to reduce the emission of CO$_2$ and convert it into a more useful compound [1]. Electroreduction of CO$_2$ becomes a popular study to resolve this problem. One of the focuses is on the use of certain types of electrodes to convert CO$_2$ into more useful products. The use of electrode in the form of metal or metal oxide is necessary to electrochemically reduce CO$_2$ [3]. Electroreduction CO$_2$ is expected not only to reduce emissions of CO$_2$, but it can produce a variety of beneficial substances such as formic acid, methane, ethylene, methanol, and ethanol [4].

Study of some metals and metal oxides, such as Pb, Cu, Sn has been reported for electrochemical reduction of CO$_2$ [3]. It was also declared that copper oxide-modified materials increased the formation of hydrocarbons in such reaction [5]. On the other hand, boron-doped diamond (BDD) electrode is established as electrode with many advantages due to its good stability, wide working potential, and very low blank current [1, 6, 7]. Electrochemical reduction of CO$_2$ at this electrode was reported to be promising in NaCl or sea water [8]. Further, modification BDD electrodes with copper for the electroreduction of CO$_2$ was reported to produce methanol [9]. In this work, the BDD was modified with copper oxide to study its influence for electrochemical reduction of CO$_2$. Comparison between BDD, copper, and BDD modified with copper was also observed.
2. Materials and method

2.1. Materials

Cu(CH₃COO)₂, CH₃COONa, CH₃COOH, H₂SO₄, NaCl, 2-propanol, HClO₄, phosphate buffer, and acetonitrile were supplied from Wako (Japan). The distilled water was prepared by using Millipore®. CO₂ and N₂ gas were supplied from local sources in Indonesia.

2.2. Method

A cell with 3-electrodes system was used with various working electrodes, including BDD, Cu and Cu₂O-BDD. Cu-BDD was also used for comparison. Ag/AgCl was used as the reference electrode, while Pt foil used as the counter electrode. Cu₂O-BDD electrode was prepared using the same procedure that have been reported before [10]. Briefly, cyclic voltammetry in the potential range of -0.2 V to -1.0 V (vs. Ag/AgCl) was performed at BDD electrode in a solution containing 1 mM Cu(CH₃COO)₂ and 0.1 M CH₃COONa (ratio was 1: 1) at pH 5.7. Then, amperometry technique at the peak potential of -0.3 V with various deposition time of 60 s, 120 s and 180 s were applied. Meanwhile, Cu-BDD was prepared based on the optimum condition of previous result by using amperometry technique in mM CuSO₄ and 5mM H₂SO₄ applied at -0.4 V (vs. Ag/AgCl) for 120 s [9].

The solution for electrochemical reduction of CO₂, i.e. 0.1 M NaCl was pre-treated by bubbling N₂ for 30 min to remove other gas. Further, cyclic voltammetry at the potential range of 0.0 to -2.0 V was conducted after bubbling CO₂ into the solution with various bubbling times of 30, 60 and 90 min. Then, chronoamperometry technique was applied at the potential of -1.3 V for 60 min at all electrodes [10]. Afterward, the solution was analyzed by using HPLC.

3. Results and discussion

Electroreduction of CO₂ was performed at Cu₂O-BDD with various deposition time of 60 s, 120 s and 180 s. Comparison was also performed by using BDD, Cu, and Cu-BDD electrodes. The preparation and characterization of Cu₂O-BDD has been reported in our previous research [9]. Prior to electroreduction of CO₂, the reduction potential of CO₂ was studied using cyclic voltammetry in 0.1 M NaCl solution with without dissolved CO₂ (figure 1).

Cyclic voltammograms in the absence of CO₂ at Cu, Cu-BDD and Cu₂O-BDD electrodes showed typical oxidation-reduction couple peaks, respectively, at -0.2 V and -0.6 V, which related to the potential reduction and oxidation of Cu. In the presence of CO₂, the peak was observed at different potentials for different electrode. The potential reduction measured at BDD, Cu, Cu-BDD, and Cu₂O-BDD with various deposition time were -1.5 V, -1.1 V, -1.2 V and -1.3 V (vs Ag/AgCl), respectively. These reduction potentials were located between Cu-BDD and BDD, indicated the influence of both BDD and Cu (figure 2). Deposition of Cu was prepared only in the optimum condition reported in the previous result [9].

CO₂ electroreduction was performed by using chronoamperometry at -1.3 V for 60 min at various working electrodes. The resulting liquid products were analyzed using HPLC and the Faraday efficiencies were calculated. Figure 3 shows the products observed as the results of CO₂ reduction at various electrodes. It can be seen that formic acid and formaldehyde could be produced at all electrodes, although at the unmodified BDD electrode, very limited products were generated. Acetic acid and methanol were not produced at unmodified BDD, while these products were observed at Cu-based electrode. Furthermore, when the BDD was modified with Cu₂O, these products increased significantly, indicated the influence of Cu₂O in the formation of methanol and acetic acid. The figure also confirmed that Cu₂O-BDD electrodes prepared with longer deposition times increased its selectivity to produce methanol and acetic acid than formaldehyde. The selectivity of the products was calculated by the percentage of a generated product in comparison to all products observed in this reaction [1, 2]. The summary is displayed in table 1.
Figure 1. Cyclic voltammograms of 0.1 M NaCl in the absence and in the presence of dissolved CO$_2$ at (a) BDD, (b) Cu, (c) Cu-BDD as well as Cu$_2$O-BDD with various deposition times of (d) 60 s, (e) 120 s and (f) 180 s, respectively.

Based on the number of products obtained from CO$_2$ reduction (table 1), a possible mechanism of the product was determined due to calculations of % Faraday efficiency. The following mechanism is proposed for the CO$_2$ electroreduction's product [4].

Formic acid, acetic acid, formaldehyde and methanol were produced by CO$_2$ electroreduction using Cu$_2$O-BDD electrode with various deposition time. The possible mechanism of methanol production (figure 4) was initiated by the formation of CO$_2^-$ radicals to form CO$_{ads}$ intermediate. Further, CO
species will be adsorbed and reduced into HCO\(_{(\text{ads})}\). HCO that has been adsorbed then will undergo further reduction to become formaldehyde. Formaldehyde continues to be reduced as well to become H\(_3\)CO\(_{(\text{ads})}\) intermediate. Furthermore, H\(_3\)CO is further reduced and reacted with hydrogen atoms so that it will produce methanol.

![Figure 2. Plots of CO\(_2\) reduction peak potentials at different electrodes.](image1)

![Figure 3. Total products of electroreduction at various electrodes.](image2)

| Electrode          | Formic acid | Acetic acid | Formaldehyde | Methanol |
|--------------------|-------------|-------------|--------------|----------|
| BDD                | 52.52       | -           | 47.48        | -        |
| Cu                 | 12.46       | -           | 87.54        | -        |
| Cu-BDD             | 8.29        | 24.49       | 64.78        | -        |
| Cu\(_2\)O-BDD 60s  | 18.54       | 12.19       | 11.76        | 65.7     |
| Cu\(_2\)O-BDD 120s | 19.92       | 17.12       | 7.98         | 63.65    |
| Cu\(_2\)O-BDD 180s | 23.6        | 23.31       | 5.59         | 60.25    |
Figure 4. Possible mechanism of methanol formation.

Table 2. Results of % efficiency faraday of electroreduction CO$_2$.

| Electrode  | Formic acid | Acetic acid | Formaldehyde | Methanol | Total |
|------------|-------------|-------------|--------------|----------|-------|
| BDD        | 0.28        | -           | 0.505        | -        | 0.78  |
| Cu         | 0.04        | -           | 0.555        | -        | 0.59  |
| Cu-BDD     | 0.06        | 0.51        | 0.677        | -        | 1.25  |
| Cu$_2$O-BDD 60 s | 0.24 | 1.14 | 0.550 | 4.61 | 6.54 |
| Cu$_2$O-BDD 120 s | 0.33 | 2.03 | 0.473 | 5.66 | 8.50 |
| Cu$_2$O-BDD 180 s | 0.46 | 3.93 | 0.472 | 7.62 | 12.48 |

Cu$_2$O that was deposited on BDD electrode surface supplying Cu (I) species and it takes a significant part in reducing CO$_2$ for the reaction of the formation of CH$_3$OH [8]. Cu (I) species can stabilize the intermediates and able to enhance the adsorption of the CO to be selective to methanol as the main product. It is also possible that Cu (I) site more likely to adsorb CO than the Cu sites. By doing determination% Efficiency Faraday the amount of electricity used during the process of CO$_2$ electroreduction will be known.

Based on the obtained faradaic efficiency (table 2), it appears that the electrical energy supplied to the electrode is used in the formation of methanol. Cu$_2$O-BDD electrode 180 s slightly has a higher faradaic efficiency of methanol, it is comparable in terms of yield methanol that can be produced at each electrode. Faradaic efficiency of each electrode is still low, this may be due to the formation of other by-products in the form of liquid or gas, so that the parameters of the product is still not yet included into the calculation.

4. Conclusion
Cyclic voltammograms of CO$_2$ dissolved in 0.1 M NaCl solution at BDD electrode, Cu and Cu-BDD showed reduction peaks at potentials of -1.5, -1.1 and -1.2 V (vs. Ag/AgCl), respectively. However, Cu$_2$O-BDD electrodes with various deposition times showed a typical reduction peak at the potential...
around -1.3 V (vs. Ag/AgCl). Applying amperometry technique at this potential using BDD electrode, Cu, Cu-BDD, and Cu$_2$O-BDD for 60 min for CO$_2$ reduction showed that modification of BDD with copper oxide produced methanol and acetic acid besides formic acid and formaldehyde. The result indicated that the modification with copper oxide is promising to form hydrocarbon with two carbon numbers.

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