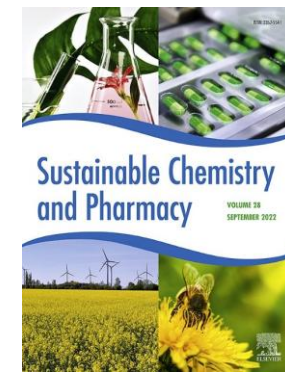


**I am happy for you to photograph or
tweet the slides from my talk**



Supporting Publication S



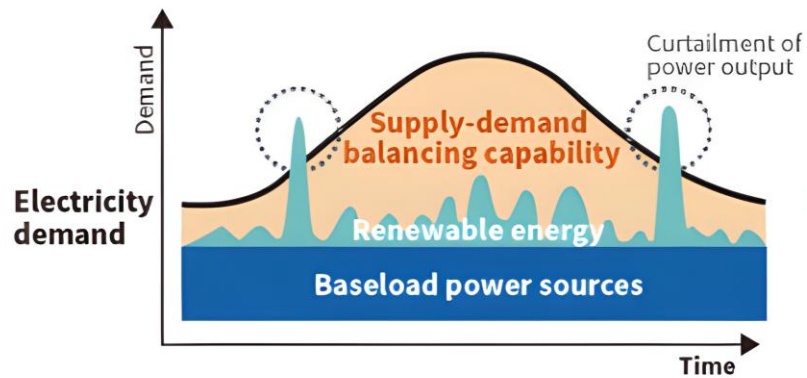
BDD-assisted acetic acid electrochemical decarboxylation for pyrolysis oil upgradation application

Turning low value crude bio liquids into energy dense biofuels for sustainable road transport

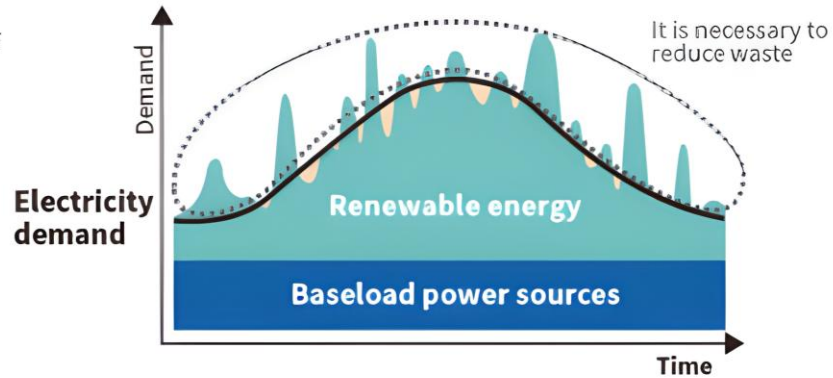
Talal Ashraf, Bastian Mei, Guido Mul
23-05-2023

Photocatalytic synthesis group (PCS)
University of Twente
Contact: t.ashraf@utwente.nl





Now

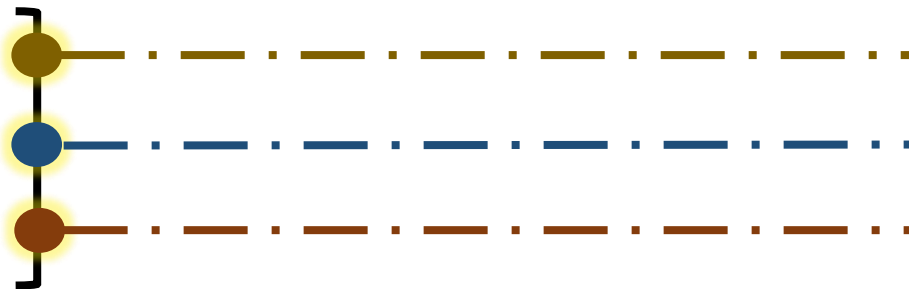


2030 ~

<https://www.global.toshiba/ww/products-solutions/hydrogen/products-technical-services/supply-chain.html>



Storing “**green electrons**” in biobased pyrolysis oil

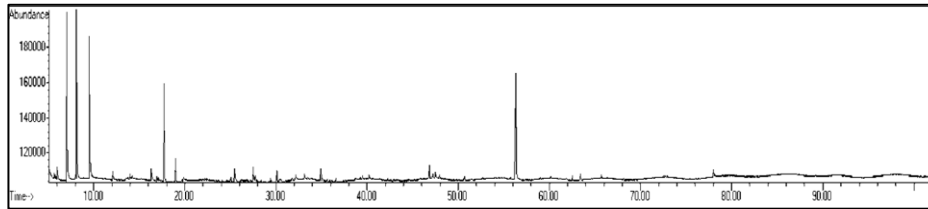


- Upgraded pyrolysis oil
- Chemicals production
- Fuels production

Pyrolysis Oil as feedstock for electrochemical conversion

Aqueous fraction

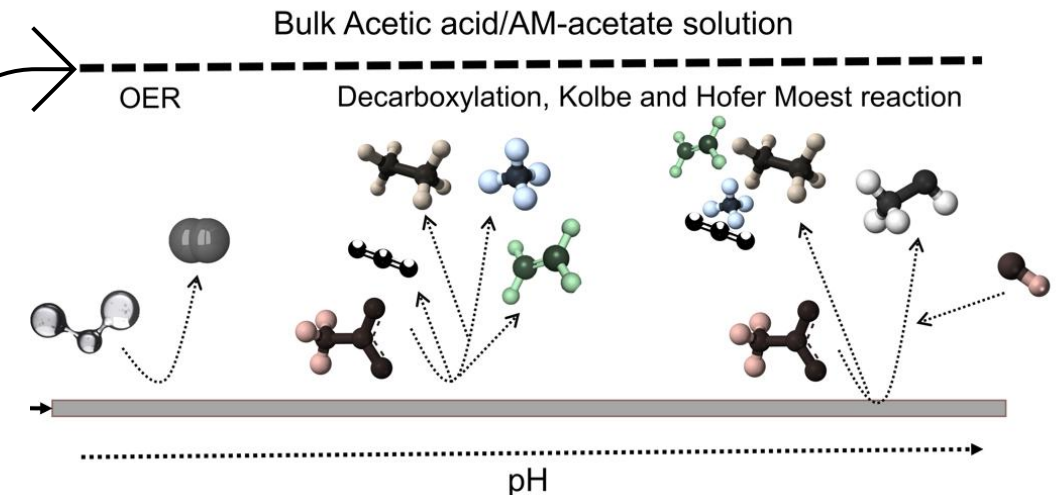
50%



- 4-methyl guaiacol
- Anhydrose mannopyranose
- Guaiacol
- Cyclopentenone
- Furfural
- Butanediol
- 2-hydroxy 3 methyl cyclopent-1-one
- Formic acid methyl ester
- Hydrazine carboxylic acid
- 1-propanol
- Acetic acid

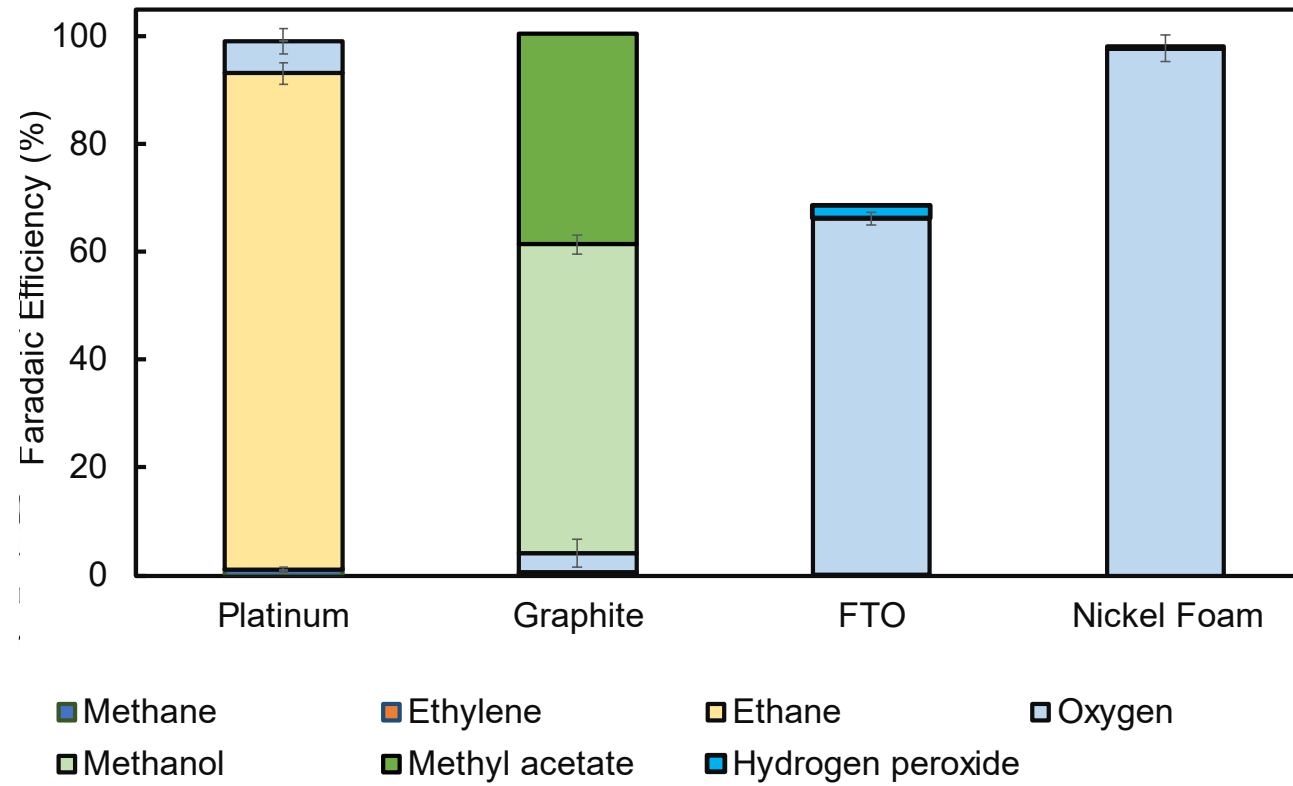
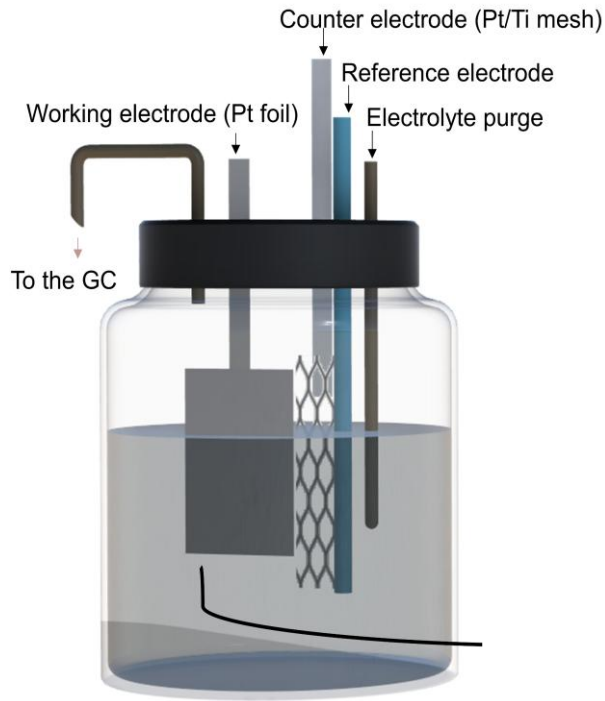
Electrochemical conversion Via Kolbe electrolysis

- Selective to electrode material (Platinum)
- Properties and reaction conditions are well defined in the literature



- Vijh, A. K., and B. E. Conway. "Electrode kinetic aspects of the Kolbe reaction." *Chemical Reviews* 67.6 (1967): 623-664.
- Smith, William B., and Hans-Georg Gilde. "The kolbe electrolysis as a source of free radicals in solution." *Journal of the American Chemical Society* 81.20 (1959): 5325-5329.
- Nordkamp, Margot Olde, et al. "Study on the Effect of Electrolyte pH during Kolbe Electrolysis of Acetic Acid on Pt Anodes." *ChemCatChem* 14.16 (2022): e202200438.

An alternative material to platinum that can withstand extreme conditions of electrochemical decarboxylation of acetic acid?



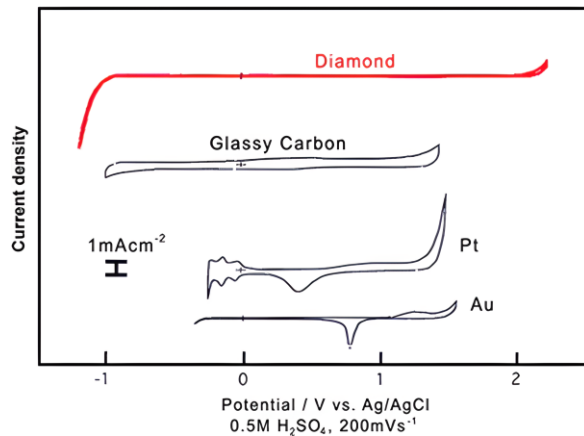
- “Platinum is prone to dissolution at high oxidation potentials”

Ranninger, Johanna, et al. "On-line Electrode Dissolution Monitoring during Organic Electrosynthesis: Direct Evidence of Electrode Dissolution during Kolbe Electrolysis." *ChemSusChem* 15.5 (2022): e202102228.

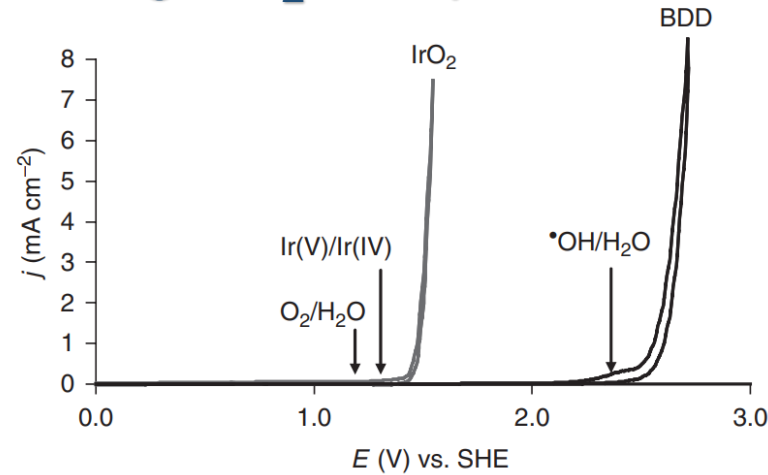
Reaction conditions: 1M acetic acid/sodium acetate pH 5 at 25 mA/cm² in batch cell reactor

Boron Doped Diamond Electrode: Alternative Electrode

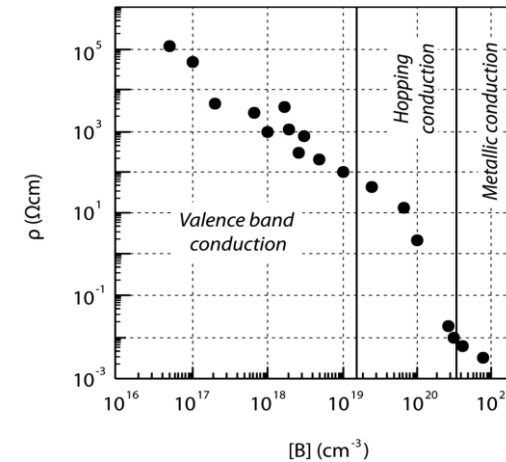
Wide potential window



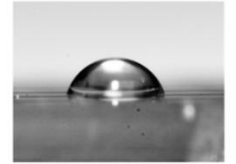
High O₂ overpotential



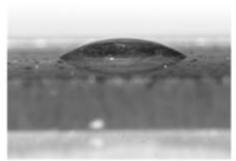
Metal like conduction



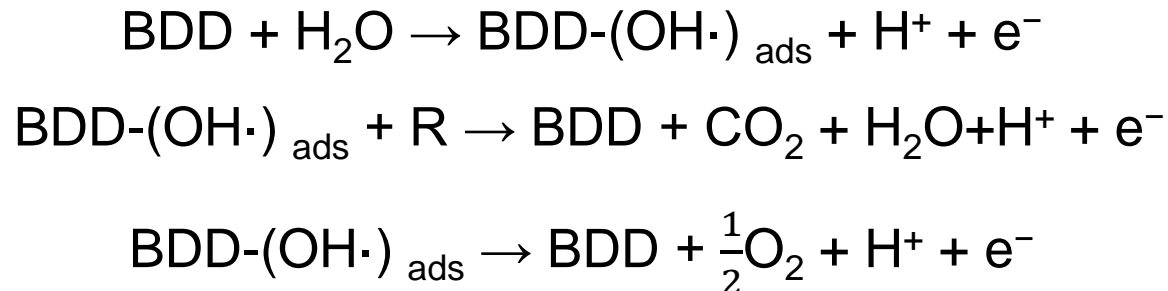
Surface termination



H-terminated



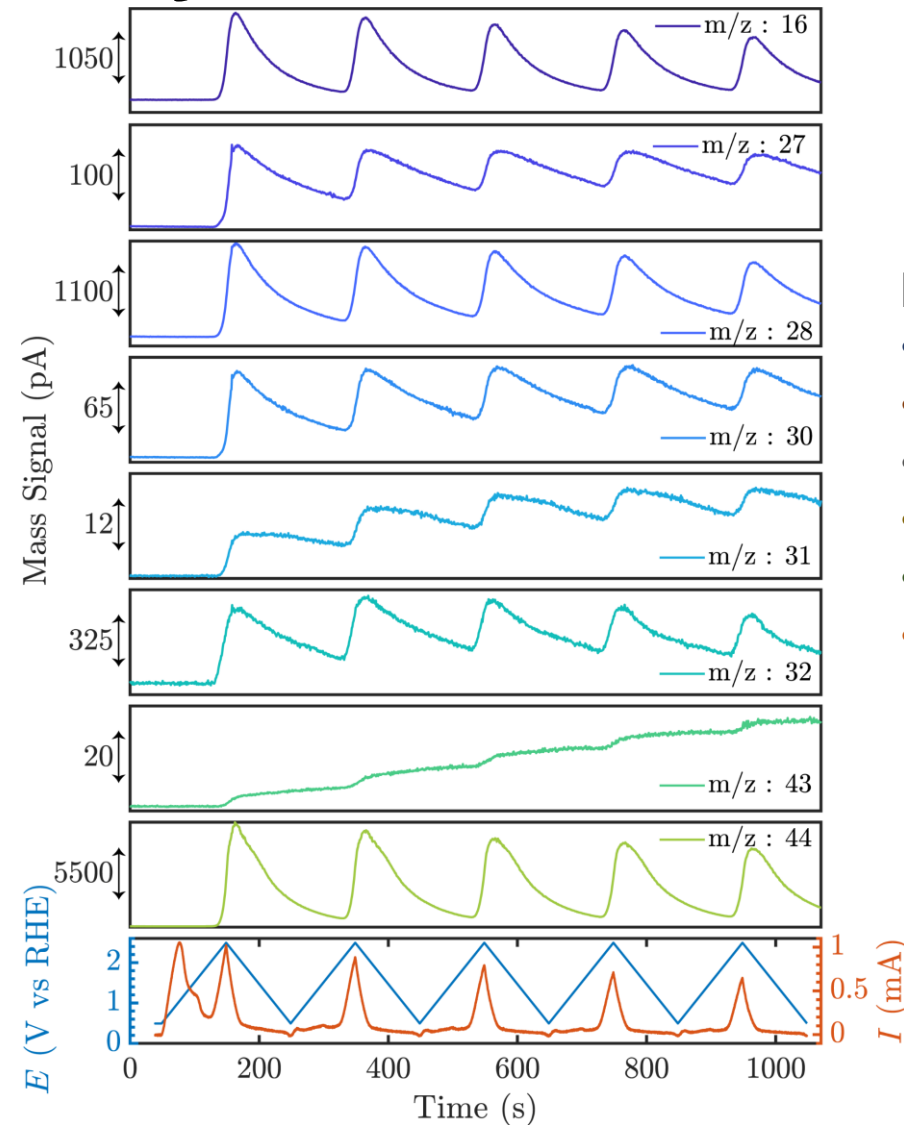
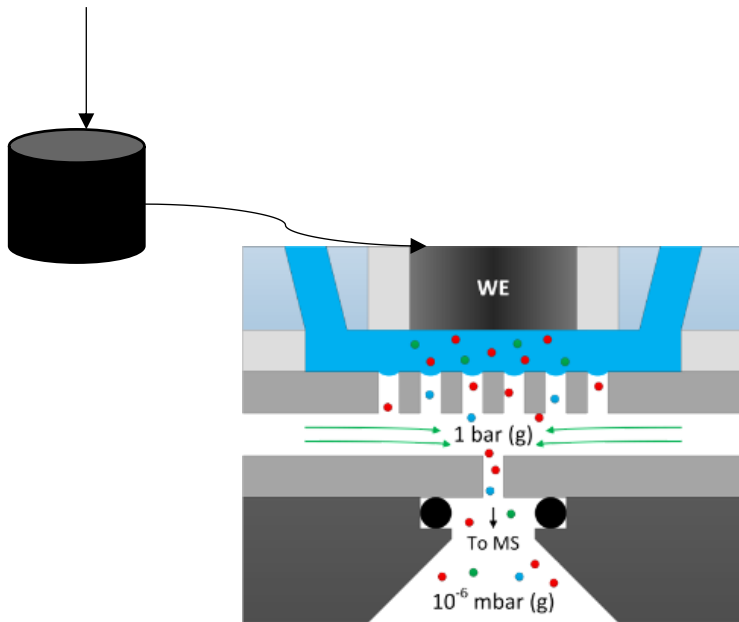
O-terminated



- Macpherson, Julie V. "A practical guide to using boron doped diamond in electrochemical research." *Physical Chemistry Chemical Physics* 17.5 (2015): 2935-2949.
- Kapalka, Agnieszka, et al. "DEMS Study of the Acetic Acid Oxidation on Boron-Doped Diamond Electrode." *Journal of The Electrochemical Society* 155.7 (2008): E96.
- Einaga, Yasuaki. "Development of electrochemical applications of boron-doped diamond electrodes." *Bulletin of the Chemical Society of Japan* 91.12 (2018): 1752-1762.

Insitu products detection by ECMS

1M acetic acid/sodium acetate (pH 5)



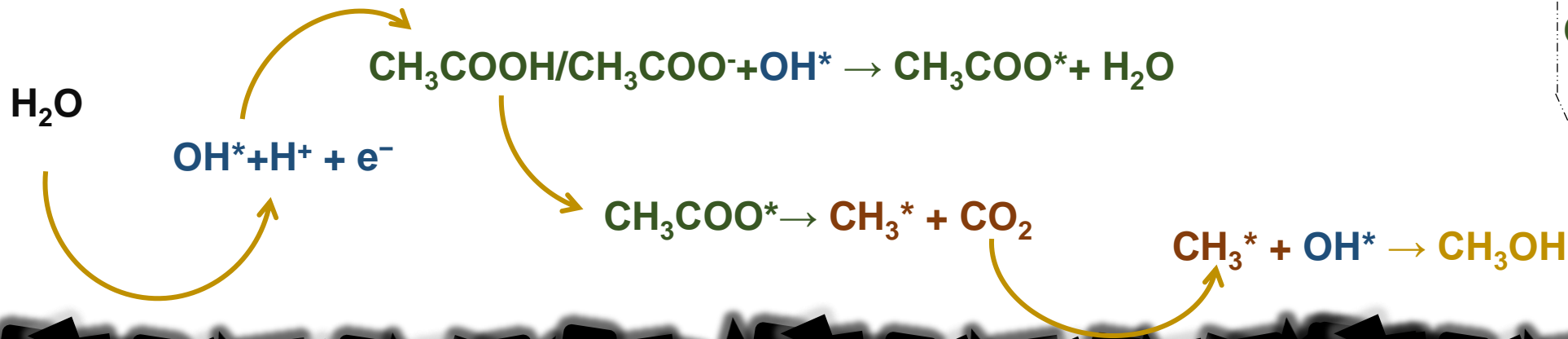
Detected products:

- Methanol (31)
- Methyl acetate (43)
- CO_2 (44)
- O_2 (32)
- Ethane (30)
- Methane (16)

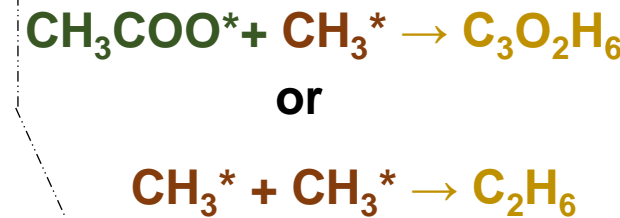
Reaction mechanism of acetic acid decarboxylation on BDD

- Electrooxidation takes place via an indirect pathway (**OH radical mediated**)
- Other side reactions are Kolbe coupling and (non)Kolbe/Hofer Moest reaction

Primary reactions



Other reactions



BDD

Effect of boron doping level in diamond properties

- Doping level

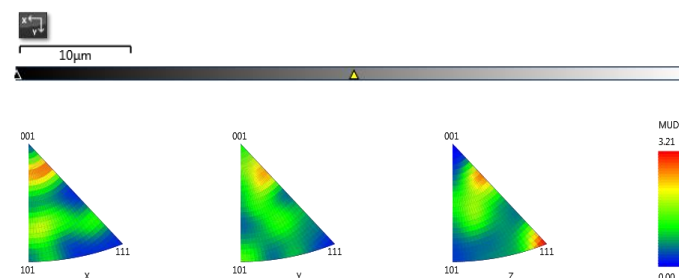
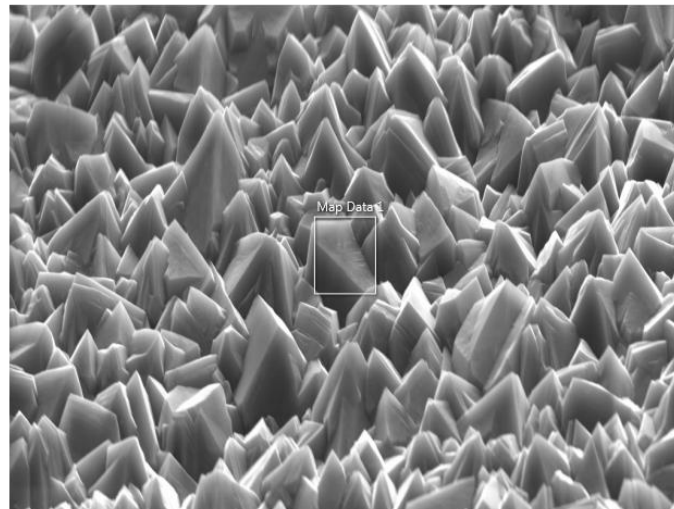
- High doped <2000-5000ppm boron atoms in diamond lattice
- Low doped >2000ppm

Triangular features represent 111 facets

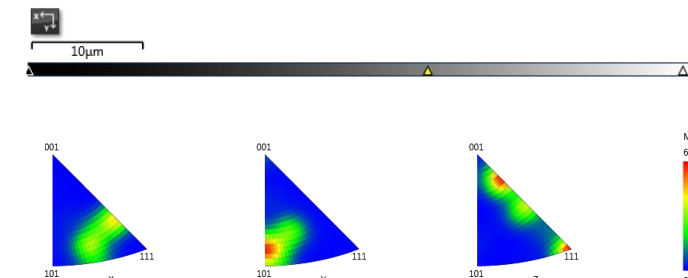
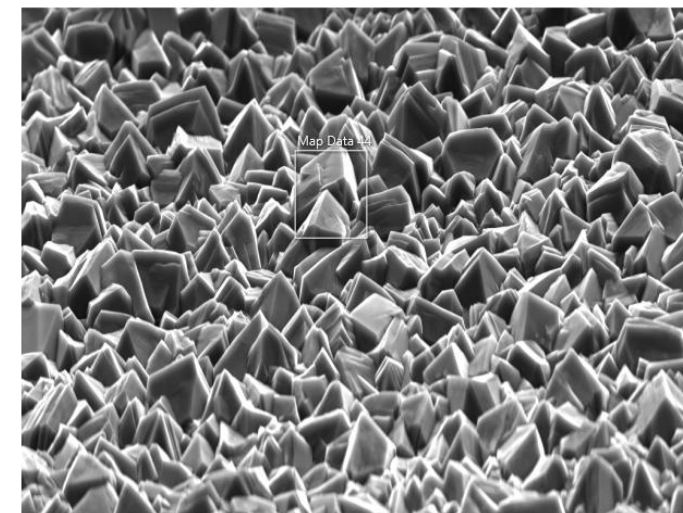
111 facets are more active for electrochemical oxidation

High doped diamond has more abundance of 111 facets

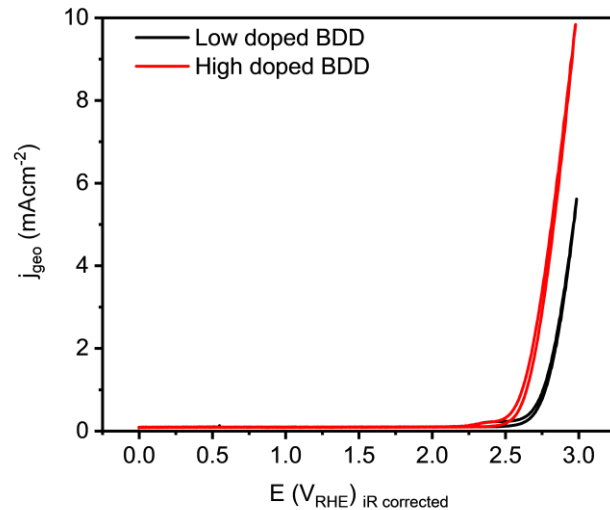
High doped diamond



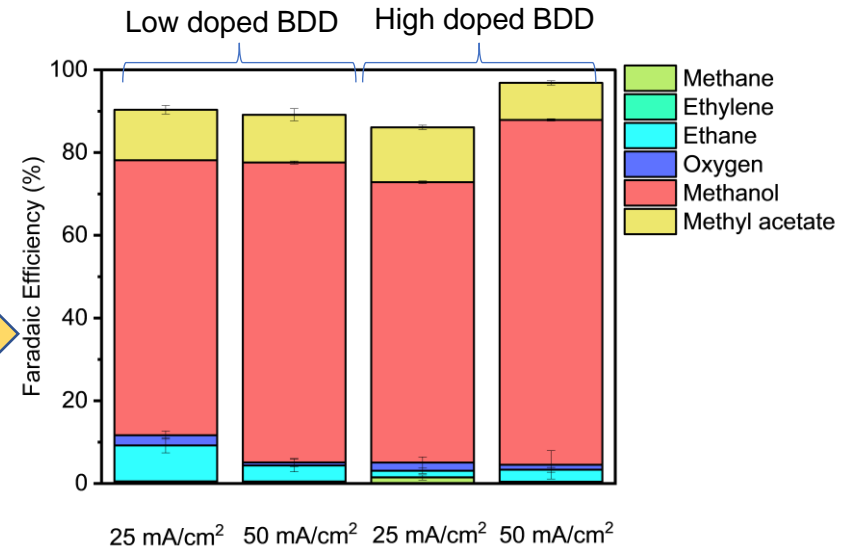
Low doped diamond



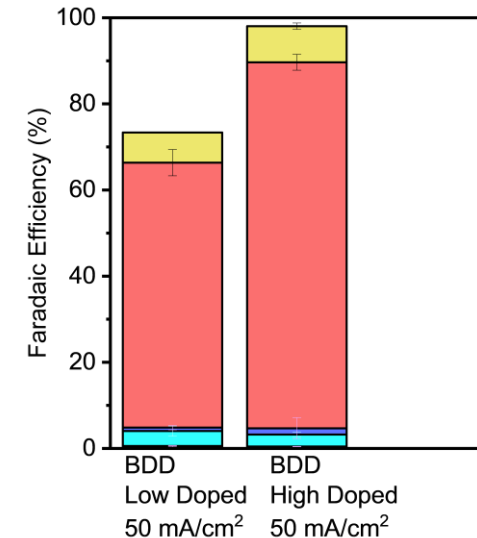
The electrochemical activity of acid acid decarboxylation



1 Hr

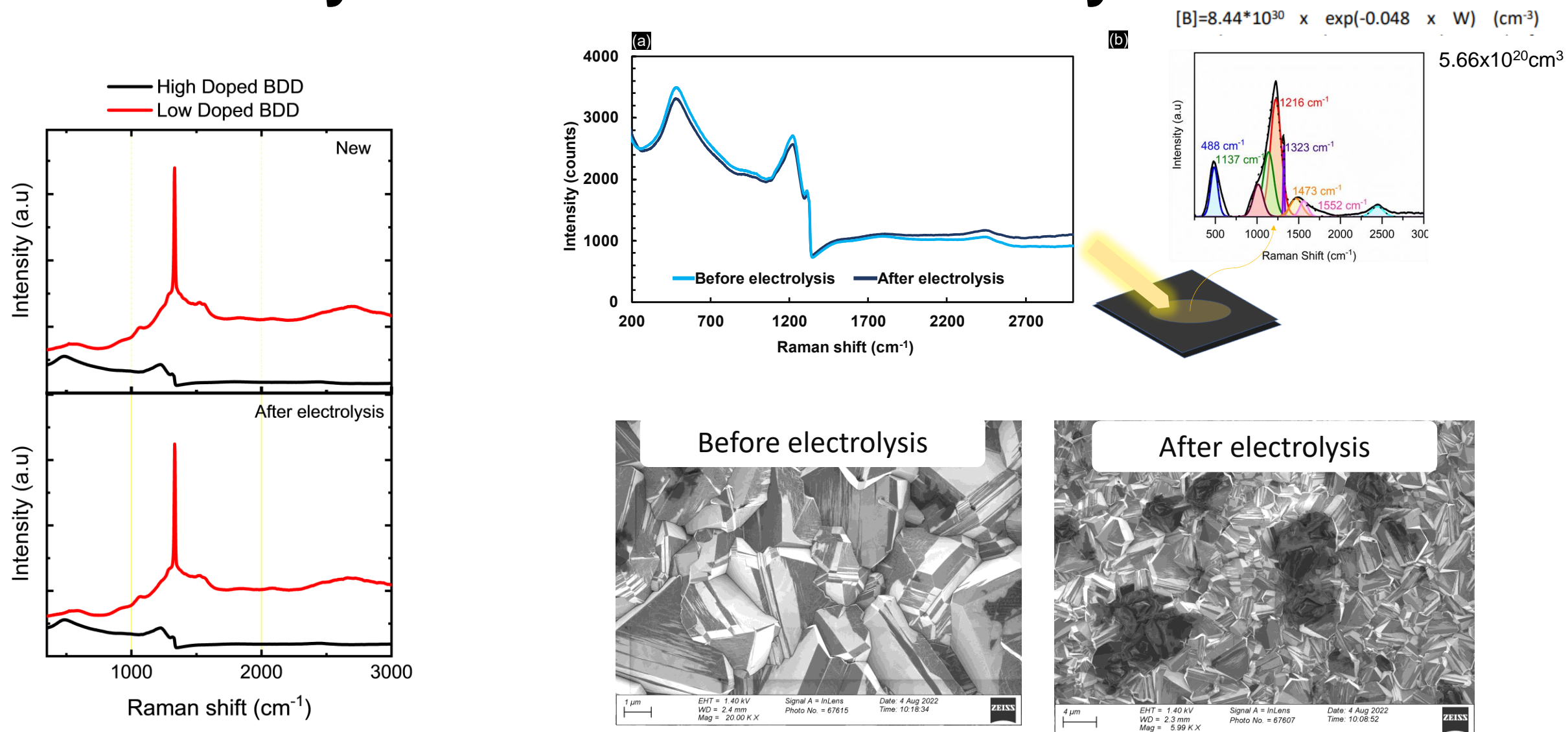


2 Hr



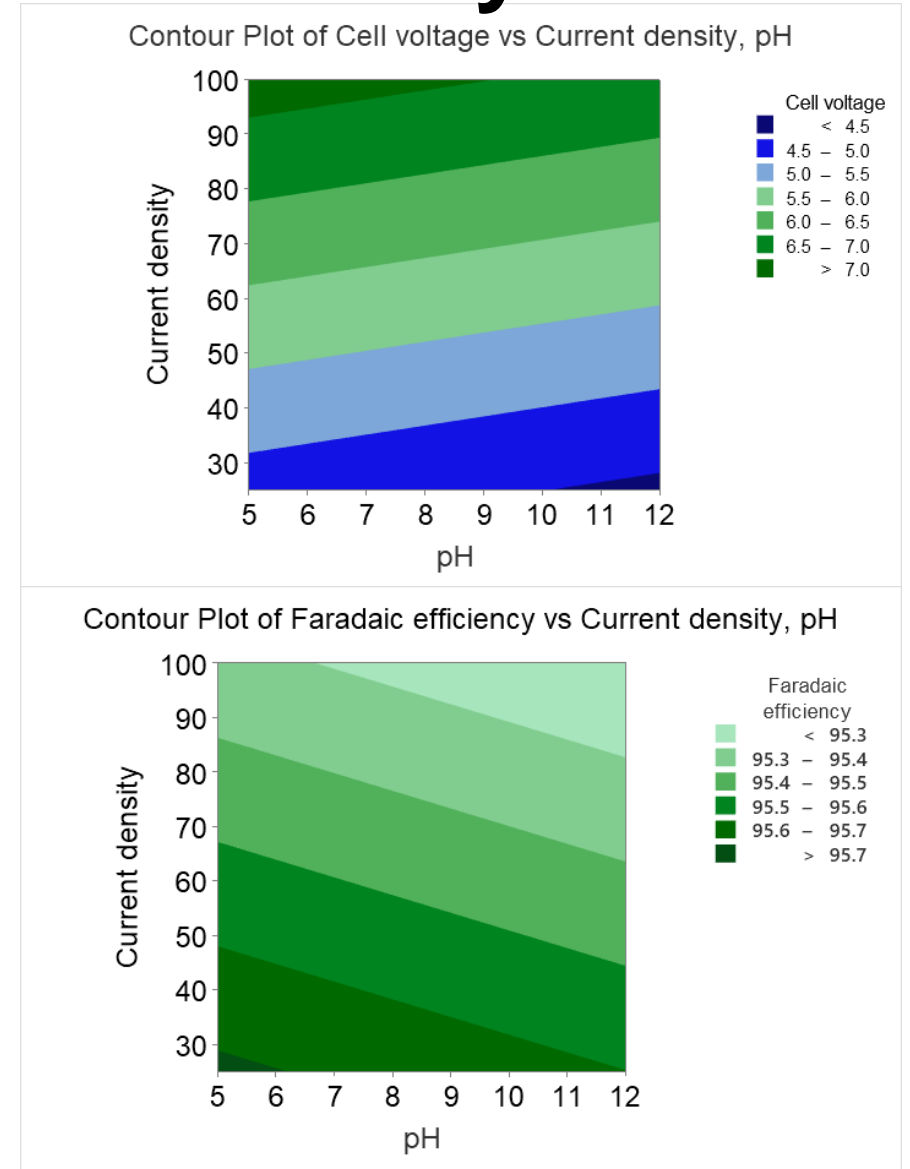
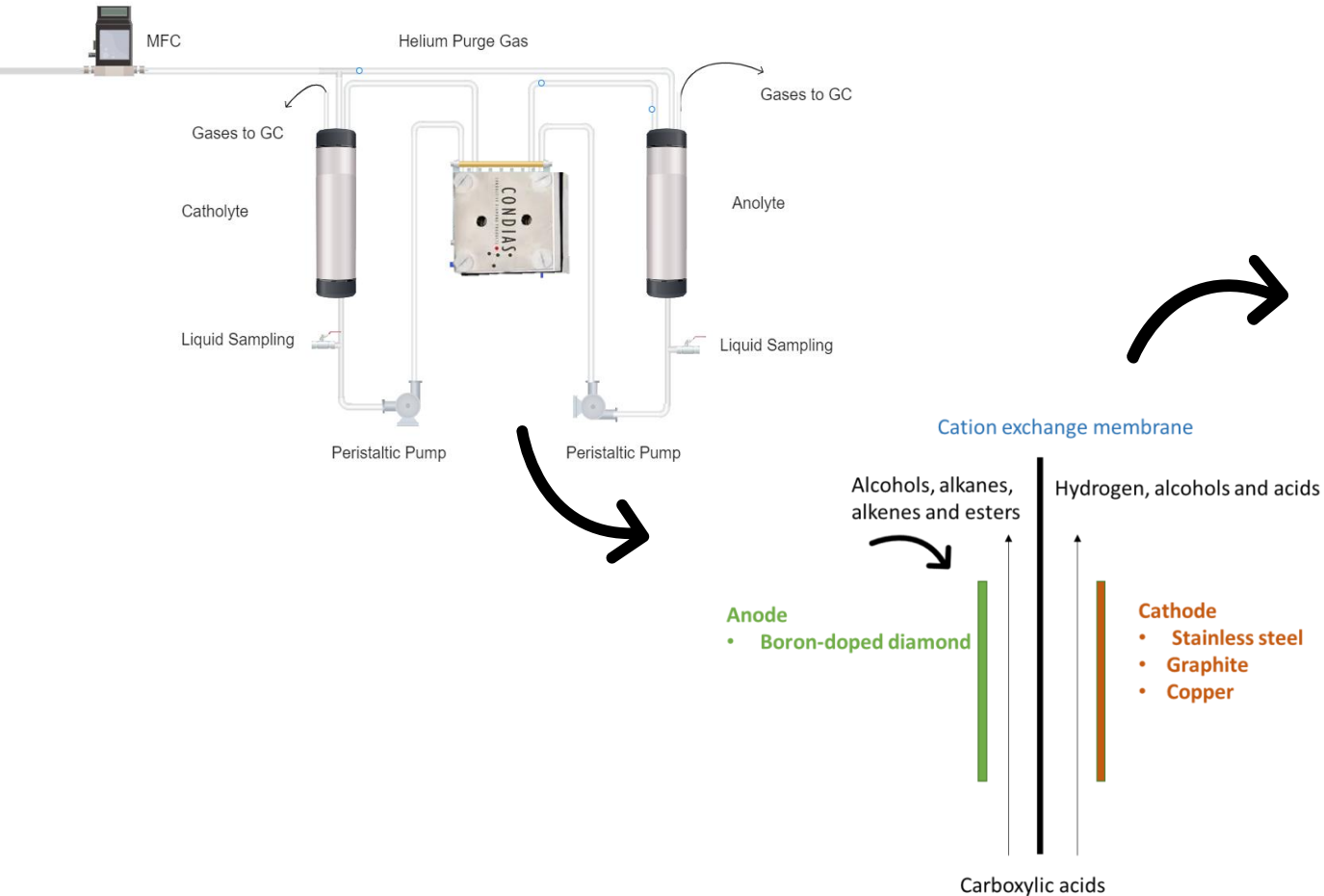
Reaction conditions: 1M acetic acid/sodium acetate pH 5 at 25 and 50 mA/cm² as catholyte and anolyte at 60ml/min in divided flow cell reactor separated by Nafion 324, reaction time 1 and 2 Hrs

BDD stability before and after electrolysis



Reaction conditions: 1M acetic acid/sodium acetate pH 5 at 25 mA/cm² as catholyte and anolyte at 60ml/min in divided flow cell reactor separated by Nafion 324, reaction time 1Hr

Optimal conditions for acetic acid decarboxylation on BDD via DoE in flow cell



Reaction conditions: 1M acetic acid/sodium acetate as catholyte and anolyte at 60ml/min in divided flow cell reactor separated by Nafion 324, reaction time 1Hr

Summary and Outlook

- Acetic acid decarboxylation on platinum takes place via Kolbe electrolysis and indirect oxidation (OH^* -mediated) on the BDD
- Compared to other electrode materials (Graphite, FTO and Nickel foam), BDD is more stable and selective to methanol formation
- High-doped diamond is more active for decarboxylation and contains 111 facets which are electrochemically more active
- Raman spectra confirm the stability of the BDD after decarboxylation
- Current density and pH don't have a very prominent effect on the faradaic efficiency of OH^- -mediated oxidation.

DoE will be used for analysing the effect of supporting electrolyte, temperature, choice of cathodic reaction and use of mixed acids, sugars and phenols oxidation along with the techno-economic analysis



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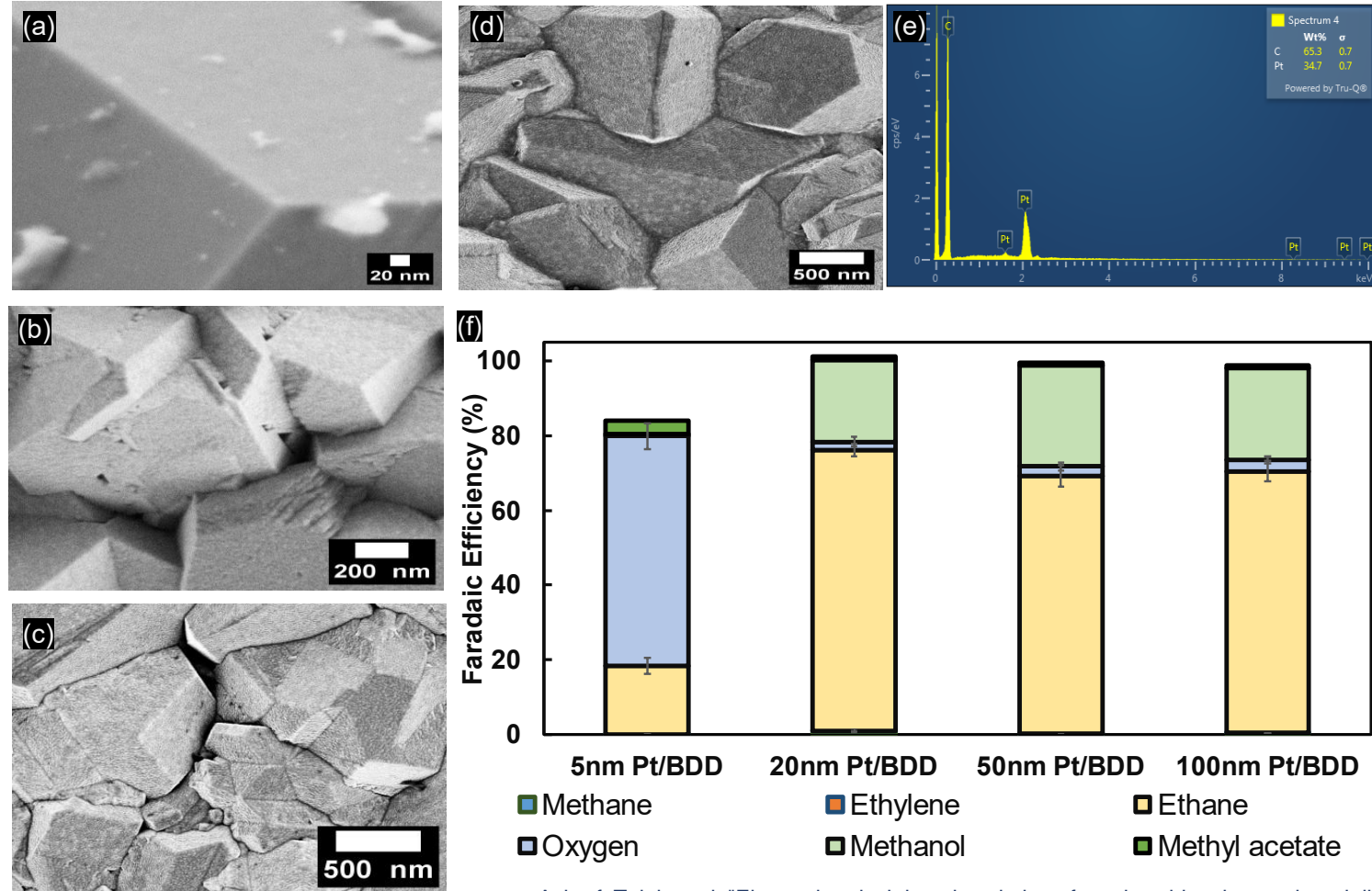
Thank you for the attention



Backup slides

BDD as substrate functionalised with thin films

- Surface functionalisation of BDD can be used to tune the selectivity of reaction, i.e. OH^* mediation oxidation to Kolbe electrolysis



Ashraf, Talal, et al. "Electrochemical decarboxylation of acetic acid on boron-doped diamond and platinum functionalised electrodes for pyrolysis-oil treatment." *Faraday Discussions* (2023)

Reaction conditions: 1M acetic acid/sodium acetate pH 5, three electrode undivided batch cell reaction at 25 mA/cm²