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Prastika Krisma Jiwanti

Department of Chemistry, Faculty of Science and Technology, University of Airlangga, Surabaya 60115, Indonesia

Rani Puspitasari Aritonang

Department of Chemistry, Faculty of Mathematics and Natural Sciences, Universitas Indonesia, Depok 16424, Indonesia

Imam Abdullah

Department of Chemistry, Faculty of Mathematics and Natural Sciences, Universitas Indonesia, Depok 16424, Indonesia

Yasuaki Einaga

Department of Chemistry, Faculty of Science and Technology, Keio University, Yokohama 223-8522, Japan

Tribidasari Anggraningrum Ivandini

Department of Chemistry, Faculty of Mathematics and Natural Science, Universitas Indonesia, Depok 16424, Indonesia, ivandini.tri@sci.ui.ac.id

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Cover Page Footnote

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Copper-nickel-modified Boron-doped Diamond Electrode for CO₂ Electrochemical Reduction Application: A Preliminary Study

Prastika Krisma Jiwanti^{1,3}, Rani Puspitasari Aritonang², Imam Abdullah², Yasuaki Einaga³,
Tribidasari Anggraningrum Ivandini^{2*}

1. Department of Chemistry, Faculty of Science and Technology, University of Airlangga, Surabaya 60115, Indonesia

2. Department of Chemistry, Faculty of Mathematics and Natural Sciences, Universitas Indonesia,
Depok 16424, Indonesia

3. Department of Chemistry, Faculty of Science and Technology, Keio University, Yokohama 223-8522, Japan

*E-mail: ivandini.tri@sci.ui.ac.id

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Abstract

CO₂ electrochemical reduction (CO₂ER) activity is known to be influenced by electrode materials. In this study, we report the fabrication of a copper-nickel-modified boron-doped diamond (CuNi-BDD) electrode using wet chemical seeding and electrodeposition. Annealing was performed to improve the stability of the modified electrode during electrolysis. Characterization of the modified BDD electrodes shows successful deposition without damage to the surface of the BDD support material. CO₂ER was conducted with the CuNi-BDD electrode, which produces various important products including methanol, formic acid, CO, and CH₄. Additionally, a different applied potential affected the product distribution. CO₂ER was also conducted on the surfaces of Cu-BDD and Ni-BDD electrodes for comparison.

Keywords: boron-doped diamond, CO₂ reduction, copper-nickel

Introduction

In the last few decades, the concentration of CO₂ gas in the atmosphere has increased tremendously. This cheap and highly abundant gas, which is a known greenhouse gas, can be converted to useful and valuable chemicals or converted back to fuel [1–3]. Many attempts to reduce CO₂ have been reported, including electrochemistry [4] and photoelectrochemistry [5], which have been widely developed in recent years. However, CO₂ER requires a high overpotential, which is a drawback of many reported methods. The applied potential remained much higher than the standard reduction potential of CO₂. Therefore, an important approach to overcoming this problem is developing a suitable catalytic system. For this purpose, a suitable electrode material is required.

Previous studies on CO₂ER have been reported mostly on copper electrodes, resulting in various product distributions, including hydrocarbons and oxygenated species [6–8]. Other studies reported that a copper-modified nickel electrode showed high catalytic activity with hydrocarbon formation [9]. Additionally, computational experiments on a copper-nickel alloy with a ratio of 3:1 for CO₂ reduction showed an increase in the CO₂ reduc-

tion electrocatalytic activity to form methane due to overpotential suppression [10].

Meanwhile, recent studies have focused on CO₂ER on the surface of a BDD electrode [11,12]. The BDD electrode is known to have a wide potential window that is considerably useful for suppressing the production of H₂ gas as a CO₂ER competitor. Additionally, the BDD electrode has high chemical and mechanical stability, making it suitable for practical application. CO₂ER on a bare BDD electrode in aqueous alkali metal solution has been known to produce HCOOH with more than 90% faradaic efficiency. However, the high overpotential (>–2 V) needed for the system remains a drawback. Therefore, modification of the BDD electrode surface is suggested to enhance the catalytic activity.

Metal modification on the BDD electrode is a simple technique for increasing the catalytic effect of the electrode. The use of a metal-modified BDD electrode for CO₂ER has been reported in several publications [13–15]. Such systems successfully decreased the overpotential or produced carbon compounds (C₂/C₃) with a longer chain, which were barely observed on the BDD electrode. Therefore, CO₂ER on other metals deposited on the BDD electrode is worth further investiga-

tion. In this study, the BDD electrode surface was modified with Cu and Ni particles. Cu is a well-known metal catalyst for CO₂ER, whereas Ni is an active metal for hydrogen production. A strategy for combining two metals with high activity but different behavior is desired to provide an overall high activity for the CO₂ER reaction to produce useful chemicals. The detailed fabrication of the modified electrodes and a preliminary report of their application to CO₂ER is presented.

Materials and Methods

Chemicals. CuSO₄·5H₂O (>99.5%), Ni(NO₃)₂, NaOH, NaCl, and Na₂SO₄ were purchased from Wako Pure Chemical Industries. NaBH₄ was purchased from Sigma Aldrich. All reagents were used without further purification. Ultrapure water was obtained from a Simply-Lab water system (Direct-Q UV3, Millipore).

Electrode Fabrication. BDD Films were deposited on Si (111) wafers using microwave plasma-assisted chemical vapor deposition (Model AX 5400, Cornes Technology Corp.) [16]. Modification of the BDD electrode surface with metal particles was performed by wet chemical seeding [17] and followed by electrochemical method. Wet chemical seeding was performed by dropping 100 μL of 1 M NaBH₄ in 0.1 M NaOH solution on the BDD surface and continuing with a 400 μL metal precursor (1 mM Ni(NO₃)₂ or CuSO₄) to prepare Ni-BDD or Cu-BDD. To prepare CuNi-BDD, we obtained a metal precursor with 3:1 v/v mixture of 1 mM Ni(NO₃)₂ and 1 mM CuSO₄. This electrode was dried at room temperature and pressure for 24 h, rinsed with water, and dried under N₂ gas. This process was repeat-

ed three times and followed by electrodeposition. Electrodeposition was performed in each 1 mM metal precursor at a potential of -1.2 V for 15 min, followed by rapid thermal annealing (RTA) at 700 °C for 5 min in N₂ atmosphere. The electrode was repeatedly activated by cyclic voltammetry thereafter and characterized using scanning electron microscopy-energy dispersive X-ray spectroscopy (SEM-EDS), Raman spectroscopy, and X-ray photoelectron spectroscopy (XPS).

CO₂ER Method and Product Analysis. CO₂ER was conducted in two cells separated by a Nafion membrane. The catholyte and anolyte were 0.1 M NaCl and 0.1 M Na₂SO₄, respectively. The modified BDD electrode, a Pt spiral, and Ag/AgCl electrodes were used as working (WE), counter (CE), and reference (RE) electrodes, respectively. All potentials were measured against Ag/AgCl unless otherwise stated. This system was also equipped with a gas trap to carry gas products from the cell (Figure 1). N₂ gas was purged through the catholyte to remove dissolved O₂ gas, followed by CO₂ gas bubbling at a flow rate of 100 sccm. Electrolysis was performed for 1 h. Subsequently, the collected gas products were analyzed by gas chromatography with a flame ionization detector and thermal conductivity detector (GC-2014, Shimadzu Corp.). The liquid products were analyzed using gas chromatography-mass spectrometry (GCMS-QP2010 Ultra, Shimadzu Corp.) using auto-injection headspace method (5 mL sample in 20 mL volume vial) with the selected ion monitoring mode and employing high-performance liquid chromatography with an electroconductivity detector (Prominence, Shimadzu Corp.).

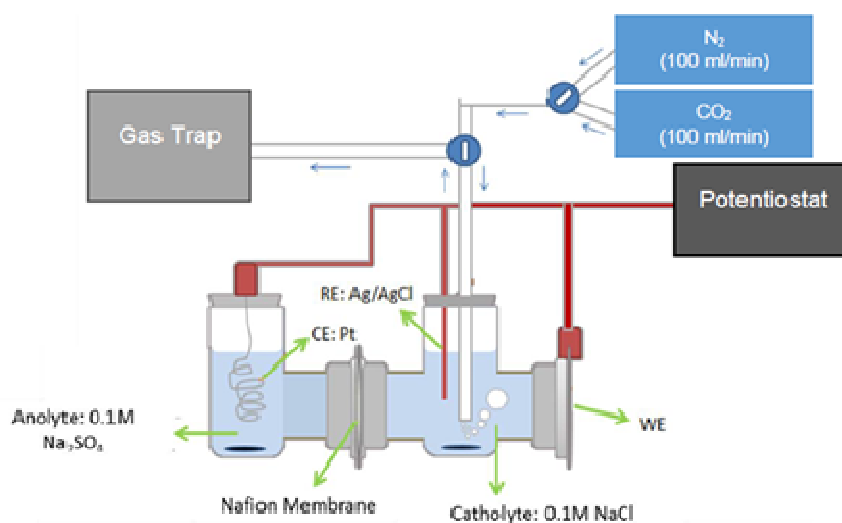


Figure 1. Scheme of CO₂ER System

Results and Discussion

Preparation and Characterization of Modified BDD Electrodes. First, wet chemical seeding was applied to modify the surface of the BDD electrode to stabilize the metal particles because the common electrodeposition method might lead to instability and detachment of metal particles. In this study, NaBH_4 was used as a reducing agent. NaBH_4 (1 M) in 0.1 M NaOH solution was dropped on the surface of the BDD electrode followed by the metal precursor. Thus, reduction occurred on the surface of the electrode, with strong adsorption to the electrode surface. Electrochemical deposition was then performed on the electrode modified by wet seeding, aiming to increase the deposited metals. However, up to this stage, the fabricated electrode could still be mechanically unstable. Therefore, RTA was conducted at 700 °C for 5 min to stabilize the particles on the BDD surface. However, RTA passivates the modified electrode, thereby requiring an additional electrochemical polishing treatment. In this work, several cycles of cyclic voltammetry were conducted as an electrochemical polishing technique.

An SEM image of the CuNi-BDD electrode shows that the Cu and Ni particles are successfully deposited on the BDD electrode surface (Figure 2), while EDS indicates that the contents of Cu and Ni particles are 0.11% and 0.14%, respectively (C 99.5% and O 0.59%). XPS was

also conducted (Figure 3). XPS spectra of the modified BDD electrode show elemental analysis of the modified BDD surface. The peak at 933.9 eV represents $\text{Cu } 2p_{3/2}$, while that at 856 eV represents $\text{Ni } 2p_{3/2}$. Thus, the presence of metal particles on the modified BDD electrode surface was confirmed.

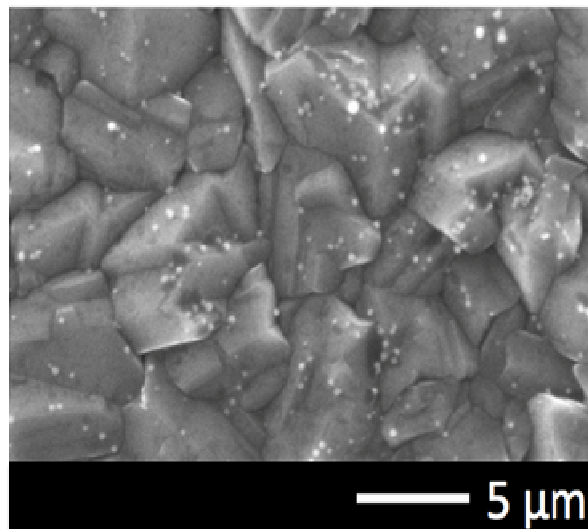


Figure 2. SEM Image of CuNi-BDD Electrode

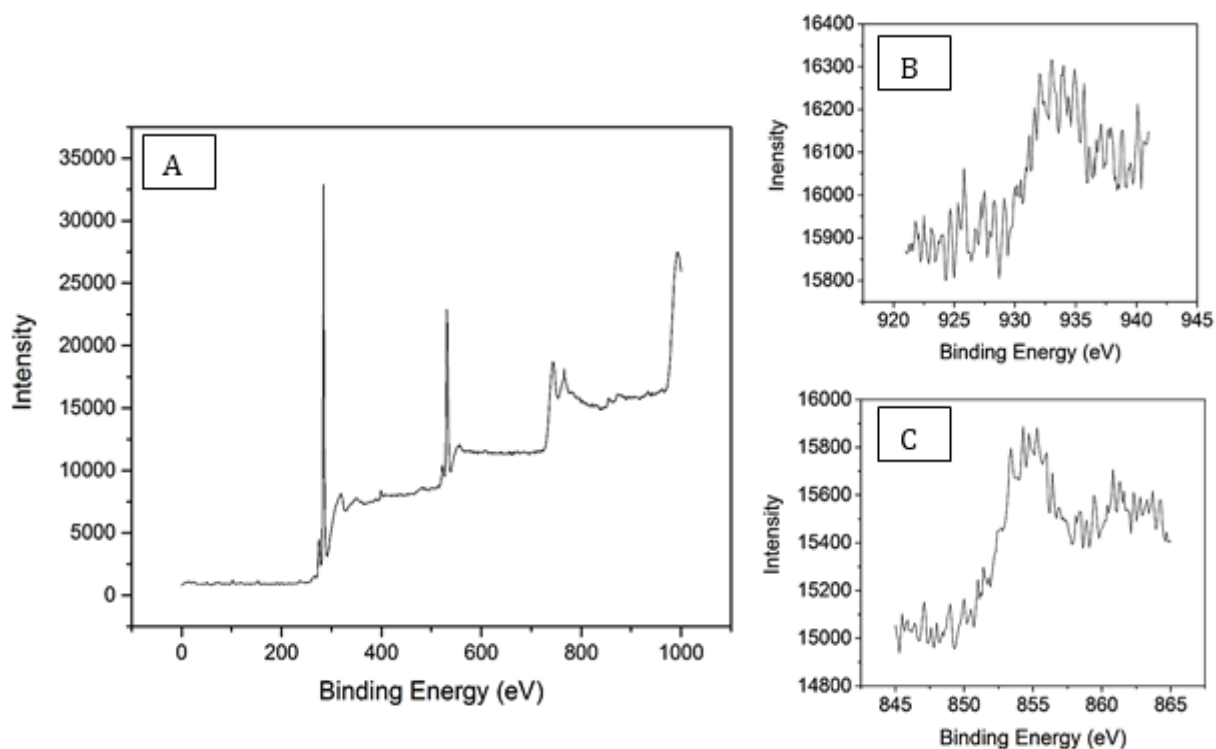


Figure 3. XPS Spectra of CuNi-BDD Electrode: Wide Scan (A), and Narrow Scan of $\text{Cu } 2p_{3/2}$ (B) and $\text{Ni } 2p_{3/2}$ (C)

Additionally, Raman spectroscopy was performed to examine the stability of the BDD electrode after all the deposition treatments (Figure 4). The high temperature of RTA and several deposition steps was previously thought to damage the sp^3 carbon bonding of BDD. However, the modified BDD electrode retained its characteristic properties, where sp^3 carbon bonding at 1332 cm^{-1} and the B-B bond peak at 1220 cm^{-1} were analyzed, and no sp^2 carbon bonding at approximately 1500 cm^{-1} was detected [18]. Therefore, the fabrication method used in this study did not damage the BDD electrode as a support for Cu and Ni deposition, confirming the high compatibility of this material for practical application.

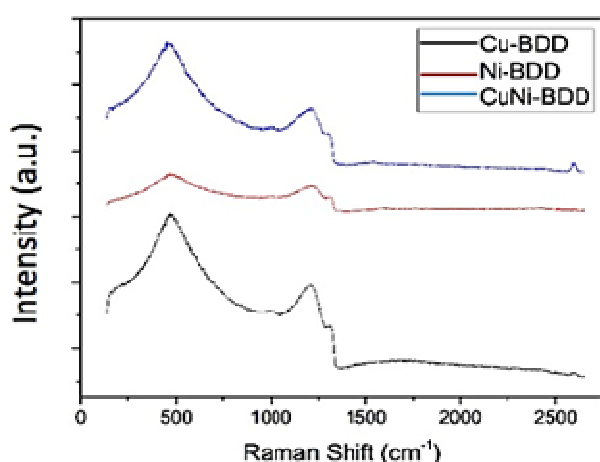


Figure 4. Raman Spectra of Fabricated Cu-BDD, Ni-BDD, and CuNi-BDD

Table 1. Total Current Density of Modified BDD Electrodes with and without RTA Treatment at Three Different Applied Potentials

Electrode	Potential (V)	Total current density (mA/cm ²)
<i>With RTA</i>		
Cu-BDD	-1.2	0.08
	-1.5	0.33
	-1.7	0.70
Ni-BDD	-1.2	0.08
	-1.5	0.37
	-1.7	1.84
Cu Ni-BDD	-1.2	0.10
	-1.5	0.20
	-1.7	0.42
<i>Without RTA</i>		
Cu-BDD	-1.2	3.94
Ni-BDD	-1.2	10.24
Cu Ni-BDD	-1.2	2.16

CO₂ER application. CO₂ER was performed for 1 h at three different potentials: -1.2, -1.5, and -1.7 V. The total current density was evaluated for each electrode at each potential. Comparison with an electrode fabricated without RTA is also presented (Table 1). The results show that BDD electrodes modified by RTA show a relatively lower total current density than those without RTA treatment. This condition could be explained by imperfect activation through cyclic voltammetry, which results in incomplete removal of the passivation layer that is known to exist after annealing [17]. Regardless of this condition, the stability of the modified BDD electrode could be improved. Thus, enhancement of the activation treatment is recommended for future work to overcome this issue.

CO₂ER on the Ni-BDD electrode shows the best performance at a potential of -1.2 V, which may be due to lower H₂ evolution providing a pathway for CO₂ER to form simple C₁ molecules, unlike Cu-BDD, which is known to be active for CO₂ER, thereby resulting in CO₂ER products at all the potentials applied in this work. However, the higher potential required to produce ethanol in this study (>-1.5 V), compared with the previous report [14], might be due to the modified BDD electrode not being fully activated or a different detailed system being used in this study.

However, as shown in Figure 5A, the CO₂ER products on the CuNi-BDD electrode include methanol and methane. Additionally, Figure 5B shows the trend of the partial current density rather than the faradaic efficiency because the total current density of CO₂ER differs considerably for each electrode. The trend of the partial current density is similar to that for the product content. The CO₂ER on the CuNi-BDD electrode, which combines the behavior of two different metals with its own, shows good performance at -1.5 V and -1.7 V. It is known that CO₂ER on Ni metal produces a large amount of H₂ gas [19] with a very low CO₂ER efficiency. Ni is also a well-known metal catalyst that can strongly adsorb CO, which is known to be a CO₂ER intermediate. However, Cu is well-known for producing various products via CO₂ER, including hydrocarbons and oxygenated species [20]. Cu also has a lower CO adsorption strength than Ni metal. Based on these results, modification of the BDD surface with bimetallic Ni and Cu, as a combination of metals with different behavior in CO₂ER, is expected to improve the catalytic performance of CO₂ER [21]. However, the performance of CuNi-BDD in CO₂ER is between those of Cu-BDD and Ni-BDD. The presence of Cu particles may decrease the production of hydrogen, which is the main product on Ni metal. Nevertheless, the behavior and product trends of CO₂ER on CuNi-BDD are not significantly different from those of the monometal-modified electrode. Thus, adjusting the metal composition can

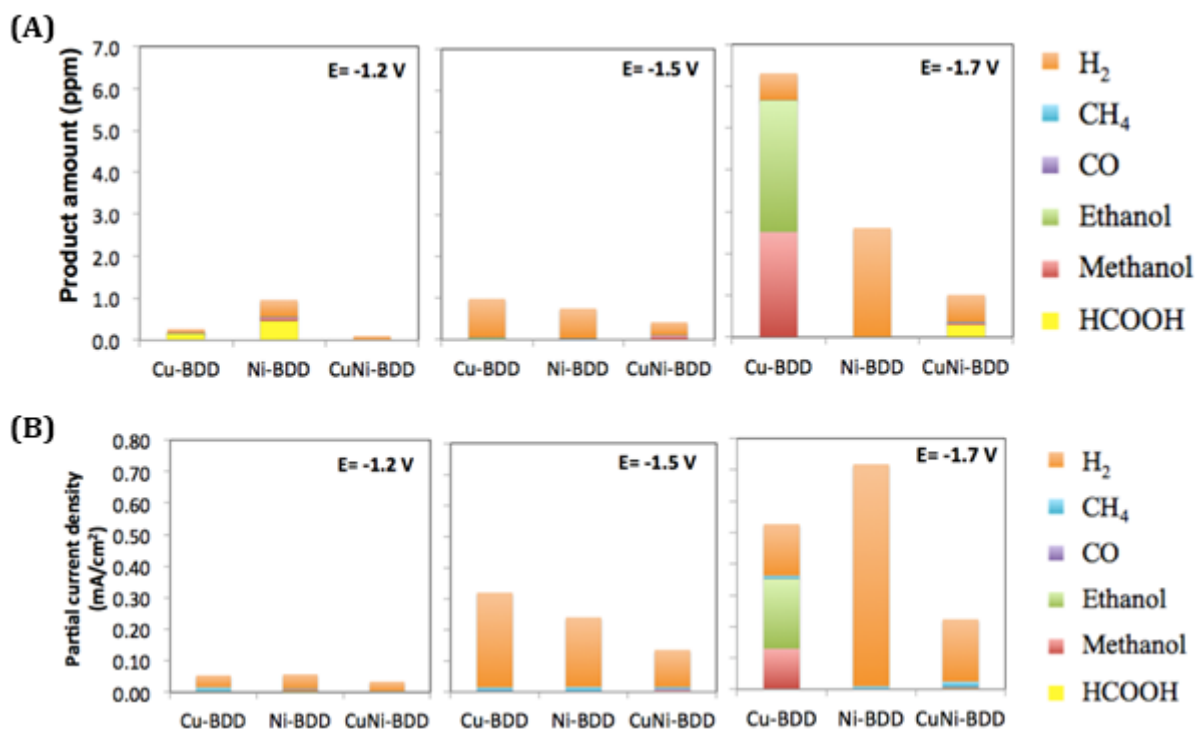


Figure 5. CO₂ER Product Distribution (A) and Partial Current Density (B) on Cu-BDD, Ni-BDD, and CuNi-BDD at Different Applied Potentials (-1.2, -1.5, and -1.7 V)

optimize the catalytic effects, including the reaction rate and even the selectivity toward CO₂ER.

Regardless of the limitations of these results, an attempt to modify the surface of a BDD electrode with metal particles, resulting in the possible generation of products other than HCOOH, has been shown in this report. For reference, previous work on CO₂ER on the surface of a bare BDD electrode in aqueous alkali metal solution produced mainly HCOOH [22]. Thus, methanol and methane production on the CuNi-BDD electrode is an important finding and worth further study to increase the amount of CO₂ER products, selectivity, and efficiency.

Conclusion

In summary, a CuNi-BDD electrode was successfully fabricated. The modified BDD electrode shows activity toward CO₂ER. Products other than HCOOH, the main CO₂ER product that used a bare BDD electrode in aqueous alkali metal solution, could be produced, including methanol and methane. However, improvement is required to achieve optimum activation of the annealed-modified electrode and increase the amount of CO₂ER products and efficiency. Finally, research on CO₂ER on the metal-modified BDD electrode is ongoing and worth further exploration as a method of overcoming the high overpotential of CO₂ER on a bare BDD electrode.

Acknowledgments

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