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Switchable Product Selectivity in the Electrochemical Reduction of Carbon Dioxide Using Boron-Doped Diamond Electrodes

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KEYWORDS: boron-doped diamond, carbon dioxide, carbon monoxide, electrochemistry, infrared spectroscopy

ABSTRACT: The main product obtained by electrochemical reduction of CO_2 depends on the electrode material, and in many cases the faradaic efficiency for this is determined by the electrolyte. Only a few investigations in which attempts to produce different products from the same electrode material have been done so far. In this work, we focus on boron-doped diamond (BDD) electrodes with which plentiful amounts of formic acid and small amounts of carbon monoxide have been produced. By optimizing certain parameters and conditions used in the electrochemical process with BDD electrodes, such as the electrolyte, the boron concentration of the BDD electrode, and the applied potential, we were able to control the selectivity and efficiency with which carbon monoxide is produced. With a BDD electrode with 1% boron used for the cathode and $KClO_4$ for the catholyte, the selectivity for producing carbon monoxide was high. On the other hand, with a BDD electrode with 0.1% boron used for the cathode and KCl for the catholyte, the production of formic acid was the most evident. *In-situ* ATR-IR measurements during electrolysis showed that $CO_2^{\bullet-}$ intermediates were adsorbed on the BDD surface in the $KClO_4$ aqueous solution. Here, switchable product selectivity was achieved when reducing CO_2 using BDD electrodes.

1. Introduction

The conversion of carbon dioxide (CO_2) into value added products has attracted the attention of many researchers. Atmospheric CO_2 is considered to be a greenhouse gas and therefore must be reduced. On the other hand, CO_2 is an abundant source of carbon and conversion of CO_2 into useful carbon-based chemicals by organic, biochemical, photochemical or electrochemical processes is desirable[1,2]. Of these methods, electrochemical conversion has some advantages, because the conditions used for this type of process are moderate and the reactions can be easily controlled by adjusting the applied potential or current.

CO_2 can be electrochemically reduced to produce formic acid, carbon monoxide, hydrocarbons, or alcohols. It is well known that the main product obtained by the electrochemical reduction of CO_2 depends on the electrode material. Metal electrodes are classified into several groups according to the adsorption strength of $CO_2^{\bullet-}$, the CO_2 anion radical, which is an intermediate in the CO_2 reduction reaction[2,3,4]. Sn, Pb, In, and Hg, which do not adsorb $CO_2^{\bullet-}$, mainly produce formic acid or formate; Ag, Au, and Zn, which do adsorb $CO_2^{\bullet-}$, mainly produce carbon monoxide. Cu, an electrode used specifically for the CO_2 reduction, produces hydrocarbons and alcohols. In addition, electrolytes can affect the faradaic efficiencies of the products, so in much previous research the effect of the cations and anions of the electrolytes on CO_2 reduction using several metal electrodes has been investigated[5,6,7,8,9,10,11]. However, it is of great interest to produce different products from the same electrode material, not by optimizing the electrode material, but by optimizing the electrolysis conditions as in previous studies[12,13].

Many metal electrodes used for the electroreduction of CO_2 have problems of toxicity or stability[2,14]. Boron-doped diamond (BDD) is a promising electrode for CO_2 reduction. Made from carbon and boron, BDD contains no metals, and has a wide potential window compared to metal electrodes in aqueous solutions, so the hydrogen evolution reaction, which is a competitive reaction, occurs at high potential and the CO_2 reduction reaction can be made the dominant one. Moreover, BDD has high chemical and physical stability[15,16,17], so the electrolysis can be continued for a long time[18]. In our previous studies[19,20,21,22,23], electrochemical reduction of CO_2 using BDD electrodes produced formaldehyde, methanol, formic acid and carbon monoxide depending on the conditions such as electrolyte, boron content of BDD, and so on. Of these products, formic acid and carbon monoxide were obtained easier than other products because they are two-electron reductants. Both formic acid and carbon monoxide are used in many industrial fields. Formic acid is an excellent fuel for direct fuel cells[24] and can be used as a carrier for hydrogen[25]. Carbon monoxide is an important raw material in C1 chemistry and is used as a ligand in inorganic chemistry. However, currently, the faradaic efficiency for the production of carbon monoxide from CO_2 reduction using BDD electrodes is much less than that for the production of formic acid. In this work, we optimized the electrolysis conditions, including the electrolyte, the boron concentration in the electrode, and the applied potential, to produce carbon monoxide selectively and more efficiently by the electrochemical reduction of CO_2 using BDD electrodes.

2. Experimental

2.1. Preparation and characterization of the BDD electrodes

The BDD electrodes were deposited onto Si wafer substrates in a microwave plasma-assisted chemical vapor deposition (MPCVD) system (AX5250M, AX6500; Cornes Technologies Ltd.). The boron-to-carbon ratio in the feed gases was 1000 ppm (0.1%) and 10000 ppm (1%) (0.1% BDD, 1% BDD) and deposition was carried out for 6 hours at 6 kW and 5 kW, respectively, using conditions reported in a previous paper[26]. For the 0.1% BDD electrode, the carbon and boron sources were methane and trimethylboron, respectively. On the other hand, for the 1% BDD electrode, the carbon and boron sources were acetone and trimethyl borate, respectively. The BDD electrodes were characterized by Raman spectroscopy (excited wavelength: 532 nm), scanning electron microscopy (SEM), and glow discharge optical emission spectrometry (GDOES). Raman spectra were recorded with an Acton SP2500 (Instruments). The SEM images were obtained with a JCM-6000Plus (JEOL Ltd.), and GDOES analysis was conducted using a GD-Profiler2 (HORIBA Ltd.) to estimate the boron concentration in the BDD films. The results of the characterizations are shown in the Supporting Information.

2.2. Chemicals

$KClO_4$, KCl, HCl, HNO_3, and $HClO_4$ were purchased from FUJIFILM Wako Pure Chemical Corporation. Formic acid (FUJIFILM Wako Pure Chemical Corp.), formaldehyde solution (37 wt.% in H_2O, contains 10-15% Methanol; Sigma-Aldrich), methanol (Tokyo Chemical Industry Co., Ltd.), and ethanol (Kanto Chemical Co., Inc.) were used to make standard solutions for quantitative analysis. All the chemicals were used without any purification. All the aqueous solutions were prepared from ultrapure water with a resistivity of 18.2 MΩ cm at 25°C obtained from a DIRECT-Q UV3 system (Millipore Corp.).

2.3. Procedure for the electrolysis

The BDD electrodes were pretreated by immersion in aqua regia for 30 min and UV- ozone oxidation using a low-pressure mercury lamp (UVB40; Sen Lights Corp.) for 30 min, as described in our previous work[23]. For the purposes of comparison, a Sn (99.9%; Nilaco Corp.) electrode was also prepared. This was pretreated by polishing with sandpaper (Ultra fine #800-1000; 3M) to get a clean surface.

A two-compartment flow cell made of PTFE[27] was used for the electrolysis of CO_2. The compartments were separated by a Nafion membrane (Nafion® NRE-212; Sigma-Aldrich). 0.1% BDD, 1% BDD, or Sn was used for the working electrode. A Pt plate and Ag/AgCl (3 mol L^{-1} NaCl) were used for the counter and reference electrodes, respectively. The geometric areas of the working and counter electrodes of this cell[27] were both 9.62 cm^2. 0.1 mol L^{-1} $KClO_4$ and KCl aqueous solutions were used for the electrolytes. The volumes of the catholyte and anolyte were each 50 mL. Unless noted otherwise, the electrolytes were circulated at a flow rate of 100 mL min^{-1}.

N_2 gas was bubbled into the catholyte for 30 min at a gas flow rate of 200 mL min^{-1} to remove the dissolved oxygen and then CO_2 gas was bubbled for 15 min at a gas flow rate of ca. 250 mL min^{-1}. At the same time the electrolytes were circulated. Electrolysis was carried out at constant potential using a potentiostat/galvanostat system (PGSTAT204; Metrohm Autolab) until the total charge had reached 69 C. CO_2 was bubbled into the solution at a flow rate of less than 25 mL min^{-1} during electrolysis. After electrolysis, N_2 gas (50 mL min^{-1}) was bubbled for 10 min to collect the gas products. All the experiments were conducted at room temperature (20-25°C) and atmospheric pressure (1 atm).

The products obtained by CO_2 reduction were quantified by a high-performance liquid chromatography (HPLC) system equipped with an electroconductivity detector or a UV-visible detector (Prominence; Shimadzu Corp.), a gas chromatography (GC) system equipped with a thermal conductivity detector or a flame ionization detector (GC-2014; Shimadzu Corp.), and a gas chromatography-mass spectrometer (GCMS-QP2010 Ultra; Shimadzu Corp.). Details of the analysis are given in our previous paper[23]. The faradaic efficiency was calculated using equation (1):

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

where n is the number of electrons used in producing the products from CO_2, F is the Faraday constant (96,485 C mol^{-1}), c is the amount of the product (mol), and Q is the total charge passed in the reduction process (69 C). All electrolysis experiments were conducted once at a time.

2.4. *In-situ* ATR-IR measurements

A submicrometer thick BDD film was deposited onto a Si ATR-IR prism using the MPCVD system described above. The carbon and boron sources were methane and trimethylboron, respectively. In order to enable isotope labeling, BDD films were prepared with both $^{12}CH_4$ (^{12}C-BDD) and $^{13}CH_4$ (^{13}C-BDD). The BDD prism was characterized by Raman spectroscopy, SEM (JSM-7600F; JEOL Ltd.), GDOES, and a stylus profiler (Dektak™; Bruker Corp.). Data are shown in Figure S2. The BDD prism, a glassy carbon rod, and Ag/AgCl (3 mol L^{-1} NaCl) were used as the working, counter, and reference electrodes, respectively. Electrical contact to the BDD film was made using Ag paste and placing Au tape at the edge of the prism. Electrochemical measurements were carried out with a PGSTAT204 (Metrohm Autolab). ATR-IR spectra were measured with a FT/IR-6600 (JASCO Corp.) using a liquid nitrogen cooled MCT detector. Each spectrum was collected at a resolution of 4 cm^{-1} and had 256 scans.

3. Results and discussion

The electrochemical reduction of CO_2 was performed using BDD and Sn electrodes in $KClO_4$ and KCl aqueous solutions. The main products obtained by CO_2 reduction were carbon monoxide and formic acid. Methanol and methane were hardly obtained. In addition, hydrogen was detected. The faradaic efficiencies for the products are summarized in Table S1. From the experiments, the conditions to produce carbon monoxide efficiently were optimized.

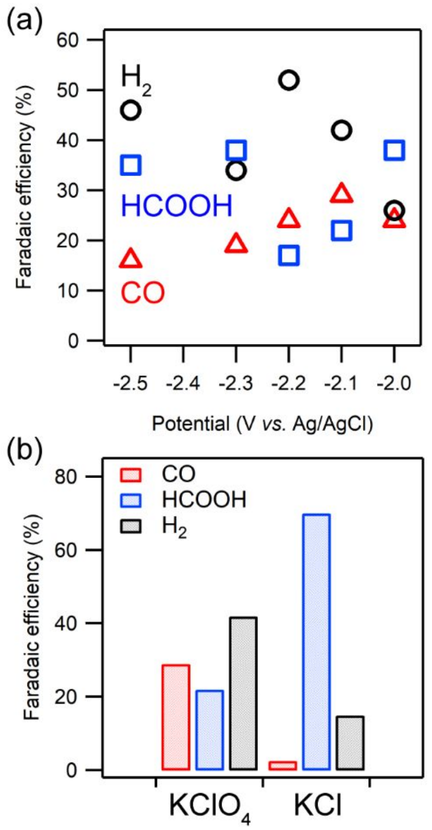

Figure 1. (a) Faradaic efficiencies for producing carbon monoxide (red triangles), formic acid (blue squares), and hydrogen (black circles) by the electrochemical reduction of CO_2 with a 0.1% BDD electrode in 0.1 mol L^{-1} $KClO_4$ aqueous solution. (b) Comparison between the electrochemical reduction of CO_2 using a 0.1% BDD electrode at −2.1 V (*vs.* Ag/AgCl) in $KClO_4$ and in KCl aqueous solutions.

3.1. The electrochemical reduction of CO_2 using BDD electrodes

3.1.1. The effect of the electrolyte on the production of carbon monoxide

First, we investigated how the electrolyte can affect the selectivity of the products. Figure 1a shows the faradaic efficiencies for producing carbon monoxide, formic acid, and hydrogen using a 0.1% BDD electrode in $KClO_4$ aqueous solution. The faradaic efficiency for the production of carbon monoxide increased when the applied potential became less negative, and reached a maximum at −2.1 V (*vs.* Ag/AgCl). The faradaic efficiency for formic acid production decreased and then increased when the applied potential became less negative. The selectivity for the production of carbon monoxide is maximum at −2.2 V (*vs.* Ag/AgCl).

In previous research[27], formic acid was produced with high efficiency by electrolysis in an aqueous solution of KCl. Electrolysis in KCl was also conducted in this study, but at the same potential at which the production of carbon monoxide was a maximum in $KClO_4$ aqueous solution (−2.1 V *vs.* Ag/AgCl). The results for the two electrolysis are shown in Figure 1b. When KCl was used for the electrolyte, the faradaic efficiency for producing formic acid was high, and very little carbon monoxide was obtained. From these experiments, it can be concluded that carbon monoxide is produced more easily when $KClO_4$ is used as the electrolyte rather than when KCl is used.

It is supposed that the anions in the electrolytes have some effect on the selectivity of the products. The effect of anions has been investigated by many research groups, and it has been suggested that the CO_2 reduction reaction can be influenced by the buffering effect of the anions, or by the specific adsorption of anions on the electrode surface[2,9,10,11]. It has also been reported that the anions have little effect on CO_2 reduction[28]. However, BDD is a carbon-based electrode, so these assertions cannot be applied directly to this research. Generally, carbon monoxide is produced using electrodes at which the intermediate in the CO_2 reduction reaction ($CO_2^{\bullet -}$) is easily adsorbed, whereas formic acid is produced using electrodes for which the adsorption of the $CO_2^{\bullet -}$ intermediate is difficult. When $KClO_4$ is used as the electrolyte, adsorption of the $CO_2^{\bullet -}$ intermediate on the electrodes can be promoted, so carbon monoxide production is high. On the other hand, when KCl is used as the electrolyte, adsorption of the $CO_2^{\bullet -}$ intermediate on the electrodes is more difficult, so the production of formic acid is promoted. From the results of electrolysis obtained by CO_2 reduction using $KClO_4$, KCl, and other electrolytes (Table S1), perchlorate ions play an important role in the electroreduction of CO_2 using BDD electrodes.

3.1.2. *In-situ* ATR-IR measurements during CO_2 reduction

In order to obtain an insight into the effect of the anions, ATR-IR measurements were conducted during electrolysis in 0.1 mol L^{-1} $KClO_4$ and KCl aqueous solutions.

Figure 2 shows time-dependent ATR-IR spectra during CO_2 reduction in 0.1 mol L^{-1} $KClO_4$ and KCl aqueous solutions, respectively. After anodic oxidation (+3 V *vs.* Ag/AgCl, 0.1 mol L^{-1} $HClO_4$ aqueous solution, 5min), a background spectrum was taken just after the reduction potential (−2.1 V *vs.* Ag/AgCl) was applied. Then, each ATR-IR spectrum was taken at 5 minute intervals. The ATR-IR spectrum with the $KClO_4$ aqueous solution (Figure 2a) has two strong peaks at 1360, and 1632 cm^{-1}. On the other hand, the ATR-IR spectrum with the KCl aqueous solution (Figure 2b) has three strong peaks at 1360, 1390, and 1616 cm^{-1}. Some chemical species relevant to CO_2 show absorption peaks between 1300 and 1400 cm^{-1} (the spectra for these are shown in Figure S3), so it is difficult to assign the peaks at around 1300-1400 cm^{-1}. In contrast, based on previous studies[29,30], the peaks at 1632 cm^{-1} (Figure 2a) and 1616 cm^{-1} (Figure 2b) can be assigned to asymmetric OCO stretching, suggesting the presence of $CO_2^{\bullet -}$. In order to distinguish this peak from H_2O vibrations, the same measurements were conducted in D2O. The peaks were also observed in D_2O, suggesting that the peaks can be assigned to $CO_2^{\bullet -}$ intermediates. Figure 2c shows a comparison of the peaks observed in $KClO_4$ and KCl aqueous solutions after 30 minutes of electrolysis.

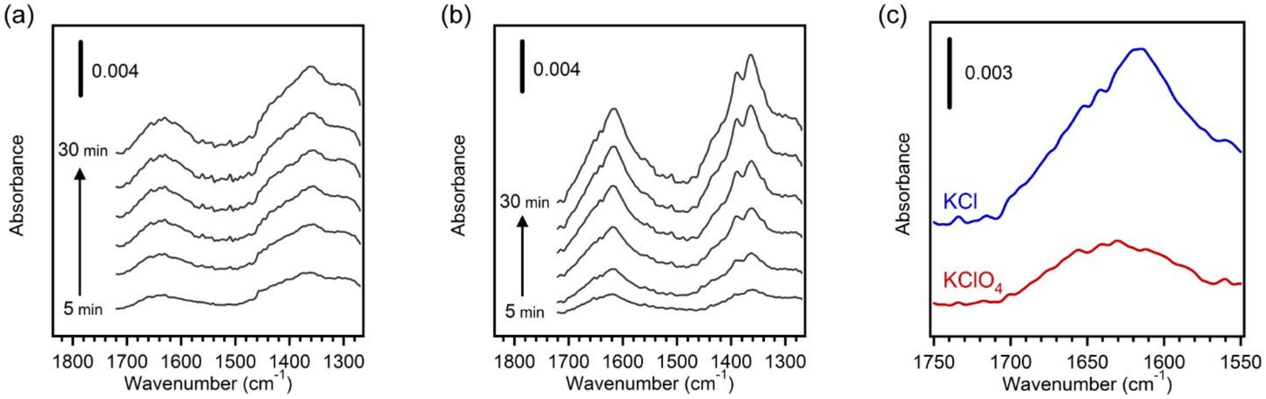

Figure 2. Time-dependent ATR-IR spectra during electrochemical reduction of CO_2 in 0.1 mol L^{-1} (a) $KClO_4$ and (b) KCl aqueous solutions at −2.1 V (*vs.* Ag/AgCl). Each spectrum was taken after every 5 minutes of electrolysis. The arrows in the figures show the direction of time. (c) Comparison between the spectra in $KClO_4$ (red) and KCl (blue) aqueous solutions taken after 30 minutes of electrolysis.

The wavenumbers of the peaks that can be assigned to asymmetric OCO stretching are different for the $KClO_4$ and KCl aqueous solutions. It is plausible that this peak shift is due to a difference in the nature of the adsorption of the $CO_2^{\bullet-}$ intermediates on the BDD electrodes in the two different solutions. The adsorption characteristics of $CO_2^{\bullet-}$ intermediates are an important determinant for the main product obtained by CO_2 electrochemical reduction[4,31]. Thus, it is anticipated that the electrolyte has an effect on the adsorption behavior of $CO_2^{\bullet-}$ intermediates when using BDD electrodes.

In order to confirm whether the electrolyte does affect the adsorption characteristics of the $CO_2^{\bullet-}$ intermediates, ATR-IR measurements were also conducted when using a BDD electrode prepared with a ^{13}C carbon source (^{13}C-BDD). ATR-IR spectra with the ^{13}C-BDD electrode were measured using the same procedure used to take the spectra shown in Figure 2.

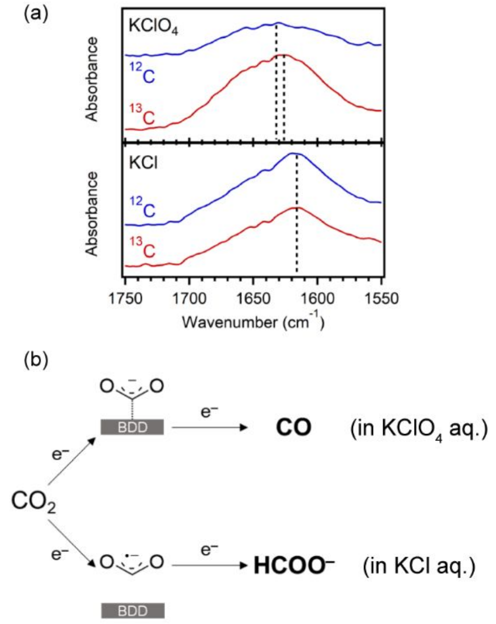

Figure 3. (a) Comparison of the in-situ ATR-IR spectra for CO_2 reduction using ^{13}C-BDD and ^{12}C-BDD electrodes in 0.1 mol L^{-1} $KClO_4$ and KCl aqueous solutions. Each spectrum was taken 30 minutes after applying −2.1 V (*vs.* Ag/AgCl). (b) The possible reaction pathway of CO_2 reduction using BDD electrodes in $KClO_4$ and KCl aqueous solutions.

Figure 3a shows a comparison of the ATR-IR spectra taken during CO_2 reduction in different electrolytes using ^{13}C- and ^{12}C-BDD electrodes. The most obvious feature is the peak assigned to $CO_2^{\bullet-}$ intermediates, which has shifted from 1632 cm^{-1} (on ^{12}C-BDD) to 1622 cm^{-1} (on ^{13}C-BDD), only in the 0.1 mol L^{-1} $KClO_4$ aqueous solution. This is possibly because $CO_2^{\bullet-}$ intermediates are directly adsorbed on BDD in $KClO_4$ aqueous solutions, and the vibrations of these are directly affected by the different carbon isotopes. In contrast, the spectra taken in 0.1 mol L^{-1} KCl aqueous solution do not show any shift due to the different isotopes. This indicates that the $CO_2^{\bullet-}$ intermediates are not adsorbed on BDD in KCl aqueous solution. From the ATR-IR analyses and the electrolysis results, it is inferred that, in $KClO_4$ aqueous solution, $CO_2^{\bullet-}$ intermediates are adsorbed on the BDD electrode, thereby promoting the production of carbon monoxide, but in the case of KCl aqueous solution many intermediates exist as free intermediates, so the production of formic acid is promoted (Figure 3b). It is of great interest that the strength of the adsorption of the $CO_2^{\bullet-}$ intermediates on BDD can be controlled by the electrolyte.

3.1.3. Optimizing the conditions to produce carbon monoxide

With a 0.1% BDD cathode and $KClO_4$ catholyte, more or equal amounts of formic acid was produced compared to carbon monoxide, so it is necessary to increase the selectivity and faradaic efficiency for the production of carbon monoxide. Research has been done focusing on the effect of the boron concentration in the BDD electrode on the electrochemical reduction of CO_2. In that study, the carbon monoxide production was somewhat higher when the boron concentration in the electrode was higher[22]. Here, in our next experiment, we used a 1% BDD electrode for the cathode.

Figure 4 shows the faradaic efficiencies for producing carbon monoxide, formic acid, and hydrogen using a 1% BDD electrode in $KClO_4$ aqueous solution at −2.1 V (*vs.* Ag/AgCl). Comparison with the results using the 0.1% BDD

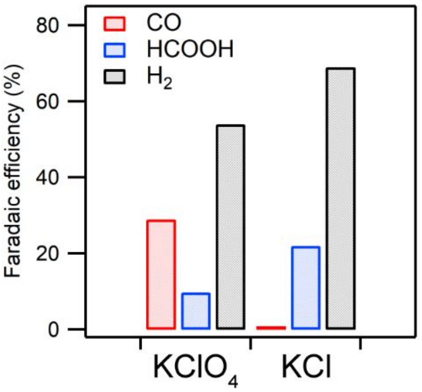

Figure 4. Faradaic efficiencies for producing carbon monoxide (red), formic acid (blue) and hydrogen (black) by the electrochemical reduction of CO_2 using a 1% BDD electrode at −2.1 V (*vs.* Ag/AgCl) in 0.1 mol L^{-1} $KClO_4$ and KCl aqueous solutions.

electrode as the cathode shows that the hydrogen production has increased due to the low hydrogen overpotential compared to 0.1% BDD[26,32], whereas the selectivity for producing carbon monoxide has increased. As mentioned before, carbon monoxide is produced on electrodes such as Au, Ag, and Zn, on which $CO_2^{\bullet-}$ intermediates can be adsorbed[4,3]. It has been reported that BDD electrodes with high boron content have more acceptor states and holes[33]. Thus, it is assumed that more intermediates can be adsorbed on 1% BDD than on 0.1% BDD, and that the production of carbon monoxide is promoted on 1% BDD. When 1% BDD was used as the cathode, the selectivity for carbon monoxide production was higher than when 0.1% BDD was used as the cathode. Moreover, when BDD electrode with much higher boron content (5% BDD) was used as a cathode (Table S1), the amounts of carbon monoxide produced were as much as or less than with the 1% BDD electrode.

KCl was also used as a catholyte (Figure 4). Formic acid production was lower compared to the results using a 0.1% BDD electrode, but carbon monoxide production was still less than formic acid production, which is much different to the results obtained using $KClO_4$ as the catholyte. The experimental results so far have shown us that to produce carbon monoxide selectively from CO_2 using BDD electrodes, it is important to use $KClO_4$ as the catholyte and 1% BDD as the cathode.

Use of 1% BDD as the cathode and $KClO_4$ as the catholyte promotes the production of carbon monoxide. With these, electrolysis was conducted at several applied potentials (Figure 5a). As shown in Figure 5a, the faradaic efficiency for the production of carbon monoxide is higher than that for the production of formic acid at all potentials. The faradaic efficiency for producing carbon monoxide increases as the applied potential becomes less negative, and the maximum faradaic efficiency is at −1.8 V (*vs.* Ag/AgCl). In addition, the selectivity for producing carbon monoxide has a maximum at −2.1 V (*vs.* Ag/AgCl).

With the applied potential at −2.1 V (*vs.* Ag/AgCl), the flow rate of the electrolyte was varied from 100 mL min^{-1} to 500 mL min^{-1} (Figure 5b). As the flow rate increases, the faradaic efficiencies for the production of carbon monoxide and formic acid increase, and that for hydrogen production decreases sharply. This infers that the increased flow rate increases the supply of CO_2 to the electrode surface, thus promoting the CO_2 reduction reaction[27]. In addition, the high flow rate would promote removal of the carbon monoxide produced by the CO_2 reduction and adsorbed on the BDD electrode, and that new CO_2 would be able to reach the electrode surface. Promotion of the CO_2 reduction reaction decreases the number of electrons available for the hydrogen evolution reaction, thereby reducing hydrogen production. The flow rate dependency was also investigated at −1.8 V (*vs.* Ag/AgCl), the potential at which the maximum faradaic efficiency for carbon monoxide production was obtained (Table S1). Increases in carbon monoxide and formic acid production and a decrease in hydrogen production were observed, but the selectivity for carbon monoxide production was lower than the results at −2.1 V (*vs.* Ag/AgCl).

3.2. The electrochemical reduction of CO_2 using a Sn electrode

To compare the performance with a metal electrode, Sn was chosen for the electrode material. It is known that BDD electrodes are inert,[16] so it is considered that reactants are

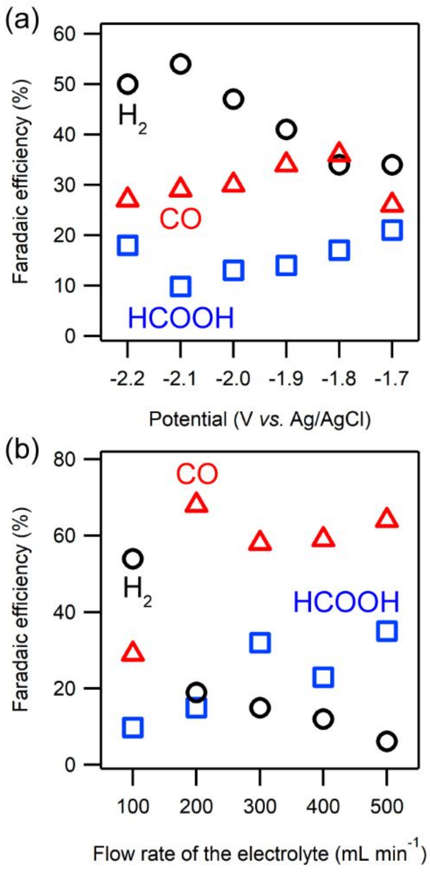

Figure 5. Dependency of (a) the applied potential and (b) the flow rate of the electrolyte on the faradaic efficiencies for carbon monoxide (red triangles), formic acid (blue squares) and hydrogen (black circles) production by the electroreduction of CO_2 using a 1% BDD electrode in 0.1 mol L^{-1} $KClO_4$ aqueous solution.

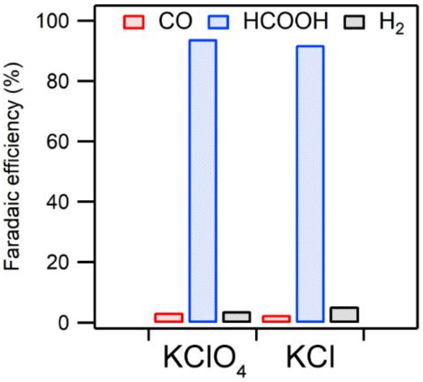

Figure 6. Faradaic efficiencies for producing carbon monoxide (red), formic acid (blue) and hydrogen (black) by CO_2 reduction using a Sn electrode at –2.0 V (*vs.* Ag/AgCl) in 0.1 mol L^{-1} $KClO_4$ and KCl aqueous solutions.

difficult to adsorb on the electrode surface. The trend of the properties and the products by CO_2 reduction of BDD electrodes[27] are similar to those of Sn. In previous researches, Sn, Pb, and Hg are known as the electrodes which do not adsorb $CO_2^{\cdot -}$ intermediates on their surfaces.[3,4] The products by galvanostatic electrolysis are mainly formic acid and small amounts of carbon monoxide.[34]

Electrolysis with the Sn electrode was conducted at –2.0 V (*vs.* Ag/AgCl) in $KClO_4$ and KCl aqueous solutions (Figure 6). In both cases, the faradaic efficiency for the production of formic acid was high, and little carbon monoxide was obtained. Unlike the BDD electrode, switching the product selectivity could not be done when Sn was used as the cathode. In addition, there were some adsorbed species on the surface of the Sn electrode after electrolysis. From previous research[14], this is due to corrosion and the formation of alkali metal deposits on the Sn electrode. It is inferred that changing the electrolyte does not affect the adsorption strength of the $CO_2^{\cdot -}$ intermediates on Sn electrodes, so highly efficient formic acid production was observed. On the other hand, with BDD electrodes the adsorption strength changes with the electrolyte, so the product selectivity can be switched by changing the composition of the electrolyte. In addition, unlike metal electrodes, the surfaces of BDD electrodes are covered with some functional groups[35,36], so the situation for the $CO_2^{\cdot -}$ intermediates is different to that of metals.

4. Conclusions

In this work, we investigated the electrochemical reduction of CO_2 using BDD electrodes and examined the conditions that would enable us to control the selectively for producing carbon monoxide or formic acid. The electrolyte, the boron concentration of the BDD electrodes, and the applied potential were optimized. We found a correlation between the product selectivity and the electrolyte. When $KClO_4$ was used as the electrolyte, the selectivity for the production of carbon monoxide tended to increase, whereas when KCl was used as the electrolyte, the selectivity for the production of formic acid tended to increase. It was deduced that when $KClO_4$ was used as the electrolyte, more $CO_2^{\cdot -}$ intermediates were adsorbed on the electrode than when KCl was used as the electrolyte. An ATR-IR study showed that the adsorption peak for the $CO_2^{\cdot -}$ intermediates only appeared when $KClO_4$ aqueous solution was used, supporting the results of the electrolysis. The selectivity for producing carbon monoxide using $KClO_4$ as the electrolyte increased when a 1% BDD electrode was used rather than a 0.1% BDD electrode. Increasing the flow rate of the electrolytes, increased the faradaic efficiency for producing carbon monoxide and formic acid, and that for hydrogen dropped significantly. This is attributed to the increase in the supply of CO_2 and promotion of carbon monoxide removal from the electrode surface. CO_2 reduction using Sn electrodes was also conducted in $KClO_4$ and KCl aqueous solutions. In both cases, formic acid was produced with high efficiency, while only small amounts of carbon monoxide were obtained. Unlike BDD electrodes, the product selectivity could not be switched when using Sn electrodes. With BDD electrodes, the product selectivity could be switched by changing the electrolyte from $KClO_4$ to KCl. Here, we found that more $CO_2^{\cdot -}$ intermediates are adsorbed on BDD in $KClO_4$ aqueous solution compared to KCl aqueous solution; however, it is still unclear why $CO_2^{\cdot -}$ intermediates are more favorably adsorbed on BDD electrodes in $KClO_4$ aqueous solution rather than in KCl aqueous solution. In addition, on which site of the BDD surface $CO_2^{\cdot -}$ intermediates are adsorbed should be investigated. To obtain the answers for these, DFT calculations are in progress.

ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available free of charge via the Internet at http://pubs.acs.org.

Characterization of BDD electrodes used for electrochemical reduction of CO_2, characterization of a BDD films used for *in-situ* ATR-IR measurements, the faradaic efficiencies of products obtained by CO_2 reduction in various electrolytes using BDD or Sn electrodes, representative ATR-IR peaks observed during CO_2 reduction, potential-dependent ATR-IR spectra during CO_2 reduction in 0.1 mol L^{-1} $KClO_4$ aqueous solution, ATR-IR spectra during electrochemical reduction of $^{13}CO_2$, ATR-IR spectra during cathodic reduction without CO_2, and linear sweep voltammograms using BDD electrodes in $KClO_4$ and KCl aqueous solutions

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Notes

The authors declare no competing financial interest.

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