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CO₂ Reduction

High-Yield Electrochemical Production of Formaldehyde from CO_2 and Seawater[**]

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Abstract: *The catalytic, electrocatalytic, or photocatalytic conversion of CO_2 into useful chemicals in high yield for industrial applications has so far proven difficult. Herein, we present our work on the electrochemical reduction of CO_2 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 H_2. 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 sp^3-bonded carbon of the BDD. Our results have wide ranging implications for the efficient and cost-effective conversion of CO_2.*

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 CO_2 is a final product of the combustion process, the back conversion and utilization of CO_2 are important areas of research from the viewpoints of conservation of resources and the development of a sustainable society.[1–3] The use of CO_2 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 CO_2 with H_2O 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 CO_2 molecule is thermodynamically stable. To efficiently convert CO_2 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 CO_2 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 CO_2 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 CO_2 molecule requires a high overpotential,[17] which means that the evolution of hydrogen is a competitive process. This can reduce the efficiency of the CO_2 reduction. Thus, efficient catalysis is needed for the successful reduction of CO_2.

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 CO_2. In particular, the wide potential window promotes the reduction of CO_2, 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 CO_2 using BDD electrodes in various electrolytes, including seawater, which acts as a source for both electrons and protons.

To confirm the reduction of CO_2 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 CO_2 in MeOH is about five times that in water, thus allowing easier detection of the reduction of CO_2. 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 N_2 was bubbled. The N_2 was then replaced with CO_2 at a pressure of 1 atm, and after bubbling with CO_2 for

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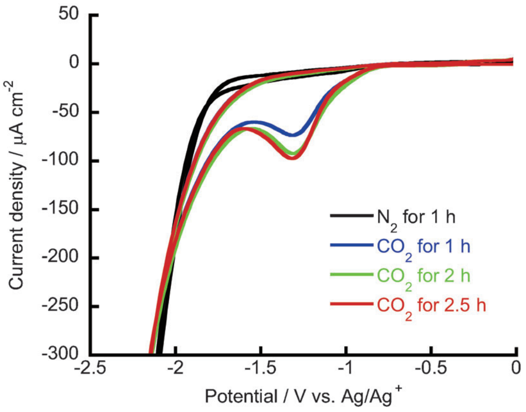

Figure 1. Cyclic voltammograms for a BDD electrode with CO_2. The cyclic voltammograms were measured in a MeOH solution (0.1 M) containing TBAP at a scan rate of 100 mV s^{-1}. First, cyclic voltammetry was performed at a pressure of 1 atm, with N_2 bubbled through the solution. After the measurement, the N_2 was replaced by CO_2 at a pressure of 1 atm. Cyclic voltammograms were measured after bubbling with CO_2 for 1 h, 2 h, and 2.5 h.

1 h, a large peak was observed at −1.3 V vs. Ag/Ag$^+$. The current density of the peak increased and became saturated to 97.5 µA 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 V vs. Ag/Ag$^+$. Formic acid was also generated with a best Faradaic efficiency of 15 % at −1.5 V vs. Ag/Ag$^+$. The efficiency for the formation of hydrogen was less than 1.1 % below −1.7 V vs. Ag/Ag$^+$. At higher potentials, above −1.9 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).

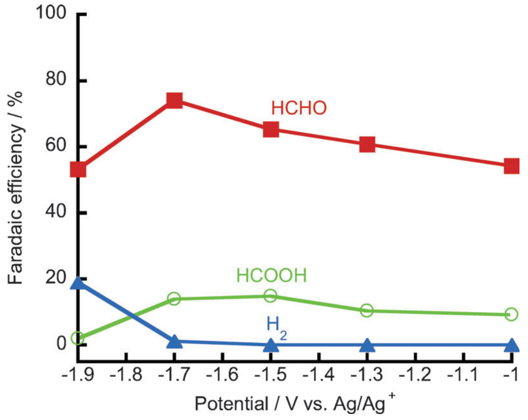

Figure 2. Faradaic efficiency of the various products obtained through the electrochemical reduction of CO_2 in a MeOH electrolyte, with respect to potential. The electrochemical reduction was performed in the range from −1.0 V to −1.9 V vs. Ag/Ag$^+$ using the BDD working electrode and platinum counter electrode in a two-compartment cell (100 mL) separated by Nafion for 1 h at room temperature and atmospheric pressure. After electrolysis, the gaseous products were collected in aluminium Tedlar bags and analyzed by gas chromatography. Products soluble in the electrolyte were analyzed by high-performance liquid chromatography.

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 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.

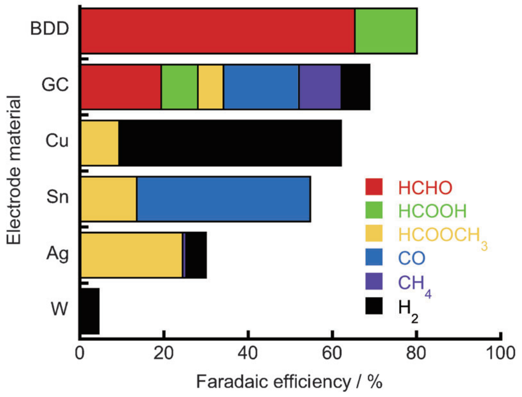

Figure 3. Faradaic efficiency of the products generated by the electrochemical reduction of CO_2 using various electrodes in a MeOH electrolyte. The electrochemical reduction was performed at −1.5 V vs. Ag/Ag$^+$ using a platinum counter electrode in a two-compartment cell (100 mL) separated by Nafion for 1 h at room temperature and atmospheric pressure.

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^3- and sp^2-bonded carbon in the production of formaldehyde, we fabricated a BDD electrode containing a large amount of sp^2-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^2-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]

$$CO_2 + 2H^+ + 2e^- \rightarrow HCOOH \quad (1)$$

$$HCOOH + 2H^+ + 2e^- \rightarrow HCHO + H_2O \quad (2)$$

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 electrochemical reduction of CO_2. For reference, we used water containing NaCl (0.1 M) 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 folmaldehyde. Indeed, the amount of formaldehyde produced was 7.5×10^{-3} M per hour for electrolysis in seawater (−1.5 V vs. Ag/AgCl), which is greater than that previously reported (for example, 1.4×10^{-3} M 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.

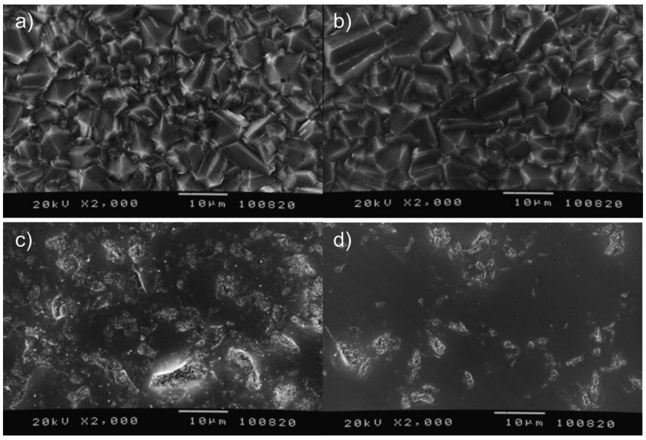

Figure 4. SEM images before and after the electrolysis for 20 h. a,b) BDD electrode before (a) and after (b) electrolysis. c,d) Glassy carbon electrode before (c) and after (d) electrolysis. Scale bars are 10 μm.

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^2-bonded carbon were prepared on Si(111) wafers in the MPCVD chamber (AX6500X, Seki 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) 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^3 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 continuum of electronic transitions. The large bands observed at around 477 cm^{-1} and 1204 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 cyclic voltammograms were taken at a scan rate of 100 $mV s^{-1}$, unless 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 $mL min^{-1}$ 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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