A New Pathway for CO₂ Reduction Relying on the Self-Activation Mechanism of Boron-Doped Diamond Cathode

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ABSTRACT: By means of an initial electrochemical carbon dioxide reduction reaction (eCO₂RR), the reaction current and Faradaic efficiency of the eCO₂RR on boron-doped diamond (BDD) electrodes were significantly improved. Here, this effect is referred to as the self-activation of BDD. Generally, the generation of carbon dioxide radical anions (CO₂⁻⁻) is the most recognized pathway leading to the formation of hydrocarbons and oxygenated products. However, the self-activation process enabled the eCO₂RR to take place at a low potential, that is, a low energy, where CO₂⁻⁻ is hardly produced. In this work, we found that unidentate carbonate and carboxylic groups were identified as intermediates during self-activation. Increasing the amount of these intermediates via the self-activation process enhances the performance of eCO₂RR. We further evaluated this effect in long-term experiments using a CO₂ electrolyzer for formic acid production and found that the electrolytico-chemical energy conversion efficiency reached 50.2% after the BDD self-activation process.

KEYWORDS: boron-doped diamond, CO₂ reduction, self-activation, energy conversion efficiency, intermediates

1. INTRODUCTION

Research on carbon dioxide (CO₂) utilization is one of the keystones to realize the artificial carbon cycle and possibly carbon neutrality. Several methods are currently under investigation, and among them, the electrochemical CO₂ reduction reaction (eCO₂RR) has been proved to be a viable and efficient approach to reduce CO₂ into small useful products. In these products, as a liquid fuel, formic acid not only possesses superiorities in transportation and storage but also has a bright application prospect in hydrogen vector and fuel cells. However, high overpotentials, poor product selectivity, and low current densities are still obstacles that hinder the technological applications of eCO₂RR.

During eCO₂RR, the main reason concerning overpotentials and poor product selectivity was found to be the energetically unfavorable CO₂ adsorption. Specific interactions between the CO₂ molecule (i.e., substrate) and electrodes (i.e., electrocatalyst) are needed to stabilize reaction intermediates, leading to lower overpotentials, high product selectivity, and faster reaction rate. Until now, the most recognized pathway for eCO₂RR is through the generation of CO₂ radical anion (CO₂⁻⁻). If the generation of CO₂⁻⁻ is the rate-determining step, then this will introduce a large overpotential, as CO₂/CO₂⁻⁻ redox couple has a standard potential that lies near −1.85 V vs SHE which limits the electrolysis potential in a highly negative range.

Kanan’s group reported that compared to pure metal, oxidized or oxide-derived metal electrodes showed more prominent Faradaic efficiency and reduced overpotential for eCO₂RR, where the increased stabilization of CO₂⁻⁻ intermediate was speculated to be the reason for this improved performance. But unfortunately, the chemical model and direct evidence of the interaction between CO₂ molecules and the surface state of the electrode is crucial to provide stabilization for intermediate species in reaction mechanisms which did not rely on the generation of CO₂⁻⁻. A possible pathway has been proposed by Baruch et al. as the mechanism involved bicarbonate functional groups and an unlikely simultaneous transfer of two electrons. Valenti et al. proposed CeO₂ as an electrocatalyst for CO₂ hydrogenation at overpotential as low as −0.02 V. From the previous examples, it is clear that oxides or oxygenated species play a central role in eCO₂RR at low overpotentials. Therefore, the specific mechanism for eCO₂RR, especially when the applied potential is insufficient to form CO₂⁻⁻ radicals, is still worth further investigation.

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Boron-doped diamond (BDD) was proposed as an outstanding candidate for mechanistic investigation of eCO2RR. BDD is chosen for its long-term stability, resistance to corrosion, and high product selectivity in eCO2RR. In addition, due to its unique properties of low capacitive current and wide potential window, BDD not only could greatly inhibit the reactivity of hydrogen evolution, which is the main competitor of eCO2RR, but also is able to show evident redox signals for the electrochemical analysis. However, so far, the mechanism for the initial eCO2RR reaction process has not been clearly determined. Therefore, in order to apply eCO2RR to industrial processes, we now urgently need clarification and optimization of the factors that determine the experimental conditions, including the pretreatment of BDD electrode surfaces.

Here, we investigated a process referred as “self-activation” of BDD that prompted us to suggest a new and efficient pathway for eCO2RR, which bypasses the mechanism involving CO2. During electrolysis, the CO2 molecules were first bound by BDD in the form of unidentate carbonate (−O–CO2) and were further transformed to carboxylic structure (−COOH) after a proton and electron transfer reaction. This process leaves a detectable amount of carboxylic groups on the surface of BDD which are dependent on time, current density, and potential, for this reason named self-activation, finally enhancing the performance in terms of Faradaic efficiency and partial current density. The application of this self-activation mechanism was evaluated on the performance of eCO2RR with a long-term two-electrode electrolysis reaching a remarkable electrical-to-chemical energy (ECE) conversion efficiency of 50.2% after 7 h of self-activation at the total cell voltage of 2.7 V for eCO2RR to formic acid.

2. EXPERIMENTAL SECTION

2.1. Materials
KCl, KOH, H2SO4, NaClO4 and 2-propanol were purchased from Wako Pure Chemical Industries Ltd. NiSO4, FeSO4, and (NH4)2SO4 were purchased from Sigma-Aldrich. All reagents were used without any further purification. The deionized (DI) water employed in this work was from a Simply-Lab water system (DIRECT-Q 3 UV, Millipore) with a resistivity of 18.2 MΩ·cm at 25 °C. Experiments were performed at room temperature (25 °C) in atmospheric pressure, unless stated otherwise. All of the electrochemical measurements were performed with the assistance of a potentiostat/galvanostat system (PGSTAT204, Metrohm Autolab). Ag/AgCl (KCl sat'd) was set as the reference electrode for all of the electrochemical measurements in this work.

2.2. Preparation of BDD electrode
The polycrystalline BDD film was deposited on a Si (100) wafer substrate with a microwave plasma-assisted chemical vapor deposition (MPCVD) system (AX6500, Cornes Technologies Ltd.). The concentration of boron in the BDD electrode was determined by the ratio between the carbon source (methane) and the boron source (trimethylboron) and was set to 0.1%. A glow discharge optical emission spectroscopy (GD-Profiler2, Horiba Ltd.) measurement was performed to further confirm the exact content of boron in BDD. Raman spectrum was recorded using an Acton SP2500 (Princeton Instruments) with a 532 nm laser (Figure S1) to confirm the crystallinity of diamond and exclude the interference caused by sp2 carbon. Surface morphology images of the BDD film were obtained with a scanning electron microscope (JCM-6000, JEOL) (Figure S1). The interference of the substrate, Si (100), was excluded by corresponding eCO2RR (Figure S2, Table S1).

2.3. Electrochemical Measurements and Product Analysis
Before each electrolysis, the BDD electrode was cleaned with 2-propanol and DI water by an ultrasonic treatment for 10 min each. Electrochemical measurements were performed in a two-compartment polytetrafluoroethylene (PTFE) flow cell which was with the same condition of our previous work. 0.1% BDD, Pt, and Ag/AgCl (KCl sat’d) were set as the cathode, anode, and reference electrode, respectively, and the two chambers of the cell were separated by Nafion NRE-212 (Sigma-Aldrich). As a pretreatment before CO2 reduction, several cyclic voltammetry (CV) scans (including 10 cycles from a potential of −3.5 to 3.5 V and 20 cycles from 0 to 3.5 V in 0.1 M H2SO4 and 0.1 M NaClO4, respectively, with a scan rate of 0.5 V/s) were performed to ensure reproducibility and cleanliness of the surface of the electrodes. The catholyte and anolyte were 0.5 M KCl and 1 M KOH, respectively (50 mL each). The catholyte was bubbled with N2 for 30 min to remove oxygen and CO2 for 60 min, resulting in a CO2-saturated solution. During electrolysis, CO2 bubbling was set at a flow rate of 10 mL min−1.

For the two-electrode electrolysis system, the nafion membrane was replaced by the bipolar membrane (fumasep FBM, FUELCELL Store). Each chamber in the cell was connected with a reference electrode (Ag/AgCl, KCl sat’d) to monitor the working potentials of both cathode and anode. In comparison experiments, the Pt anode was further replaced by Ni (Nilaco), NiFeOx, and dimensional stable electrode (DSE, DE NORA). The NiFeOx electrode was synthesized through electrodeposition. In brief, a Ni foil was immersed in a mixture solution of 9 mM NiSO4, 9 mM FeSO4, and 25 mM (NH4)2SO4 (pH adjusted at 2.5 by H2SO4) and was electrolyzed under a constant current of 10 mA/cm2 for 30 s and repeated for 50 cycles.

At the end of each CO2 reduction experiment, all of the products were quantified. Formic acid was quantified by high-performance liquid chromatography (HPLC, CDD-10A, Shimadzu Corp.). The gaseous products (CO and H2) were collected in an aluminum gas bag (GL Sciences) and quantified by gas chromatography (GC-2014, Shimadzu Corp.). Formic acid for HPLC calibration was obtained from FUJIFILM Wako pure Chemical Corporation. Hydrogen and carbon monoxide for GC calibration were obtained from GL Sciences.

2.4. XPS Measurements
The specific elemental information about the surface of BDD electrode was measured with an X-ray photoelectron spectrometer (XPS, JPS-9010 TR, JEOL). The C 1s spectra were deconvoluted with Gaussian functions. Peaks deconvoluted from the C 1s spectra were assigned to the following components: 283.0 eV (sp2 C bond), 284.75 eV (sp3 C bond), 285.3 eV on membrane was set at a 3.5 V and 20 cycles from 0 to 3.5 V in 0.1 M H2SO4 and 0.1 M NaClO4, respectively, with a scan rate of 0.5 V/s) were performed to ensure reproducibility and cleanliness of the surfaces of the electrodes. The catholyte and anolyte were 0.5 M KCl and 1 M KOH, respectively (50 mL each). The catholyte was bubbled with N2 for 30 min to remove oxygen and CO2 for 60 min, resulting in a CO2-saturated solution. During electrolysis, CO2 bubbling was set at a flow rate of 10 mL min−1.

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2.5. In Situ Attenuated Total Reflectance Infrared Spectroscopy Measurements
A thin 0.1% BDD film was deposited on a Si attenuated total reflectance infrared (ATR-IR) prism using MPCVD with the same method as mentioned before. The quality of the BDD film was verified by Raman spectrum (Figure S3). A one chamber PTFE cell was used to perform the electrolysis in which BDD, glassy carbon rod, and Ag/AgCl (KCl sat’d) were set as the working electrode, counter electrode, and reference electrode, respectively. Supporting electrolytes as 0.1 M H2SO4 and 0.1 M NaClO4 were used for the pretreatment, while 0.5 M KCl for CO2RR. The ATR-IR spectra were measured through a FT/IR-6600 (JASCO Corp.) with a liquid-nitrogen-cooled mercury-cadmium-telluride detector. All of the spectra were collected at a resolution of 4 cm−1 and had 256 scans. The baseline spectrum and pretreated comparison spectrum were measured in N2-saturated DI water. After the electrolysis, the BDD electrode was washed by DI water for three times, and then the ATR-IR spectrum was measured again in N2-saturated DI water.
The BDD electrode was activated by incubation with 10 mM 1-(3-(dimethylamino)propyl)-3-ethylcarbodiimide hydrochloride (EDC, Tokyo Chemical Industry Co. Ltd.), 10 mM N-hydroxysuccinimide (NHS, Sigma-Aldrich), and 0.1 M 2-morpholinoethanesulfonic acid (MES, DOJINDO) for 1 h in DI water. After rinsed with 0.1 M MES, the BDD electrode was further incubated with 0.01 M aminoferrocene (Fc-NH₂, Sigma-Aldrich) in 0.1 M carbonate buffer solution (pH 9.8) for 1 h. Fc-NH₂ was previously dissolved in the minimum amount of acetonitrile. Before electrochemical measurements, BDD was rinsed with the mixed solvent DI water and acetonitrile 50:50 v/v. Cyclic voltammetry (CV) scan rate was set to 50 mV s⁻¹ with the mixed solvent DI water and acetonitrile 50:50 v/v. Cyclic voltammetry (CV) scan rate was set to 50 mV s⁻¹ in the potential range of 0.1−0.6 V. All measurements were performed in a one chamber PTFE cell with 0.5 M KCl as supporting electrolyte.

3. RESULTS AND DISCUSSION

3.1. Self-Activation Process of BDD

To investigate and verify the self-activation process of BDD, we first performed the eCO₂RR with a BDD cathode in a three-electrode system in a flow cell. As shown in Figure 1AB, 3 h eCO₂RR experiments were carried out at the potential of −2 V.

Galvanostatic CO₂ reductions for 1 h at current densities of −0.1 mA cm⁻², −0.5 mA cm⁻², −1 mA cm⁻², −1.5 mA cm⁻², and −2 mA cm⁻² were adopted as activation processes and performed before the formal eCO₂RR. Without activation, current density and Faradaic efficiency at BDD are −0.17 mA cm⁻² and 73.81%, respectively. In contrast, by the activation processes, the current density reached −0.22 mA cm⁻², −0.3 mA cm⁻², −0.59 mA cm⁻², −0.23 mA cm⁻², and −0.35 mA cm⁻², and the Faradaic efficiency for formic acid achieved 81.29%, 88.65%, 91.01%, 87.51%, and 87.32%, respectively. An activation current of −1 mA cm⁻² resulted in the best conditions, as the current density was improved more than three times and the Faradaic efficiency increased by 17.2% compared to BDD without activation.

To confirm the benefit of activation, electrolysis experiments of eCO₂RR were performed at different potentials from −2.2 V to −1.8 V, where the activation current density was set as −1 mA cm⁻². According to Figure 1C, an improvement of the Faradaic efficiency took place in the region of low potentials, also associated with higher current densities and product concentration (Figure S4), indicating that the reaction current of the activated BDD was significantly improved. When the reduction potential was −2.2 V, the Faradaic efficiencies of the activated and nonactivated BDD were at the same level, while at reaction potentials of −2 V, −1.9 V, and −1.8 V, the Faradaic efficiencies of the activated BDD increase of 17.2%, 18.72% and 20.7%, respectively, compared with those by nonactivated BDD.

Previously, we proposed that the generation of CO₂⁺−intermediate (E° = −2.05 V vs Ag/AgCl, KCl (sat’d)) is a reliable pathway for BDD cathode to achieve efficient eCO₂RR. Without the activation process, a Faradaic efficiency higher than 80% could be realized only when the applied potential is sufficiently negative to generate the CO₂⁺. However, the results in Figure 1 proved that with the aid of the activation process, the performance of eCO₂RR was greatly improved for more positive potentials (−100−150 mV) and a Faradaic efficiency of more than 80% could be obtained even at potentials where the CO₂⁺ was hardly produced. Besides, it is worth noting that in the eCO₂RR with BDD cathode, the faradic current keeps increasing with time, a tendency observed previously. Therefore, we speculate that during eCO₂RR, BDD will be subjected to a self-activation process that increases the electroactive area available for CO₂ reduction, and reaction intermediates other than CO₂⁺ might be generated on the surface which will gradually increase along with the reaction time.
3.2. Mechanistic Investigation

A combination of X-ray photoelectron spectrometer (XPS), in situ attenuated total reflectance infrared (ATR-IR) spectroscopy and electrochemical measurements have been used to investigate the changes of BDD surface state before and after the activation process by eCO2RR.

The comparison of XPS spectra for C 1s signal was depicted in Figure 2 and fitted to account for five carbon species including sp2 C–C, C–H, sp3 C–C, C–O, and C==O. The deconvolution of the C 1s signal revealed that with the activation by eCO2RR, the content of C–H bonds decreased, while the amount of oxygen-containing groups increased, where the increment of C–O bond was 5% and the content of C==O group increased to 12.6%. From this increment of oxygen moieties, we presumed that during eCO2RR, the CO2 molecules were first bound on BDD in the form of chemisorption and then reacted into oxygen-containing intermediates. The relative abundance of these components is summarized in Table 1.

![Figure 2. Deconvoluted C 1s spectra for the BDD and BDD with activation electrodes. The components are shown as follows: (1) sp2 C–C, (2) C–H, (3) sp3 C–C, (4) C–O, and (5) C==O.](image)

| Table 1. Relative Abundance of the Components (%) on the Surface of BDD Electrodes |
|-----------------------------------|---|---|---|---|---|
|                                   | sp2 C–C | C–H | sp3 C–C | C–O | C==O |
| BDD                               | 1.5     | 22.3| 48.8    | 27.4| –    |
| BDD w/activation                  | –       | 5.8 | 48.2    | 33.4| 12.6 |

To confirm the XPS results and verify the existence of such oxygen-containing intermediates, in situ ATR-IR spectroscopy measurements were further carried out (Figure 3). Before eCO2RR, the background ATR-IR spectrum did not show any feature, even during CO2 bubbling, meaning that signals of CO2 chemisorption could not be observed (Figure S5–S6). During eCO2RR, new absorption peaks emerged in the region of 1900 cm−1–1200 cm−1 (Figure 3). The strong absorption at 1530–1470 cm−1 and 1370–1330 cm−1 was assigned to the vibration of unidentate carbonate (–COO−),33 and showed an increasing trend with time of eCO2RR. Because the intense absorption peaks at 1650 cm−1 and 3400–3200 cm−1 showed a similar time-dependent variation (Figure 3 and Figure S7), both have been assigned to water vibration modes. Conversely, to water vibrations, the shoulder peak at 1720–1710 cm−1 kept increasing during the eCO2RR. Therefore, we suggested that the shoulder peak at 1720–1710 cm−1 and peak at 1460–1370 cm−1 could be assigned to the characteristic absorption of C=O and –OH groups in carboxylic structure (–COOH), respectively,32 moreover, this signal cannot be mistaken for formic acid in solution (Figure S8). Even after rinsing the BDD in ultrapure water, the characteristic peaks of unidentate carbonate and carboxylic structure on the surface could be observed clearly (Figure 3). In addition, the presence of the carboxylic structure on BDD after eCO2RR was further verified by reaction with aminoferrocene (Fc-NH2, Figure S9)33,34 and detected electrochemically (Figure 4A).

![Figure 3. In situ time-dependent ATR-IR spectra during CO2 reduction at −2 V vs Ag/AgCl, KCl (sat’d). The gray line shows the ATR-IR spectrum after rinsing BDD in ultrapure water. # and * indicate the νs vibration of unidentate carbonate and the stretching vibration of carboxylic C=O group, respectively.](image)

The schematic diagram showing the modification process of Fc-NH2 was described in Figure S9. With the help of 1-(3-(dimethylamino)propyl)-3-ethylcarbodiimide hydrochloride (EDC) and N-hydroxysuccinimide (NHS), the carboxylic structure on the surface of BDD can be activated to react with the amino group of Fc-NH2, and consequently the redox process of Fc-NH2 can be monitored by CV. A clear redox signal, corresponding to ferrocene, was observed for BDD electrode after eCO2RR, but not for the comparison BDD (Figure 4A), thus confirming that carboxylic functionalities were available on the surface of BDD only after eCO2RR. Considering that aldehyde groups can react with Fc-NH2 as well, and without activation by EDC/NHS, we performed the Fc-NH2 functionalization without EDC/NHS. Because the CV did not show any redox peak, we could exclude the presence of aldehydes on BDD surface after eCO2RR (Figure 4A). Therefore, the formation of carboxylic functionalities could be demonstrated through ATR-IR spectra and redox signals from the functionalization with Fc-NH2. Furthermore, to evaluate the time dependence on the formation of carboxylic groups, we measured the ferrocene redox signal at increasing time of eCO2RR (Figure 4B). The current increment for the redox peak of ferrocene demonstrates that the amount of carboxylic functionality intermediates generated on the surface of BDD electrode increased gradually with the time of eCO2RR.

On the basis of the measurements described previously, we demonstrated that during eCO2RR, unidentate carbonate and carboxylic structure were generated on the surface of BDD. The amount of both intermediates increased with the time of electrolysis, and these two groups could remain on the surface of BDD even after the CO2 reduction. Therefore, we concluded that CO2 molecules would be bound on the surface of BDD in the form of unidentate carbonate first, then...
undertook a proton-coupled electron transfer reaction\textsuperscript{35} at negative potentials to generate carboxylic groups, and finally released from the surface of BDD as formate. During electrolysis, the increase of unidentate carbonate and carboxylic intermediates on the surface of BDD brings the direct consequence of enhancing the Faradaic efficiency of CO$_2$ reduction because activation will not only improve the reaction current but also enhance the competitiveness of eCO$_2$RR for protons, which is an essential reactant for both hydrogen evolution and eCO$_2$RR. The supposing schematic diagram of this pathway is shown in Figure 5 and Figure S10.

![Figure 4](image)

**Figure 4.** (A) CVs of BDD electrodes after the modification with Fc-NH$_2$: Comparison sample without CO$_2$ reduction (black), CO$_2$ reduction-activated BDD without the addition of EDC/NHS before the Fc-NH$_2$ functionalization (blue), and CO$_2$ reduction-activated BDD coupled with the addition of EDC/NHS before the Fc-NH$_2$ functionalization (red); BDD activation by galvanostatic eCO$_2$RR at −1 mA cm$^{-2}$. (B) SWVs showing the variation of the Fc-NH$_2$ signals along with the time of eCO$_2$RR. Scan rate: 50 mV s$^{-1}$, supporting electrolyte: 0.5 M KCl, reference electrode: Ag/AgCl, KCl (sat’d).

In support for the reaction mechanism beyond the experimental evidence, we performed first-principles calculations based on density functional theory. The BLYP functional\textsuperscript{16,37} was used to calculate the electronic structures of the surface of interest. The effects of electrolyte solution and electrode potential on the electronic structures were taken into account by using the reference interaction site model\textsuperscript{18} and the effective screening medium method,\textsuperscript{39} respectively. The surface state with unidentate carbonate was calculated as a stationary point where the negative charge of $-0.75\, e$ resides on the surface under the experimental electrode potential condition of ca. $-2.0\, V$ vs Ag/AgCl (Figure S11A). This starting point has been set at $0\, kcal/mol$. Concerning the other intermediate, the carboxylic surface state was calculated to be nearly electrically neutral with a neighboring hydroxyl group (Figure S11C). This carboxylic intermediate was found to be more stable by ca. $31\, kcal/mol$ in grand potential than the unidentate carbonate surface state. This result indicates that the reaction proceeds through the unidentate carbonate intermediate followed by the carboxylic structure. The final hydroxyl terminated surface was estimated to be more stable by ca. $85\, kcal/mol$ in grand potential than the carboxylic surface state, which was due to the release of the energy storage compound, that is, formic acid (Figure S11D). Noteworthy, all these defined reaction steps, as reported in Figure 5, proceed exothermically. In conclusion, the calculation results are consistent with the experimental observations and in agreement with the reaction pathway that has been proposed where unidentate carbonate and carboxylic groups are available on the BDD surface. Further insights are available in the Supporting Information (Figure S12 and Table S2).

### 3.3. Long-Term Self-Activation

To evaluate the time dependence of the self-activation process on BDD and the overall effect on Faradaic and energy efficiency, the eCO$_2$RR was tested in an electrolysis system. The electrochemical cell comprised two compartments, equipped with a flow electrolyte setup, where BDD was set as the cathode. The electrochemical flow cell was first optimized by testing the performance for different membranes, which separate the anode and cathode chambers (i.e., Nafion and bipolar membrane), and for electrolyte flow rate. As a result, the bipolar membrane was selected to ensure that both sides would not be contaminated by cation crossover, in particular by metal ions from the anode electrode\textsuperscript{40,41} (Figures S13–S16), while 400 mL/min was selected as the optimal flow rate of electrolyte (Figure S17 and Tables S3 and S4).

Furthermore, we investigated the performance of four selected anodes such as Pt, Ni, NiFeO$\textsubscript{2}$, and dimensional stable electrode (DSE, Ti/IrO$_x$Ta$_2$O$_5$) to ensure an efficient oxygen evolution reaction (OER).\textsuperscript{42} This aspect is crucial because the anode material, completing the electrochemical cell, will affect both the potential distribution between anode and cathode and the current density achievable. The CVs and XPS spectra of anode electrodes are shown in Figures S18 and S19, respectively. We performed the eCO$_2$RR with the BDD-cathode electrolyzer at different total voltages to find the most suitable potential that maximizes Faradaic efficiency and electrical-to-chemical energy (ECE) conversion efficiency. During this investigation, we observed that both efficiencies are positively correlated with improved OER according to the anode materials. In particular, at $2.7\, V$ the ECE conversion efficiency reached $48\%$, while the Faradaic efficiency is stable between $85\%$ and $95\%$ (Figure S20 and Tables S5 and S6).

The improvement of the ECE conversion efficiency was mainly attributed to the low-energy consumption attained by using efficient OER anodes (Figures S21 and S22 and Tables S7 and S8). The repeatability of the activation process was further verified in two electrode eCO$_2$RR (Figures S23 and S24).

The time dependence of the self-activation process on BDD was evaluated over 7 h of eCO$_2$RRs at the best ECE conversion efficiency potential of $2.7\, V$ (Figure S20) by...
monitoring the current, Faradaic efficiency, and ECE conversion efficiency (Figure 6).

![Figure 6](image)

**Figure 6.** (A) Current densities, (B) production rate, and (C) Faradaic efficiencies/ECE conversion efficiencies of the BDD-based CO2 electrolyzers which were coupled with different anodes including Pt, Ni, NiFeOx, and DSE. CO2 reduction electrolysis experiments were performed at the applied voltage of 2.7 V.

Current and formic acid production rate increased continuously with the reaction time, suggesting an ongoing activation of the surface (Figure 6A,B) in agreement with previous results, therefore confirming our hypothesis of BDD “self-activation” during eCO2RR. The Faradaic efficiency of formic acid could reach more than 90% with an average ECE conversion efficiency of 50.2% after 7 h of continuous eCO2RR, viz. self-activation (Figure 6C). The effect of different OER anodes is clearly evident in the current values (Figure 6A), as lower overpotentials for OER lead to higher currents and then enhanced self-activation that turns into higher production rates (Figure 6B and Figure S25) with the series DSE(IrOx) > NiFeOx > Ni > Pt.

Additionally, we would like to draw attention to the reaction pathways on activated and nonactivated BDD which is the same; this is also the reason to choose the term “self-activation”. As shown in Figure 6, in the BDD-based long-term eCO2RR, both the reaction current density and the Faradaic efficiency for the production of formic acid were continuously improved. This is the essential performance of self-activation, and it indicates that during eCO2RR, the activity of BDD for CO2 reduction will keep increasing, which means an improvement of the electroactive surface area. However, due to the low initial reaction current, the process of self-activation is very slow; therefore, it benefits by additional galvanostatic CO2 reduction performed before the formal eCO2RR to accelerate the activation process, as demonstrated clearly in Figure 1.

Finally, we compared the ECE conversion efficiency of the present work with other representative electrocatalysts,29,40,41,43−49 to show that BDD can reach remarkable performances (Figure 7). Although the efficiency of BDD does not reach the level of noble metal electrocatalysts (e.g., Au or Pd), the advantages of BDD are in terms of raw material cost, chemical resistance, and physical stability in long-term applications where the carbon nanostructure coupled with noble metal electrocatalysts face structural changes and activity loss.50,51 We are aware that at present, the electrolysis current density of BDD cannot meet the standard of the industrial application, therefore improving the current density of BDD, for example, by gas diffusion electrode system, will be our research direction for the future work.

**CONCLUSION**

Here we investigated the mechanism of CO2 reduction on BDD highlighting a new and until now uncovered mechanism which leads to “self-activation” of the BDD surface during the eCO2RR. Characterization of the BDD surface by spectroscopic techniques such as XPS and ATR-IR combined with electrochemical analysis with aminoferrrocene demonstrated that unidentate carbonate and carboxylic intermediates were generated on the surface of BDD and kept increasing during eCO2RR. Based on the presence of these intermediates, a new pathway for electrochemical CO2 reduction was proposed, which was independent of the generation of CO2−.

![Figure 7](image)

**Figure 7.** Summarized ECE conversion efficiencies of the reported representative CO2 electrolyzers. The energy efficiencies with * were calculated by ourselves.
to a carboxylic intermediate and finally to formate. During eCO\textsubscript{2}RR an increasing amount of carboxylic intermediates are generated on the BDD surface, meaning an improvement of the self-activation effect was further estimated by 7 h eCO\textsubscript{2}RR in a flow electrolyzer. Benefiting from the self-activation effect, the BDD electrode reaches an ECE conversion efficiency of 50.2% for the single product of formic acid. This work provides new insights on the mechanism of electrochemical CO\textsubscript{2} reduction at BDD electrodes and demonstrates its potential application as working electrode for eCO\textsubscript{2}RR.

### ASSOCIATED CONTENT

**Supporting Information**

The Supporting Information is available free of charge at https://pubs.acs.org/doi/10.1021/jacsau.2c00081.

Details for the “self-activation” process for BDD electrode, the computational methods and calculation results, nafion and bipolar membrane: optimization experiments, electrolyte flow rate; optimization experiments, anode electrodes characterizations, Faradaic efficiency and ECE conversion efficiency, calculation of the energy distribution in the two-electrodes cell, Faradaic efficiency, ECE conversion efficiency, and energy distribution in the two-electrodes cell; results and Raman spectra of BDD electrodes (PDF)

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**Notes**

The authors declare no competing financial interest.

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**ABBREVIATIONS**

BDD, boron-doped diamond; eCO\textsubscript{2}RR, electrochemical carbon dioxide reduction reaction; ECE, electrical-to-chemical energy

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