Preparation of platinum-modified boron-doped diamond for electroreduction of CO$_2$

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Abstract. Metal-modified boron-doped diamond has been prepared for preliminary study of CO$_2$ electroreduction. Pt was electrodeposited at boron-doped diamond (BDD) by using chronoamperometry technique. The precursor metal solution concentration of 6 mM was applied with deposition potentials of -0.3 V (vs Ag/AgCl). Characterization by using FESEM and XPS confirmed the presence of Pt on the surface of BDD. Cyclic voltammetry was applied to obtain an optimum condition for electroreduction of CO$_2$. CO$_2$ dissolved in 0.1 M NaCl and 0.1 M Na$_2$SO$_4$ solutions were applied. A reduction peak, attributable to CO$_2$, appeared at a potential of -0.7 V (vs Ag/AgCl) in NaCl solution, while no peak was observed in Na$_2$SO$_4$ solution. The result indicated that the metal-modified electrodes has successfully prepared as a working electrode for CO$_2$ electroreduction.

Keywords: platinum, boron-doped diamond, CO$_2$ electroreduction

1. Introduction

Research on electrochemical reduction of CO$_2$ has been performed since a long time ago. Various products of the CO$_2$ reduction into a more useful substances are widely discovered, such as formaldehyde, formic acid, methanol, methane, etc. [1, 2]. Electrochemical reduction of CO$_2$ employing metal electrodes has been carried out for Pt [2, 3]. Pt belongs to d group metals with an incompletely filled d orbital [2].

On the other hand, boron-doped diamond (BDD) electrodes provide a wide potential window and high electrochemical stability, which establish BDD as an attractive candidate for the electrochemical reduction of CO$_2$ [1, 4]. Nakata et al. [1] reported that electroreduction of CO$_2$ using BDD generates formaldehyde in a high percentage. Moreover, the electroreduction was affected by the solvent or electrolyte as well as the type of electrodes [1, 5].

In this work, platinum-modified BDD electrodes were prepared in order to improve the catalytic properties of the BDD electrodes for CO$_2$ electroreduction.

2. Materials and methods

2.1. Materials

H$_2$PtCl$_6$ were purchased from WAKO chemicals (Japan), Pt wire was obtained from Nilaco (Japan), and Ag/AgCl (saturated KCl) system was supplied from BAS Inc. (Japan). Double distilled water was obtained from Simply Lab water system (DIRECT-Q 3 UV, Milipore).
2.2. Preparation of platinum-modified BDD (Pt-BDD)
Preparation of Pt-BDD were performed following the previous methods [6]. Briefly, BDD was cleaned in 2-propanol, followed by double distilled water for about 10 min. Then, amperometry technique was applied at BDD by using 6 mM H₂PtCl₆ in 0.1 m H₂SO₄. A deposition potential of -0.3 V (vs Ag/AgCl) was then selected to deposit platinum at BDD electrodes. This treatment was carried out using single cell with a spiral platinum counter electrode and Ag/AgCl as a reference electrode.

2.3. Electrochemical behavior study of CO₂ at Pt-BDD
Cyclic voltammetry of 0.1 M NaCl solution with and without the presence of CO₂ was performed at BDD and Pt-BDD electrodes. Prior to bubbling with CO₂, the solution was bubbled with N₂ gas to remove other gases contained in the solution. After bubbling with CO₂ for 30 minutes, the cyclic voltammetry measurement was performed at a potential range from 0 to -2.0 V (vs. Ag/AgCl) with a scan rate of 100 mV/s.

3. Results and discussion

3.1. Characterization of Pt-BDD electrode
Characterization to confirm the existence of Pt deposited on BDD was performed by FESEM and XPS data of BDD and Pt-BDD. SEM Images of BDD (figure 1a) shows grain crystals of about 5 μm size. In the SEM image of Pt-BDD, the presence of particles on the surface of BDD (figure 1b) indicated that Pt has been deposited on BDD. Since Pt provided a higher conductivity than BDD, the particles of Pt were observed to be lighter than BDD. The shiny color corresponds to the metallic properties of d group metals, which emits light when hit by electrons.

Figure 2 shows the XPS spectra of BDD and Pt-BDD. Without modification, only the peaks of C 1s and O 1s were observed at BDD. On the contrary, in the presence of Pt particles peaks at 71 and 75 eV attributed to Pt were observed. The data confirmed that Pt particles were successfully deposited at BDD [6, 7].

![Figure 1](image-url)
3.2. Cyclic voltammetry of CO$_2$

Cyclic voltammograms (CVs) of CO$_2$ in 0.1 M NaCl solutions were performed to obtain the suitable solution to reduce CO$_2$ using Pt-BDD electrode. Figure 3 shows CVs of CO$_2$ in 0.1 M NaCl at unmodified BDD (figure 3a) and at Pt-BDD (figure 3b) electrodes. Since the solution was bubbled with N$_2$ gas to remove other gases before it was saturated by CO$_2$ gas, the observed reduction peak can be attributed to the reduction of CO$_2$. The peak was appeared at a potential of -0.7 V (vs Ag/AgCl) at BDD electrodes, while it was observed at -0.5 V at Pt-BDD, suggested that reduction of CO$_2$ at Pt-BDD can be performed at lower potential.

4. Conclusions

Preparation of Pt-BDD as a working electrode for CO$_2$ electrochemical reduction has been successfully performed. It was confirmed by the characterization of electrodes with FESEM and XPS data. Additionally, electrolyte determination suggested that reduction potential of CO$_2$ at Pt-BDD was occurred at a lower potential than at unmodified BDD.
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References
[1] Nakata K, Ozaki T, Terashima C, Fujishima A and Einaga Y 2014 Angew. Chemie - Int. Ed. 53 871-4
[2] Jitaru M, Lowy D A, Toma M, Toma B C and Oniciu L 1997 J. Appl. Electrochem. 27 875-89
[3] Saeki T, Hashimoto K, Kimura N, Omata K and Fujishima A 1996 J. Electroanal. Chem. 404 299-302
[4] Yang N, Gao F and Nebel C E 2013 Anal. Chem. 85 5764-9
[5] Lee J and Tak Y 2001 Electrochim. Acta 46 3015-22
[6] Ivandini T A, Sato R, Makide Y, Fujishima A and Einaga Y 2004 Chem. Lett. 33 1330-1
[7] Ivandini T A, Sato R, Makide Y, Fujishima A and Einaga Y 2005 Diamond Relat. Mater. 14 2133-8