Electrochemical study of nickel-cobalt deposited on boron-doped diamond as working electrodes for urea fuel cells

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Abstract. Urea as one of the most abundant compounds that can be used as a fuel in fuel cells. It contains a nitrogen–hydrogen bond that can easily be broken by electrochemical processes to produce two molecules of hydrogen. The hydrogen released can generate electricity as in a fuel cell. In this research, boron-doped diamond (BDD) was modified using nickel and/or cobalt electrodeposition to provide Ni-Co-BDD, Ni-BDD, and Co-BDD working electrodes for enhanced urea electro-oxidation. The highest power density and potential was achieved using Ni-Co-BDD (96.4 mW cm\(^{-2}\) and 0.92 V, respectively), while the highest current density was achieved using Co-BDD (165.34 mA cm\(^{-2}\)). Overall, the results indicate that the best and most stable electrode for fuel cells is that based on Ni-Co-BDD.

Keywords: boron-doped diamond, fuel cell, surface modification, nickel, cobalt

1. Introduction
Electricity demand in Indonesia continues to increase in line with increasing national economic growth. Electrical energy is currently mainly produced from fossil fuels, which are a limited resource and produce large quantities of pollutants. Therefore, alternative energy sources that can satisfy increasing demands while remaining efficient and environmentally friendly are essential.

A fuel cell is a device that can instantly convert chemical energy into electricity with high efficiency [1]. Fuel cells can be used for various purposes, including as power sources for portable devices and electric vehicles, as well as stationary energy storage devices. Therefore, the use of fuel cells is expected to replace fossil-fueled electric energy.

Urea is considered as a potentially excellent source of hydrogen owing to its abundance, stability, and non-toxicity [2]. Furthermore, electricity can be generated if the hydrogen gas is released via electrochemical processes [3]. Accordingly, Guo et al. [2] used urea as a fuel in a fuel cell using a nickel–cobalt electrode in 2016 [2]. Previously, Boggs et al. [4] had used urea as a fuel in a fuel cell using a nickel electrode in 2009. Nickel is known to be a good catalyst and has a high current density and low oxidation potential in urea electro-oxidation. The catalytically active component of Ni electrodes for urea electro-oxidation is NiOOH [4]. The formation potential of NiOOH from Ni(OH)_2 can reach \(\approx 0.25\) V (vs. Ag/AgCl) in 5.0 M KOH. Accordingly, a large over potential is required to operate direct urea fuel cell [4]. Theoretically, urea fuel cells produce water, electric energy, and heat by the following processes [2]:

Overall reaction:

\[
\text{CO(NH}_3\text{)} + 8\text{KOH} + 3\text{H}_2\text{O} + 3\text{H}_2\text{SO}_4 \leftrightarrow \text{N} + 12\text{H}_2\text{O} + \text{K}_2\text{CO}_3 + 3\text{K}_2\text{SO}_4, (E^\circ = 2.51\text{ V})
\]
On the contrary, boron-doped diamond (BDD) is known as an electrode with high stability and wide potential window [5]. Furthermore, Asgari et al. [6] reported that the charge acceptance of nickel can be increased by doping with cobalt, lowering the NiOOH formation potential [6]. Therefore, in the present study, BDD was modified with nickel and/or cobalt to synthesize three different electrodes (Ni-BDD, Co-BDD, and Ni-Co-BDD), which were compared and assessed for urea fuel cells [1].

2. Experimental

2.1. Preparation of Ni-BDD, Co-BDD, and Ni-Co-BDD

BDD film was obtained from Einaga Laboratory, Keio University, Japan. To prepare Ni-BDD, NiSO₄·6H₂O (0.53 g) was dissolved in 0.1 M acetate buffer solution (pH 5). This solution was used to electrodeposit onto a BDD at a potential of −1.2 V for 600 s using an amperometric electrodeposition technique. The same procedure was performed using CoCl₂·6H₂O (0.951 g), followed by electrodeposition at −1.0 V to prepare Co-BDD. Ni–Co–BDD was prepared by dissolving NiSO₄·6H₂O (0.84 g) and CoCl₂·6H₂O (0.19 g) in acetate buffer solution (pH 5), followed by electrodeposition at −1.2 V for 600 s. The modified electrodes were then placed in 1 M KOH, and cyclic voltammetry (CV) was performed 300 times at 100 mV s⁻¹ to generate Ni(OH)₂ layers [7]. The electrodes were characterized using scanning electron microscopy (SEM).

2.2. Fuel cell test

For the fuel cell tests, Nafion 115 (Dupont) was placed between the anodic and cathodic chambers. Prior to use, the Nafion was boiled in 5% H₂O₂ and deionized water, respectively. The membranes were immersed in deionized water before use. The anolyte contained urea and KOH while the catholyte contained H₂O and H₂SO₄ [2]. Direct urea/H₂O fuel cell tests were carried out with a potentiostat using the eDAQ Chart application.

3. Results and discussion

3.1. Characterization of Ni-BDD, Co-BDD, and Ni-Co-BDD

For Ni-BDD, Ni(OH)₂ layer was performed by cyclic voltammetry for 300 times in 1M KOH at the scan rate of 100 mV s⁻¹ [7]. The same procedure was applied to Co-BDD and Ni–Co–BDD. Then all the electrodes were characterized using SEM. Representative SEM images are presented in figure 1.

![SEM images of (a) bare BDD, (b) Ni-BDD, (c) Co-BDD, and (d) Ni-Co-BDD.](image-url)
This treatment is required to form two crystallographic species, i.e., hydrated α-Ni(OH)$_2$ and anhydrous β-Ni(OH)$_2$. [7]. β-Ni(OH)$_2$ is more stable than α-Ni(OH)$_2$ and is thus formed by performing 300 cycles.

The CV results for Ni-BDD, Co-BDD, and Ni-Co-BDD are shown in figure 2. The oxidation peak of the last cycle for both Ni-BDD and Ni-Co-BDD is shifted to the right of the previous oxidation peaks as shown in figure 2a and figure 2b. This indicates the formation of the more stable β-Ni(OH)$_2$ structure. However, as shown in figure 2c, this phenomenon is not observed for Co-BDD because it has no Ni(OH)$_2$ layer.

3.2. Fuel cell tests
Plots of time versus power density for direct urea/H$_2$O fuel cells operating for 1 h at room temperature are presented in figure 3a. Ni–Co–BDD, Ni–BDD, and Co–BDD were used as the working electrodes with a platinum spiral as the counter electrode and a saturated Ag/AgCl electrode as the reference electrode. Nafion was used to transfer protons from the anode to the cathode chambers. The anolyte
was 0.001 M KOH and 0.33 M urea, and the catholyte was 2 M HSO₄ and 2 M H₂O. In this fuel cell system, Ni–Co–BDD presented a maximum power density of 96.4 mW cm⁻², while Ni–BDD presented a maximum power density of 73.9 mW cm⁻² and Co–BDD presented a maximum power density of 52.74 mW cm⁻².

Figure 3b shows plots of time versus current density. The maximum current density for Ni–Co–BDD is 104.3 mA cm⁻², while it is 103.1 mA cm⁻² for Ni–BDD and 165.34 mA cm⁻² for Co–BDD.

Figure 3c shows plots of time versus potential. The highest potential is that for Ni–Co–BDD (0.92 V), then Ni–BDD (0.71 V), and Co–BDD (0.32 V). The power was stable for ~3,500 s with the best working electrode (Ni–Co–BDD), which indicates that our system is promising for direct urea fuel cells.

4. Conclusions
Application of Ni–Co–BDD, Ni–BDD, and Co–BDD as electrode materials in fuel cells containing urea provided maximum power densities of 96.4, 73.9, and 52.74 mW cm⁻², respectively. The highest current density for the three electrodes was provided by Co–BDD (165.34 mA cm⁻²), while those of Ni–Co–BDD, and Ni–BDD were 104.3 and 103.1 mA cm⁻², respectively. However, Co–BDD provided the lowest power density and potential, making it unsuitable as a working electrode for fuel cells. The highest potential for the three electrodes was that of Ni–Co–BDD (0.92 V). Thus, the data indicate that the best working electrode material is Ni–Co–BDD, and that this material has great promise as a urea fuel cell electrode material.

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