Electrochemical CO_2 Reduction by Boron-Doped Diamond Electrodes

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Boron-doped diamond (BDD) electrodes are very attractive material, because of their wide potential window, low background current, chemical inertness, and mechanical durability.[1] In these years, we have reported several examples for electrochemical sensor applications including novel microsensing systems for *in vivo* real time detection of local drug kinetics.[2] Furthermore, applications for electrochemical organic synthesis[3] and electrochemiluminescence (ECL) systems[4] are also reported. Here, recent developments on electrochemical CO_2 reduction using BDD electrodes are presented.

In 2018, we investigated the electrochemical reduction of CO_2 in a flow cell using BDD electrodes. The faradaic efficiency (FE) for the production of HCOOH was as high as 94.7%. Furthermore, the selectivity for the production of HCOOH was more than 99%. The rate of the production was increased to 473 μmol $m^{-2}s^{-1}$ at a current density of 15 mA cm^{-2} with a FE of 61%. The FE and the production rate are almost the same as or larger than those achieved using Sn and Pb electrodes. In addition, the stability of the BDD electrodes was confirmed by 24 hours operation.[5]

Then, in 2019, we were able to control the selectivity and efficiency with which carbon monoxide (CO) is 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. 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.[6]

Recently, in order to operate on a large scale for industrial applications, an intermittent flow cell system was presented. A stop-start motion of the flow conditions in the intermittent cell was created using a piston pump, and this considerably increases the rate of electrochemical conversion of CO_2 to HCOOH compared to a continuous flow system.[7] Furthermore, we found that an initial electrochemical CO_2 reduction reaction could significantly improved the reaction current and Faradaic efficiency of the CO_2 reduction on BDD electrodes.[8] The effect is referred to as the "self-activation" of BDD. Here, the mechanisms and the effect of self-activation is discussed.

References

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