The Utilization of Boron-doped Diamond Electrodes for the Electrochemical Reduction of CO₂: Toward the Production Compounds with a High Number of Carbon Atoms

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ABSTRACT

The utilization of boron doped diamond (BDD) as an electrode material for the electrochemical reduction of CO₂ has been studied in recent decades. Its stability and ability to suppress hydrogen evolution makes it an attractive choice for the electrochemical reduction of CO₂. It has been confirmed that, when using a bare BDD electrode, very high selectivity and productivity can be achieved in the production of formic acid. Moreover, by modifying the surface of a BDD electrode with copper (Cu) particles, we have been able to produce compounds with a high number of carbon atoms. In this article, we summarize the results of our work on the electrochemical reduction of CO₂ using BDD electrodes, with the specific aim of the producing compounds with a high number of carbon atoms.

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1. Introduction

In the past few decades, because of climate change issues, the conversion of CO₂ to useful chemicals has attracted the attention of researchers around the world.^{1,2} A major source of CO₂ gas in the atmosphere is fuel combustion; there have, therefore, been many attempts to close the carbon cycle by converting CO₂ gas back to fuel.^{3–5} CO₂ gas in the atmosphere is cheap and abundant, but it is worth noting that its value will increase as it becomes used for producing other chemicals.

Many methods for converting CO₂ have been studied. Currently, electrochemical techniques are being widely developed, using either power supplied from the usual electrical sources,⁶ or by combining the technique with a photocathode or a solar panel.^{7–9} The standard potentials for reducing CO₂ and the hydrogen evolution reaction are summarized in Table 1. It is easy to apply the reduction potential to the electrode; however, in practice, some additional activation energy is needed to obtain the products by direct electron transfer to the CO₂ molecule. Thus, developing a system that is suitable for reducing CO₂ is challenging.

It is well known that the working electrode plays an important role in electrochemical techniques. The electrochemical reduction of CO₂, using either carbon based electrodes,¹² metal or metal complex based electrodes,^{13–15} or semiconductor based electrodes, has been widely studied. In our work, we have focused on using BDD electrodes for the electrochemical reduction of CO₂. BDD has a

Table 1. Standard potentials for the reduction of CO₂ and the hydrogen evolution reaction.^{10,11}

Reaction	E ⁰ [V vs. (SHE)] at pH 7
2H ⁺ _(aq) + 2e [−] → H _{2(g)}	−0.414
CO _{2(g)} + e [−] → CO ₂ [−] _(aq)	−1.85
CO _{2(g)} + H ₂ O _(aq) + 2e [−] → CO _(g) + 2OH [−] _(aq)	−0.52
CO _{2(g)} + H ₂ O _(aq) + 2e [−] → HCOO [−] _(aq) + OH [−]	−0.67
CO _{2(g)} + 5H ₂ O _(aq) + 6e [−] → CH ₃ OH _(l) + 6OH [−] _(aq)	−0.40
2CO _{2(g)} + 9H ₂ O _(aq) + 12e [−] → C ₂ H ₅ OH _(l) + 12OH [−] _(aq)	−0.33

wide potential window that can help suppress H₂ evolution in favor of the competitive CO₂ reduction reactions, especially in aqueous solutions. In addition, BDD electrodes are chemically inert and have high mechanical durability, which makes them suitable for practical applications.^{16,17}

BDD electrodes have been examined for applications to sensors and electrochemical synthesis.^{18,19} However, there have not been many studies in which they have been utilized for the reduction of CO₂. In the last few years, we have studied the electrochemical reduction of CO₂ using bare BDD electrodes and modified BDD electrodes. With a bare BDD electrode and using a circulation flow cell, formic acid was successfully produced with a faradaic

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Figure 1. Faradaic efficiency of formic acid produced in several types of electrolytes with different cations and anions. Reprinted with permission from Ref. 27. Copyright (2018) John Wiley and Sons.

efficiency as high as 94.7% and selectivity of more than 99%.²⁰ Studying the production of other chemicals with higher numbers of carbon atoms using BDD as the carbon based electrode is equally attractive, and also challenging. In this review article, we summarize the application of BDD electrodes for the electrochemical reduction of CO₂ to C₁ products and its potential to produce compounds with higher numbers of carbon atoms (C₂/C₃/... species) by metal modification of the BDD electrodes.

2. Using Bare BDD Electrodes

Our group has carried out studies of the electrochemical reduction of CO₂ to useful chemicals using bare BDD electrodes and developed processes applicable for industrial production. Many parameters have been studied, such as the influence of the electrolyte and the amount of boron in the diamond.

In the electrochemical reduction of CO₂ gas in aqueous solutions, the CO₂ gas has to be absorbed in the catholyte, so the type of electrolyte used in the system is quite important.^{21,22} The electrolyte determines the solubility of the CO₂ gas in solution. The carbon capture and sequestration (CCS) process has been widely used in industrial processes. This captures waste CO₂ gas using a strong absorber, namely an amine solution, and transports it to a storage site. On the other hand, aqueous ammonia solution is also known as a strong CO₂ absorber and has become an alternative to the widely used amine solutions.²³ Accordingly, we used a BDD electrode in ammonia solution to electrochemically reduce CO₂, producing methanol as the main product at a potential of −1.3 V vs. (Ag/AgCl).²⁴ The maximum faradaic efficiency we obtained in the production of methanol was 24.3% (Table 2).

The reduction of CO₂ (at pH 7.7) is believed to be through the reduction of bicarbonate ions by the following reaction (Eq. (1)):

Bicarbonate ions are formed during the absorption of CO₂ gas in the solution which decreases the pH. The pH determines the dominant species in the solution. At pH < 5, pH 7.5 to 9, pH > 12, the dominant species are dissolved CO_{2(aq)}, HCO₃[−], and CO₃^{2−} respectively.

Table 2. The faradaic efficiency of products in the electrochemical reduction of CO₂ in ammonia solution under different applied potentials.²⁴

Potential/ V vs. (Ag/AgCl)	Faradaic Efficiency (%)			
	CH ₃ OH	CO	CH ₄	H ₂
−1.2	2.61	0	0.24	0
−1.3	24.3	0.05	0.13	19.7
−1.4	15.1	0.12	0.03	25.8
−1.5	2.02	0.20	0	57.2

Moreover, considering the solubility of CO₂, the electrochemical reduction of CO₂ using BDD electrodes in a methanol electrolyte containing tetrabutylammonium perchlorate (TBAP) was also performed, since the solubility of CO₂ in methanol is five times higher than in water. The main product in this case was formaldehyde which was produced at a potential of −1.7 V vs. Ag/Ag⁺ with a faradaic efficiency of 74%. A small amount of formic acid with a maximum faradaic efficiency of 15% was also produced.²⁵

Nevertheless, studies of CO₂ reduction in aqueous solutions have been carried out since BDD electrodes themselves have the ability to suppress the production of H₂. The effects of alkali metal-cations have been studied using alkaline solutions, generating formic acid as the main product.²⁶ NaOH, KOH, RbOH, and CsOH have all been tested. Of those electrolytes, CO₂ reduction in a RbOH solution (pH 6.2) gives the highest efficiency for formic acid, as high as 71%. From this point on, studies of the effects of different cations and anions was continued by Tomisaki, et al.²⁷ Several cations with different anions were used, and a current density of −2 mA cm^{−1} was applied for 1 hour to electrochemically reduce the CO₂. The results are summarized in Fig. 1. The efficiency for the production of formic acid was increased to 95% in RbBr aqueous solution. It is said that larger cations can maintain the pH near the surface of electrode, thus the CO₂ concentration near the surface of the electrode remained stable. In addition, some other anions were also studied, including SO₄^{2−} and NO₃[−]. The results show that the production of formic acid was maintained with adsorbed anions such as sulfate and halides, whereas with NO₃[−], the electrons reduced the NO₃[−], resulting in a low conversion efficiency for CO₂.

Another important aspect of this study is the role of the BDD electrode for the CO₂ electrochemical reaction itself. This can be evaluated by performing experiments on the surfaces of BDD electrodes which have been prepared with different parameters, such as the surface termination, the amount of sp² carbon impurities, and the amount of boron in the diamond.²⁸

To evaluate the effect of the boron content, BDD electrodes with 0.01%, 0.1%, 0.5%, 1%, and 2% boron were prepared and used in the electrochemical reduction of CO₂. It is known that the

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Figure 2. Faradaic efficiency of products from the electrochemical reduction of CO₂ using BDD electrodes with different amounts of boron. Reprinted with permission from Ref. 28. Copyright (2018) Elsevier.

electrochemical reactivity of BDD electrodes depends on the level of boron in the electrode. The electrochemical reactivity increases with the boron content. The experiments showed that the optimum boron content for the production of formic acid was 0.1%, with an efficiency as high as 75% (Fig. 2). The formic acid production was lowest at the lowest boron level (0.01%), which can be explained by the low electrochemical reactivity of this electrode. On the other hand, using electrodes with higher boron levels increases the hydrogen evolution, which competes with the CO₂ reduction, resulting in lower formic acid production.

3. Using Metal Modified BDD Electrodes

As the studies described above demonstrate, the production of compounds with higher numbers of carbon atoms ($C_2/C_3/\dots$ species), which would enable the development of processes using BDD electrodes to produce ready-to-use fuel, is still challenging, since at the moment C_1 products only (formic acid, formaldehyde, and methanol) have been reported. In addition, the high overpotential required is still a drawback.

BDD electrodes are known to be very stable and relatively inert, thus the adsorption of CO, which can operate as an active intermediate to produce compounds with higher numbers of carbon atoms through cross-coupling reactions, hardly occurs. Modifying the BDD surface may enable efficient methods for initiating CO adsorption to be developed. There have been many types of surface

modification that have increased the catalytic behavior of BDD electrodes, such as covalent organic modification,^{29,30} the use of metal complexes,³¹ or simply by metal deposition.³²

As is well known, metals are widely used as catalysts for CO₂ reduction. The products generated are highly correlated with the intrinsic behavior of the metals and also the pretreatment conditions of the electrode itself. Thus, the choice of a suitable metal to modify the surface of the BDD electrode is very important. Many metals have been studied for the electrochemical reduction of CO₂ and these are summarized in a diagram of the periodic table (Fig. 3).³³ However, the product distribution is not strictly as shown, since it depends on operating conditions that may vary or even change the main product, for example with Sn CO can be produced instead of formate.^{4,34} In addition, it is known that each metal has a specific behavior toward the adsorption of CO. CO binds weakly to Ag, Au and Zn, while it binds strongly to Pt, Ni and Fe, and moderately to Cu.³⁵ The stronger the binding, the lower the current efficiency for CO₂ reduction is. However, a strong bond between CO and the surface of the electrode is necessary to bring about a coupling reaction; thus, CO is not detached from the surface of the electrode as a product.

The high stability of BDD makes it a good candidate for the electrode support material. However, until recently, few studies on the electrochemical reduction of CO₂ using metal modified BDD electrodes have been done. Several reports have been published in which the surfaces of BDD electrodes have been modified with metal or metal oxides of Ag, Ru, or Cu-Sn.³⁶⁻³⁸ All those modifications have successfully increased the productivity of CO, except modification with the oxide of Ru, which produced mainly HCOOH and methanol at relatively low overpotentials (−0.5 V vs. SCE). This shows that the deposited metal provides a catalytic effect, thus decreasing the applied potential required to reduce CO₂.

Meanwhile, copper (Cu), for which the CO binding is moderate, is the only metal well known to produce hydrocarbons and oxygenated species.^{13,39} Therefore, this is clearly an interesting metal for modifying the surface of BDD electrodes and applying to the electrochemical reduction of CO₂.⁴⁰ A simple electrochemical deposition method is carried out by applying a specific potential to modify the surface of a BDD electrode with Cu particles (Cu-BDD). The concentration of the metal contained in the solution, the applied potential/current and the deposition time affects the characteristics of the deposited particles including how many particles can be deposited. Figure 4 shows that the amount of deposited Cu particles increases as the deposition time becomes longer. However, the Cu particles detach more easily from the surface of the electrode as the

Figure 3. Diagram of periodic table showing the CO₂ reduction products of each metal and carbon electrode. Reprinted with permission from Ref. 33. Copyright (2015) American Chemical Society.

Figure 4. SEM images of Cu-BDD electrodes prepared with different deposition times. Cu-BDD deposited for (a) 50 s (b) 100 s (c) 300 s at a potential of -0.6 V vs. (Ag/AgCl) in 0.1 M H_2SO_4 containing 1 mM CuSO_4 before electrochemical reduction. (a'), (b'), and (c') are the same electrodes after electrochemical reduction at -1.0 V vs. (Ag/AgCl) for 2 hours at room temperature and pressure.⁴⁰ Reprinted with permission from Ref. 40. Copyright (2018) Elsevier.

amount of particles increases. This lack of stability of the deposited particles is still a challenging problem. This drawback can be solved by a step by step thermal deposition method or annealing at a particular temperature.^{37,41}

Finally, the faradaic efficiencies of all the electrodes were evaluated. Ethanol, acetaldehyde, and acetone are the main products. The faradaic efficiency of these products varies depending on the amount of deposited Cu particles as well as the applied potential (Fig. 5A–5B). The maximum production of ethanol was with a Cu-BDD electrode that had Cu deposited at a potential of -1.0 V vs. (Ag/AgCl) for 100 s.

The importance of BDD as a support electrode for the deposition of Cu particles was also shown by comparing these with glassy carbon (GC) electrodes. Hardly any C_2/C_3 species were produced with Cu modified GC (Cu-GC) electrodes. This can be explained by the fact that the size of the Cu particles on BDD electrodes tends to be larger than on GC electrodes. Moreover, the narrower potential window of GC electrodes promotes high hydrogen gas production thereby reducing the efficiency of CO_2 reduction products ($<5\%$).

4. Conclusion

Although BDD electrodes have been used to produce C_1 products (i.e. HCOOH , HCHO , methanol), the production of compounds containing more than one carbon atom is difficult; however, by modifying the surface of BDD electrodes with Cu particles this can be achieved. BDD is an excellent support electrode, with which the production of hydrogen gas can be suppressed, and thus the production of ethanol, acetaldehyde, and acetone, which are not produced with high efficiency using Cu electrodes, can be improved. Studies of the electrochemical reduction of CO_2 using other metal modified BDD electrodes is on going and worth exploring, in order to find new systems with BDD electrodes that produce compounds with higher numbers of carbon atoms or else lower the high applied overpotential used with BDD electrodes.

Figure 5. Faradaic efficiencies for the production of ethanol, acetaldehyde, and acetone depending on (A) the Cu deposition time on the Cu-BDD electrode at a potential of -1.0 V vs. (Ag/AgCl), and (B) the applied potential for the electrochemical reduction of CO_2 on the surface of a Cu-BDD electrode that had a deposition time of 100 s.⁴⁰ Reprinted with permission from Ref. 40. Copyright (2018) Elsevier.

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