High-Yield Electrochemical Production of Formaldehyde from CO₂ and Seawater**

Kazuya Nakata,* Takuya Ozaki, Chiaki Terashima, Akira Fujishima, and Yasuaki Einaga*

Abstract: The catalytic, electrocatalytic, or photocatalytic conversion of CO₂ into useful chemicals in high yield for industrial applications has so far proven difficult. Herein, we present our work on the electrochemical reduction of CO₂ in seawater using a boron-doped diamond (BDD) electrode under ambient conditions to produce formaldehyde. This method overcomes the usual limitation of the low yield of higher-order products, and also reduces the generation of H₂. In comparison with other electrode materials, BDD electrodes have a wide potential window and high electrochemical stability, and, moreover, exhibit very high Faradaic efficiency (74%) for the production of formaldehyde, using either methanol, aqueous NaCl, or seawater as the electrolyte. The high Faradaic efficiency is attributed to the sp³-bonded carbon of the BDD. Our results have wide ranging implications for the efficient and cost-effective conversion of CO₂.

The demand for fossil fuels has continued to increase because of our reliance on it as a source of energy by combustion and as a resource for the production of plastics and industrial chemicals. As CO₂ is a final product of the combustion process, the back conversion and utilization of CO₂ are important areas of research from the viewpoints of conservation of resources and the development of a sustainable society.[1–3] The use of CO₂ as an alternative to fossil fuels is also inherently promising, both from ecological and economical standpoints, and has received much attention owing to the fact that the reaction of CO₂ with H₂O using an external energy source is a simplified model of artificial photosynthesis. It has been an aim of chemists to harness this naturally occurring carbon fixation process as a model for manufacturing synthetic chemicals.

The CO₂ molecule is thermodynamically stable. To efficiently convert CO₂ into a desired product, suitable activation mechanisms and reaction conditions must be found. Among the various possible approaches, electrochemical reduction is a promising one, mainly because it has the advantages that the products from the electrochemical reduction of CO₂ can be tuned by the reaction conditions, and that water can be used as both a source of electrons and a source of protons to produce hydrocarbons.[4–8] In most of the studies made using metal electrodes, the main products obtained through CO₂ reduction have been CO or formic acid, although higher reduction products, such as formaldehyde, methanol, and methane, have also been obtained with semiconductor or other metal electrodes[9,10] under atmospheric or high-pressure conditions.[11–16] However, direct electron transfer to a CO₂ molecule requires a high overpotential,[17] which means that the evolution of hydrogen is a competitive process. This can reduce the efficiency of the CO₂ reduction. Thus, efficient catalysis is needed for the successful reduction of CO₂.

Boron-doped diamond (BDD) electrodes with p-type surfaces exhibit interesting properties, such as a wide potential window, a low background capacitive current, and a very high stability, which renders them chemically inert and mechanically durable. These properties are significantly different from those of other electrodes, such as glassy carbon (GC)[18–24] and make BDD an attractive candidate for the electrochemical reduction of CO₂. In particular, the wide potential window promotes the reduction of CO₂, which may be masked by the decomposition of solvents produced with other electrodes. Other desirable properties, such as the intrinsically inert nature of BDD, are expected to lead to practical applications.

In the present work, we report on the results of an investigation into the reduction of CO₂ using BDD electrodes in various electrolytes, including seawater, which acts as a source for both electrons and protons.

To confirm the reduction of CO₂ using the BDD electrode, we first performed cyclic voltammetry in a methanol solution containing tetrabutylammonium perchlorate (TBAP). Methanol was chosen as the electrolyte because the solubility of CO₂ in MeOH is about five times that in water, thus allowing easier detection of the reduction of CO₂. Cyclic voltammograms for the BDD electrode are presented in Figure 1. A cathodic current with an onset potential of −1.8 V vs. Ag/Ag⁺ was observed at a pressure of 1 atm in a solution through which N₂ was bubbled. The N₂ was then replaced with CO₂ at a pressure of 1 atm, and after bubbling with CO₂ for...

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1 h, a large peak was observed at $-1.3 \, \text{V vs. Ag/Ag}^+$. The current density of the peak increased and became saturated to 97.5 $\mu$A cm$^{-2}$ after 2.5 h bubbling CO$_2$, thus indicating that the CO$_2$ concentration in the methanol electrolyte had saturated.

After saturation of the MeOH electrolyte with CO$_2$, electrolysis was performed with the BDD electrode at various potentials for 1 h at room temperature and atmospheric pressure. The reaction products were formaldehyde, formic acid, and hydrogen (Figure 2). A maximum Faradaic efficiency for formaldehyde (74%) was observed at $-1.7 \, \text{V vs. Ag/Ag}^+$. Formic acid was also generated with a best Faradaic efficiency of 15% at $-1.5 \, \text{V vs. Ag/Ag}^+$. The efficiency for the formation of hydrogen was less than 1.1% below $-1.7 \, \text{V vs. Ag/Ag}^+$. At higher potentials, above $-1.9 \, \text{V vs. Ag/Ag}^+$, the Faradaic efficiency for formaldehyde and formic acid decreased, whereas that for hydrogen increased, because of the electrochemical decomposition of the electrolyte, which suppressed the direct reduction of CO$_2$, as observed in the cyclic voltammogram. Note that longer electrolysis (20 h) produced formaldehyde with a Faradaic efficiency of 74%, which is the same as that for a shorter electrolysis time (1 h).

Although there have been reports regarding the formation of formaldehyde during the electrochemical reduction of CO$_2$, the production of formaldehyde with such a high yield is quite difficult.[10] Formaldehyde is an industrially important material used for the production of plastics, such as resins, and of industrial chemicals for adhesives, paint, and preservatives. Presently, formaldehyde for industrial use is typically obtained from the catalytic oxidation of methanol, so an alternative high-yielding method for the production of formaldehyde, such as from CO$_2$, is desirable. Figure 3 shows a comparison of the Faradaic efficiency of products obtained through the electrochemical reduction of CO$_2$ in a methanol electrolyte at $-1.5 \, \text{V vs. Ag/Ag}^+$ using different electrodes. No formaldehyde was observed with metallic Cu, Sn, Ag, or W electrodes. With a glassy carbon electrode, a low Faradaic efficiency for formaldehyde (19%) was observed. Thus, the high-yield production of formaldehyde is an inherent property of BDD electrodes.

The mechanism for the production of formaldehyde in this case may be due to the presence of sp$^3$-bonded carbon on the BDD. Glassy carbon electrodes have a large amount of sp$^2$-bonded carbon, which results in a low Faradaic efficiency for formaldehyde. To compare the role of sp$^2$- and sp$^3$-bonded carbon in the production of formaldehyde, we fabricated a BDD electrode containing a large amount of sp$^3$-bonded carbon by controlling the preparation conditions. Characterization was done by Raman spectroscopy (Supporting Information, Figure S1). The BDD electrode with a large amount of sp$^3$-bonded carbon gave a low Faradaic efficiency (15%)
during electrochemical reduction of CO$_2$ in MeOH at $-1.5$ V vs. Ag/Ag$^+$. Thus, sp$^3$-bonded carbon may have specific properties beneficial for the production of formaldehyde. Formaldehyde can be formed by two electron reduction of formic acid.$^{[10]}$

$$\text{CO}_2 + 2\text{H}^+ + 2e^- \rightarrow \text{HCOOH}$$  \hspace{1cm} (1)

$$\text{HCOOH} + 2\text{H}^+ + 2e^- \rightarrow \text{HCHO} + \text{H}_2\text{O}$$  \hspace{1cm} (2)

Thus, CO$_2$ is reduced to form formic acid, which is then continuously reduced to produce formaldehyde. To test this hypothesis, we performed the electrochemical reduction of formic acid instead of CO$_2$ in MeOH at $-1.5$ V vs. Ag/Ag$^+$, for which a high Faradaic efficiency of formaldehyde production was obtained (85%). For comparison, a glassy carbon electrode and some metal electrodes (Cu, Sn, Ag, and W) were also used for the electrochemical reduction of formic acid. These exhibited quite low Faradaic efficiency, 6.4% and less than 0.1% for the glassy carbon and all of the metal electrodes, respectively. Thus, the BDD electrode is particularly efficient in the process of reducing formic acid to formaldehyde. Furthermore, it has been reported that BDD electrodes have an electrocatalytically inactive surface.$^{[18,20]}$ It has been reported in previous papers that electrocatalytically inactive surfaces preferentially produced formic acid.$^{[25,26]}$

Thus, the production of formaldehyde with the BDD electrode can be attributed to the reduction of formic acid produced from the reduction of CO$_2$. The formation of hydrogen competes with the electrochemical reduction of CO$_2$; therefore, it is very important to suppress the formation of hydrogen in order to avoid wasting energy on hydrogen evolution instead of using it for reducing CO$_2$. In this experiment, the wide potential window of BDD reduced the Faradaic efficiency for the formation of hydrogen.

As mentioned previously, the electrochemical reduction of CO$_2$ requires electrons and protons. Seawater is a better option as a source of both electrons and protons because of its abundance and conductivity. Thus, we next used seawater as an electrolyte. The use of seawater as the electrolyte yielded formaldehyde (36%) at room temperature and atmospheric pressure (Table S1). The poorer Faradaic efficiency, compared with the MeOH electrolyte, is due to the narrow potential window in water and the inorganic and organic impurities in seawater, which lower the chemical reduction of CO$_2$. For reference, we used water containing NaCl (0.1m) as the electrolyte, which gave a Faradaic efficiency of 62%. The higher Faradaic efficiency versus that of seawater can be attributed to the absence of impurities. In practice, the high conductivity of the BDD electrode is beneficial for the high production rate of formaldehyde. Indeed, the amount of formaldehyde produced was $7.5 \times 10^{-3}$ mol per hour for electrolysis in seawater ($-1.5$ V vs. Ag/AgCl), which is greater than that previously reported (for example, $1.4 \times 10^{-3}$ mol per hour for TiO$_2$).$^{[10]}$ These results suggest that formaldehyde can be effectively produced from CO$_2$ and seawater. Note that the BDD electrode has extremely good corrosion resistance compared to other electrodes, which is also beneficial for practical applications.

Finally, as durability is an important issue for industrial applications, we analyzed the electrochemical durability of a BDD electrode used in the electrochemical reduction of CO$_2$. The morphology of the BDD was examined by FE-SEM, which showed that it had not changed after electrochemical reduction, even after 20 h (Figure 4). The results were compared with those obtained for a glassy carbon electrode, whose surface was dramatically changed after 20 h of electrolysis, thus demonstrating another significant advantage that BDD has over other electrode types.

In conclusion, we have demonstrated the electrochemical reduction of CO$_2$ using a BDD electrode, which produces formaldehyde in high yield. Furthermore, the production of formaldehyde was performed using seawater as a source of both electrons and protons, which suggests that formaldehyde can be simply prepared from CO$_2$ and seawater under ambient conditions. If the electrical energy required for the reduction could be obtained from solar cells, we might thereby achieve artificial photosynthesis through the production of CO$_2$, water, and solar energy.

**Experimental Section**

BDD thin films were grown using a microwave plasma assisted chemical vapor deposition (MPVCD) system (ASTeX Corp. Woburn, MA). The boron source, B(OCH$_3$), was dissolved in acetone (as a carbon source) with a B/C atomic ratio of 1.0 w/w. BDD was deposited on Si(111) wafers in an MPCVD chamber at 5 kW using high-purity hydrogen as a carrier gas. BDD thin films with a high amount of sp$^3$-bonded carbon were prepared on Si(111) wafers in the MPCVD chamber (AX6500X, Scklo Technotron Corp.) at 6 kW using methane and B(OCH$_3$) as sources.

The surface morphology and crystalline structures were characterized using scanning electron microscopy. The typical size of the diamond crystals on the BDD electrodes was about 5 µm. To confirm the ratio of boron atoms in the BDD, glow discharge-optical emission spectroscopy (GDOES) was carried out on the obtained BDD and a BDD electrode with a known atomic ratio measured by secondary ion mass spectrometry (SIMS). The boron atomic ratio of the BDD was 1.45%.
To confirm the film quality of the BDD, Raman spectroscopy was carried out with Ar laser illumination (Acton-SP2500). Raman spectra were measured for the BDD electrodes. The presence of a narrow peak at 1324 cm\(^{-1}\) is attributed to the D band of sp\(^2\) bonded carbon in a BDD with a boron atomic ratio of 1.45%, which was shifted from 1332 cm\(^{-1}\) in natural diamond (Figure S1). This peak shift, which is usually observed in heavily doped diamond, is attributed to the quantum interference between this phonon and a narrow peak at 1324 cm\(^{-1}\) in the spectra of all BDD films are usually observed in metallic heavily doped BDD. In the spectrum of BDD with a high amount of sp\(^2\)-bonded carbon, an additional peak appeared at 1538 cm\(^{-1}\), which may be attributed to the G band of sp\(^2\)-bonded carbon. Further detail of morphology of the surface of BDD is shown in Figure S2. The apparatus for the electrochemical reduction of CO\(_2\) are shown in Figure S3. All of the electrochemical experiments were performed in a two-compartment cell (100 mL), using a platinum counter electrode and a Ag/Ag\(^+\) electrode as a reference. Methanol (99%, Nacalai Tesque, Japan) was used as received. Water was obtained from a Millipore Milli-Q Plus system. BDD electrodes were sonicated in ultrapure water prior to use. All experiments were performed in a two-compartment cell (100 mL), otherwise stated. The electroreduction procedure was as follows: First, N\(_2\) gas was bubbled into the electrolytes for 1 h at a rate of 100 mL/min to remove oxygen, after which CO\(_2\) gas was bubbled into the methanol for 2.5 h at a rate of 100 mL min\(^{-1}\). The obtained CO\(_2\)-saturated solution was electrolytically reduced at cathodic polarization. Stirring of the electrolyte was done with a magnetic bar. The Faradaic efficiency of formation for the products was calculated assuming that a total charge passed through the cell.

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Boron is a diamond's best friend: A boron-doped diamond (BDD) electrode exhibited very high Faradaic efficiency (74%) for the production of formaldehyde using either methanol, aqueous NaCl, or seawater as the electrolyte at room temperature and ambient pressure.