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

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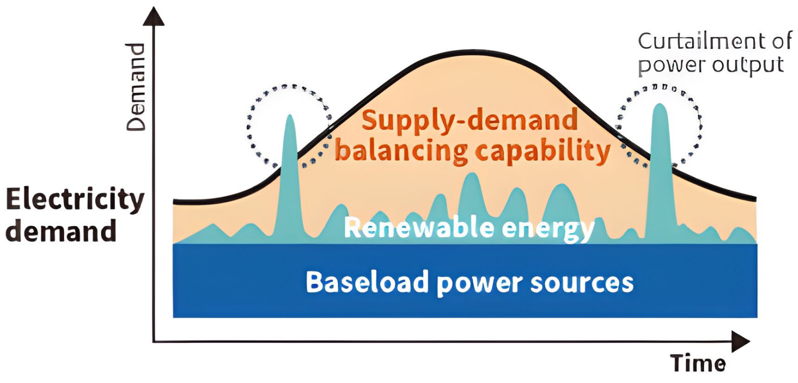

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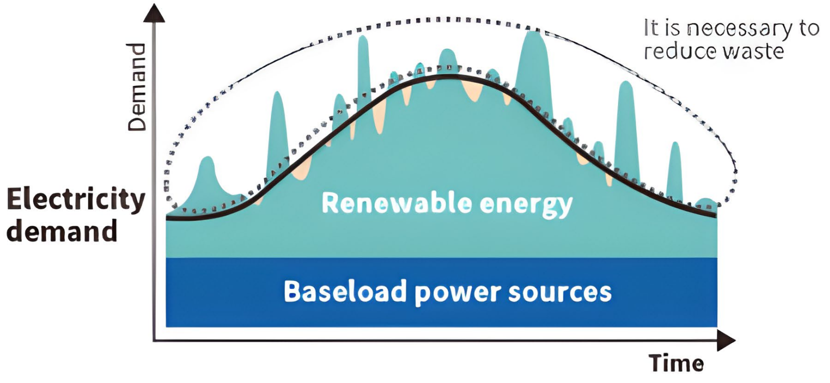

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https://www.global.toshiba/ww/products-solutions/hydrogen/products-technical-services/supply-chain.html

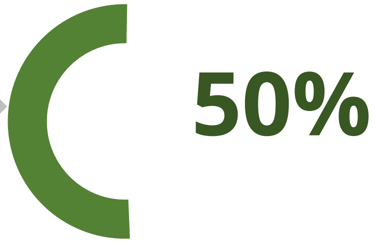
EBIO

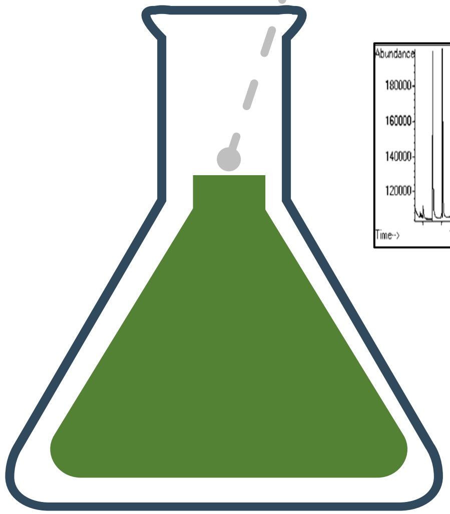
Storing “green electrons” in biobased pyrolysis oil

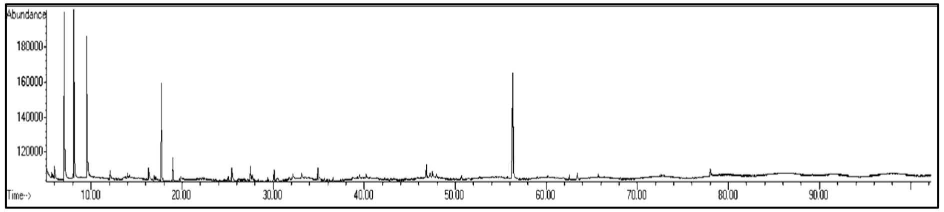
- Upgraded pyrolysis oil
- Chemicals production
- Fuels production

Pyrolysis Oil as feedstock for electrochemical conversion

Aqueous fraction



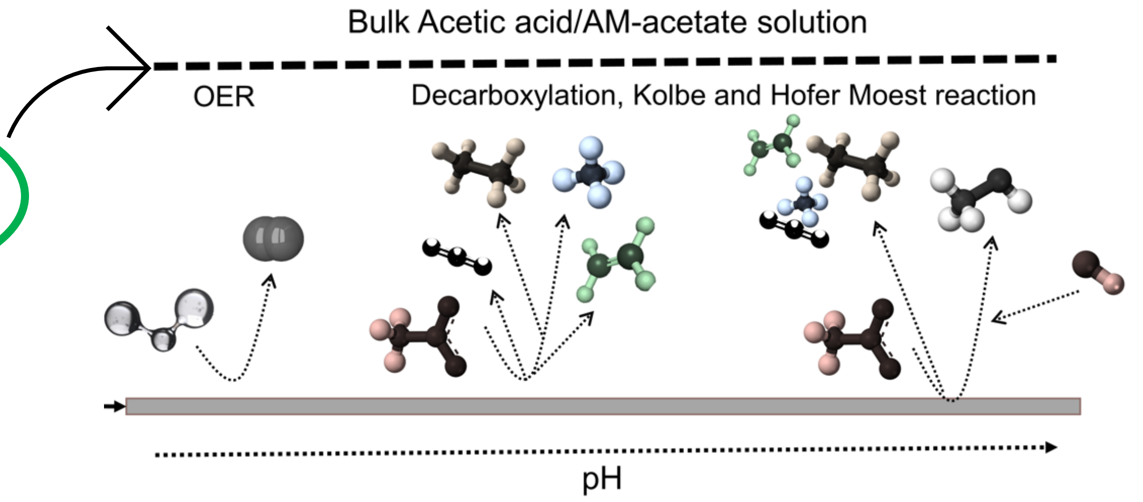




- 4-methyl guaiacol
- Acetic acid
- Anhydrose mannopyranose
- 1-propanol
- Guaiacol
- Hydrazine carboxylic acid
- Cyclopentenone
- Formic acid methyl ester
- Furfural
- 2-hydroxy 3 methyl cyclopent-1-one
- Butanediol

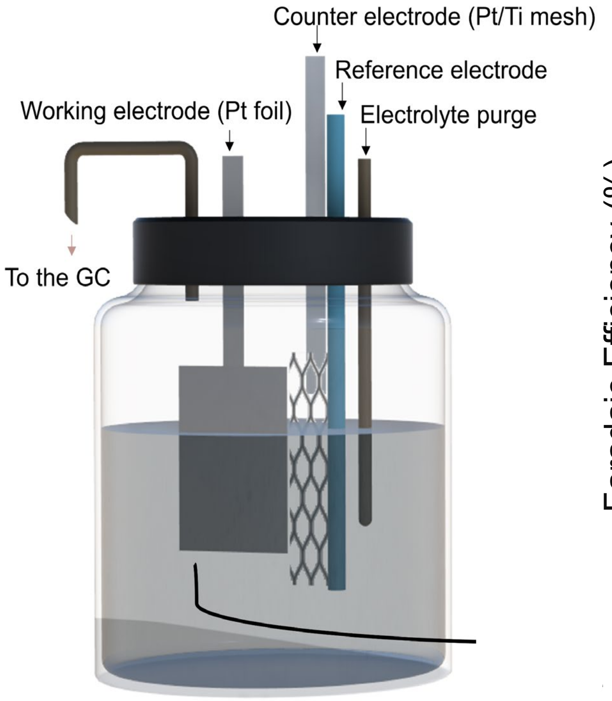
Electrochemical conversion Via Kolbe electrolysis

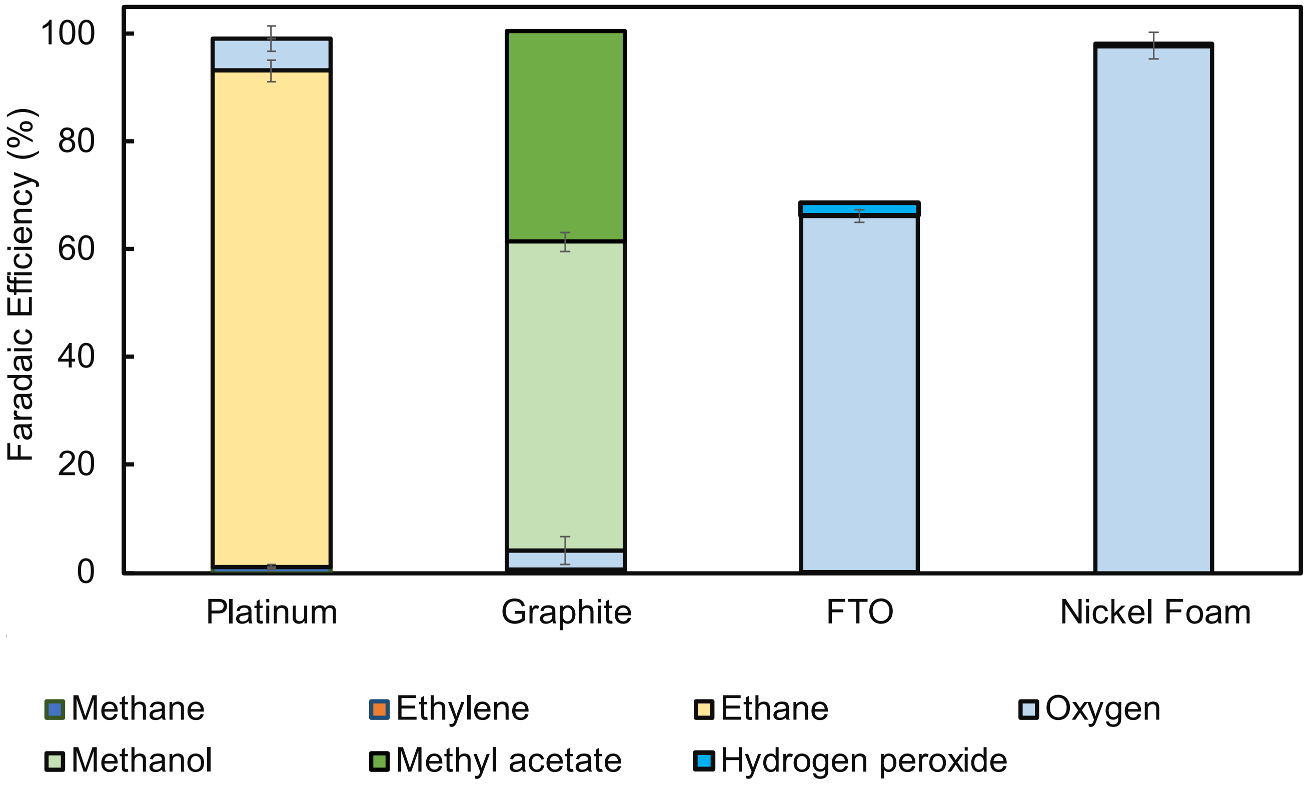
- Selective to electrode material (Platinum)
- Properties and reaction conditions are well defined in the literature



- 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?





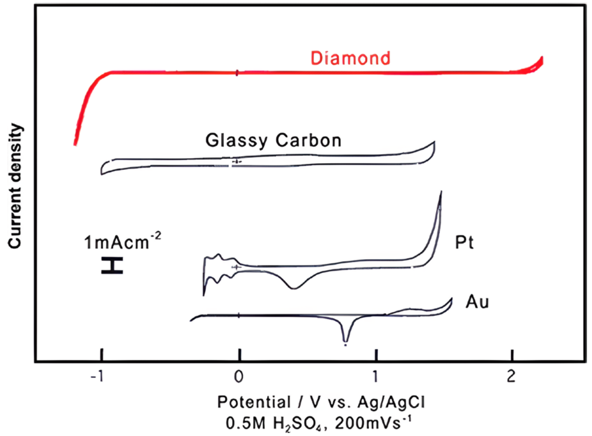
- "Platinum is prone to dissolution at high oxidation potentials"

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.

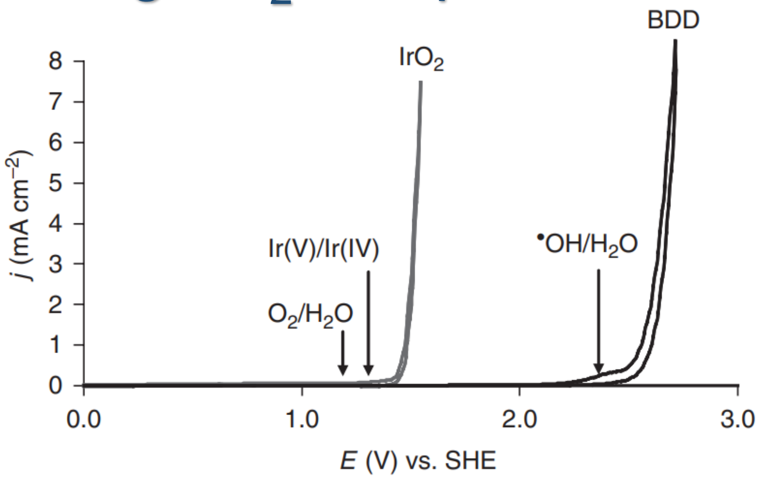
Reaction conditions: 1M acetic acid/sodium acetate pH 5 at 25 mA/cm^2 in batch cell reactor

Boron Doped Diamond Electrode: Alternative Electrode

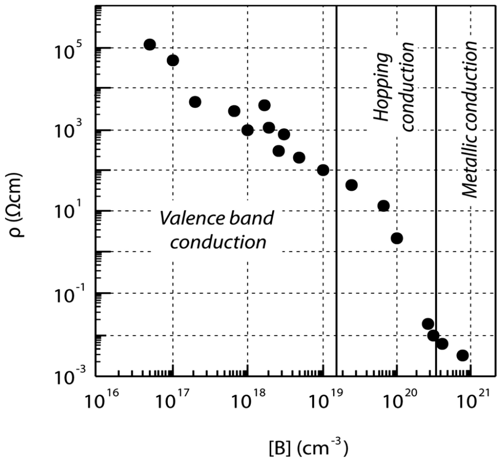
Wide potential window



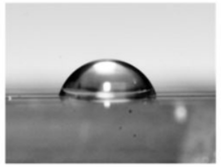
High O_2 overpotential



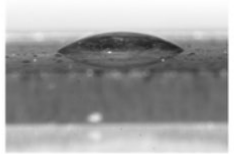
Metal like conduction



Surface termination



H-terminated



O-terminated

$$BDD + H_2O \rightarrow BDD\text{-}(OH\cdot)_{ads} + H^+ + e^-$$

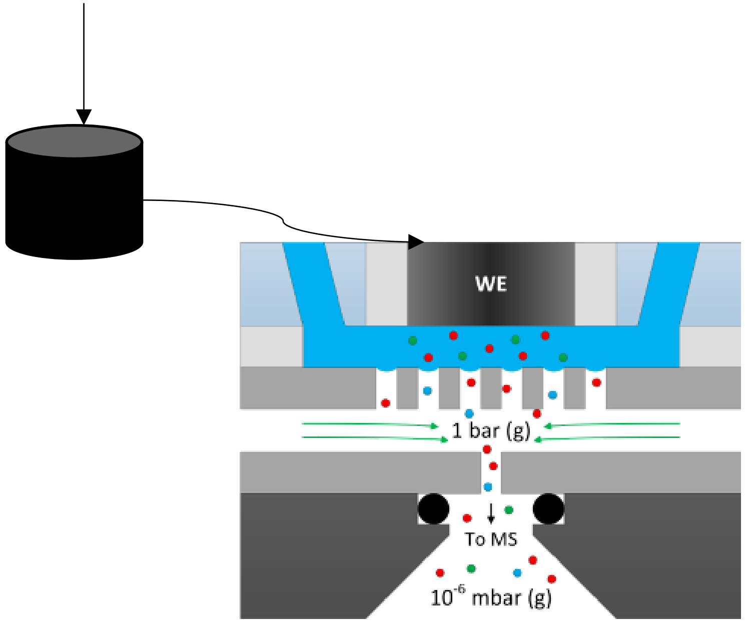
$$BDD\text{-}(OH\cdot)_{ads} + R \rightarrow BDD + CO_2 + H_2O + H^+ + e^-$$

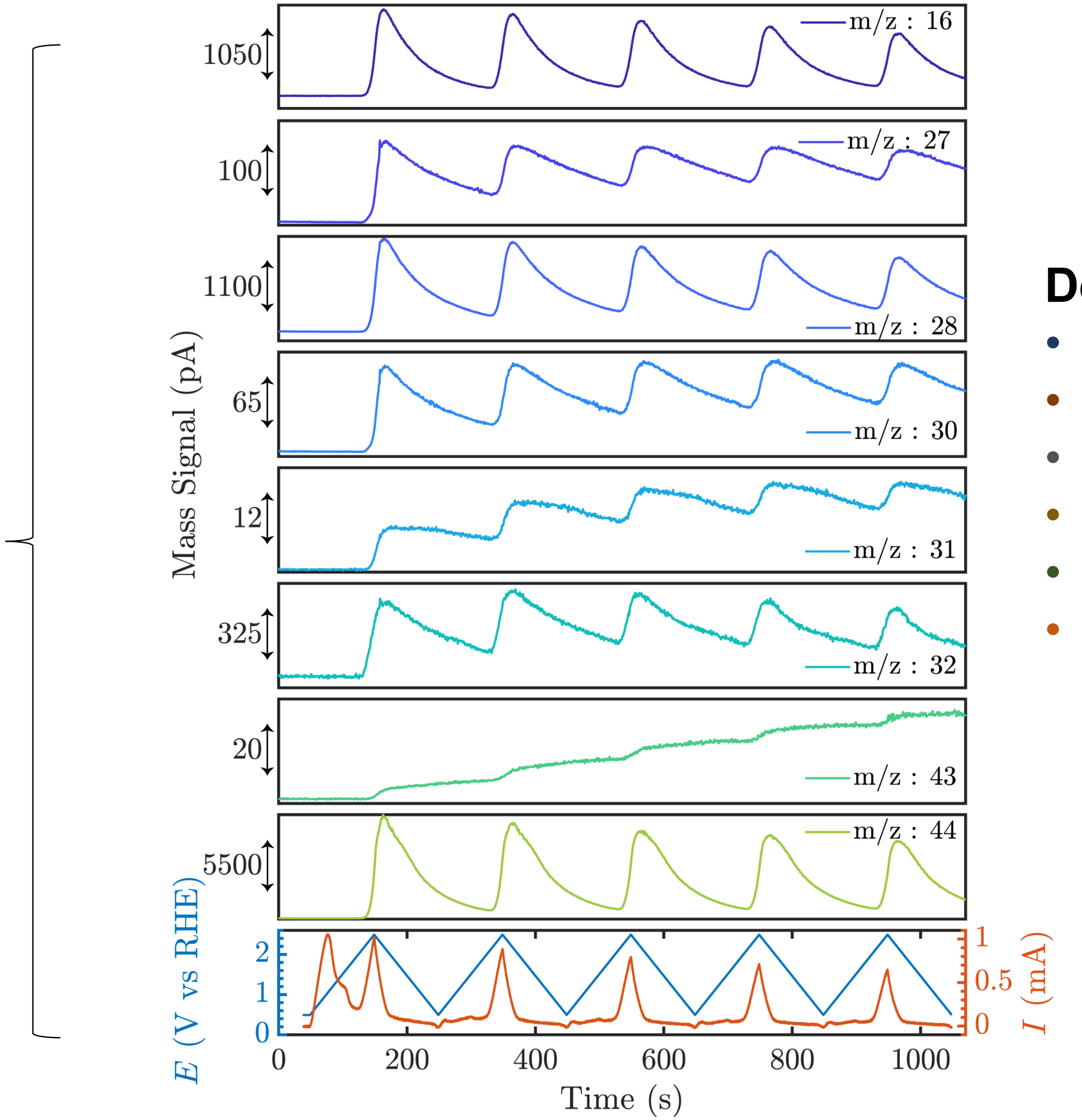
$$BDD\text{-}(OH\cdot)_{ads} \rightarrow BDD + \frac{1}{2}O_2 + H^+ + e^-$$

- Macpherson, Julie V. "A practical guide to using boron doped diamond in electrochemical research." *Physical Chemistry Chemical Physics* 17.5 (2015): 2935-2949.
- Kapałka, Agnieszka, et al. "DEMS Study of the Acetic Acid Oxidation on Boron-Doped Diamond Eelectrode." 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)





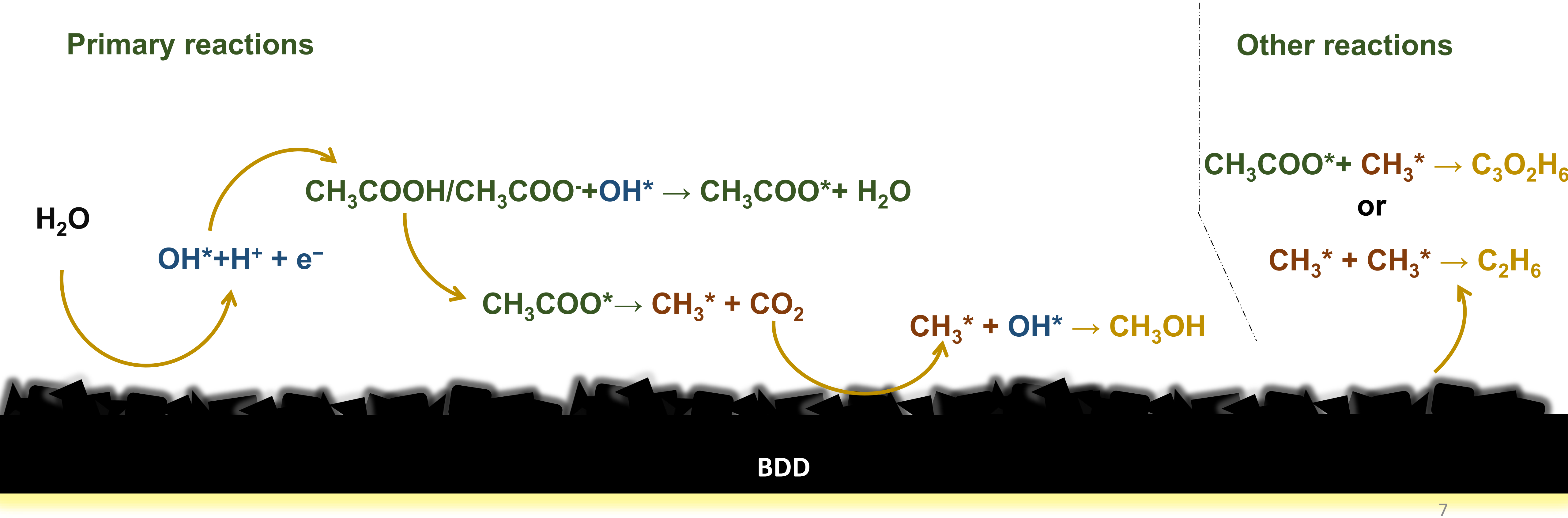
Detected products:

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

- Ashraf, Talal, et al. "Electrochemical decarboxylation of acetic acid on boron-doped diamond and platinum functionalised electrodes for pyrolysis-oil treatment." *Faraday Discussions* (2023)
- Kapałka, Agnieszka, György Fóti, and Christos Comninellis. "I. nvestigation of the anodic oxidation of acetic acid on boron-doped diamond electrodes." *Journal of the Electrochemical Society* 155.3 (2008): E27.

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



- Kapałka, Agnieszka, et al. "DEMS Study of the Acetic Acid Oxidation on Boron-Doped Diamond Eelectrode." Journal of The Electrochemical Society 155.7 (2008): E96.

Effect of boron doping level in diamond properties

CONDIAS
CONDUCTIVE DIAMOND PRODUCTS

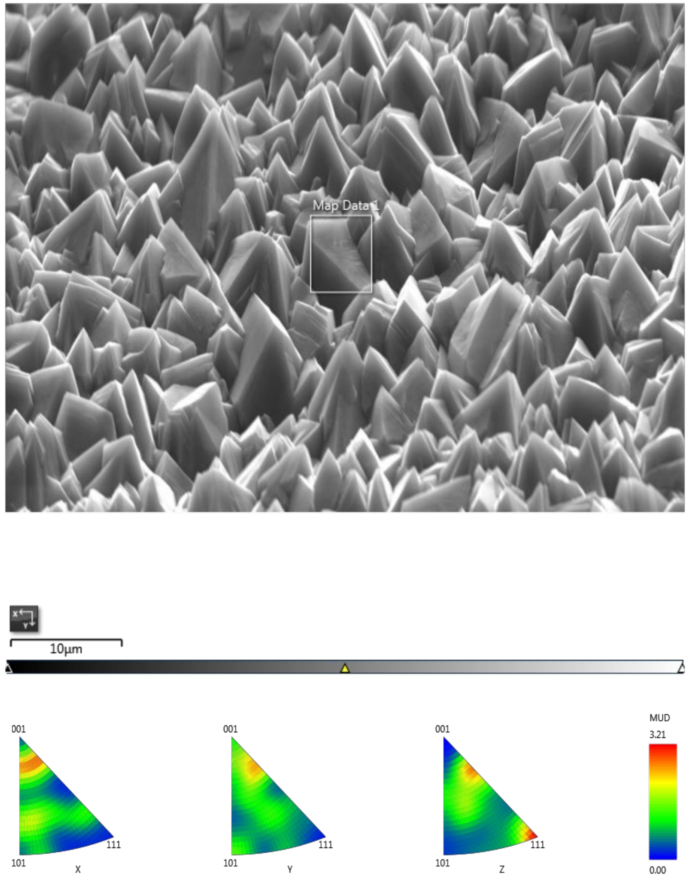
- **Doping level**
  - High doped <2000-5000ppm boron atoms in diamond lattice
  - Low doped >2000ppm

Triangular features represent 111 facets

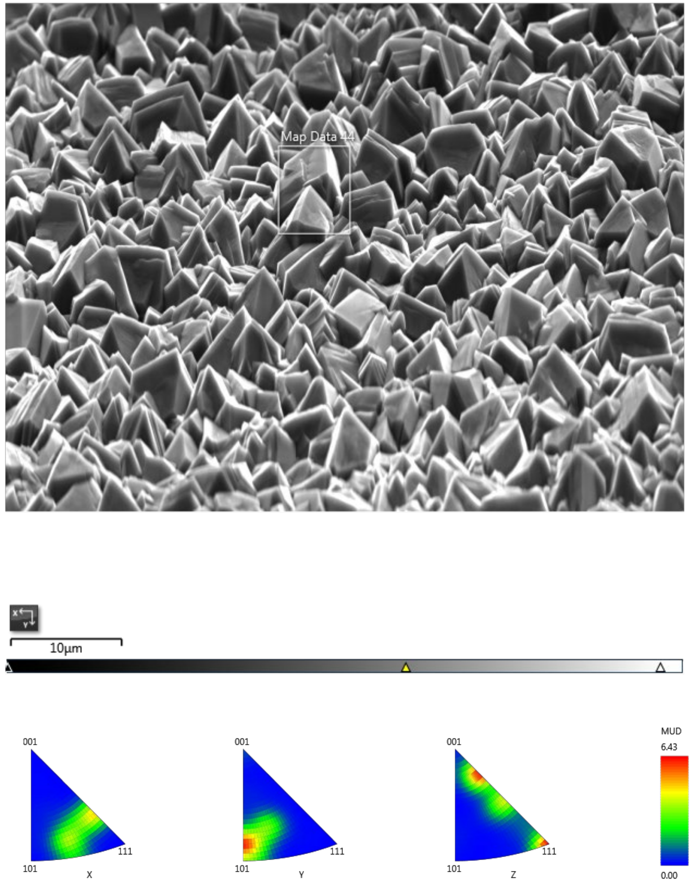
111 facets are more active for electrochemical oxidation

High doped diamond has more abundance of 111 facets

High doped diamond

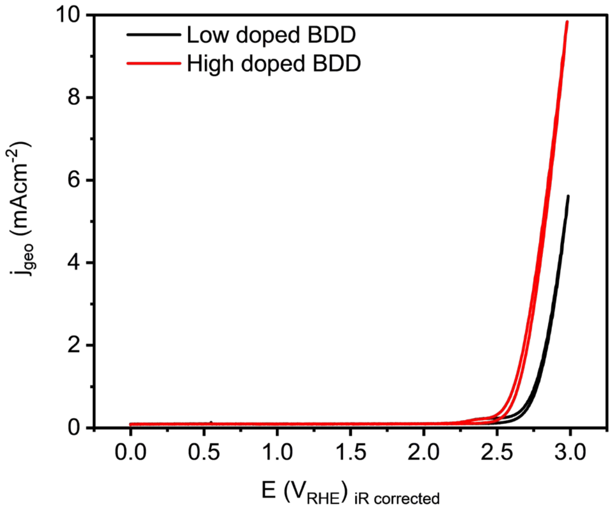


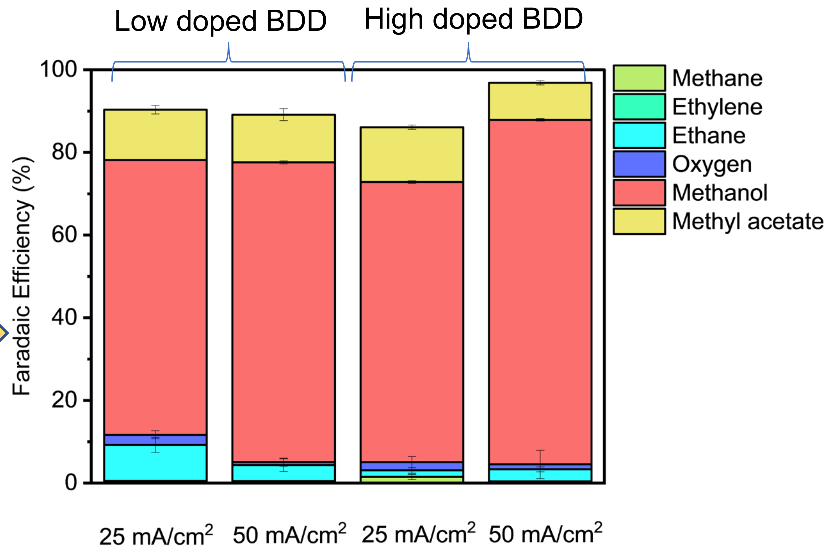
Low doped diamond

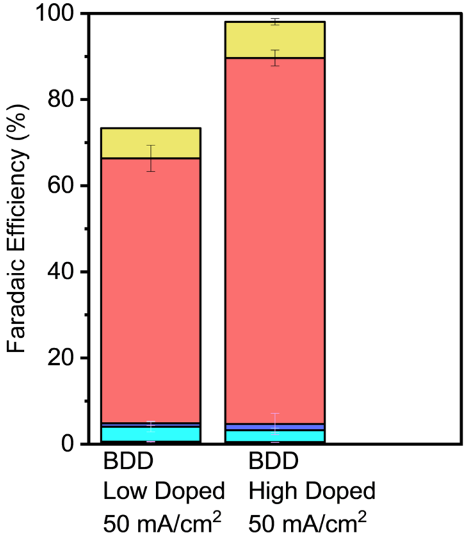


Kashiwada, Takeshi, et al. "A study on electrolytic corrosion of boron-doped diamond electrodes when decomposing organic compounds." ACS Applied Materials & Interfaces 8.42 (2016): 28299-28305.

The electrochemical activity of acid acid decarboxylation

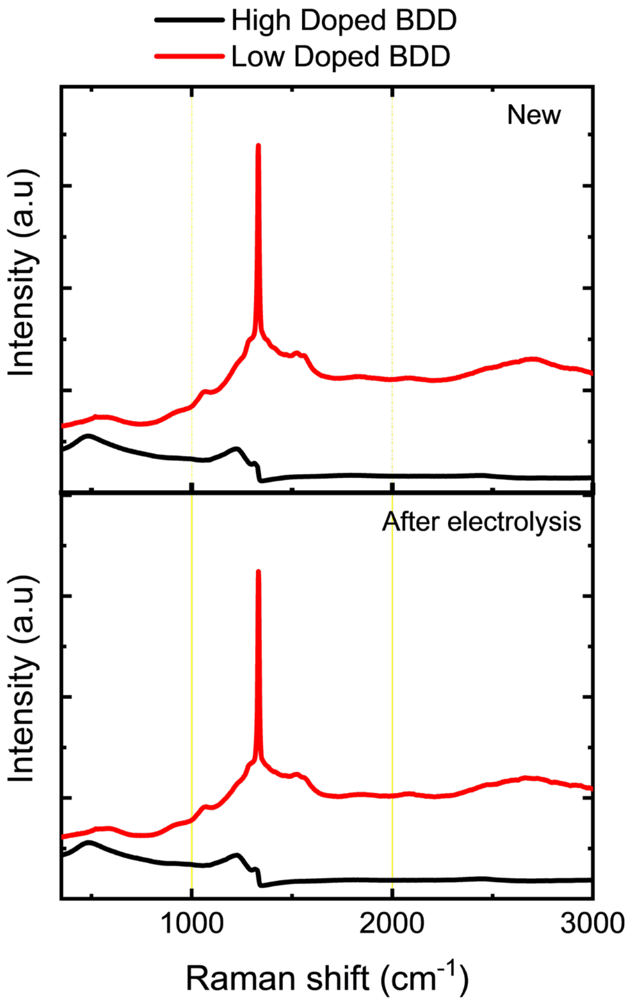


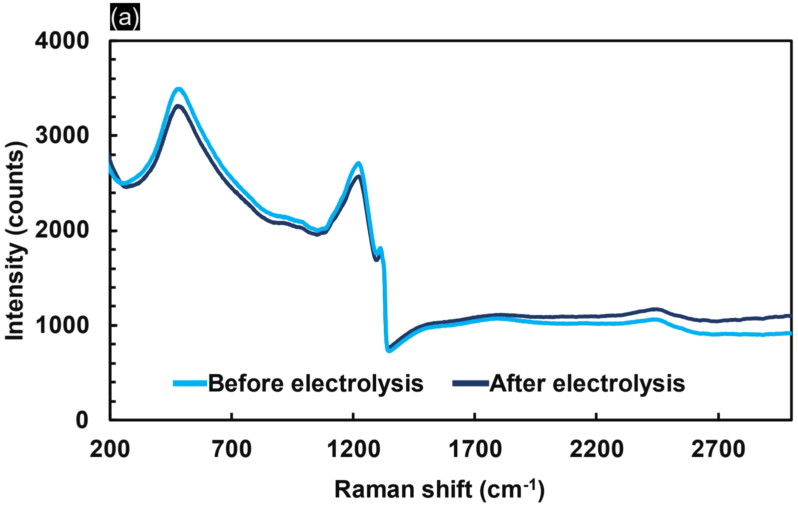




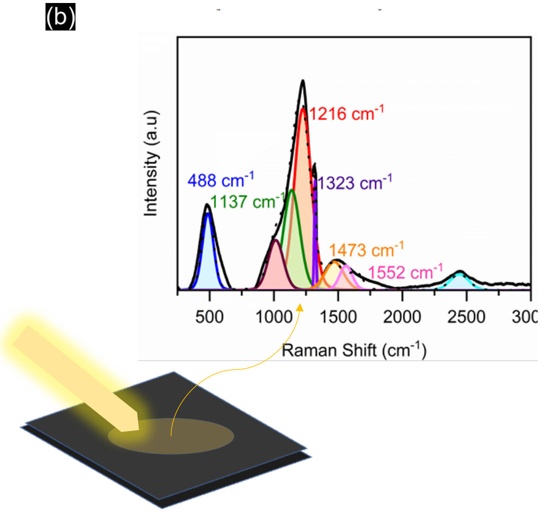
Reaction conditions: 1M acetic acid/sodium acetate pH 5 at 25 and 50 mA/cm^2 as catholyte and anolyte at 60ml/min in divided flow cell reactor separated by Nafion 324, reaction time 1 and 2 Hrs

BDD stability before and after electrolysis

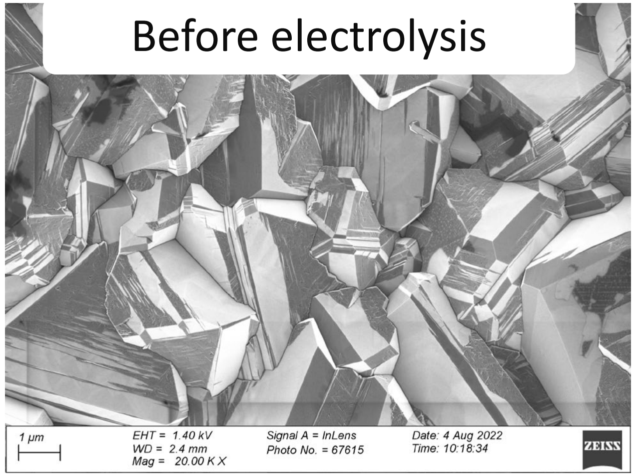


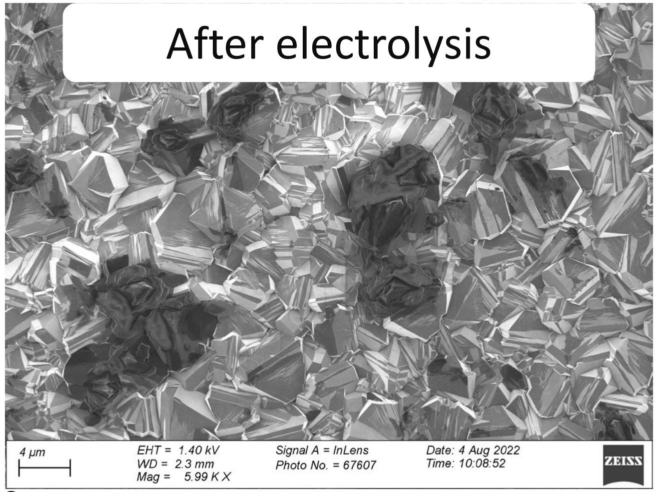


$[B]=8.44*10^{30}$ x exp(-0.048 x W) (cm^{-3})



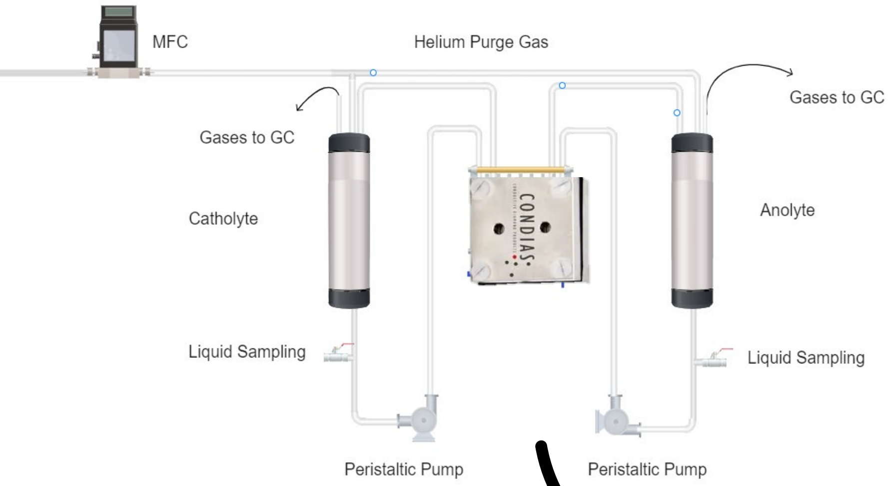
$5.66x10^{20}cm^3$

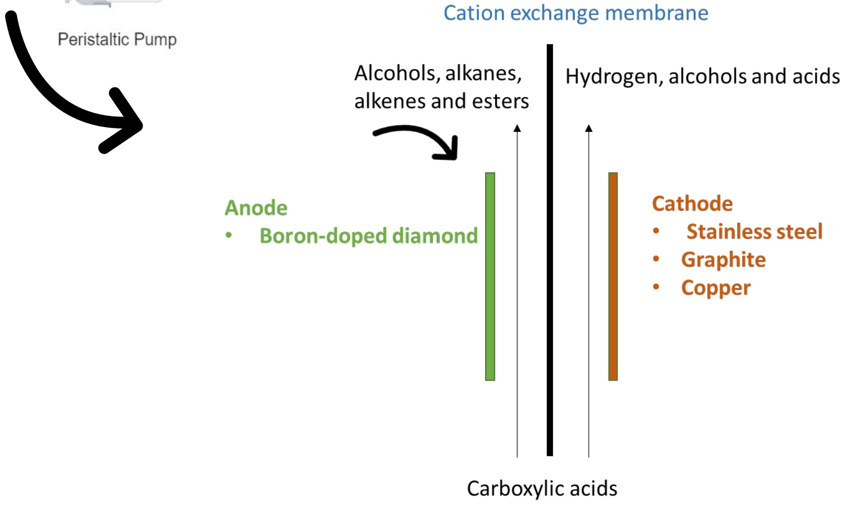


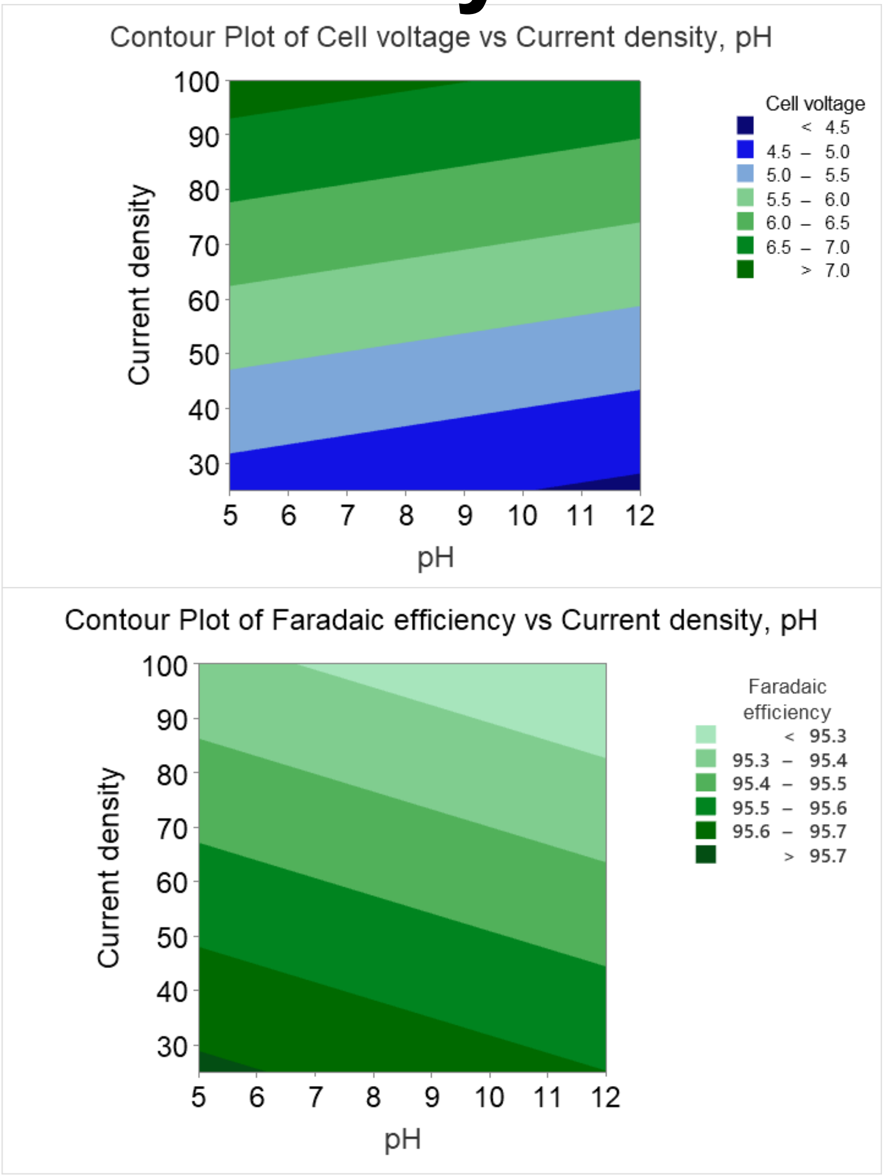


Reaction conditions: 1M acetic acid/sodium acetate pH 5 at 25 mA/cm^2 as catholyte and anolyte at 60ml/min in divided flow cell reactor separated by Nafion 324, reaction time 1Hr

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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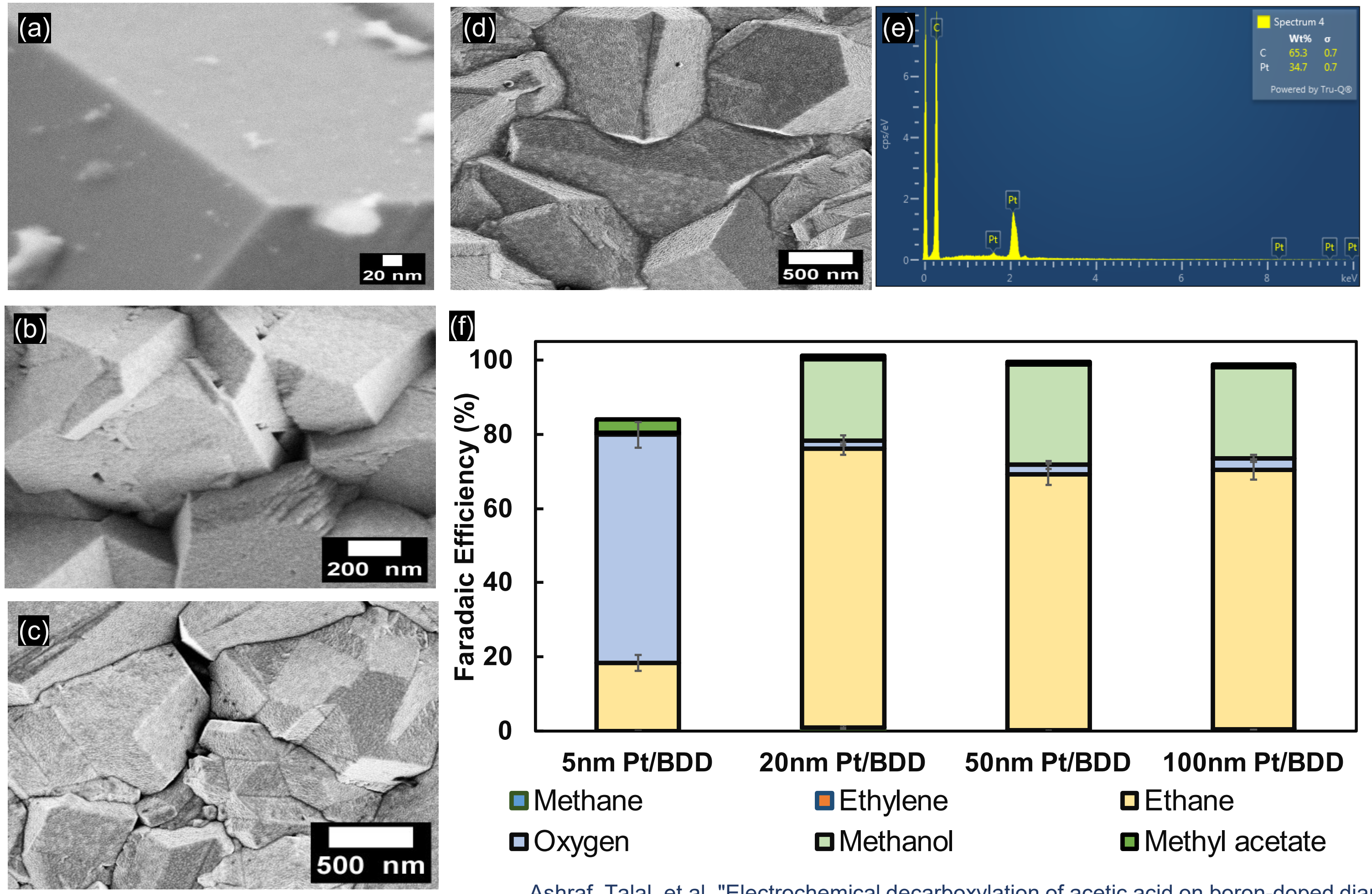
Wiktoria Kowalczyk (Utwente)

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