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Stable and Highly Efficient Electrochemical Production of Formic Acid from Carbon Dioxide Using Diamond Electrodes

Keisuke Natsui,[a] Hitomi Iwakawa,[a] Norihito Ikemiya,[a] Kazuya Nakata,[b] and Yasuaki Einaga*[a,c]

Abstract: High faradaic efficiencies can be achieved in the production of formic acid (HCOOH) by metal electrodes, such as Sn or Pb, in the electrochemical reduction of carbon dioxide (CO_2). However, the stability and environmental load in using them are problematic. Here, we investigated the electrochemical reduction of CO_2 to HCOOH in a flow cell using boron-doped diamond (BDD) electrodes. BDD electrodes have superior electrochemical properties to metal electrodes, and, moreover, are highly durable. The faradaic efficiency for the production of HCOOH was as high as 94.7%. Furthermore, the selectivity for the production of HCOOH was more than 99%. The rate of the production was increased to 473 μmol m^{-2} s^{-1} at a current density of 15 mA cm^{-2} with a faradaic efficiency of 61%. The faradaic efficiency and the production rate are almost the same as or larger than those achieved using Sn and Pb electrodes. In addition, the stability of the BDD electrodes was confirmed by 24 hours operation.

Carbon dioxide (CO_2) is well known as the most significant greenhouse gas, and the continual increase in the atmospheric concentration of CO_2 have lead to climate change. It is a serious problem for the world. Consequently, many researchers have made great efforts to develop solutions for reducing CO_2 in the atmosphere, such as the development of renewable energy sources[1] and carbon capture and storage (CCS) technology.[2] From another point of view, CO_2 is a cheap and abundant source of carbon, so the utilization of CO_2 is of great interest. In the past few decades, various methods to convert CO_2 into useful chemicals and fuels have been tried, such as photochemical,[3-5] electrochemical,[6-9] and photoelectrochemical methods.[10-12] Of these, a great deal of attention has been devoted to electrochemical methods, since these can be performed under ambient temperature and pressure conditions, and, moreover, these methods are relatively easy to operate on a large scale for practical applications. Various chemicals can be produced by the electrochemical reduction of CO_2, such as formic acid/formate ($HCOOH/HCOO^-$), carbon monoxide (CO), methane (CH_4), alcohol, and hydrocarbons.[9]

HCOOH is an important chemical for industry (leather, rubber, medicine, fiber, etc.). In addition, HCOOH has recently become regarded as an excellent fuel for direct fuel cells[13] and a useful hydrogen-storage material.[14] There are many reports on the production of HCOOH by the electrochemical reduction of CO_2 using various cathode materials such as Sn, Pb, Cd, Hg, In, Pd-Pt nanoparticles, and so on.[15-19] Especially, Sn and Pb electrodes have been frequently used, because they are cheap and high faradaic efficiencies for producing HCOOH can be achieved (e.g. 88.4% and 97.4%, respectively).[15] However, their environmental load is very high, and their stability also seems to be problematic.[20]

Boron-doped diamond (BDD) is the most promising alternative to these electrodes, because BDD is metal-free and, as such, is environmentally friendly. It also has excellent electrochemical properties such as a wide potential window in aqueous solutions and high durability derived from intrinsic diamond.[21] It is expected that the wide potential window will enable the suppression of hydrogen evolution, which is a competing reaction in the reduction of CO_2, leading to more efficient production of the desirable products. In fact, using BDD for the electrochemical reduction of CO_2, we were able to produce formaldehyde[22], methanol[23], and HCOOH[24] with high faradaic efficiencies. However, in our previous paper, the maximum faradaic efficiency for HCOOH was only 71% using a two-compartment batch cell.[24]

In this paper, in an effort to achieve greater efficiency in the production of HCOOH, we investigated the electrochemical reduction of CO_2 with BDD electrodes using a circulation flow cell (Figure 1). With this cell the mass-transport of CO_2 onto the electrode is improved, and we were able to obtain a high faradaic efficiency for the production of HCOOH (94.7%) at a high production rate.

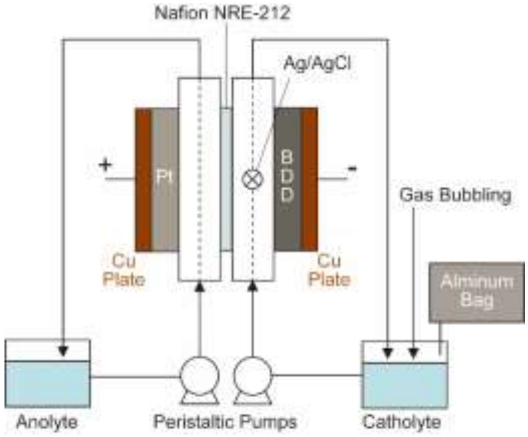

Figure 1. Schematic diagram of two-compartment flow cell.

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First, we investigated the effect of the flow rate of the electrolyte on the electrochemical reduction of CO_2 using a BDD electrode. The electroreduction of CO_2 was performed with a BDD electrode at a current density of 2 mA cm^{-2} for 60 min with various flow rates. The main product was HCOOH, plus a small amount of CO. Moreover, H_2 was also obtained, which is a competing reaction. The amounts of other products were negligible. The production rates of HCOOH and the faradaic efficiencies for the products are summarized in Table 1. Note that the measurements were repeated three times (n = 3) for each condition, and we calculated the means and standard deviations of the faradaic efficiencies and production rates. The production rate is defined as the quantity of HCOOH (mol) produced per unit cathode area (m^2) and unit time (s). The faradaic efficiency for the production of HCOOH increased to 94.7% with increasing flow rate to 200 mL min^{-1}, whereas the faradaic efficiency for the production of H_2 decreased. In addition, the selectivity for the production of HCOOH by CO_2 reduction was more than 99%. The selectivity for end products by CO_2 reduction depends on the binding ability of electrode surface for the produced intermediates ($CO_2^{\bullet-}$).[7] HCOOH/HCOO$^-$ is formed on the electrodes which can hardly bind the $CO_2^{\bullet-}$. As the BDD surface is inert,[25] the $CO_2^{\bullet-}$ could be hardly bound. Thus, the highly selective production of HCOOH could be achieved on the BDD electrode. In a previous work,[26] nitrogen-doped diamond also can produce HCOO$^-$, though acetate is the main product. This implies that diamond surface seems to have a tendency for HCOOH production. At 20 mL min^{-1}, the combined faradaic efficiency was less than 100%, possibly due to H_2 gas partially leaking from the electrolysis cell.

Table 1. Electrochemical reduction of CO_2 using a BDD electrode in a flow cell at 2 mA cm^{-2} for 60 min with various flow rates of the electrolytes.

Flow rate (ml min^{-1})	Production rate of HCOOH (μmol m^{-2} s^{-1})	Faradaic efficiency (%)			
		HCOOH	CO	H_2	Total
20	36.6±9.8	35.4±9.4	0.4±0.1	40.8±9.6	76.6±5.1
50	87.7±2.0	84.7±2.0	0.9±0.6	8.6±2.5	94.2±0.7
100	94.3±0.8	91.1±0.7	0.5±0.4	3.6±1.3	95.2±0.9
200	97.9±2.3	94.7±2.3	0.6±0.5	4.1±1.9	99.4±0.6
500	91.4±1.9	88.4±1.8	2.7±2.6	8.1±3.4	99.2±0.8

Figure 2 shows chronopotentiograms during CO_2 reduction using a BDD electrode at various flow rates of the electrolyte. As can be seen in Figure 2, the reduction potential shifts to more positive values with increasing flow rate. In addition, linear sweep voltammograms after CO_2 saturation on a BDD electrode with a scan rate of 100 mV s^{-1} at various flow rates of the electrolytes showed that the reduction current increased and the onset potential shifted to more positive values with increasing flow rate (Figure S2). These suggest that the reduction reaction can proceed at a lower potential because fresh reactants are brought more frequently to the electrode surface due to the increased flow rate. Therefore, it is assumed that as the mass-transport of the CO_2 increases, so also does the faradaic efficiency for the production of HCOOH compared to the H_2 evolution reaction. In addition, the highly efficient CO_2 reduction is probably related to not only the use of a flow cell, but also the property of the BDD electrode. Referring to the previous report,[26] the positively charged B atoms, which caused by polarization of B-C bonds due to low electronegativity of B, and defects on BDD may stabilize the produced $CO_2^{\bullet-}$ on the BDD surface by the electronic interaction, and thus the energy barrier is reduced, resulting in the acceleration of CO_2 reduction. Moreover, the high H_2 overpotential of the BDD electrode can suppress the H_2 evolution reaction, leading to the improvement of the efficiency for CO_2 reduction. On the other hand, the faradaic efficiency for the production of HCOOH decreases slightly from 94.7% at 200 mL min^{-1} to 88.4% at 500mL min^{-1}. This may be because the rate is so fast that it inhibits electron transfer from the electrode to the CO_2 at a current density of 2 mA cm^{-2}, and H_2O, of which there is a greater amount than CO_2, is preferentially reduced to H_2 gas. Thus far, the maximum faradaic efficiency for the production of HCOOH, 94.7%, is the best value achieved for CO_2 reduction using a BDD electrode. Recently, we reported on the production of HCOOH by CO_2 reduction using a BDD electrode in an H-type cell.[24] In that case, the maximum faradaic efficiency was 71% using Rb$^+$ cations, which are relatively high cost. Also, the production rate of HCOOH was lower (76.5 μmol m^{-2} s^{-1}) than the present case operating at the same current density (2 mA cm^{-2}). The improvements here are due to the increased mass-transport of CO_2 using the flow cell.

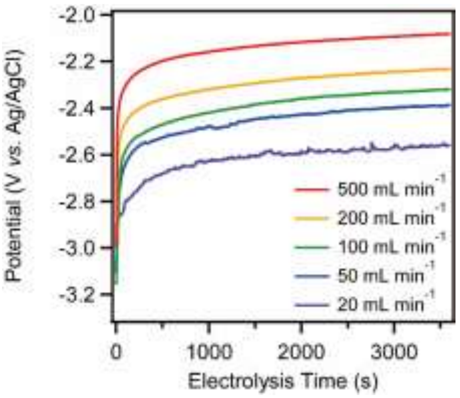

Figure 2. Chronopotentiograms with a BDD electrode at 2 mA cm^{-2} for 60 min with flow rates of 20 mL min^{-1} (purple), 50 mL min^{-1} (blue), 100 mL min^{-1} (green), 200 mL min^{-1} (orange), and 500 mL min^{-1} (red).

Next, we investigated the dependence of the faradaic efficiency and the production rate of HCOOH on current density. In order to obtain increased amounts of HCOOH, the current density was increased. Electroreduction of CO_2 was performed using a BDD electrode at current densities of 2, 5, 10, 15, and 20 mA cm^{-2} for 60 min with flow rates of 200 mL min^{-1} and 500 mL min^{-1}. Figure 3 shows the faradaic efficiency and the production rate of HCOOH as functions of the applied current density. At 20 mA cm^{-2}, the faradaic efficiency for HCOOH has dropped to just 19%, and the production rate has also been significantly reduced, because H_2 evolution occurs much easily compared to CO_2 reduction.

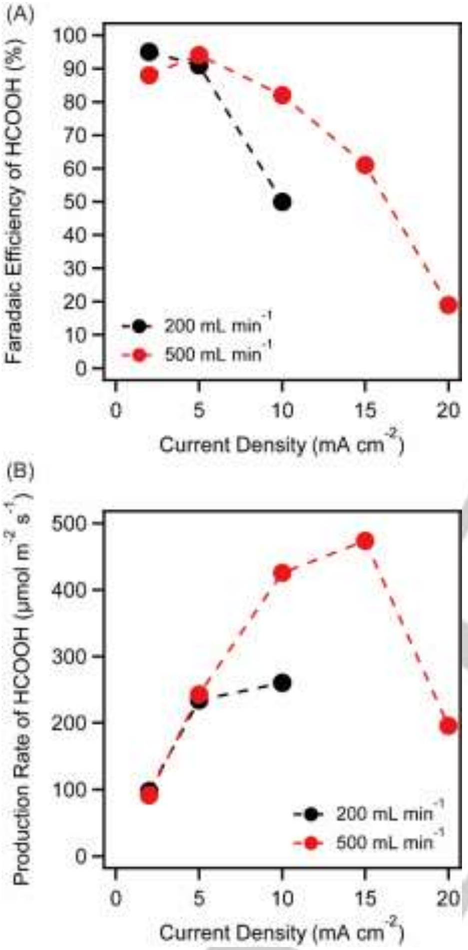

Figure 3. Faradaic efficiency (A) and production rate (B) of HCOOH by electrochemical reduction of CO_2 with a BDD electrode at various current densities with flow rates of 200 mL min^{-1} (black) and 500 mL min^{-1} (red). The dashed lines in the figures are guides for eye.

In Figure 3A, the faradaic efficiency for HCOOH decreases with increasing applied current density. Note that no other products were obtained and H_2 evolution increases with increasing current density. Increasing the current density means that the rate of electron transfer between the electrode and the reactants is increased. Thus, it is assumed that the transport rate of CO_2 onto the cathode becomes slower than the rate of electron transfer as the current density increases, so that the faradaic efficiency for the production of HCOOH decreases. In addition, the faradaic efficiencies at 500 mL min^{-1} are larger than those at 200 mL min^{-1} when a high current density is applied. This is also because the mass transport of CO_2 at 500 mL min^{-1} is higher than at 200 mL min^{-1}. On the other hand, the production rate of HCOOH is 473 μmol m^{-2} s^{-1} at 15 mA cm^{-2} and 500 mL min^{-1} (Figure 3B). This value is larger than the rates for Sn and Pb electrodes using a similar flow cell as this work in a previous work (e.g. 440 μmol m^{-2} s^{-1} at a faradaic efficiency of around 70% with Sn).[27]

Finally, we investigated the electrochemical reduction of CO_2 at 2 mA cm^{-2} with a flow rate of 200 mL min^{-1} for 24 hours to confirm the stability of the production of HCOOH and the durability of the BDD electrode. These conditions are those that gave the highest faradaic efficiency for the production of HCOOH achieved in this work. During the electrolysis, CO_2 gas was bubbled to maintain saturation. In Figure 4A, the faradaic efficiency remained at around 90% for 24 hours. Moreover, the concentration of HCOOH increased linearly with the electrolysis time, as shown in Figure 4B. Therefore, we confirmed the stability of the production of HCOOH by CO_2 reduction using a BDD electrode in a flow cell under the above conditions for at least 24 hours. In addition, no degradation of the BDD electrode was observed by SEM after 24 hours of electrolysis (data not shown).

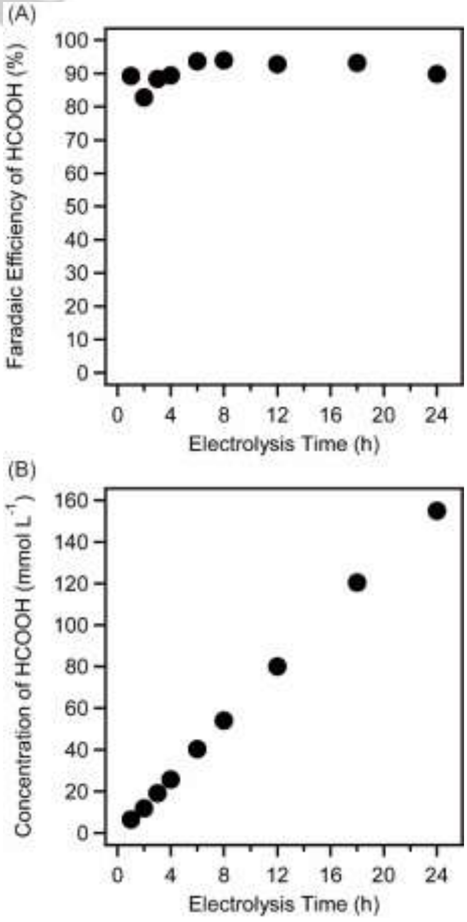

Figure 4. Faradaic efficiency (A) and concentration (B) of HCOOH by the electrochemical reduction of CO_2 with a BDD electrode at 2 mA cm^{-2} and a flow rate of 200 mL min^{-1}.

In this work, we investigated the electrochemical reduction of CO_2 using a boron-doped diamond (BDD) electrode in a two-compartment flow cell to obtain HCOOH efficiently. The faradaic efficiency for the production of HCOOH increased with increasing flow rate of the electrolyte, reaching a maximum of 94.7%, due to the greater mass transport of CO_2 onto the BDD surface. This value is almost equivalent to that achieved with other metal electrodes, such as Sn (88.4%) and Pb (97.4%).[15] In addition, the selectivity for the production of HCOOH by CO_2 reduction was more than 99%. On the other hand, although the faradaic efficiency for the production of HCOOH decreased with increasing applied current density, the production rate of HCOOH was as much as 473 μmol m^{-2} s^{-1} at 15 mA cm^{-2} and 500 mL min^{-1} with a faradaic efficiency of 61%. This production rate is also comparable to the values for Sn and Pb electrodes using a similar flow cell (440 μmol m^{-2} s^{-1} with a faradaic efficiency of around 70%).[27] Moreover, we confirmed the stability of the BDD electrode after electrochemical reduction of CO_2 for 24 hours at 2 mA cm^{-2}. Consequently, we found that the use of BDD electrodes is a viable alternative to other metal electrodes with which HCOOH can be produced, such as Sn and Pb. However, so far, the detailed mechanisms about highly selective and efficient production of HCOOH on the BDD electrodes using the flow cell are unclear. To elucidate the mechanisms, the investigations into the concentration of CO_2 near the electrode surface and the intermediates of CO_2 reduction using *in situ* infrared attenuated total reflection (IR-ATR) technique are now in progress. In the next phase, it should be possible to further improve the faradaic efficiency and the production rate by making a gas diffusion electrode system[28] using BDD.

Experimental Section

BDD electrodes were prepared on Si wafer substrates using a microwave plasma-assisted chemical vapor deposition system (AX5400, Corns Technologies Ltd.) following a procedure described in our previous paper.[29] The boron-to-carbon ratio in the feed gases was 1000 ppm, and the deposition time was 6 hours. Characterization of the BDD was performed by Raman spectroscopy (excited wavelength: 532 nm) and a scanning electron microscope (SEM). Raman spectra were recorded using an Acton SP2500 (Prinston Instruments), and SEM images were taken with a JCM-6000 Plus (JEOL). The Raman spectra of the obtained BDD showed an asymmetrical sharp peak at 1332 cm^{-1} due to the zone-center optical phonon of diamond.[30] This asymmetrical feature is attributed to the Fano-effect,[31] which is typically observed in semimetallic BDD (boron concentration $\geq 10^{20}$ cm^{-3}).[32] SEM images of the BDD showed that it had a polycrystalline nature with a grain size of about 10~20 μm.

KCl, KOH, and H_2SO_4 were purchased from Wako Pure Chemical Industries Ltd., and used without any further purification. Deionized water with a resistivity of 18.2 MΩ cm at 25 °C was obtained from a Simply-Lab water system (DIRECT-Q 3 UV, Millipore).

Electrochemical measurements were performed under atmospheric pressure and temperature in a two-compartment PTFE flow cell separated with Nafion NRE-212 (Sigma-Aldrich) membrane using a potentiostat/galvanostat system (PGSTAT204, Metrohm Autolab), as shown in Figure 1. The construction details of the flow cell are shown in Figure S1. BDD, a Pt plate, and Ag/AgCl (saturated KCl) were used as the working, counter, and reference electrodes, respectively. The geometric area of the BDD electrode in the contact with electolyte was 9.62 cm^2 (diameter: 3.5 cm). The interelectrode gap between the BDD electrode and the Pt plate was 3 cm. Electrical contacts were made between Cu plates and the back sides of the BDD electrode and the Pt plate. Before each electrolysis, the BDD electrode was cleaned using an electrochemical pretreatment (10 cycles between potentials of −3.5 V and 3.5 V and then 20 cycles between potentials of 0 V and 3.5 V with a scan rate of 1 V s^{-1} in a 0.1 M H_2SO_4 aqueous solution). 0.5 M KCl aqueous solution (50 mL) was used as the catholyte, and 1.0 M KOH (50 mL) was used as the anolyte. The catholyte was bubbled with N_2 for 30 min to remove dissolved oxygen, and then bubbled with CO_2 for 60 min. After saturation with CO_2, the pH of the catholyte was around 3.9. Linear sweep voltammetry (LSV) after CO_2 bubbling was performed with a scan rate of 100 mV s^{-1} from −0.5 to −2.5 V (*vs*. Ag/AgCl), while circulating the electrolytes using peristaltic pumps with the flow rates of 20, 50, 100, 200, and 500 mL min^{-1} (Figure S2). Electrolysis of the CO_2 was performed at current densities of 2, 5, 10, 15, and 20 mA cm^{-2} for 60 min. CO_2 bubbling was maintained during electrolysis. The electrolytes were circulated during electrolysis using peristaltic pumps, and the flow rates of the electrolytes were 20, 50, 100, 200, and 500 mL min^{-1}. After electrolysis, N_2 gas was bubbled through the catholyte for 15 min to collect the gas products into an aluminum bag. The liquid products were analyzed using a high-performance liquid chromatograph equipped with an electroconductivity detector (CDD-10A, Shimadzu Corp.), and the gas products were analyzed using a gas chromatograph equipped with a flame ionization detector and a thermal conductivity detector (GC-2014, Shimadzu Corp.). The faradaic efficiency was estimated using the following equation:

$$\text{Faradaic efficiency (\%)} = nFc/Q \times 100 \qquad (1)$$

where n is the number of electrons involved in reducing the CO_2 to the product, F is the Faraday constant (96,485 C mol^{-1}), c is the amount of product (mol), and Q is the total charge passed through the reduction process (C).

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Conflict of interest

The authors declare no conflict of interest.

Keywords: boron • diamond • electrochemistry • carbon dioxide • formic acid

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COMMUNICATION

Efficient CO_2 conversion: Formic acid could be obtained with high faradaic efficiency, as high as 95%, by the electrochemical reduction of CO_2 on boron-doped diamond (BDD) electrodes using a circulation flow cell. Moreover, the stability of the BDD electrodes was confirmed by operating the system for 24 hours. We found that the use of BDD electrodes is a viable alternative to other metal electrodes with which formic acid can be produced.

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