

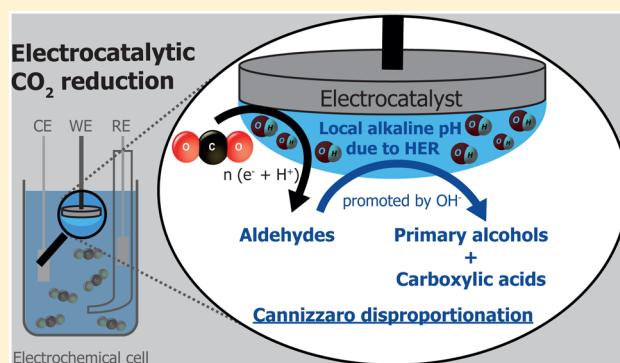
The Importance of Cannizzaro-Type Reactions during Electrocatalytic Reduction of Carbon Dioxide

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S Supporting Information

ABSTRACT: A seemingly catalytically inactive electrode, boron-doped diamond (BDD), is found to be active for CO₂ and CO reduction to formaldehyde and even methane. At very cathodic potentials, formic acid and methanol are formed as well. However, these products are the result of base-catalyzed Cannizzaro-type disproportionation reactions. A local alkaline environment near the electrode surface, caused by the hydrogen evolution reaction, initiates aldehyde disproportionation promoted by hydroxide ions, which leads to the formation of the corresponding carboxylic acid and alcohol. This phenomenon is strongly influenced by the electrolyte pH and buffer capacity and not limited to BDD or formaldehyde, but can be generalized to different electrode materials and to C₂ and C₃ aldehydes as well. The importance of these reactions is emphasized as the formation of acids and alcohols is often ascribed to direct CO₂ reduction products. The results obtained here may explain the concomitant formation of acids and alcohols often observed during CO₂ reduction.



INTRODUCTION

The production of fuels or fine chemicals from water, CO₂, and sunlight is a promising way to store solar energy and alleviate CO₂ accumulation in the atmosphere, one of the main causes of global warming since the industrial revolution. Research activities on (photo)electrocatalytic reduction of CO₂ have therefore increased exponentially, especially in the past few years. Different reaction products have been observed depending on, e.g., the nature of the electrocatalyst, the electrolyte, the pH, etc.^{1–3} Unfortunately, the existing electrocatalysts for the CO₂ reduction still suffer from the competing hydrogen evolution reaction (HER), high overpotentials, and poor selectivity toward a desired product.

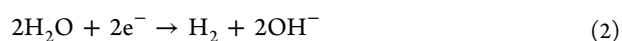
Boron-doped diamond (BDD) is a popular electrode material in electrochemistry, because of its interesting properties such as a wide potential window, high stability, robustness under extreme conditions (potential, temperature, pressure), and low background capacitive currents. BDD finds its use in electrochemistry mainly as a substrate for electrodeposition or nanoparticles and for electroanalytical purposes.^{6,7} In the field of electrocatalytic CO₂ reduction, BDD has been used as a substrate for catalysts as diverse as RuO₂ layers,⁸ Cu nanoparticles,⁹ and metal complexes.¹⁰ BDD has not been investigated as an electrocatalyst for CO₂ reduction until recently, when Nakata et al. reported high faradaic efficiency toward formaldehyde (HCHO) as well as a small amount of formic acid (HCOOH).¹¹ The standard equilibrium potentials for HCOOH, HCHO, and CO are obtained from formation energies in aqueous media at atmospheric pressure and 25 °C¹²

and given in Table 1. Note that E_{eq}^0 for HCOOH is pH-dependent for pH > 4, due to the dissociation of HCOOH into HCOO⁻ and H⁺.

Table 1. Standard Equilibrium Potentials for Reactions:
 $p\text{CO}_2 + q(\text{e}^- + \text{H}^+) \rightarrow \text{Product} + r\text{H}_2\text{O}$

<i>p</i>	<i>q</i>	product	<i>r</i>	E_{eq}^0 (V _{RHE})
1	2	HCOOH	0	-0.20 (pH ≤ 4) -0.20 + 0.059(pH - 4) (pH > 4)
1	4	HCHO	1	-0.08
1	2	CO	1	-0.11

It is well-known that the local pH at the electrode–electrolyte interface plays a crucial role for numerous electrochemical reactions.^{13–19} In aqueous media, cathodic potentials lead to a local alkaline environment caused by the consumption of protons and/or production of hydroxide ions (eqs 1 and 2).



The influence of the local pH variations is often neglected, although it is very important, as the local pH change may lead not only to a shift in the effective overpotential but also to the

Received: November 21, 2016

Published: January 18, 2017

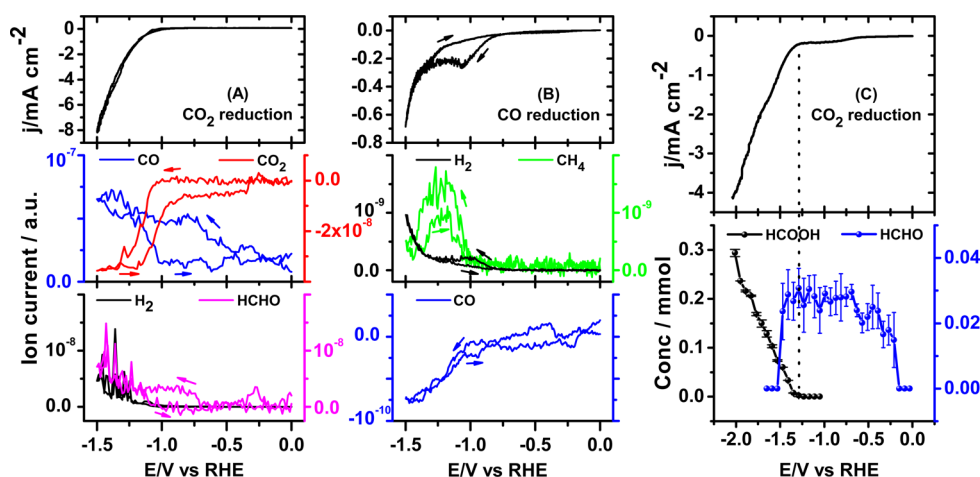


Figure 1. Volatile products detected during reduction of (A) CO_2 and (B) CO , and liquid products detected during (C) CO_2 reduction on BDD in 0.001 M HClO_4 + 0.099 M NaClO_4 electrolyte. Scan rate: 1 mV s^{-1} .

formation of other species by base-catalyzed chemical or disproportionation reactions. It is evident that the effect of the local pH should be known for a correct interpretation of the data, especially for mechanistic studies. Possible organic transformations related to the reduction of CO_2 have recently been discussed from a general point of view.²⁰ In this context, aldehydes are the most important intermediates/products, because of their diverse reactivity. The Cannizzaro reaction is a base-catalyzed disproportionation reaction of an aldehyde, devoid of α -H atoms, into the corresponding carboxylic acid and alcohol.^{21–23} Aldehydes with α -H atoms do not undergo the Cannizzaro disproportionation, as the aldol reaction is much faster. In the aldol reaction, C–C bond formation occurs by addition of the α -carbon of one aldehyde/ketone molecule to the carbonyl carbon of another molecule under the influence of a base.^{24,25}

In this work we elaborate on the utilization of BDD as electrocatalyst for the electrochemical CO_2 reduction under ambient conditions in acidic media. We will discuss the importance of disproportionation and chemical reactions on product distributions often encountered with CO_2 electroreduction also on other electrode materials. We will show that a supposedly inactive material such as BDD is active for the reduction of CO_2 to methane and the concomitant formation of methanol and formic acid, as a result of base-catalyzed Cannizzaro reactions.

EXPERIMENTAL SECTION

The electrochemical experiments were carried out in a conventional three-electrode cell where the working electrode and counter electrode compartments were separated by a nafion membrane (Nafion 115). BDD discs of 3 mm or 10 mm diameter (Windsor Scientific Ltd., UK) were embedded in Teflon and used as working electrodes. The counter and reference electrodes were a platinum gauze and a reversible hydrogen electrode (RHE), respectively. For correct measurements versus the RHE scale, the luggin capillary and the RHE compartment were filled with CO_2 -saturated electrolyte before CO_2 reduction. Electrolyte solutions were prepared with high-purity perchloric acid (Merck Suprapur), sodium perchlorate (Sigma-Aldrich, ACS reagent), and ultrapure water (Millipore Milli-Q gradient A10 system, $18.2 \text{ M}\Omega\text{-cm}$). The reported current density is IR corrected and normalized by the geometric surface area of the BDD disc. During voltammetry, online electrochemical mass spectrometry (OLEMS) was utilized for the detection of volatile reaction products and online high-performance liquid chromatography (online HPLC) for the

analysis of nonvolatile reaction products, as described before.^{26,27} The reported concentrations of liquid products are an average of two or three independent measurements. Additionally, the data points of each specific experiment are recorded as the average of two injections of one sample in HPLC, since a slightly different chromatogram also adds an uncertainty to the calculated concentration. The latter source of error is more important for low concentrations ($<0.05 \text{ mM}$), while the deviation in concentration resulting from repeated experiments is dominant for high concentrations.

RESULTS AND DISCUSSION

Prior to each experiment, the BDD electrode was cleaned by ultrasonication in concentrated HNO_3 and water. A Raman spectrum of the BDD electrode is given in the Supporting Information (Figure S.1). After ultrasonication, blank cyclic voltammograms were recorded in 0.001 M HClO_4 + 0.099 M NaClO_4 at a scan rate of 500 mV s^{-1} until a stable voltammogram was obtained (typically around 50 cycles) to ensure a clean surface, as shown in Figure S.2a. Experiments on BDD in a CO_2 -saturated electrolyte show higher current densities compared to those using an Ar-saturated electrolyte, implying that BDD is active for CO_2 reduction (Figure S.2b). Figure 1 shows the formation of volatile species during (A) CO_2 reduction and (B) CO reduction, and (C) the formation of nonvolatile species during CO_2 reduction. Besides H_2 , CO_2 , and CO , the mass fragment of HCHO is observed, which is in agreement with the literature¹¹ and our HPLC data (Figure 1C), except for lower faradaic efficiencies for HCHO and HCOOH , as shown in Figure S.3. The lower faradaic efficiencies are the result of an electrolyte with higher proton concentration, leading to the formation of a significant amount of H_2 compared to the work by Nakata et al.¹¹ Remarkably, Figure 1B shows the formation of CH_4 during CO reduction on BDD. The current measured during CO_2 reduction is much higher compared to the current measured during CO reduction, probably due to suppression of the HER by CO . The reason why no CH_4 is detected during CO_2 reduction is assumed to be related to the small amount of CO produced, needed for further reduction to CH_4 . The production of CH_4 during CO reduction is not limited to pH 3, but is also observed in electrolytes with a pH between 1 and 7. Our previous experiments and DFT calculations suggest that CH_3OH is an intermediate in the further reduction toward CH_4 on cobalt protoporphyrins immobilized on pyrolytic

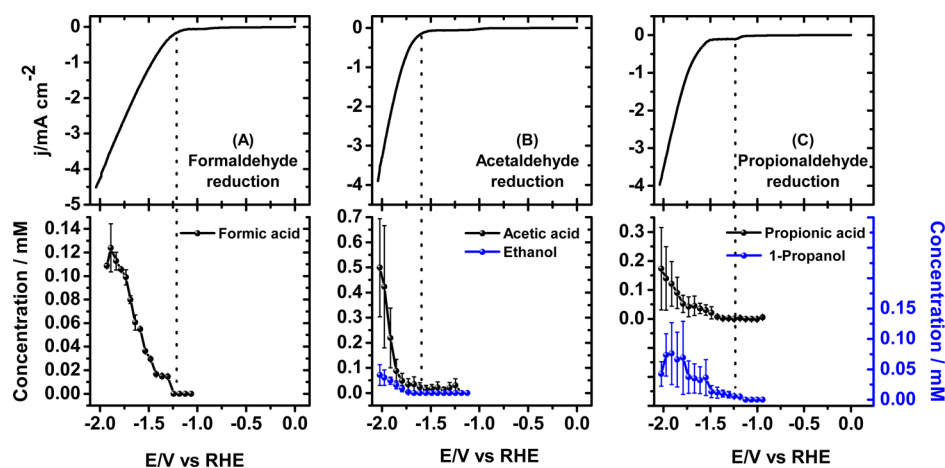


Figure 2. Liquid products detected during reduction of (A) 100 mM formaldehyde, (B) 100 mM acetaldehyde, and (C) 100 mM propionaldehyde on BDD in 0.001 M HClO₄ + 0.099 M NaClO₄ electrolyte. Scan rate: 1 mV s⁻¹.

graphite.^{28,29} However, a similar pathway is not likely for CO₂ or CO reduction on BDD, since CH₄ is not detected with OLEMS during methanol reduction on BDD. Even though the amount of CH₄ is not expected to be high, this finding is very intriguing as BDD activity for CO₂ reduction beyond formaldehyde has not been reported before. Very recently it was shown that metal impurities in catalysts and electrolytes can have significant effects on the catalytic activity for CO₂ reduction.^{30,31} Since our experiments are conducted on high surface area BDD electrodes and on relatively small time scales, the catalyst poisoning by metal ion impurities in the electrolyte as discussed by Wuttig et al. are assumed to be negligible. Moreover, the promotion of CO₂ reduction by impurities in carbon materials, especially trace levels of copper leading to CH₄, is assumed not to affect our experiments on BDD, since a cleaning procedure is followed similar to one suggested by Lum et al. needed for removal of these metallic impurities and the voltammogram recorded afterward does not show additional redox peaks (Figure S.2a inset). For these reasons we believe that the formation of CH₄ on BDD is not the result of metallic impurities promoting the CO₂ reduction toward CH₄, but can be ascribed to the electrochemical activity of BDD for CO₂ reduction. As pristine pyrolytic graphite is not active for CO₂ reduction²⁸ and does not produce HCHO, HCOOH, CH₃OH, or CH₄, the activity of BDD is likely associated with its sp³-hybridized carbon atoms.

In addition to the formation of HCHO, Figure 1C shows the formation of HCOOH at more cathodic potentials (< -1.3 V_{RHE}). This could be due to the fact that BDD has some activity for CO₂ reduction to HCOOH,¹¹ but the same trend for HCOOH is observed during direct reduction of HCHO, as shown in Figure 2A. Importantly, the onset potential of HCOOH production is the same as the onset of the HER. The formation of HCOOH, an oxidation product of HCHO, under reducing conditions is believed to be the result of a disproportionation reaction such as the Cannizzaro reaction. The H₂ evolution at less negative potentials (approximately between -0.5 and -1.3 V_{RHE}) is the result of proton reduction, and at more negative potentials (< -1.3 V_{RHE}) caused by direct water reduction similar to results obtained previously on pyrolytic graphite in perchloric acid of pH 3.²⁸ The direct water reduction produces OH⁻ ions in the vicinity of the electrode surface (eq 2), which promote the disproportionation reaction. The Cannizzaro reaction is expected to form CH₃OH as well

which is not detected with HPLC due to sensitivity limitations. However, as shown in Figure S.4, CH₃OH is detected with OLEMS and with HPLC when the HCHO concentration is increased.

We also investigated the formation of liquid products from the C₂ and C₃ aldehydes, acetaldehyde and propionaldehyde, under reducing conditions as shown in Figure 2B,C. Both, the primary alcohols and carboxylic acids, are observed commencing together with the HER akin to HCHO reduction. This observation justifies and generalizes the involvement of a disproportionation reaction at negative potentials. The product distributions suggest a Cannizzaro type disproportionation reaction, although the classical Cannizzaro reaction does not take place with aldehydes having α -H atoms. However, Cannizzaro products from aldehydes with α -H atoms have been observed before.³² When the C₁-C₃ aldehydes are treated with different concentrations of NaOH, the carboxylic acids and alcohols are formed, as displayed in Figure S.5. It can be seen that the amount of alcohol and carboxylic acid formed depends on the concentration of NaOH analogous to a higher local concentration of OH⁻ at more negative potentials. If self-disproportionation is the dominant mechanism, the expected yields of alcohol and carboxylic acid should be around 50:50%, which is not obtained in our aldehyde reduction experiments. A factor 10 higher yield is observed for propionic acid compared to 1-propanol during propionaldehyde reduction (Figure 2C), which suggests the involvement of at least one other reaction pathway or a mechanism not corresponding to the classical Cannizzaro mechanism.

The formation of C₂-C₃ alcohols and carboxylic acids is probably associated with a catalytic or kinetic effect, where near the BDD surface the aldol reaction is suppressed or the Cannizzaro reaction is preferred over the aldol reaction. Ethanol and acetic acid as products of disproportionation reactions of acetaldehyde have been reported before. Cook et al. have reported a homogeneously catalyzed disproportionation of acetaldehyde into acetic acid and ethanol.³³ Nagai et al. found several products including acetic acid and ethanol formed by a noncatalytic reaction pathway of acetaldehyde under hydrothermal conditions.³⁴ A catalytic effect of BDD for the disproportionation reactions is unlikely as the reduction of the C₁-C₃ aldehydes on a pyrolytic graphite electrode in the same electrolyte also leads to the formation of carboxylic acids and alcohols as shown in Figure S.6. Additionally, the Cannizzaro

products for formaldehyde disproportionation, HCOOH and CH₃OH, are also observed on gold and copper electrodes as depicted in Figure S.7. The fact that no aldol reaction products are detected suggests that the presence of the electrode surface plays a role. Even though the classical Cannizzaro and aldol reactions were originally reported for homogeneous alkaline solutions, a variety of heterogeneous and catalytic systems for these reactions have been investigated for formaldehyde^{35–38} and acetaldehyde^{39–42} as well. Several groups have reported that surface OH[−] can initiate Cannizzaro disproportionation of surface adsorbed HCHO leading to formate ions and methoxy groups.^{35–37} A mechanism including a nucleophilic-addition transformation of HCHO to dioxymethylene (CH₂O₂) which subsequently reacts with a HCHO molecule to form formate and methoxy groups has been proposed.⁴³

The importance of the local pH (gradient) near the electrode is demonstrated by the reduction of formaldehyde in different electrolytes as shown in Figure 3. A small amount HCOOH is

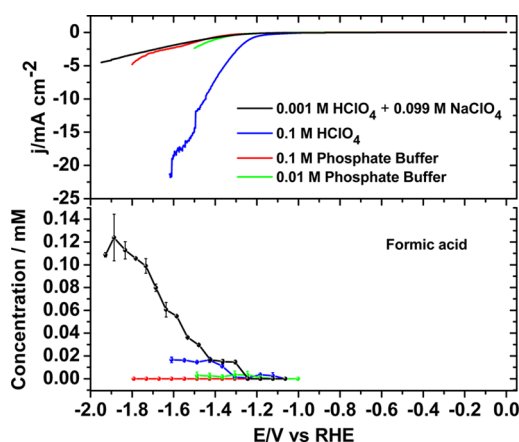


Figure 3. Formic acid formation during reduction of formaldehyde in perchloric acid (pH 1 and pH 3), 0.1 M phosphate buffer pH 6.8, and 0.01 M phosphate buffer pH 6.8. Scan rate: 1 mV s^{−1}.

observed in a 0.1 M HClO₄ electrolyte while trace amounts or no HCOOH are observed in phosphate buffers of pH 6.8, depending on the buffer capacity. The higher the buffer capacity, the less sensitive the local pH is to changes, the smaller the possibility of disproportionation reactions to occur. In case of the 0.1 M HClO₄ electrolyte, the local environment is very acidic and the local concentration of hydroxide ions near the electrode surface is lower compared to perchloric acid of pH 3, which results in the formation of less HCOOH.

In the recent literature there are several studies where formaldehyde, methanol, formic acid or acetaldehyde, ethanol, acetic acid or propionaldehyde, propionic acid, and 1-propanol have been observed during CO₂ electroreduction in different electrolytes on different electrodes.^{44–49} Our results show that one should be careful not to misinterpret the observation of carboxylic acids and alcohols to be a result of direct CO₂ reduction. Especially in the quest for novel catalytic materials for CO₂ electroreduction toward liquid products, the involvement of disproportionation reactions should be evaluated. Specifically, ethanol formation always seems to go hand-in-hand with acetate formation, suggesting that they may be (partially) formed from acetaldehyde disproportionation. Moreover, the use of buffer solutions is recommended in order to avoid disproportionation reactions and control experiments

are recommended when using alkaline electrolytes to evaluate the stability of products and intermediates.

CONCLUSION AND SUMMARY

In conclusion, this work has illustrated the existence and the importance of disproportionation reactions during electroreduction of CO₂. These reactions lead to product distributions which should be distinguished from direct CO₂ reduction products. The formation of carboxylic acids and alcohols is shown to be the result of disproportionation of aldehydes, which is promoted by the local alkaline environment in the vicinity of the electrode surface, caused by the HER. This phenomenon is strongly affected by the pH and buffer capacity of the electrolyte and can be generalized to other electrode materials and to C₂ and C₃ aldehydes as well. Moreover, it is revealed that BDD has the ability to further reduce CO to methane. The BDD activity should therefore be taken into account when BDD is used as a substrate for catalysts for CO₂ and CO reduction. The involvement of the disproportionation reactions results in a pathway leading to desirable products such as formic acid, acetic acid, methanol, and ethanol during CO₂ electroreduction, different from the direct CO₂ reduction pathway toward these liquid products.

ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/jacs.6b12008.

Characterization of the BDD electrode (blank cyclic voltammograms and Raman spectra); cyclic voltammograms in Ar- and CO₂-saturated electrolyte; Faradaic efficiency for liquid products; methanol formation during reduction of formaldehyde; formation of Cannizzaro products from C₁–C₃ aldehydes when treated with NaOH; formation of liquid products from the reduction of C₁–C₃ aldehydes on pyrolytic graphite and from formaldehyde on gold and copper (PDF)

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Notes

The authors declare no competing financial interest.

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