

Preparation of boron doped diamond modified by iridium for electroreduction of carbon dioxide (CO₂)

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Abstract. Electroreduction of carbon dioxide (CO₂) at iridium oxide-modified boron-doped diamond (IrOx-BDD) electrodes in aqueous electrolytes was studied by voltammetric method. The aim of this study was to find out the catalytic effect of IrOx to produce fine chemicals contained of two or more carbon atoms (for example acetic acid) in high percentage. Characterization using FE-SEM and XPS indicated that IrO₂ can be deposited at BDD electrode, whereas characterization using cyclic voltammetry indicated that the electrode was applicable to be used as working electrode for CO₂electroreduction.

Keywords: Electroreduction, carbon dioxide, iridium oxide, boron-doped diamond

1. Introduction

CO₂ produced by human's activity offers a great value to overcome the global warming issues. CO₂ can be recycled to O₂ naturally, during the photosynthesis process, however this process is limited due to the decrease of plant population. The remaining CO₂ then continuously increases at the surface of the earth. This problem prompted some researchers to investigate the alternative process to decrease CO₂ content in the atmosphere. One of the alternative method to reduce CO₂ is to convert the gas electrochemically to industrial chemicals such as formic acid [1], methanol [2], and acetic acid [3, 4]. Le *et al.* [2] reported that direct reduction of CO₂ to form methanol can be performed by using copper as the working electrode, while several other studies reported the reduction of CO₂ to formic acid with cadmium, indium, tin and lead as the working electrodes [5]. In addition, the use of gold or silver as the working electrode with KOH-methanol as the electrolyte was also reported [6] whereas methane can be produced electrochemically through CO₂ reduction using copper electrode with lithium as a supporting electrolyte [7].

Furthermore, Nakata *et al.* [8] reported that the use of boron-doped diamond (BDD) electrodes in the reduction of CO₂ can produce formaldehyde. BDD is reported to be a better electrode compared to the previous electrode used in this application, because it generates higher products percentage. BDD is also known to have a wide potential window as well as a high electrochemical stability [9, 10]. The use of a single element for the working electrode such as copper, BDD and other working electrode also showed the tendency to form organic compounds consists only one carbon atom, such as methane, methanol, formic acid and formaldehyde. Meanwhile, Panglipur *et al.* [4] reported an indication of the formation of acetic acid from CO₂ reduction process using BDD modified by copper at its surface [3, 4]. It was proposed that the use of composite consisted of BDD and copper correlates to the formation of organic compounds with two carbon atoms.



This research studies the preparation of iridium-modified BDD electrodes for an application in electrochemical reduction of CO₂. Iridium was used as a composite metal at the BDD surface due to its electrocatalytic effect. The use of iridium oxide nanoparticles composite with cobalt oxide electrode on water oxidation and mercury detection have been reported [11, 12]. Characterization with SEM, XPS, EDX and cyclic voltammetry was performed to confirm that the iridium-modified electrode is ready to be employed as the working electrode in CO₂ electroreduction.

2. Materials and methods

2.1. Chemicals

H₂IrCl₆ · xH₂O, KNO₃, NaCl, and 2-propanol were supplied from Sigma and used in this study without purification.

2.2. Experimental

Boron doped diamond (BDD) was characterized by cyclic voltammetry in 0.1 M KNO₃ prior to be modified by Iridium. As the modified solution, a solution consisted of 0.5 M H₂IrCl₆ and 0.1 M KNO₃ (1:1) was aged by heating for a specified time at 80°C in closed vials, and cooled to room temperature [9]. Then, the solution was used as a modified solution to BDD by performing cyclic voltammetry for several times from a potential of +0.2 to 1.20 V (vs. Ag/AgCl). The iridium-modified BDD was characterized using SEM, EDX, XPS and cyclic voltammetry.

3. Results and discussion

3.1. Electrochemical behavior of iridium at Boron Doped Diamond (BDD)

Before the BDD electrode was modified by iridium, cyclic voltammetry using KNO₃ as the electrolyte was performed in the potential range of -1.0 to +1.5 V with a scan rate of 100 mV/s (figure 1). No oxidation and reduction peak were observed in the applied potential indicated that the BDD was electrochemically stable and no contamination of other analytes that can go through redox reactions in the applied potential range on the cyclic voltammetry system was observed.

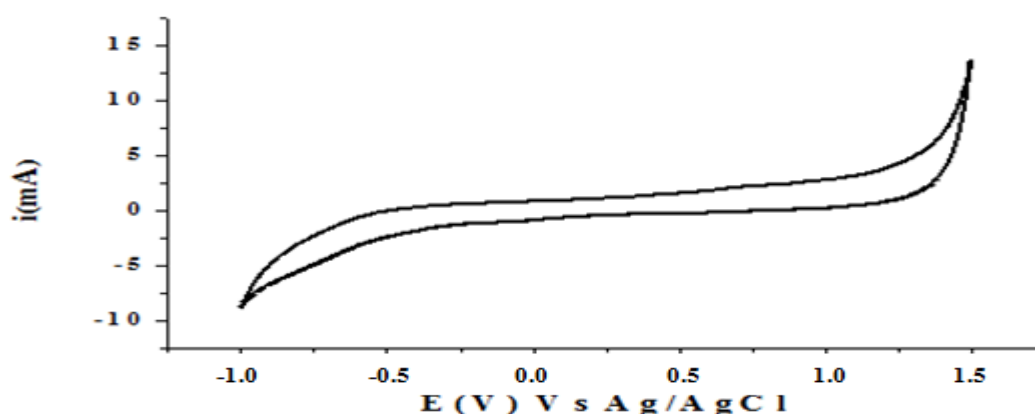


Figure 1. Voltammogram of BDD in 0.1 MKNO₃

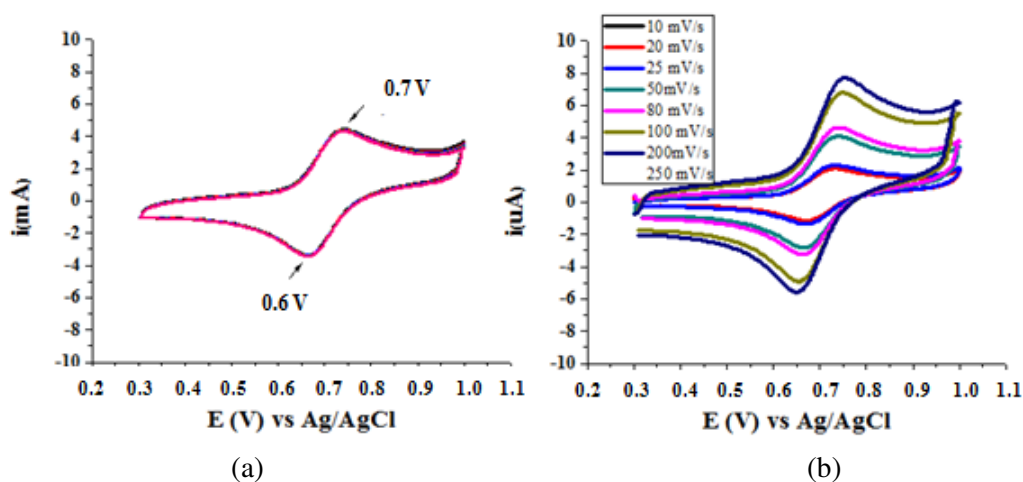


Figure 2. (a) Repeating cyclic voltammetry process (10 Cycles) of 0.3 mM Ir in 0.1 M KNO₃ (1:1) and (b) variation of scan rate on Ir 0.3 mM in 0.1 M KNO₃ (1:1)

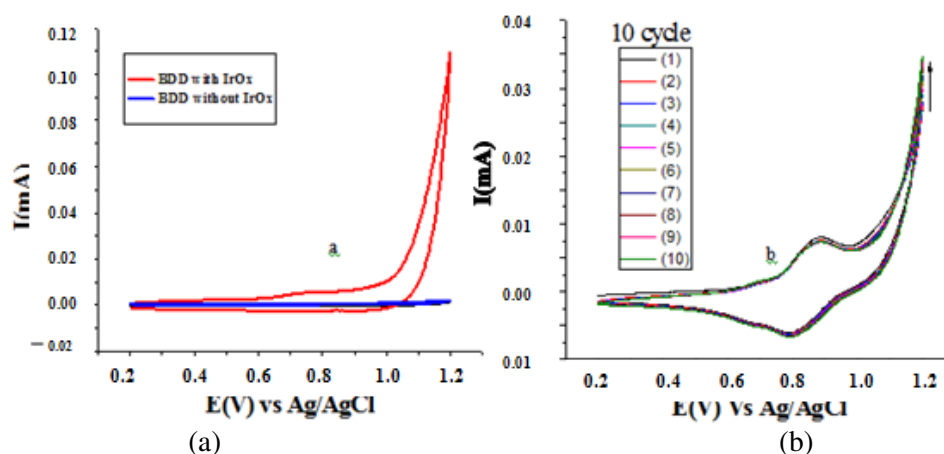


Figure 3. The voltammograms of (a) the unmodified and the iridium-modified BDD and (b) the iridium-modified BDD after 10 cycles of voltammetry in the solution consisted of 0.5 mM Ir and 0.1 M KNO₃ (1:1)

In the presence of 0.3 mM Ir in 0.1 M KNO₃ (1: 1), the cyclic voltammograms (figure 2a) shows an oxidation-reduction couple peaks in the potential range of +0.7 V and +0.6 V. The peaks shows a good reproducibility, which indicates the stability of the working electrode as well as the electrolyte solution and analytes during the measurements. Meanwhile, characterization using the same solution by varying the scan rate (figure 2b) also shows that the current increases proportionally, scan rate suggested a good performance of the working electrode to generate the current [13].

3.2. Deposition IrO_x-BDD

Deposition of iridium oxide on the surface of BDD was performed using chronoamperometry with applied potential of +1.2 V for 10 minutes. As the depositing solution, a solution consisted of 0.5 mM Ir and 0.1 M KNO₃ (1: 1) was used after aging by heating for 1 hour at 80°C.

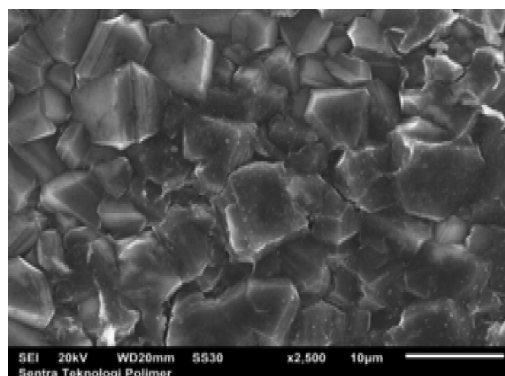


Figure 4. Characterization of BDD by FE-SEM

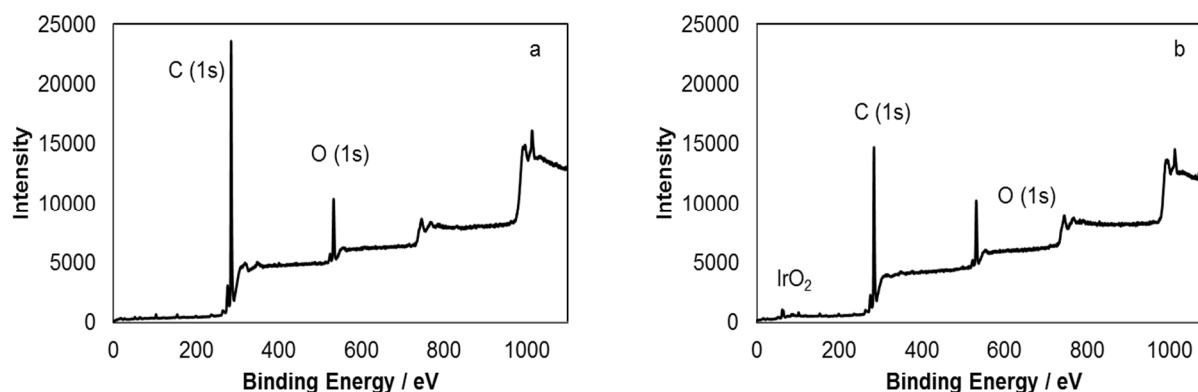


Figure 5. XPS characterization of BDD (a) before and (b) after deposition with iridium

The characterization using cyclic voltammetry was performed in 0.1 M KNO_3 (figure 3a). Whereas the unmodified BDD generates very low background current, a higher current at a potential 1.2 V was observed for the modified BDD, suggested the formation of an electroactive compound at the surface of BDD. The current becomes higher when more of cyclic voltammetry process was performed and then saturated after 10 cycles, indicated that the deposition was saturated at the surface of BDD (figure 3b).

3.3. Characterization of IrOx -BDD by using FE-SEM

The electrode was also characterized by using FE-SEM with a magnification of $10000\times$ (figure 4). In BDD which deposited by Ir, Ir particles on the surface of BDD marked with the brighter dotted area than the BDD.

3.4. XPS characterization

Elements composition at the BDD surface was characterized with XPS. The characterization before and after modification (figure 5) shows a peak at 284 eV attributable to C 1s and another peak at 532 eV attributed to O 1s. On the other hand, at the Ir-modified BDD the peak at 86 eV was observed, while it was not appeared at unmodified BDD. This peak was identified as IrO_2 which was formed on the surface of BDD after the deposition.

4. Conclusions

Modification of boron-doped diamond by iridium was successfully performed by chronoamperometry technique. Characterization of the electrode by FE-SEM and XPS indicated the formation of IrO_2 on

the surface of BDD, whereas cyclic voltammetry suggested that the electrode is promising to be applied for electrochemical reduction of CO₂.

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