Electroreduction of carbon dioxide using platinum-iridium modified boron-doped diamond (BDD) with various platinum-iridium ratios

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Abstract. Modification of boron-doped diamond (BDD) electrodes with bimetallic platinum-iridium was studied. Combination techniques of wet chemical seeding and electrochemical deposition were performed with various Pt-Ir precursor ratios of (1:1), (1:2) and (2:1). These electrodes were then applied for electrochemical reduction of CO dissolved in 0.1 M NaCl solution at the potentials of -1.1 V, -1.2 V, -1.3 V, and -1.5 V (vs Ag/AgCl) for 60 min. Electroreduction of CO applied at PtIr(2:1)-BDD at the potential of -1.1 V (vs Ag/AgCl) produced formic acid, methanol and hydrogen as the main products.

Keywords: boron-doped diamond, bimetal, CO, electroreduction, iridium, platinum.

1. Introduction

Total of CO in atmosphere reaches 72 % and increases about 3 % each year [1]. The abundance of CO attracts researcher’s interest to produce valuable chemical products. One promising technique to reduce CO is electrochemical reduction because the products can be controlled by changing the electrochemical parameters, such as potentials and electrolytes [2–4]. Moreover, water can be used as both electron and proton sources to produce hydrocarbons [4].

On the other hand, boron-doped diamond (BDD) is established as a superior electrode with many advantages, such as wide working potential and low background current in water solution as well as excellent stability of its surface [5]. However, sometimes it needs to modify the BDD surface with catalysts to improve its electroactive ability. Meanwhile, bimetallic electrocatalysts have attracted great attention as a good candidate to enhance the catalytic activity as well as selectivity over their monometal ones [6-9]. Recently, Kortlever et al. [10] reported that modification of carbon with PtPd provide a exceptionally low onset potential for the CO reduction to form formic acid [10].

Platinum, which is known as inert material, provides favorable activation and conversion of CO to CO [11,12]. Electroreduction CO on Pt-BDD electrode at potential of -2.5 V (vs Ag/AgCl) was reported to produce formic acid as the main product with 14.6 % faradaic efficiency [11]. On the other hand, iridium, either in the forms of metal complexes or nanoparticles, has a great electrocatalytic activity [13]. The use of iridium on cobalt electrode in water electrolysis system was reported to increase the product yields [14]. Iridium was also reported to react with water to generate Ir–OH species, that can integrate with Pt–CO species to eliminate surface-adsorbed CO at the lower potential compared to pure Pt [12,15]. Furthermore, our previous research using PtIr(3:4)-BDD for
electroreduction CO, at potential -1.7 V (vs. Ag/AgCl) showed the formation of acetic acid and formic acid [16]. In this research, modification of BDD with bimetallic Pt-Ir with various ratios was studied for electrochemical reduction of CO.

2. Experimental

2.1. Materials

BDD electrodes (B:C ratio of the precursor gas was 1:1000) were self-prepared in Einaga Laboratory, Chemistry Departement, Faculty of Science and Technology, Keio University, Japan. Hydrogen hexachloroplatinate (IV), potassium hexachloroiridate (IV) and sodium borohydride (NaBH₄) were from Sigma, while NaOH, NaCl, NaSO₄ and other chemicals were from Merck. Ultra-pure deionized water was obtained from a Millipore Direct® Q5-UV with a resistivity of 18.2 MΩ cm.

2.2. Preparation of PtIr-BDD electrodes

Platinum iridium (Pt-Ir) was deposited onto BDD (PtIr-BDD) by wet chemical seeding followed by electrochemical overgrowth. A volume of 10 μL 1.0M NaBH₄, in 0.1M NaOH solution and 40 μL 1mM H₂PtCl₆.KIrCl₃, or Pt-Ir solution (mole ratios were 1:1, 1:2, and 2:1) was dropped on BDD surface to provide the wet chemical seeding technique. Then, chronoamperometry in Pt-Ir solution at -0.5 V (vs. Ag/AgCl) for 15 min was conducted to provide the electrochemical overgrowth.

2.3. Electroreduction of CO

The prepared PtIr-BDD was employed as the working electrode, while a platinum wire as the counter and an Ag/AgCl system as the reference electrodes. In a two-compartment electrochemical cell, 0.1 M NaCl was placed in the cathode room, while 0.1M NaSO₄ in the anode room. Then, CO gas was dissolved in 0.1M NaCl for 30 min with 100 mL/min flow rate. The CO electroreduction were applied using chronoamperometry for 1 h and the products were analyzed using High Performance Liquid Chromatography (HPLC), Gas Chromatography and Mass Spectrometry (GC-MS), and GC with Total Ion Chromatogram (TIC) and Flame Ionization Detector (FID).

3. Results and discussion

3.1. Modification of BDD electrode and its characterization

Preparation of PtIr-BDD electrodes was carried out by electrodeposition method. Prior to the deposition, the BDD surface was treated by Pt and Ir seeds to increase the metal adsorption on the surface. The presence of NaBH₄ in the seeding step helps to bind the metal particles on the BDD surface and to reduce Pt and Ir ions to produce the metal forms. The metals then acted as the seeds on the BDD surface, where the metal particles were further grown in the electrodeposition step [17]. The reactions between NaBH₄ and Pt-Ir salt solutions are shown below [17,18]:

\[ \text{NaBH}_4 + 3\text{H}_2\text{O} + \text{H}_2\text{PtCl}_6 \rightarrow \text{Pt} + \text{H}_2\text{BO}_3 + 5\text{HCl} + \text{NaCl} + 2\text{H}_2 \]  \hspace{1cm} (1)

\[ \text{NaBH}_4 + 3\text{H}_2\text{O} + \text{K}_2\text{IrCl}_6 \rightarrow \text{Ir} + \text{H}_2\text{BO}_3 + 3\text{HCl} + 2\text{KCl} + \text{NaCl} + 2\text{H}_2 \]  \hspace{1cm} (2)

The electrodeposition was performed by using chronoamperometry technique at a potential of -0.5 V (vs Ag/AgCl) for 15 min. SEM images in figure 1a and figure 1b show that smaller amount of metal
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**Figure 2.** XPS Spectrum of PtIr-BDD Electrodes for (a) the wide scan as well as the narrow scan of (b) Pt and (c) Ir particles was deposited at PtIr-(1:1)-BDD and PtIr (1:2)-BDD in compare to that at PtIr (2:1)-BDD (figure 1c). However, at PtIr (1:2)-BDD particle aggregation on the surface was observed, indicated the influence of iridium in the deposition of Pt.

Energy Dispersive X-Ray Spectroscopy (EDS) characterization was performed to determine the composition of Pt and Ir at each BDD electrodes. At PtIr(1:1)-BDD surface, 3.67 \% of Pt and 1.17 \% of Ir could be successfully deposited, while 1.73 \% Pt and 0.15 \% Ir were deposited at PtIr(1:2)-BDD and 3.84 \% Pt and 0.39 \% Ir were deposited at PtIr(2:1)-BDD. Roughly, the ratios of Pt-Ir (3:1), (11:1) and (10:1) could be deposited on PtIr(1:1)-, PtIr(1:2)-, and PtIr(2:1)-BDD, respectively. The composition shows that all electrodes exhibit larger mass percentage of Pt than Ir probably because the electrodeposition was generated at potential reduction of Pt [13]. Therefore, Pt particles were easier to be deposited on BDD surface than Ir particles.

The X-Ray Photoelectron Spectroscopy (XPS) spectra for all three electrodes were performed. The wide scans (figure 2a) show typical peaks with high intensity at a binding energy of 284.8 eV and 532.75 eV related to C and O. Beside these peaks, Pt and Ir peaks were observed with smaller intensities. The narrow scans performed to clarify the peak of Pt and Ir at all PtIr-BDD electrodes shows the peak of Pt observed at binding energy around 71 eV (figure 2b), while the peak of Ir appeared at binding energy of 60 eV (figure 2c). The results indicated that Pt (0) and Ir (0) species were deposited on BDD electrodes [19].

3.2. Electroreduction of CO

Prior to CO electroreduction, the reduction potential of CO was determined by using cyclic voltammetry in 0.1M NaCl solution containing of CO. Cyclic voltammogram (CV) at PtIr-BDD electrodes with various Pt-Ir ratios show that the reduction peak CO was typically observed at the potential of -1.3 V vs. Ag/AgCl (figure 3). Accordingly, the electrochemical reduction of CO, was performed at around -1.1 V, -1.2 V, -1.3 V, and -1.5 V (vs. Ag/AgCl).

3.3. Product analysis of electroreduction CO

Product analysis of the electrochemical reduction CO was performed by using HPLC, LC-MS, and GC. The faradaic efficiency of each product obtained was then compared to that of the products resulting from the other electrodes as shown in figure 4. Application of PtIr (2:1)-BDD electrode at the potential -1.1 V resulted the largest total faradaic efficiency (44.88\%) composed of 23.71\% formic, 13.12\% methanol and 7.71\% hydrogen.

Furthermore, figure 5 shows that with the decrease of applied potentials from -1.3 V, the faradaic efficiency of formic acid and methanol increased. On the contrary, hydrogen decreased due to the
3.4. Performance of electrode
Stability of the modified BDD electrodes for electroreduction of CO was checked by before and after used. Table 1 shows a decrease of Pt and Ir mass percentage on BDD surface after used for electroreduction of CO. The most stable electrode was PtIr(2:1)-BDD with mass loss percentage of
13.12% Pt particles and 4.88% Ir. The results showed that although wet chemical seeding has been done before electrochemical deposition, the bimetallic Pt-Ir particles was not deposited very stable on BDD surface. Therefore, it needs to redepositing the particles on BDD surface for applying electroreduction of CO with the same electrode. In other words, performance of Pt-Ir modified BDD electrode by these modification methods are only capable for one time application in electroreduction of CO.

4. Conclusions
Preparation of PtIr-BDD by using combination techniques of wet chemical seeds and electrodeposition provided homogenous distribution of particles at Pt-Ir ratio of (1:1), whereas the increase of Ir ratio caused aggregation of the deposited particles. Examination of these electrodes for electrochemical reduction of CO indicated the most efficient result was at Pt-Ir ratios of (2:1) using an applied potential of -1.1 V with formic acid, methanol, and hydrogen as the main products.

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Table 1. Mass percentage of Pt-Ir particles deposited on BDD before and after used for electroreduction of CO.

| Electrodes       | Mass percentage of Pt (%) | Mass percentage of Ir (%) | Mass loss | before | after | before | after | mass loss |
|------------------|---------------------------|---------------------------|-----------|--------|-------|--------|-------|-----------|
| PtIr (1:1) - BDD | 3.67                      | 1.59                      | 56.68     | 1.17   | 0     | 100.00 |
| PtIr (1:2) - BDD | 1.73                      | 0.96                      | 44.51     | 0.15   | 0.12  | 20.00  |
| PtIr (2:1) - BDD | 4.42                      | 3.84                      | 13.12     | 0.41   | 0.39  | 4.88   |

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