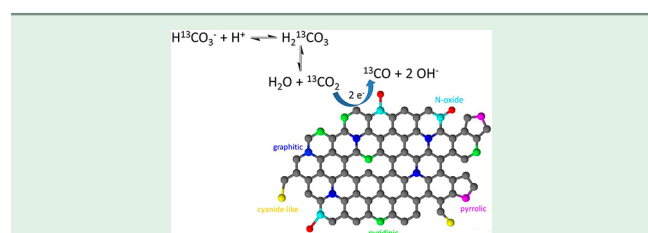# Electrochemical Reduction of Carbon Dioxide on Nitrogen-Doped Carbons: Insights from Isotopic Labeling Studies

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S *Supporting Information*

ABSTRACT: Isotopic labeling experiments were performed to better understand the electrochemical reduction of carbon dioxide on nitrogen-doped porous carbon electrodes. By using nonequilibrated solutions of selectively labeled initial carbon sources (i.e., $^{13}CO_2$ and $H^{13}CO_3^-$), bicarbonate anion was identified as the predominant source of the carbon monoxide reduction product.

Nitrogen-doped carbon materials are increasingly studied in energy-oriented electrochemical and photo-electrochemical reactions as active materials and conductive scaffolds.[1] After demonstrating their catalytic activity in the electrochemical oxygen reduction reaction,[2,3] there is growing interest toward H_2 evolution[4] and CO_2 conversion, too.[5−9] Impressive activities were reported in CO_2 reduction, which makes these cheap materials potential rivals to their more expensive inorganic counterparts. Both experimental and theoretical studies investigated mechanistic aspects to identify the active center. The chemical nature of the C−N moiety seems to be a decisive factor, where pyridinic N and a C atom next to pyridinic N were the most active.[6] Despite the steeply growing number of papers on CO_2 electroreduction using carbon-based electrodes, there are only a very few papers where any kind of isotopic labeling was performed to confirm the source of CO_2 reduction products.[5,9,10] On the other hand, detailed studies were carried out on gold[11] and copper[12] electrodes, where the electroreduction process was monitored by surface-sensitive infrared spectroscopy and mass spectrometry. In other instances, NMR spectroscopy was employed to identify ^{13}C in the liquid phase reduction products on gold and copper electrodes.[13,14] At the same time, the question still holds, what is the source of the assumed CO_2 reduction products in such cases? The dissolved CO_2, the bicarbonate ions, CO_2 furnished through the carbon dioxide−bicarbonate equilibrium, or the electrode material itself? To answer this question, we performed the *first systematic isotopic labeling study employing a N-doped carbon electrode*. The fact that it takes around 2 h to reach the equilibrium conditions between the bicarbonate ions and CO_2 (Figure S2) allowed selective or joint labeling of the carbon sources (CO_2 and HCO_3^-), and electrogenerated CO was analyzed by GC−MS.

A highly porous, high surface area N-doped carbon catalyst (HPG-PPy) was synthesized by adaptation of a literature procedure[15] (see details in the SI). Product analysis during potentiostatic electrolysis revealed the formation of CO and H_2 as main products (Figure S1D). The amounts of CO and H_2 were similar at moderate overpotentials (−0.61 and −0.71 V) and scaled linearly with the reduction charge (Figure 1A). First, joint isotopic labeling experiments (i.e., both the CO_2 gas- and bicarbonate-labeled) were carried out, and the exclusive formation of ^{13}CO confirmed that indeed the CO_2/bicarbonate feedstock was converted (Figure S3). To have a deeper understanding of the CO_2 reduction mechanism on the carbon catalyst, especially to find out whether the bicarbonate or the aqueous CO_2 is the reacting species, the two carbon sources were selectively labeled. When the bicarbonate was the labeled component and we were operating under nonequilibrium conditions (see SI section 1.3 for details), in the first hour of electrolysis, the majority of the CO was ^{13}C-labeled. Within this time frame, the isotopic equilibrium was not yet established between bicarbonate ions and CO_2 gas (Figure S2). The $^{13}CO/^{12}CO$ ratio gradually decreased and approached the ratio characteristic of the equilibrium conditions during the 2 h electrolysis (Figure 1B). On the other hand, when the CO_2 gas was labeled, the opposite trend was observed (Figure 1C). As in the case of nonequilibrated precursor solution, the isotopic composition of the CO product mirrored that of bicarbonate ions; it seems that CO either originates directly from the reduction of bicarbonate or from the aqueous CO_2 supplied through the fast equilibrium with the bicarbonate ions (but not from the dissolved CO_2 in the bulk solution). This latter mechanism was suggested for Au and Cu electrodes.[11,12]
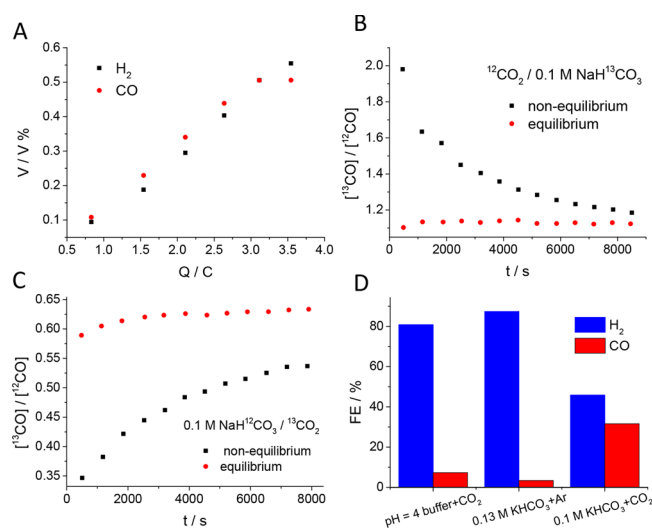
Figure 1. (A) Concentration of CO and H_2 generated on the HPG-PPy electrode with increasing reduction charge during potentiostatic electrolysis at −0.71 V (vs RHE) in a CO_2-saturated 0.1 M $KHCO_3$ electrolyte. (B) Ratio of the concentration of ^{13}CO to ^{12}CO formed during potentiostatic electrolysis at −0.71 V (vs RHE) in a $^{12}CO_2$-saturated 0.1 M $NaH^{13}CO_3$ electrolyte under nonequilibrium and equilibrium conditions. (C) Ratio of the concentration of ^{13}CO to ^{12}CO formed during potentiostatic electrolysis at −0.71 V (vs RHE) in a $^{13}CO_2$-saturated 0.1 M $NaH^{12}CO_3$ electrolyte under nonequilibrium and equilibrium conditions. (D) Faradaic efficiencies of H_2 and CO formation at the 75th minute of electrolysis at −0.61 V (vs RHE) in different electrolytes: (i) CO_2-saturated 0.1 M phosphate buffer (pH = 3.8); (ii) Ar-saturated 0.13 M $KHCO_3$ (pH = 8.8); (iii) CO_2-saturated 0.1 M $KHCO_3$ (pH = 6.6).

To decide whether the CO_2 or the HCO_3^- is the actual reacting species, a set of control experiments was performed. The concentration of bicarbonate ions and $CO_{2,aq}$ and the pH cannot be controlled independently because of the existing equilibrium. We can operate at pH values, however, where dominantly only one species is present. If the pH is below 5, almost all of the dissolved CO_2 is in the form of $CO_{2,aq}$, while between pH 7 and 9, mainly bicarbonate is present in the solution.[16] Thus, we performed electrolysis in (i) CO_2-saturated 0.1 M phosphate buffer (pH = 3.8), (ii) 0.13 M $KHCO_3$ solution saturated with Ar (pH = 8.8), and (iii) CO_2-saturated 0.1 M $KHCO_3$ (pH = 6.6), at −0.61 V vs RHE in all cases (Figure 1D). The Faradaic efficiency of CO formation (FE_{CO}) was 31.6% in the CO_2-saturated 0.1 M $KHCO_3$, while it was only 3.4% in the Ar-saturated 0.13 M $KHCO_3$. Although the total dissolved CO_2 content of the two electrolytes is approximately the same, the $CO_{2,aq}$ concentration is around 40 times higher for the CO_2-saturated 0.1 M $KHCO_3$ (see SI section 5). In the CO_2-saturated pH = 3.8 buffer, the FE_{CO} was 7.3%, higher than that in the case of the Ar-saturated electrolyte, probably because of the much higher $CO_{2,aq}$ concentration. The fact that FE_{CO} in the CO_2-saturated pH = 3.8 buffer is *much* lower than in the CO_2-saturated 0.1 M $KHCO_3$ solution suggests the vital role of bicarbonate ions acting as a CO_2 source. Notably, a very similar trend was seen in the partial current densities to what was presented for the FE values.

Overall, findings from selective isotopic labeling and pH-dependent studies demonstrated that the reacting species at the surface of a N−C electrode is most likely $CO_{2,aq}$. Dissolved

CO_2 at the electrode surface, however, is rapidly supplied by bicarbonate ions (acting as a "CO_2 buffer"), if present, rather than gas-phase CO_2 or that dissolved in bulk solution. This assumption explains why the isotopic composition of the CO product is similar to that of bicarbonate when the isotopic equilibrium is not yet established. The fact that the highest FE_{CO} was obtained for the bicarbonate/CO_2 system and that it was significantly lower when $CO_{2,aq}$ was present without bicarbonate further supports this hypothesis. Direct bicarbonate reduction is unlikely as only very small amounts of CO were produced when practically only bicarbonate ions were present. This mechanism was also suggested for a Ni−N−C catalyst based on the dependence of the CO partial current density on bicarbonate concentration.[17] Further efforts are ongoing to elucidate the mechanism of the electrochemical CO_2 reduction on N-doped carbon electrodes because these insights are very important in designing new electrode and electrochemical cell configurations to scale up this promising technology.[18,19]

■ ASSOCIATED CONTENT

Ⓢ Supporting Information

The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/acsenergylett.8b00212.

Electrode preparation, electrochemical measurements, and related mass spectrometry data (PDF)

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Notes

The authors declare no competing financial interest.

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