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Electrocatalytic CO₂ reduction toward liquid fuels : on heterogeneous electrocatalysts and heterogenized molecular catalysts

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Supporting Information to Chapter 3

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

A.1 Characterization of the BDD electrode

Figure A.1 displays the spectra of the Boron Doped Diamond and Pyrolytic Graphite (PG) electrodes, indicating the sp^3 and sp^2 bonded carbon atoms. In Figure A.2 (a) the blank voltammograms and (b) CO_2 reduction and hydrogen evolution on the BDD electrode are shown in 0.001 M $HClO_4$ + 0.099M $NaClO_4$ electrolyte.

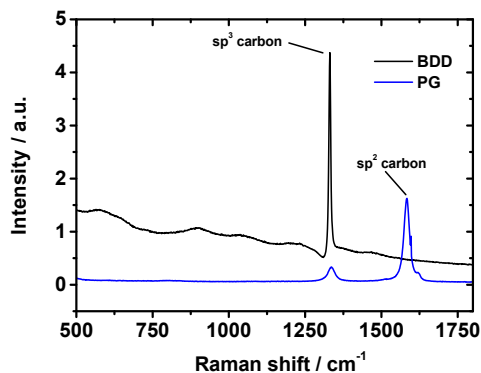


Figure A.1 Raman spectra of the BDD electrode and the PG electrode

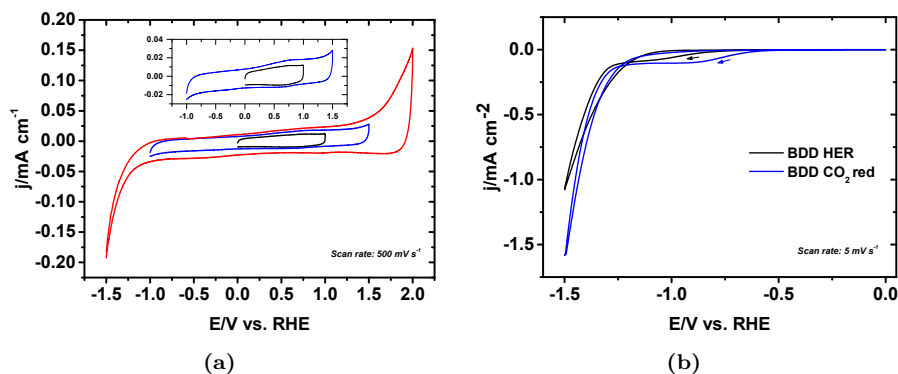


Figure A.2 (a) Blank voltammograms on BDD in 0.001 M $HClO_4$ + 0.099M $NaClO_4$ electrolyte. Scan rate: 500 $mV s^{-1}$ and (b) CO_2 reduction & hydrogen evolution on BDD in 0.001 M $HClO_4$ + 0.099M $NaClO_4$ electrolyte. Scan rate: 5 $mV s^{-1}$.

A.2 Faradaic efficiency liquid products

Potentiostatic bulk electrolysis experiments are performed for 90 minutes to determine the faradaic efficiency of the major liquid products from CO_2 reduction,

A.2. Faradaic efficiency liquid products

HCHO and HCOOH. 100 μ l samples are taken at specific times and analyzed with HPLC. The faradaic efficiency is calculated using equation A.1, where z_i is the number of electrons needed for the formation of product i , n_i the amount of product i formed (in moles), F the Faraday constant and Q the total charge calculated by the integration of the measured (IR corrected) current with respect to time.

$$FE_i = \frac{z_i n_i F}{Q} \cdot 100\% \quad (\text{A.1})$$

The faradaic efficiency towards HCHO and HCOOH are shown in Figure A.3 for $E = -0.95$ V and $E = -2.1$ V. These values are lower compared to the results of Nakata et al.,^[1] which is ascribed to the use of an electrolyte with higher proton concentration in our experiments. The total faradaic efficiency of HCHO and HCOOH is less than 100 %, where the remaining charge is assumed to be used for the production of H_2 and CO as detected by OLEMS. As described in chapter 3, the concomitant hydrogen evolution leads to a local alkaline environment and since the aim of this paper is to elucidate the effects of this local pH gradient and not on optimizing catalyst efficiency, we have not determined the faradaic efficiency at other reaction conditions (pH, potential etc.). At $E = -2.1$ V, HCHO was not detected, which is in agreement with our online HPLC measurement (Figure 3.1C). Moreover, the faradaic efficiency for HCHO decreases with time, while the faradaic efficiency towards HCOOH increases in time. This could be due to disproportionation of formaldehyde as discussed in chapter 3.

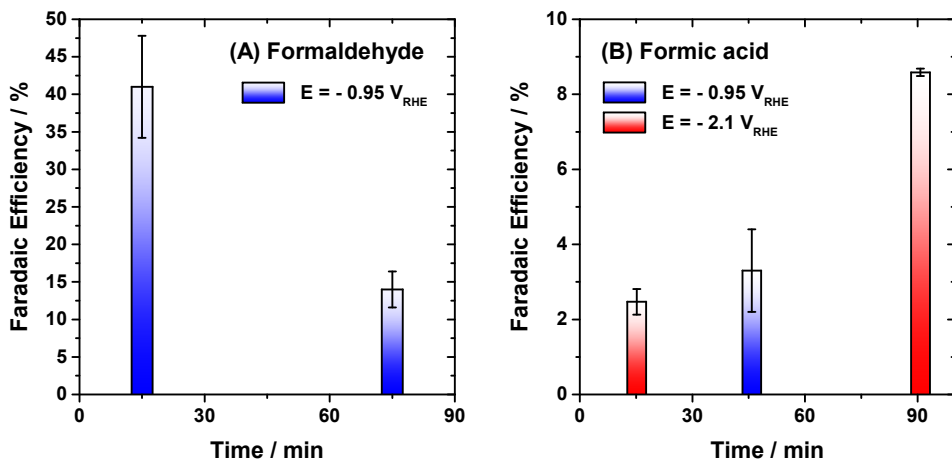


Figure A.3 Faradaic efficiency towards (A) formaldehyde and (B) formic acid at $E = -0.95 \text{ V}_{\text{RHE}}$ and $E = -2.1 \text{ V}_{\text{RHE}}$ on BDD in $0.001 \text{ M HClO}_4 + 0.099 \text{ M NaClO}_4$ electrolyte

A.3 Methanol formation during formaldehyde reduction

In addition to the online HPLC measurements, Online Electrochemical Mass Spectrometry has been utilized to investigate the products formed by reduction of formaldehyde on BDD in 0.001 M HClO_4 + 0.099M NaClO_4 electrolyte. As seen in Figure A.4a, $m/z = 31$ is observed with an onset potential similar to H_2 . This mass fragment is associated with methanol (CH_2OH^+). The reason why no methanol was detected with HPLC (Figure 3.2A) is due to the very low concentrations of methanol formed. In order to prove this, a higher concentration of formaldehyde was reduced and methanol was detected as shown in Figure A.4b. Now formic acid is not observed which is due to overlap in the chromatograms of the large formaldehyde peak with that of formic acid.

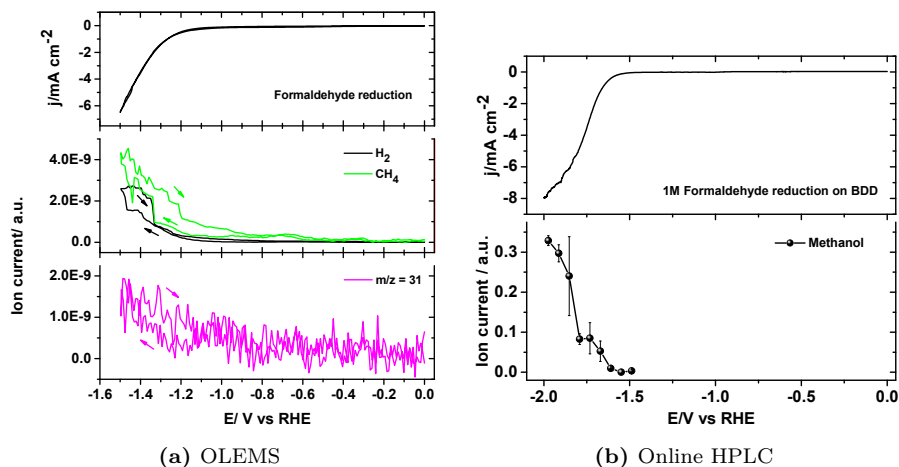


Figure A.4 (a) Formation of H_2 and methanol during 100 mM formaldehyde reduction and (b) formation of methanol during 1 M formaldehyde reduction in 0.001 M HClO_4 + 0.099M NaClO_4 electrolyte. Scan rate: 1 mV s^{-1} .

A.4 Formation of Cannizzaro products from C_1 - C_3 aldehydes and NaOH

Experiments were performed to investigate the products formed by the C_1 - C_3 aldehydes treated with OH^- . 50 mM of the aldehydes was mixed with different concentrations of NaOH and analyzed with HPLC. In all cases the carboxylic acids and primary alcohols were detected as shown in Figure A.5. The higher

A.5. Liquid product formation on other electrodes

the hydroxide concentration, the higher the concentration of carboxylic acid and primary alcohol.

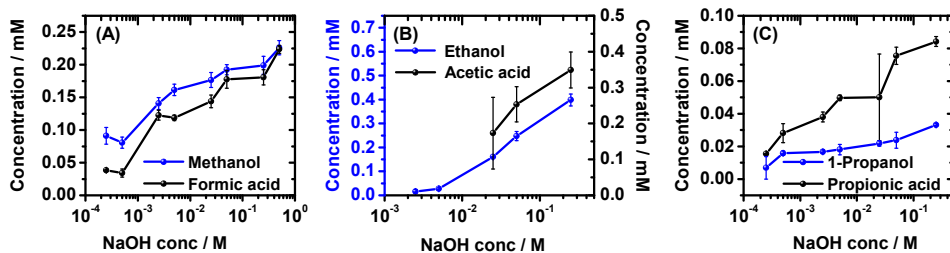


Figure A.5 Formation of carboxylic acids and alcohols during reduction of (A) Formaldehyde, (B) Acetaldehyde and (C) Propionaldehyde as function of OH^- concentration

A.5 Liquid product formation on other electrodes

The formation of the carboxylic acids and primary alcohols during reduction of the C_1 - C_3 aldehydes on a Pyrolytic Graphite electrode in perchloric acid of pH 3 is shown in Figure A.6. Figure A.7 displays the reduction of formaldehyde on gold and copper in 0.001 M HClO_4 + 0.099M NaClO_4 electrolyte, leading to formic acid and methanol. In both figures the onset of the carboxylic acid and alcohol is similar to the HER onset potential.

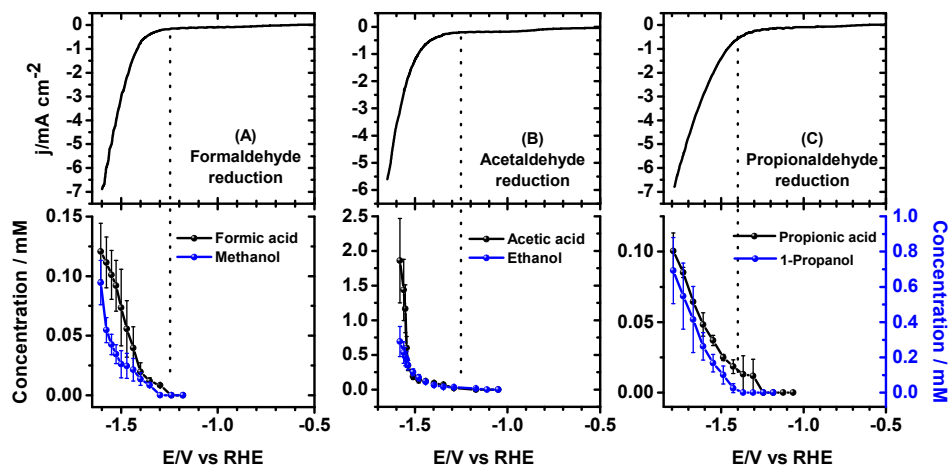


Figure A.6 Liquid products detected during reduction of (A) 50 mM Formaldehyde, (B) 100 mM Acetaldehyde and (C) 100 mM Propionaldehyde on pyrolytic graphite in 0.001 M HClO_4 + 0.099M NaClO_4 electrolyte. Scan rate: 1 mV s^{-1}

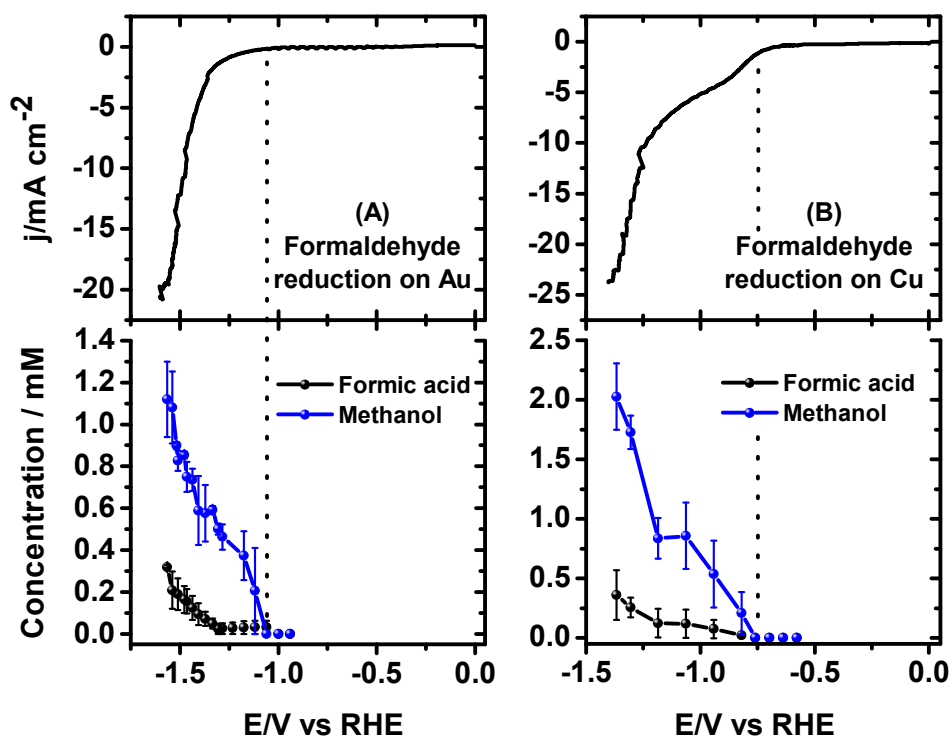


Figure A.7 Liquid products detected during reduction of 50 mM Formaldehyde on (A) gold and (B) copper in 0.001 M HClO_4 + 0.099M NaClO_4 electrolyte. Scan rate: 1 mV s^{-1}

A.6 References

- [1] K. Nakata, T. Ozaki, C. Terashima, A. Fujishima, Y. Einaga, *Angew. Chem. Int. Ed.* **2014**, *53*, 871–874.