ELECTROCHEMICAL CO_2 REDUCTION TO FORMALDEHYDE YES, WE CAN? AN FTIR CAMPAIGN

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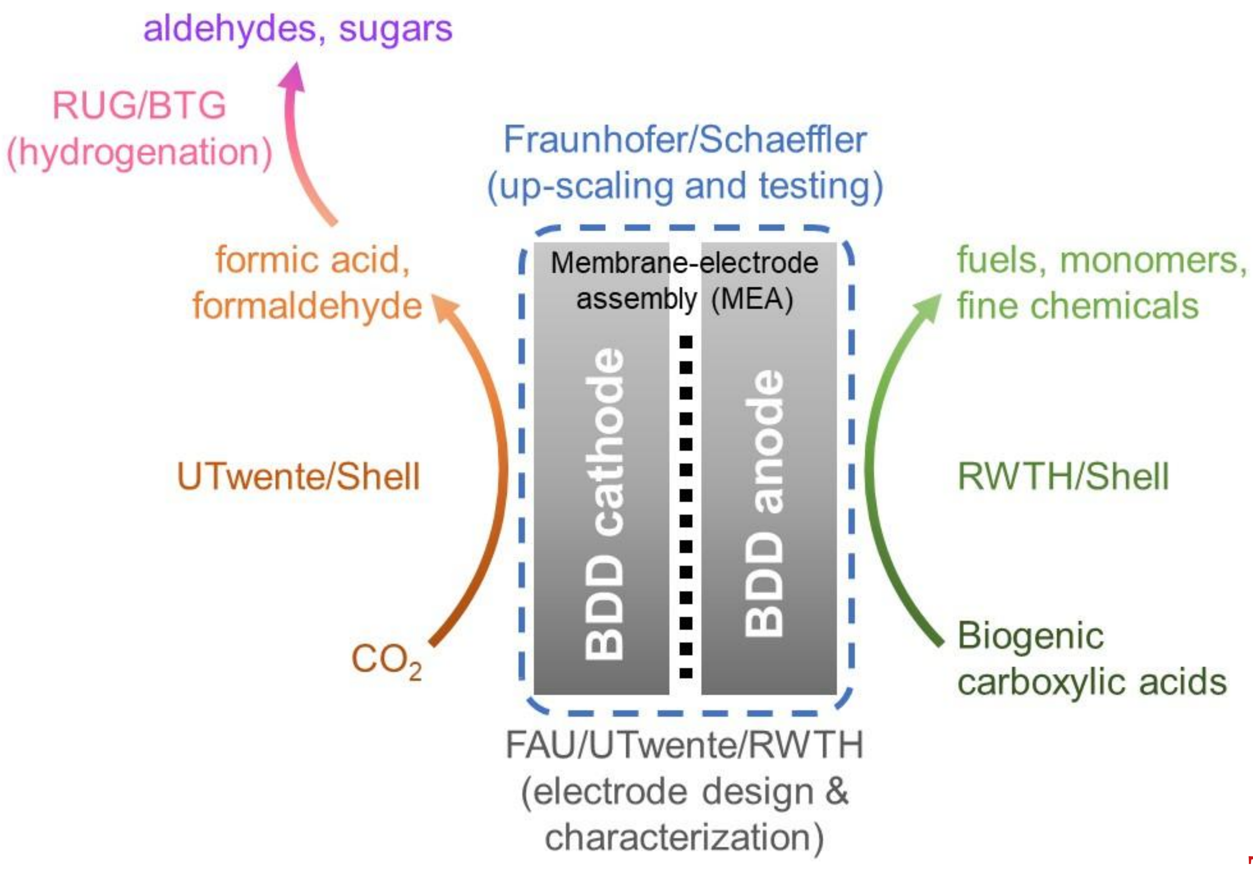
What process are we developing?

- CO_2 as feedstock to produce platform chemicals
- Electrochemical production of formaldehyde directly or via downstream hydrogenation of formic acid [1]

$$CO_2 + 4H^+ + 4e^- \longrightarrow CH_2O + H_2O$$
$$HCOOH + 2H^+ + 2e^- \longrightarrow CH_2O + H_2O$$

- Formaldehyde is a valuable platform chemical (e.g. for artificial sugars, coatings)
- Paired with oxidative valorization of biobased oils via Kolbe electrolysis instead of energy intensive production of "cheap" O_2



Fraunhofer (1PhD), Schaeffler & Shell Testing electrodes, MEA lifetime analysis and process scalability

RUG (1PhD) & BTG Hydrogenation to high-value aldehydes/sugars

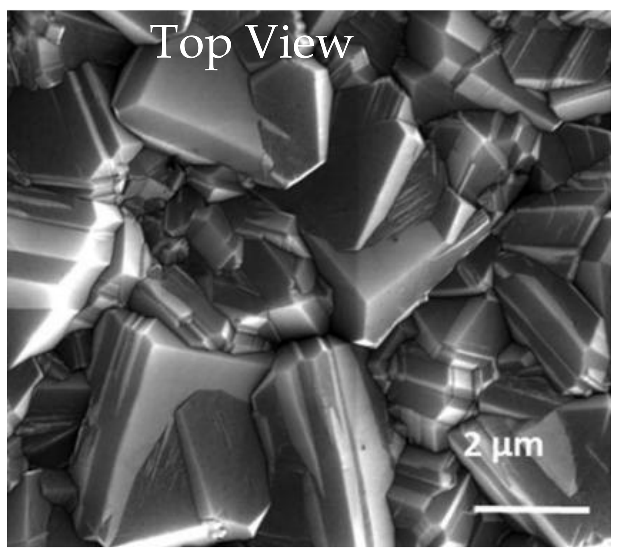
FAU (1 PhD) Advanced and durable boron-doped diamond electrodes

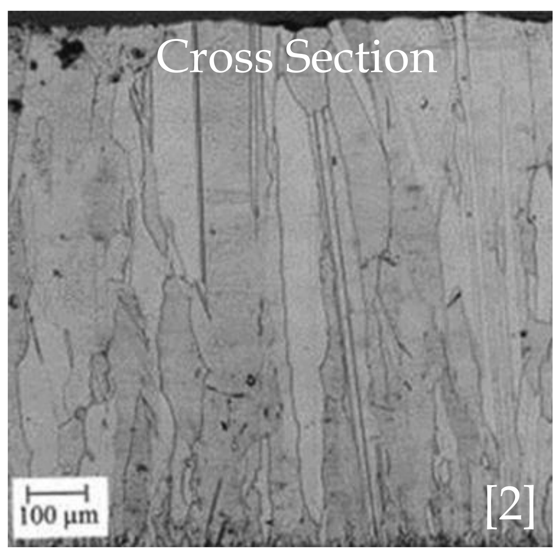
RWTH (1 PhD) Anodes characterization, performance evaluation, and mechanistic study by spectro-electrochemistry

UTwente (2 PhDs) Cathodes characterization, performance evaluation, mechanistic study by spectro-electrochemistry

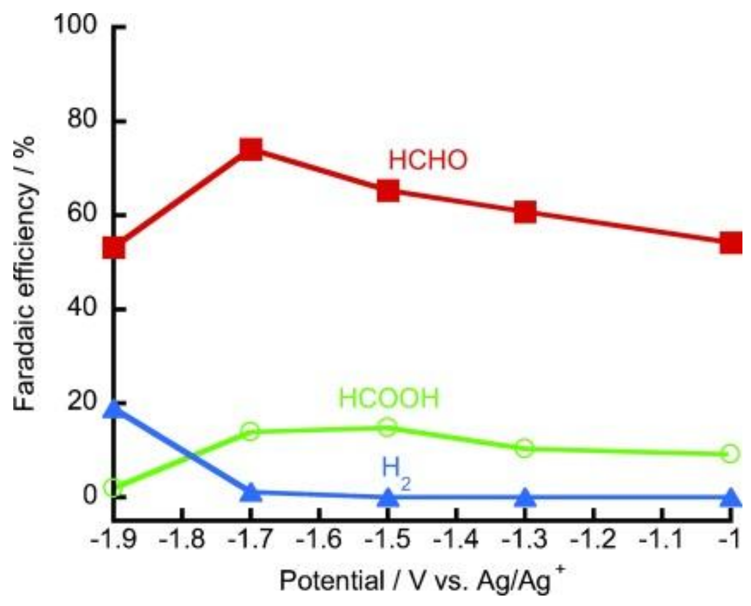
Why BDD as cathode material?

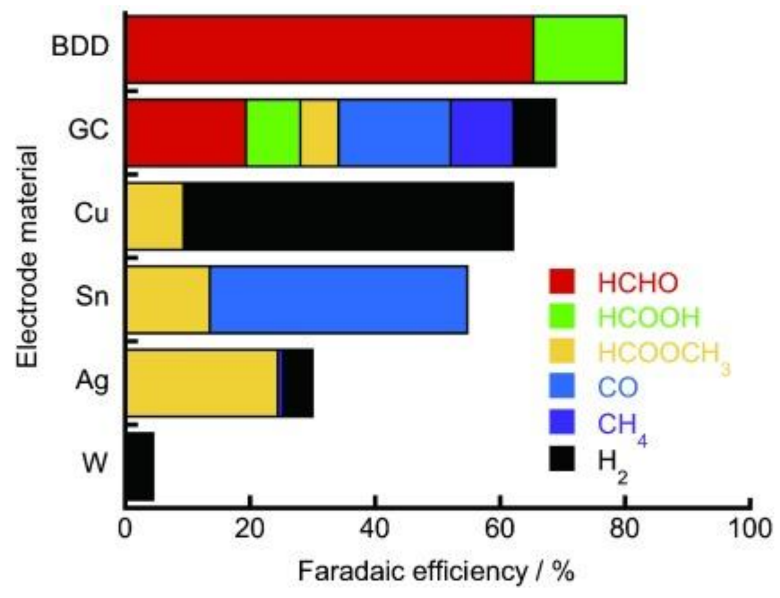
- High stability (Diamond)
- Earth abundant (Carbon)
- High overpotential for HER
- Non-corroding
- Production through Hot Filament CVD





- High faradaic efficiencies towards formaldehyde (up to 74%) for conversion of CO_2 to formaldehyde, reported by Einaga et. Al. [1]





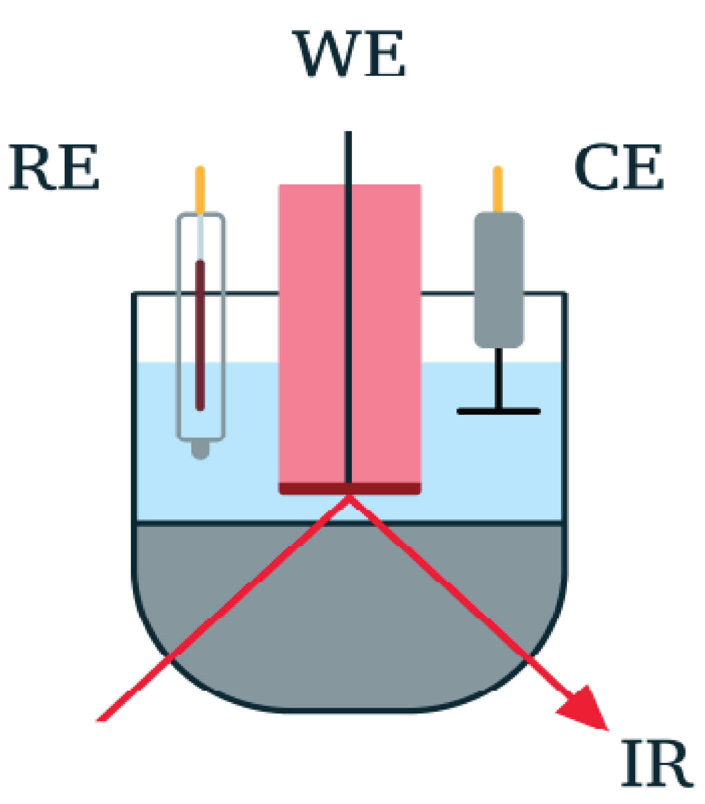
How do we study the mechanism?

FT-IR RAS

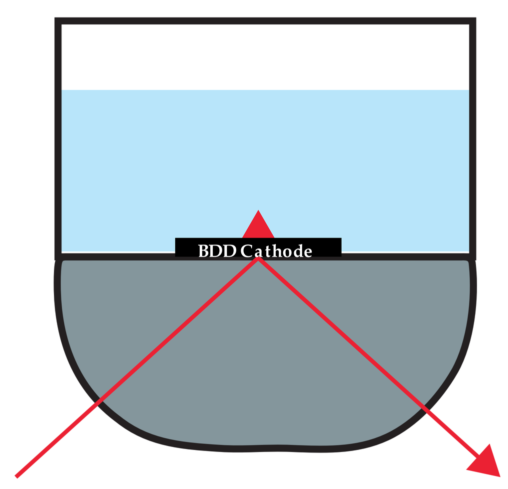
- **F**ourier **T**ransform-**I**nfra**R**ed **R**eflection-**A**bsorption **S**pectrosopy
- Surface sensitivity through the use of P- and S- polarized light
- In the process of realizing a flow-cell configuration to reduce mass transport limitations.
- Future measurements with **sub µs** time resolution

FT-IR ATR

- **F**ourier **T**ransform-**I**nfra**R**ed **A**ttenuated-**T**otal-**R**eflection **S**pectroscopy
- Thin layer (10 – 100nm) of BDD on Silicon wafers
- Grazing angle FT-IR ATR using polarized light can yield surface sensitive information
- Further depth information through varying the incident angle and BDD thickness
- Future measurements with **sub µs** time resolution



FT-IR RAS



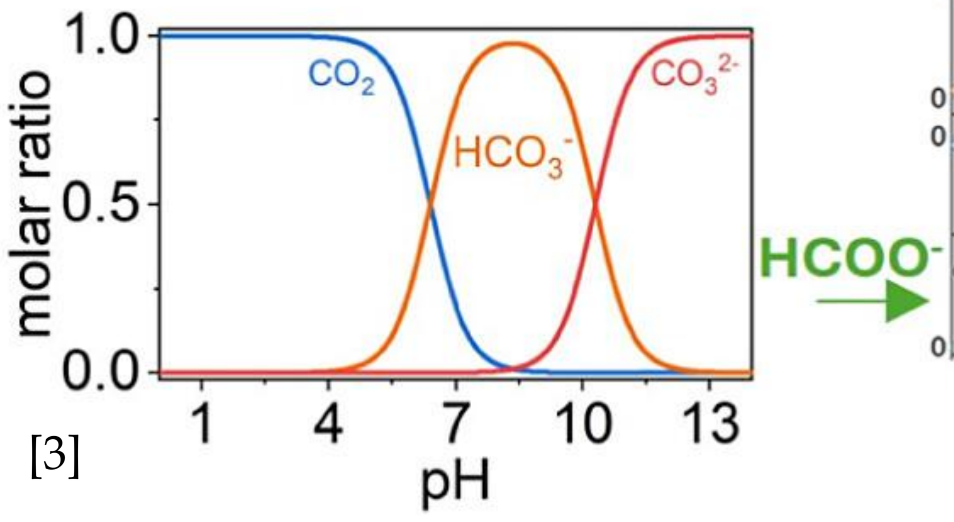
FT-IR ATR

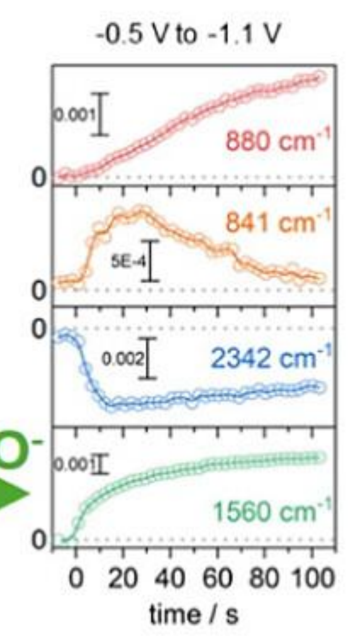
What results have we achieved?

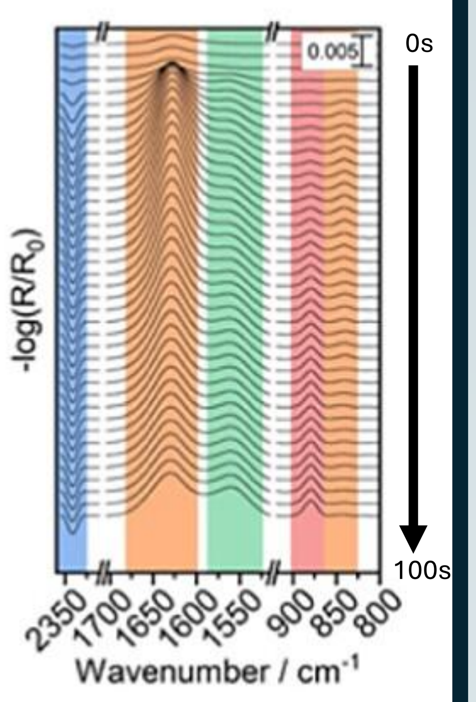
Preliminary work on Cu electrodes

Interfacial pH	4-9	9-12	>12
H_2			
$HCOO^-$			

H^+/CO_2 reduction rate: fast, slow, stopped







- Determination of interfacial pH through bicarbonate equilibrium
- Low pH (~pH 4) favors production of formate
- 3 regimes in the kinetics of formate production
  1. When CO_2 is abundantly available, the formation of formate is maximized. This implies the presence of a CO2 pathway towards formate
  2. When CO2 is depleted and bicarbonate is abundantly available, the formation of formate continues at a slower rate, implying a bicarbonate pathway
  3. When bicarbonate is depleted, the formation of formate comes to a halt

REFERENCES:
[1] Nakata K, Einaga Y. Angew Chem Int Ed Engl. 2014;53(3):871-874
[2] Macpherson J. Phys. Chem. Chem. Phys., 2015,17, 2935-2949
[3] G. Katsoukis et. al, H. Heida, G. Mul. Acs Catalysis. 2024, 14 (18)

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