Study of carbon dioxide electrochemical reduction in flow cell system using copper modified boron-doped diamond

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Abstract. High concentrations of CO_2 in the atmosphere may cause climate and environmental changes. Therefore, various research has been extensively performed to reduce CO_2 by converting CO_2 directly into hydrocarbons. In this research, CO_2 electrochemical reduction was studied using boron-doped diamond (BDD) modified with copper nanoparticles to improve BDD electrodes' catalytic properties. The deposition was performed by chronoamperometry technique at a potential of -0.6 V (vs. Ag/AgCl) and characterized using SEM, EDS, XPS, and cyclic voltammetry (CV). CO_2 electrochemical reduction on BDD and Cu-BDD was carried out at -1.5 V (vs. Ag/AgCl) for 60 minutes. The products were analyzed using HPLC and GC. The product was mainly formic acid with a concentration of 11.33 mg/L and 33% faradaic efficiency on a Cu-BDD electrode.

1 Introduction

High concentrations of CO_2 in the atmosphere promotes climate change and severe effect on the environment. Therefore, various efforts were made to reduce the increase of CO_2 gas emissions. Of the many techniques that have been examined, the electrochemical reduction is one of the most widely used [1-3]. Electrochemical is an effective method of converting CO_2 into more valuable compounds due to several advantages such as applicative, simple, and selective on the product produced. The specifications of CO_2 reduction products can be adjusted under various reaction conditions [4-7]. One of the factors that influence the variety of CO_2 electrochemical reduction products is the type of electrodes used.

In this study, the boron-doped diamond (BDD) electrode is used as working electrodes because they have the advantages of a wide potential window, low background current, and high stability, making them chemically inert and mechanically reliable [4,8]. However, the

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BDD electrode has disadvantages, namely relatively low catalytic activity, resulting in a high overpotential CO_2 electrochemical reduction requirement. So, it is necessary to modify BDD to increase its catalytic activity.

BDD surface modification with metal particles is expected to increase the BDD electrode's catalytic effect and performance [9–13]. The metal particles deposited on the BDD surface act as the electrodes' active site to stabilize the reaction intermediate to lower the overpotential [14] and produce a more varied product compared to bare BDD. Previous studies reported that BDD surface modification with copper metal could improve BDD electrodes' catalytic activity and performance to produce various CO_2 reduction products, especially hydrocarbons and oxygenated species [15–19]. Besides, a flow cell system in CO_2 electrochemical reduction using BDD electrodes has been reported to improve the CO_2 mass transport and produce formic acid as the main product with a faradaic efficiency of 94.7% [20]. This study was conducted using Cu-BDD electrodes with a flow cell system to achieve higher efficiency or suppress the overpotential. The characteristics of Cu-BDD electrodes before and after CO_2 reduction, the analysis of the resulting compounds, and the effect of using a flow cell system compared to a static system using the Cu-BDD electrode will be presented in this report.

2 Method

2.1 Materials

KCl (>99.5%), KOH (85%), CuSO$_4$·5H$_2$O (>99.5%), H$_2$SO$_4$ (95%), and 2-propanol were purchased from Wako Pure Chemical Industries Ltd. and used without further purification. Ultra-pure water was obtained from a Symply-Lab water system (Direct-Q 3 UV, Millipore).

2.2 Working electrodes preparation

Boron-doped diamond electrodes were prepared on Si(100) wafers as substrates using a microwave plasma-assisted chemical vapor deposition system (AX 5400, Cornes Technologies Ltd.) following a procedure described elsewhere [21]. The boron-doped diamond (BDD) electrode modification was carried out by the electrodeposition method. This method uses a chronoamperometric technique with 1 mM CuSO$_4$ in a 0.1 M H$_2$SO$_4$ solution. Cu deposition was carried out on the BDD working electrode in one compartment cell with Ag/AgCl and Pt spiral as a reference and counter electrode, respectively. The electrodeposition was applied at a potential -0.6 V for 25 s (Cu-BDD 25s), 50 s (Cu-BDD 50s), 100 s (Cu-BDD 100s), and 150 s (Cu-BDD 150s). Characterization of the electrodes was performed by Scanning Electron Microscopy (SEM) (JCM-600, JEOL), Energy Dispersive X-ray analysis (EDX), and X-Ray Photoelectron Spectroscopy (XPS) (JPS-9010TR, JEOL).

2.3 CO$_2$ electrochemical reduction method

The electrochemical cell used in CO_2 electrolysis is a two-compartment PTFE flow cell separated by a Nafion membrane (Fig. 1). The working electrode was Cu-BDD, Ag/AgCl as a reference electrode and a Pt plate as a counter electrode. The area of the working electrode is 9.62 cm^2 [20]. The catholyte used was 0.5 M KCl 50 mL, and the anolyte used was 0.1 M KOH 50 mL. Before electrolysis, the catholyte was bubbled with N$_2$ gas for 30 minutes, followed by CO_2 gas bubbled for 15 minutes, both at a flow rate of 200 sccm. The

CO_2 reduction process was recorded using a potentiostat (Autolab PGSTAT204, Metrohm Autolab B.V.) for 1 hour and carried out at a potential of -1.5 V. CO_2 gas at a low flow rate was flowed during the reduction process to maintain CO_2 concentration in the flow cell system. Gas chromatography (GC-2014, Shimadzu Corp.) analyzed the gas products, and the liquid product was analyzed using high-performance liquid chromatography with an electroconductivity detector (Prominence, Shimadzu Corp.).
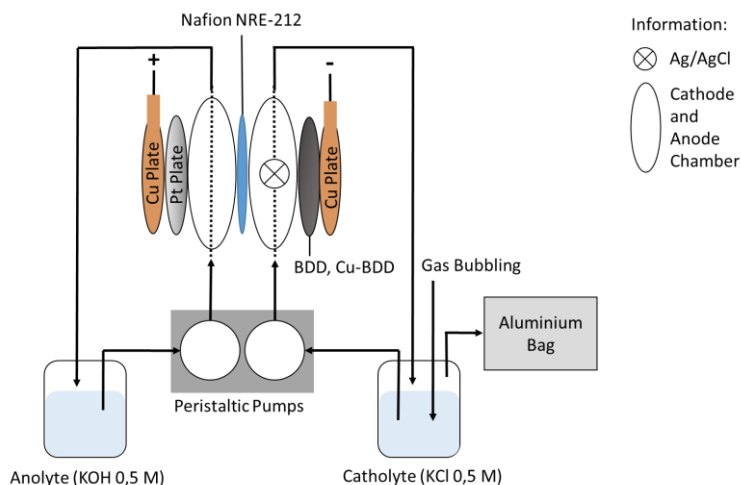

Fig. 1. Flow cell for electrochemical reduction.

3 Results and discussion

3.1 Working electrodes characterization

Cyclic voltammogram of Cu-BDD electrodes at various deposition times was performed from -0.8 V to +0.8 V (vs. Ag/AgCl) with a scan rate of 100 mV/s (Fig. 2). Cu dissolution, following the various Cu phases deposited during the potential negative sweep, is indicated by peak currents at a positive potential. With the negative-going potential, the first reduction peak of Cu^{2+} to Cu^+ occurs at a potential of around -0.19 V, -0.19 V, -0.15 V, and -0.25 V in Cu-BDD 25s, Cu-BDD 50s, Cu-BDD 100s, and Cu-BDD 150s, respectively. The reduction of Cu^{2+} to Cu^0 contained a potential around -0.34 V, -0.40 V, -0.25 V, and -0.45 V in Cu-BDD 25s, Cu-BDD 50s, Cu-BDD 100s, and Cu-BDD 150s, respectively. This phase is indicating Cu deposition on the BDD electrodes surface. The steep drop in potential around -0.60 V is due to hydrogen evolution, which causes a slight change in the BDD surface termination. Based on the CV data obtained, it shows that Cu-BDD 100s has an advantage in reducing Cu. The process of reducing Cu at a more positive potential in Cu deposited having a density and evenly distributed over the BDD surface [22].
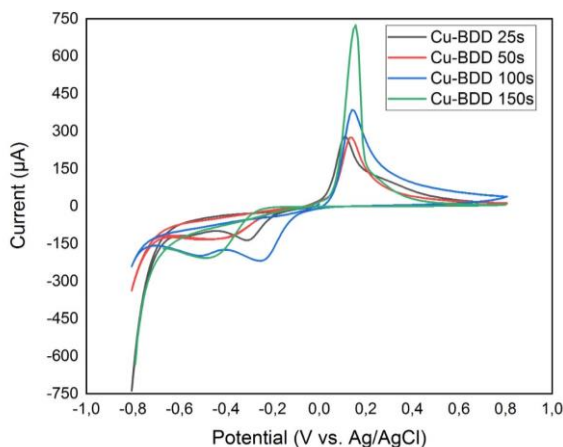
Fig. 2. Cyclic voltammogram of Cu-BDD electrodes at various Cu deposition times.

SEM-EDX examined all the Cu-BDD electrodes after electrodeposition. Based on Fig. 3 (a) and (b), there is no visible deposition of Cu. In Fig. 3 (c), a white dot shows that the deposited Cu particles were evenly uniformly distributed on the BDD surface, with average particle sizes of around ~148 nm. In contrast, Fig. 3 (d) shows the Cu particles have agglomerated. Based on the SEM images, the Cu-BDD 100s electrode showed significant characteristics compared to other deposition time variations. This case can be proven by EDX Spectroscopy, which can determine the atomic percentages on each electrode's surface, and the results are summarized in Table 1.
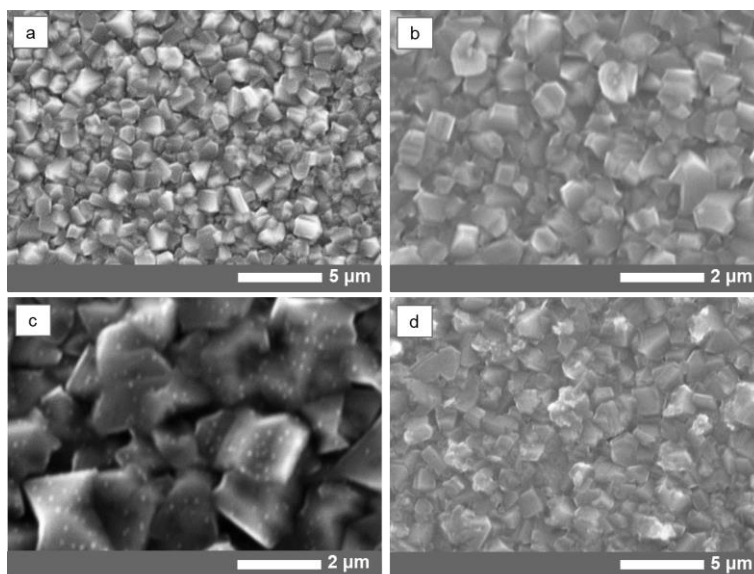

Fig. 3. SEM images of Cu-BDD electrodes with deposition times of 25 s (a), 50 s (b), 100 s (c), and 150 (d).

Moreover, the Cu particles on the electrode surfaces were also characterized using XPS. XPS spectra showed a pair of energy peaks at 933 eV and 952.4 eV, which are representative of Cu $2p_{3/2}$ and Cu $2p_{1/2}$ binding energy in Cu^0 for all Cu-BDD variations.

XPS also showed the % mass of the Cu-BDD electrodes, with the highest percentage being ~13% belonging to Cu-BDD 100s. Based on this, Cu-BDD 100s was used as an electrode for CO_2 electrochemical reduction.

Table 1. Mass percentage of each deposited material.

Element	% Mass			
	Cu-BDD 25s	Cu-BDD 50s	Cu-BDD 100s	Cu-BDD 150s
C	99.96	99.67	99.10	99.11
O	0.04	0.02	0.07	0.11
Cu	0	0.02	0.83	0.78

3.2 CO_2 electrochemical reduction

CO_2 electrochemical reduction was carried out for 1 hour using the Cu-BD 100s electrode at -1.5 V potential. After the CO_2 electrochemical reduction reaction was done, the Cu-BDD 100s electrode was characterized using SEM-EDS to see their performance after being used in CO_2 electrochemical reduction. SEM images in Fig. 4 show significant differences in the Cu-BDD 100s surface before and after CO_2 electrochemical reduction, indicating that the deposited Cu particles were detached from the surface of the BDD surface. The change in the mass% of the Cu-BDD electrode element decreased the mass% of Cu by 97.59%. This decrease happens both before and after the analysis of CO2 reduction using EDS.
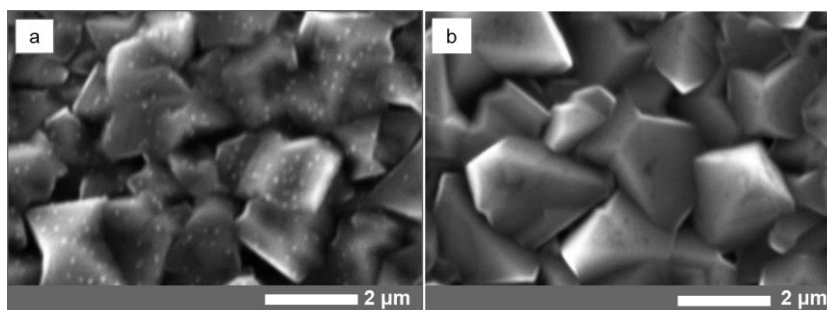

Fig. 4. SEM Images of Cu-BDD 100s (a) before and (b) after CO_2 electrochemical reduction.

The produces products were analyzed using HPLC and GC instrumentation. Fig. 5 shows the efficiencies with which formic acid, carbon monoxide, methane, and hydrogen gas were produced by using Cu-BDD 100s electrode at -1.5 V potential for 1 hour. The highest faradaic efficiency was achieved for formic acid, carbon monoxide, methane, and hydrogen gas, 33%, 1.67%, 0.05%, and 21.25%. Furthermore, the CO_2 electrochemical reduction using bare BDD electrodes was carried out in the same experimental system to compare the product. On the bare BDD electrode, formic acid, carbon monoxide, or hydrogen gas were observed on the Cu-BDD 100s electrode. The highest faradaic efficiency was achieved for formic acid, carbon monoxide, and hydrogen gas, 14.69%, 12.96%, and 49.57%. In conclusion, Cu-BDD 100s and bare BDD electrodes show insignificant differences in the produce products.
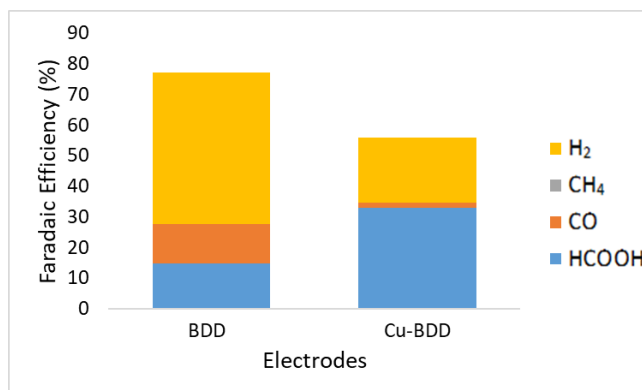
Fig. 5. Product produced by the electrochemical reduction of CO_2 on a bare BDD and Cu-BDD 100s electrodes at potential -1.5 V for 1 h.

Table 2 shows the concentration and the faradaic efficiency of the product's reduction process on bare BDD or Cu-BDD electrodes. In this study, the main product was formic acid because diamonds tend to produce formic acid [20]. The Cu-BDD electrode has a more remarkable ability than the bare BDD electrode in producing formic acid. This ability can be seen from the resulting faraday efficiency, which is 14.69% and 33% in BDD and Cu-BDD electrodes, respectively.

Table 2. The concentration and faradaic efficiency of CO_2 reduction products

Products	Concentration (mg/L)		Faradaic Efficiency (%)	
	BDD	**Cu-BDD**	**BDD**	**Cu-BDD**
HCOOH	2.59	11.33	14.69	33.00
CO	0.05	0.01	12.96	1.67
CH_4	0	9.05×10^{-5}	0	0.05
H_2	0.17	0.14	49.57	21.25

The use of Cu metal in reducing CO_2 tends to produce products in hydrocarbons, aldehydes, and alcohol. However, based on the reduction data, no aldehyde or alcohol products were formed because the use of flow cells affects the electrodes' ability to bind the intermediates produced ($CO_2^{\bullet-}$) [3]. The use of Cu-BDD electrodes in flow cells and dormant cells [17] has differences in reduction. CO_2 reduction reaction with Cu-BDD using a flow cell produces methane gas, while the static cell produces methanol. Static cells tend to produce C_2/C_3 products, while flow cells cannot because the use of flow cells makes electrolytes or reactants hit the electrodes' surface more often so that no intermediate products are formed.

4 Conclusion

The use of Cu metal in reducing CO_2 tends to produce products in hydrocarbons, aldehydes, and alcohol. However, based on the reduction data, no aldehyde or alcohol products were formed because the use of flow cells affects the electrodes' ability to bind the intermediates produced ($CO_2^{\bullet-}$) [3]. The use of Cu-BDD electrodes in flow cells and dormant cells [17] has differences in reduction. CO_2 reduction reaction with Cu-BDD using a flow cell produces methane gas, while the static cell produces methanol. Static cells tend to produce C_2/C_3 products, while flow cells cannot because the use of flow cells makes

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Acknowledgement

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