

Preparation of copper oxide modified boron-doped diamond electrodes and its preliminary study for CO₂ reduction

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Abstract. Preparation of boron-doped diamond (BDD) modified with Cu₂O (Cu₂O-BDD) electrodes was conducted to study the electrochemical reduction of CO₂. The electrodes were prepared by electrochemical reduction using a solution containing 1mM Cu(CH₃COO)₂ and 0.1 M CH₃COONa (1: 1) at pH 5.7 for 60 s. The electrodeposition of Cu₂O at BDD surface was performed by chronoamperometry technique at -0.4 V (vs Ag/AgCl). SEM-EDS and XPS were utilized to characterize the electrodes. At Cu₂O-BDD electrodes, cyclic voltammetry of dissolved CO₂ in 0.1 M NaCl solution exhibited a reduction peak at around -1.3 V (vs Ag/AgCl), indicated the possibility for application in electrochemical reduction of CO₂.

Keywords: Copper oxide, boron-doped diamond, carbon dioxide, electrochemical reduction

1. Introduction

Carbon dioxide is one of main components contained in the atmosphere and is known as one of the greenhouse gas that causes global warming. Since the 19th century, emission of carbon dioxide gas increases dramatically with the rate of around 2 ppm every year. Pletcher [1] has stated that the current content of CO₂ gas has reached around 400 ppm. This phenomenon has attracted the interest of researchers to reduce the emission of CO₂ converting it to more useful compounds. In order to achieve this purpose, some electrochemists have applied certain types of electrodes, including Sn, Pb, Cu, and their related oxides [2, 3] to study the electrochemical reduction of CO₂. It was reported that electrode surface contained copper oxide and can increase the formation of hydrocarbons [4]. The use of copper as a catalyst in CO₂ electroreduction by coating the electrode with Cu₂O was also reported to efficiently produce hydrocarbons in ambient temperature [5].

On the other hand, boron-doped diamond (BDD) electrodes are reported to have various advantages, such as high stability, wide working potential, as well as very low background current [6, 7]. Nakata *et al.* [8] reported that the electrochemical reduction of CO₂ by using BDD electrodes can be performed in NaCl or sea water as the electrolyte. Further, Panglipur *et al.* [9] have employed copper-modified BDD electrodes for the electroreduction of CO₂. In this work, we modify BDD with copper oxide. It is expected that by applying this electrode the percent yield of useful products can be increased.

2. Materials and methods

The materials used were CO₂, N₂, Cu(CH₃COO)₂, CH₃COONa, CH₃COOH, H₂SO₄, NaCl, 2-propanol, HClO₄, phosphate buffer, and acetonitrile.



Prior to copper deposition, cyclic voltammetry of a solution containing 1 mM Cu (CH₃COO)₂ and 0.1 M CH₃COONa with a ratio of 1: 1 at pH 5.7 was performed using BDD as the working electrode in the potential range of -0.2 V to -1.0 V (vs. Ag/AgCl). Chronoamperometry technique with a deposition time of 60 s was then applied at the peak potential attributed to the Cu(I) formation. The characterization of the modified was performed using SEM-EDS and XPS.

Electrochemical reduction of CO₂ was performed in a cell with three-electrode system with 0.1 M NaCl as the electrolyte. Cu₂O-BDD was employed as the working electrode, while Ag/AgCl and Pt foil were used as the reference and the counter electrodes, respectively. In order to remove other gas in the solution, N₂ was bubbled to the solution for 30 min. Further, CO₂ was bubbled followed by performing the cyclic voltammetry of the solution at the potential range of 0.0 to -2.0 V. The solution produced was characterized using HPLC.

3. Results and discussion

Cyclic voltammograms of the solution containing 1 mM Cu(CH₃COO)₂ and 0.1 M CH₃COONa (1:1) pH 5.7 (figure 1a) shows that two reduction peaks of copper were observed. The first peak at -0.40 V was attributed to the formation Cu(I), while the second peak at -0.60 V indicated the formation of Cu(0). Accordingly, Cu₂O-BDD was prepared by electrochemical reduction of the same solution at the potential of -0.40 V. Calculation based on the amperogram (figure 1b) indicated that 1.72 µg Cu₂O could be deposited at the surface of BDD.

SEM image of the electrode surface (figure 2 a) showed that copper particles could be deposited at the surface of the electrode with the average size of ~1 µm. EDS result showed the surface contained copper with the percent yields of 25.71% as well as oxygen with the percent yields of 10.67%. Meanwhile, the XPS spectrum shows that besides the peaks of C 1s at 285 eV and of O 1s at 530.5 eV, which characterized the surface of BDD [10], a couple peaks of Cu 2p_{3/2} and 2p_{1/2} at 952.8 eV and 933 eV, respectively (figure 2b) were also observed. The results confirmed the existence of bonds associated with Cu⁺ in Cu₂O [11].

The cyclic voltammogram (figure 3) of the solution showed that the longer the time of CO₂ bubbling, the higher the current which starting at about -1.2 V, suggested that onset of electrochemical reduction of CO₂ was around the potential. Chronoamperometry technique at this potential was then required to investigate the products of electrochemical reduction of CO₂ in NaCl solution.

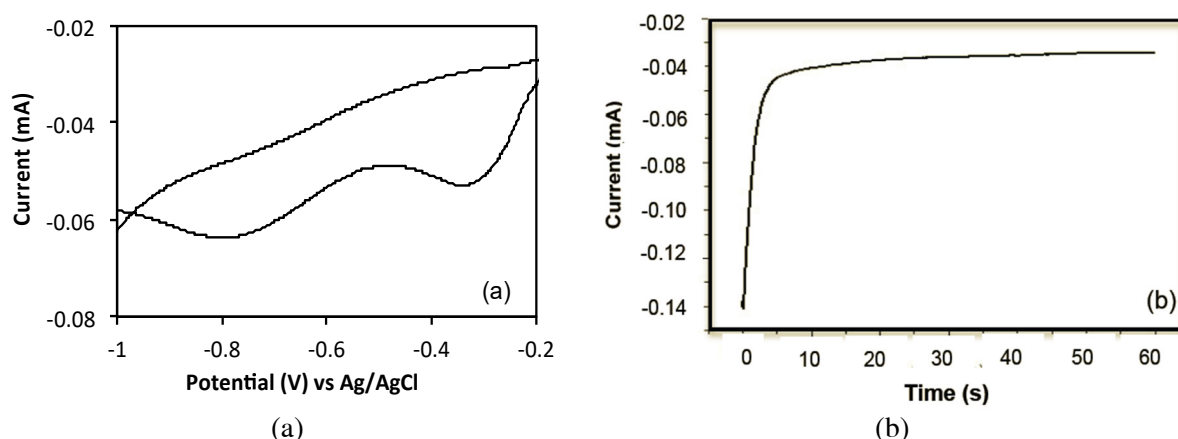


Figure 1. (a) Cyclic voltammogram and (b) chronoamperogram of the solution containing 1 mM Cu(CH₃COO)₂ and 0.1 M CH₃COONa (1:1) pH 5.7. Scan rate of 100 mV/s was applied with BDD electrode as the working electrode.

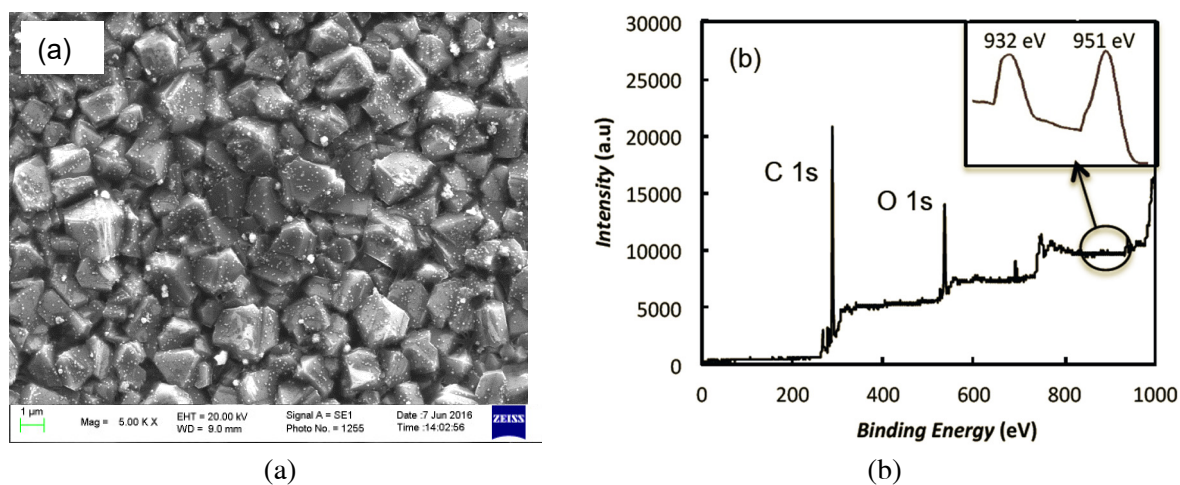


Figure 2. The characterization of the prepared Cu_2O -BDD electrodes shown by (a) SEM image and (b) XPS spectrum with the magnification of Cu 2p peaks shown in the inset.

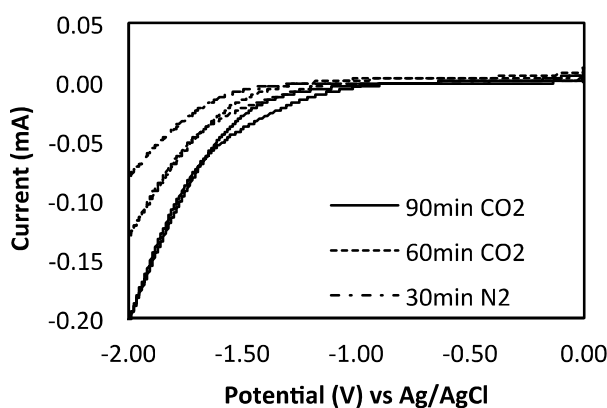


Figure 3. Cyclic voltammograms of 0.1 M NaCl solution containing N_2 (solid line) and CO_2 (dashed lines) at Cu_2O -BDD

4. Conclusions

Cu_2O -modified boron-doped diamond electrodes have been successfully prepared. The electrodes showed the onset of CO_2 reduction in 0.1 M NaCl solution at the potential around -1.3 V (vs. Ag/AgCl), indicated that the electrode is promising for application in CO_2 reduction. More experiments will be conducted to investigate this possibility.

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References

- [1] Pletcher D 2015 *Electrochemistry Communications* **61** 97-101
- [2] Chang T Y, Liang R M, Wu P W, Chen J Y and Hsieh Y C 2009 *Materials Letters* **63** 1001-3
- [3] Albo J, Alvarez-Guerra M, Castano P and Irabien A 2015 *Green Chemistry* **17** 2304-24
- [4] Ohya S, Kaneco S, Katsumata H, Suzuki T and Ohta K 2009 *Catalysis Today* **148** 329-34

- [5] Kas R, Kortlever R, Yilmaz H, Koper M T M and Mul G 2015 *Chem. Electro. Chem.* **2** 354-8
- [6] Fujishima A, Einaga Y, Rao T N and Tryk D A 2005 *Diamond Electrochemistry* (Tokyo: BKC; Amsterdam: Elsevier)
- [7] Pino F, Ivandini T A, Nakata K, Fujishima A, Merkoçi A and Einaga Y 2015 *Anal. Sci.* **31** 1061-8
- [8] Nakata K, Ozaki T, Terashima C, Fujishima A and Einaga Y 2014 *Angew. Chem. Int. Ed.* **53** 871-4
- [9] Panglipur H S, Ivandini T A, Wibowo R and Einaga Y 2016 *AIP Conference Proceedings* **1729** 020047
- [10] Ivandini T A, Saepudin E, Wardah H, Dewangga N and Einaga Y 2012 *Anal. Chem.* **84** 9825-32
- [11] Zhao W *et al.* 2011 *Crystal Eng. Comm.* **13** 2871-7