BOOK A

AURORA 80g

Remote desktop connection.

PC - EC

computer: ut151928.ad.utwente.nl
username = LabAdmin LabAdmin
password = Secret123! Geheim123!

PC - GC

computer: ut165657.ad.utwente.nl
user name : labadmin
password : Secret123!

PC GC pin
lfafe @ 2018.

Schematics

Connections:

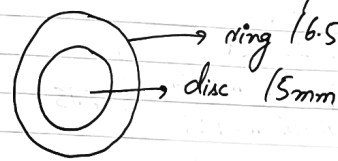
Disc: → WE1
Ring: → WE2

Cables

WE: Ref3 + CE/CA1
CE: Ref1 + ground
RE: white Ref cable.

WE: Ref3 + CE/CA1
CE: Ref + ground
RE: white Ref cable.

Metrohm RRDE



Area of circular ring (Annulus)
$= \pi (R_{out} - R_{in}) \times (R - R_{out\ in})$

Disc area = $0.19635\ cm^2$
Ring area = $0.07\ cm^2$
theoritical ring collection efficiency

Pine RRDE.

Disc dia: 5mm $\simeq 0.19635\ cm^2$
Ring dia =

Goal:
Onset for RRDE: OER during kolbe.

1.5 M acetate ✓
① 0.1M acetate ✓
② 0.5M acetate ✓
③ 1M acetate ✓
④ 1M acetate + 0.1M glucose
⑤ 1M acetate + 0.5 M glucose
⑥ 1M acetate + 1M glucose.
} → pH5

⑦ 1M acetate → pH 3, 9, 12
↳ to show methanol oxidation + ORR.

⑧ 1M acetate + 0.1M cresol
⑨ 1M acetate + 0.5M cresol
⑩ 1M acetate + 1M cresol
} → pH5

⑪ 1M acetate + 1M propionic acid
⑫ 1M acetate + 0.5M propionic acid
⑬ 1M acetate + 0.1M propionic acid
⑭ 0.5M acetate + 1M propionic acid
⑮ 0.1M acetate + 1M propionic acid.
} pH5

⊙ On Platinum.
Disc: 0 - 3 VRHE
Ring: 0.2 VRHE

+ try to do it with ultrasonication.

20230614

from a paper: inspiration.
"Bio-electrocatalytic conversion of food waste to ethylene via succinic acid as the central intermediate"
→ they used graphite ink onto the gold ring and performed Koutechky-Levich analysis
RPM: 800 - 4000 rpm
Potential: 2.1 - 2.8 1.3 VRHE to 2.8 VRHE
in alkaline conditions.

pH5 : RDE: metro-ohm: only RDE

⊙ Exp 1 K
→ 1M acetate pH5 100 rpm ✓
300 rpm ✓
600 rpm ✓
1200 rpm ✓
2000 rpm ✓
3000 rpm ✓
5000 rpm → not good.

Performed LSV from 1.3 VRHE to 3 VRHE at 10 mV/s

⊙ Exp 2
0.5 M K acetate pH5 100 ✓
acetate + water. 300 ✓
600 ✓
1200 ✓
2000 ✓
3000 ✓

Performed LSV from 1.3 VRHE to 3 VRHE @ 10 mV/s.

⊙ Exp 3 :
0.1 M K acetate pH5 100 ✓
(acetate + water) 300 ✓
600 ✓
1200 ✓
2000 ✓
3000 ✓

Performed LSV from 1.3 VRHE to 3 VRHE @ 10 mV/s

⊙Exp4

1.5M Kacetate pH5

Performed LSVs from 1.3 V_{RHE} - 3 V_{RHE} @ 10 mV/s

rpm 100 ✓
300 ✓
600 ✓
1200 ✓
2000 ✓
3000 ✓

Exp 5: RRDE

1.5M Kacetate pH5

B - disc - Ch2 : 1.3 V_{RHE} - 3 V_{RHE} @ 10 mV/s
S - ring - Ch3 : 0.3 V_{RHE}

rpm 100 → ✓ → bubbles problem
300 → ✓ → bubbles problem
600 → ✓ → bubbles problem
1200 → ✓
2000 → ✓
3000 → ✓

pH5

V_{RHE}	$V_{Ag/AgCl}$
1.3	→ 0.795
3	→ 2.495
0.3	→ -0.205

100rpm, 100cycles in 1.5M kacetate: acetate layer on the ring (picture: mobile)

Try the same experiment with ultrasonication

Exp 6: RRDE 1.5M Kacetate pH5 with sonication.

1.3 V_{RHE} - 3 V_{RHE} @ 10 mV/s → disc, 0.3 V_{RHE} → ring.

100rpm. ✓ more severe
300rpm ✓
600rpm ✓

HPLC data: Wiktoria.

Remote desktop connection.

address: UT145738.ad.utwente.nl
User: .\labuser
password: HPLC1200

Exp #7

Exp 7

Goal: Scans RRDE for inflection zone at many cycles.

→ 1500 rpm @ 1mV/s → 50 cycles.

1M K acetate
1M Na acetate
1M Cs acetate
1M Li acetate

CH: Bdisk : CH2
S ring : CH4

01_K acetate (1M): from 1.3 V Ag/AgCl to 2.495 V Ag/AgCl
nc = 50 @ 1mV/s
Ring = 0.3 V RHE = -0.205 V Ag/AgCl.

tried with 100 mV/s, no ORR was detected on ring bcz the detection limit, at 1mV/s, we produce very low O_2 and thus not in detectable range
O_2 wrong hypothesis.

Perfect visibility of inflection zone

Peak current at 3 V RHE = 8.32 mA
inflection current = 3.5 mA at 2.1 V Ag/AgCl

So only doing one CV: because on CV taking 43 mins

02_K acetate (1M): from 1.3 V Ag/AgCl to 2.495 V Ag/AgCl
nc = 50 @ 50 mV/s.
Ring: 0.3 V RHE = -0.205 V Ag/AgCl

03_Li acetate (1M) pH5 from 1.3 V Ag/AgCl to 2.495 V Ag/AgCl
nc = 1 @ 1mV/s
Ring = 0.3 V RHE = -0.205 V Ag/AgCl

04_Li acetate (1M) pH5 from 1.3 V Ag/AgCl to 2.495 V Ag/AgCl
n = 12 @ 50 mV/s
Ring: 0.3 V RHE = -0.205 V Ag/AgCl

FE LiOH+KOH
20230627

KOH: 30mins. at 50mA (O_2 before = 0.0370)
from injection 6 to 11 (O_2 before = 0.0396)
0.0329 inj 2

LiOH 30 mins
from injection 24
27 to

Experimental plan (tuesday, wednesday)
Mix acids (make a complete profile)

① Check the effect of O_2 oxidation (radiolysis)

experiment: He purge, O_2 purge, no purge

O_2 purge: They mentioned that this effect is significant for low current density.

To find
→ effect of O_2 flow rate
effect of current density

Total run 8

run order	Flow rate (O_2)	Current density (50 mA/cm²)	experiment id O_2
1	30	50	01 ✓
2	30	25	02 ✓
3	30	10	03 ✓
4	30	100	04 ✓
5	10	10	05 ✓
6	10	50	06 ✓
7	10	25	07
8	10	100	08

→ do this for propionic acid C_4 mix

→ find the concentration of OH radicals in presence of acetic acid, propionic acid → simulation
→ use the pt wire tip for DMPO
→ RDE
→ EC-MS
→ use of supporting electrolyte
→ divided vs undivided
→ Raman insitu

TMA ①

Raman spectra of membrane
Nafion 324

→ many peak visible:
→ partially successful.

tried with 785 nm Raman for BDD
visible signal for Boron, diamond and distorted structure: but due to high power BDD got ~~to~~ black spots, seems like carbon is burning:
partially successful.

PS: power supply

CH

(S1010) (W175) CH1

20230812_BDD_flow_1M pH5_Divided W175

Membrane N7 flow rate 60ml/min

BDD A

Analyte : 120ml 1M acetic acid + K acetate pH5

Catholyte : 100ml 1M acetic acid + K acetate pH5

01_C1 = 11.784

02_CP = 100 mA/cm^2 = 314.16

14:16

15:16

12503

From here, i will filter full sample

MeAC = 15337, 15706

MeOH: 98722, 98879

pH5

(404)
M7
B

W178 178

PAS

18.268

625mA/cm² . 19625

15.011

MeOH 58820, 66075
MeAc 9902, 11884

(406)
M7
C

W178 179

PAS

CH3

11.878

25mA/cm² = 785mA

16207

MeOH . 27728, 26828, 28998
MeAc . 6109, 5401, 6159

(1508)

W178

PH5

M7

D

Cl before 11.734

100mA/cm² = 314.16

Cl after 12.457

Me Ac	18286	23704
Me OH	99284	118815

Std 9

W181

CH3

(A)

20230814

M7

PH12

Cl before = 8.708

12.09

CC = 25mA/cm² = 78.5mA

Cl after = 9.467

MeOH 26724, 20967, 29415

MeAc 5064, 4373, 4788

Std 5 (B) M7 W182 CH1

pH 12 V

Cl before = 11.447

CC = 100 mA/cm² ⌀ 314.16 mA

Cl after = 12.770

MeOH 92286, 92580, 94165

MeAc 13674, 13959, 12890 } weird check again

Std (7) (C) M7 W183 potentiostat

V

pH 12

Cl before 12.497

CC: 25 mA/cm² = 78.5 mA

Cl after = 13.847

MeOH 26461, 20128, 25946

MeAc 5307, 4854, 4891

(Std 3) (1)

W184 - CH2 ✓

M7

P#12

Cl before : 9.197

CC → 62.5 mA ⇒ 196.25 mA

Cl after : 9.673

MeOH 8325, 7583, ~~8254~~ 8605

MeAC 62347, 58254, 59550

(A) (CH3)

W185

Sto. 12

M7

D#5

01_CL before = 11.294

02_CC = 25 mA/cm² = 78.5 mA

03_CL after = 11.539

14:56

MeAc = 6851, 7109, 6636

MeOH = 29587, 31165, 27377

W186

Sto 1

B
CH1

m7

pH 8.5

01_CL before = 10.705

02_CC = 100 mA/cm² = 314.16 mA

10.771

MeAc = 13770, 12139, 13144

MeOH = 96615, 97329, 96461

Sto 13

W187

C
CH2

m7

pH 8.5

01_C2 before = 9.377

02_CC = 62.5 mA/cm² = 19625 mA

9.651

MeAc = ~~5060, 6318, 5537~~ 7889, 9840, 9031

MeOH = 57916, 54732, ~~8888~~

SHO 2

W188

Potentiostat

(D) M7

DH 8.5

O1_Cl before = 10.627

O2_CC = 25 mA/cm² = 78.5 mA

12.667

MeAc 5060, 6318, 5537

MeOH 29851, 27743, 27183

After finishing M7.

experiments: ① CO_2 evolution at high current density (100 mA/cm²)
- in presence of Helium.
- → in presence of O_2

if will also required. ~~the cost~~ to do SEM.

SEM: after 25, 62.5 and 100 mA/cm², + cleaning.

Wild

Mn membrane of gut is to check the gas exchange rate

expt was time 2hr

1hr for analysis gas analysis

1hr for analysis gas analysis

at 100 ml/min

in presence of the

at 0, before 0.1172 ml membrane; the flow analysis block from gut=8

until injection 20 M:15 CC catalase

gut for changed the gas for gas analysis

to before purge to catalase tank same flow 30 ml/min

from in 21 to onwards catalase gas analysis

= no more over detected

(28)

Mcat.	~~89994~~	33509	28909	29686
Mcat.	~~288273~~	262233	30309	261805

Wild

Mn membrane gut is to check the gas exchange

= presence of the membrane

1hr for analysis gas analysis

1hr for catalase gas analysis } no gas analysis

at 100 ml/min ~~presence of the catalase~~

pH 7, Mn membrane

2hrs of electrolysis

11:57 to 13:50

Mcat. 49109, 48949, 46958

Mcat. 20605, 249342, 28477

Wild

Membrane Mn divided cell

- 2hr of continuous electrolysis
- Gas liquid product switching
  10 ml, 20 ml, 30 ml, 45 ml

60 ml/min 120 ml

60 ml/min 120 ml

60 ml/min 120 ml

30 ml (120 ml)

146

(Used sample taken each time

min	Mcat	Mcat
10	5846, 6452	269280, 46500
20	16769, 9810	48348, 49134
30	12511, 11352	48114, 46182
45	19857, 16949	105908, 99491
60	28498, 22498	1402051, 1800408

W192

200 mA/cm² divided cell
M7

pH Catholyte	pH anolyte
13.9	4.7

(D) CC = 0.628 A.

14.14 → 16.14

	MeOH	MeAc
Anolyte	407544, 441364, 351505	62690, 65869, 51611
Catholyte	15853, 10765, 9744	11, 352, 204

W193 → for cross over

100 mA/cm² divided non purged flow. pH5
M7

	MeAc	MeOH
Anolyte :	96845, 99521, 93429	18607, 18082, 18628
Catholyte :	None	None -

no cross over.

W194

pH 12
100 mA/cm² divided non purged BDD
M7 (both sides).

	MeOH	MeAc
Anolyte :	101088, 96209, 94279	14045, 14072, 13413
Catholyte :	None	None

↳ no cross over

20230806_P1

1M propionic acid / sodium propionate
pH5
Vol = 120ml
Free electrode cell.
CC at 25 mA/cm²

He flow = 30 ml/min

O_2 before = 0.0688

(total electrolysis time 1hr ~~5min~~)
↳ ~~because 5 mins are extra for one ge first injection for 0~~

CV after
0.3V RHE = -0.505 to 2.495 (pH5)
Cl = 7.605
CV to check if acetate adsorbed on the surface.

Et OH	39437, 39064, 32344
Et Pr	11265, 11585, 9151

20230806_P2

1m propionic acid / sodium propionate (Batch)

Vel = 120ml/batch

He flow: 30ml/min

O_2 before

CE = at 50 mA/cm²

O_2 before: 0.404 injection 8.

from injection 9

EtOH 62458, 63849, 57378

Et Pr 19062, 19352, 18906

20230806

1m propionic acid / sodium propionate (Batch)

Vel = 120ml

He flow: 30ml/min

O_2 before = 0.0724 injection no: 13

~~O_2 after~~

Start from injection = 14

EtOH 103996, 107271, 129035

EtPr 30662, 29761, 33876

P4

20230821

1M propionic acid / sodium propionate
Vol = 120 ml
He flow = 30 ml/min
O_2 before

CC = 10 mA/cm²
O_2 before = 0.0281 (1hr) injection = 13
from injection 14

EtOH	14990, 17694
EtPro	10012, 6916

P4 needs repitition.

P5

1M propionic acid / sodium propionate
Vol = 120 ml
He flow = 30 ml/min
O_2 before = 0.0332 (injection 9) injection

CC = 150 mA/cm² = 0.575A
(due to limitation by potentiostat to go above 400 mA. ; used the power supply, made the two electrode setup: so now (P_1, P_2, P_3, P_4) are three electrode experiment batch (cell) while P_5 is two electrode.
13:39 - 14:39

Liquid product:

EtOH	104967, 104375, 108960
EtPro	24017, 22517, 23677

P6

repitition of P5

O_2 before. 0.0375 , injection. 2

EtOH	14058, 13720, 14216
EtPro	8334, 7497

P7 20220822

1M propionic acid / sodium propionate

flow cell (purged) at 50 mA/cm²

so to check if the products are reducing at counter reaction along with the effect of batch vs flow + purged and non purged electrolyte, this experiment is being performed

purged with helium + gc + liquid products at 60 mA/cm²

pH 5 Membrane N7

WE : BDD

CE: S.S

divided two electrode flow 60 ml/min both catholyte and anolyte

40 ml/min He

CC: 157.08 mA ⇒ 50 mA/cm²

11:46

O_2 before = 0.1314 (inj 7) from injection. 8

	Et	EtPro
	51492, 53008	9785, 10967
EtOH (8.045)	57568, ~~57865~~ 54930	10967, 9786

P8 20230822

[M7]

Membrane M7
at 50 mA/cm² = 157.8

Same conditions as P7 but not purged + not connected with gc.

no purge

EtOH	47577	7679 , 16527
EtPrO	40266	

[CH2]

$$H_2O_{(l)} \rightleftharpoons OH^{\cdot}_{(aq)} + H^+ + e^-$$

$$E^\circ = -\frac{\Delta G_r^\circ}{zF}$$

OH· conc. profile during OER

$$H_2O_2 \rightarrow O_2 + 2H^+ + 2e^-$$

$$H_2O_2 \rightarrow 2OH^{\cdot} + 2H_2O$$

By using fick law of molecular diffusion in a stagnant layer, the mass balance can be expressed as

$$-D_{OH^{\cdot}}\left[\frac{d C_{OH^{\cdot}}}{dx}\right]_x - 4K_{OH^{\cdot}} \cdot C_{OH^{\cdot}}^2 \cdot \Delta x = -D_{OH^{\cdot}}\left[\frac{d C_{OH^{\cdot}}}{dx}\right]_{x+\Delta x}$$

Goal.

to check methanol & ethanol oxidation on BDD.

1 lit of 0.1M Na_2SO_4

add. 14.20g Na_2SO_4 in 1 lit of H_2O

(P#5)

(pH5) adjusted with Na_2SO_4

(pH_5)

H_2S

100mM methanol in 0.1M Na_2SO_4 pH5

↳ 240 ml.

PA

0.1M → 0.9697 ml ⇒ 1.9394 ml for 200mM

100mM ethanol in 0.1M Na_2SO_4 pH5

↳ 240 ml

→ 0.13843 ml. = 0.2766 ml for 200 mM

id: A

20230921

Solution H_2SO_4 (0.1M) NaOH 100mM pH5 (Na_2SO_4)

WE: BDD

CE: Pt/Ti

RE: Ag/AgCl

Clean electrode:

A1 | Run: blank CV: 0.1M Na_2SO_4

A2 → 100mM methanol in 0.1M Na_2SO_4: CV:, CC: 25 (30 mins)

GC: ~~A2~~ - 3 to 8.

A3 → 100mM methanol in 0.1M Na_2SO_4: CV, CC: 25 (30 mins)

A4 → 100mM methanol in 0.1M Na_2SO_4: CV:, CC = $\frac{100\ mA}{cm^2}$ (30 mins)

A5 → 100mM ethanol in 0.1M Na_2SO_4: CV: CC = $\frac{100\ mA}{cm^2}$ ⇒ 30 mins

A6 → 100mM methanol in 0.1M Na-acetate: CV: CC = $25\ mA/cm^2$

A7 → 100mM methanol in 0.1M Na-acetate: CV: CC.

A8

A9

36-7.8V

i think at DPSO FiD it is alcohol methanol peak.

Hydroxyl radicals detection by DMPO

at 1500 rpm
disc: BDD : needs to be cleaned after each experiment
ring: gold : electrodeposited
Reference electrode Ag/AgCl
DMPO concentration 10.5mM

experiment:

Acetic acid
0.1 M
0.5 M
1 M
Blank + 0.1M Na_2SO_4

Propionic acid
0.1M
0.5M
1M

acetic + Propionic acid (optimal concentration) :

OH radical detection by DMPO

Blank: at 1.2V, 1.5, 1.7, 2.1, 2.3, 2.5, 2.7, 2.9 & 3.2

0.1M Na_2SO_4 pH 5

CV scan from -0.35 to 1.0 V Ag/AgCl

setting disc at constant potential 2.3

do CV on the ring (gold) scan speed 20mV/s

Electrodeposition 2.5mM AgCl (-0.2V Ag/AgCl : 10mins) 500rpm

Experiment:	conc (M)	DMPO	Total solution volume	DMPO to add
		10.5mM	1 ml	0.0213g
AA	0.1	"	"	
	0.5	"		density DMPO
	1	"	"	1.015g/ml
Pr	0.1	"		$\rho = \frac{m}{V}$
	0.5	"	"	$V = \frac{m}{\rho}$
	1	"		$= \frac{0.0213g}{1.015g/ml}$
AA + Pr (fixed AA conc 0.5, change Pr conc)	0.1	"	"	$= 0.0209ml$
	0.5	"	"	20.9µl
	1	"	"	

OH series

Electrodeposition on ring: (Au on PE)

Cable C : channel 5

-0.2 for 15 mins

BDD cleaning: 25 mA/cm² 15 min = 4.908 mA

Connection

disc → BDD → channel C : 5

ring Au → channel B : 3

OH 1

0.1M AA

weird results: could be due to contamination or DMPO degraded.

Electrode cleaning required

so testing again:

first cleaning BDD : 0-3 V RHE : CV

Try OH_2

		CH.
Cab	B: connected to lung	5
	C: dis	4

OH_3: 0.1M AA + 10.5mM DMPO ✓

OH 2_1: 0.5M AA + 0.5mM DMPO ✓

OH3: 1M AA + 10.5mM DMPO ✓

MeOH: 200mM MeOH 0.1M Na_2SO_4 pH5 ✓

EtOH: 200mM EtOH in 0.1M Na_2SO_4, pH5 ✓

Blank: 0.1M Na_2SO_4 pH5

: Bubble were blocking surface so increase rpm 1800

In very nice blank: CV6

OH4: 0.1M PrAA ~~+10.5mM DMPO~~

no dmpo: blank

→ CV blank at 1000 rpm

→ CV + DMPO

CV dmpo 2 at 500 rpm ✓

OH5: 0.5M PrAA dmpo CV at 500 rpm ✓

OH6: 1M PrA dmpo CV at 500 rpm ✓

High current DMPO:OH means: OH radical concentration high.

OH 7: new dmpo + 0.5M AA ✓

OH8: new dmpo + 1M AA ✓

OH9 new dmpo + 0.5M AA + 0.5M PrA

new CV cuz i suspect that i used wrong electrolyte

CV 2 is repeated

OH10: new dmpo + 1M AA + 1M PrA

10.5mM.

DOE : UI medium: Talal : Propionic acid based propionic acid only.

	Conc (M)	pH	Current density	
1	1	5	100	P9
2	0.55	8.5	62.5	P10
3	1	12	100	P11
4	0.1	5	25	P12
5	0.1	12	25	P13
6	1.0	5	100	P14
7	0.1	12	25	P15
8	1.0	12	100	P16
9			25	P17

Calibration co-efficient

MeAc: $4e^{-8}$
MeOH: $7e^{-8}$
EtOH: $4e^{-8}$
Et Pro: $2e^{-8}$
acetaldehyde: $3e^{-8}$

GC gas: → instrument method

(Chromeleon local / Instrument data / Talal / New method / Universal 024.seq
low-split method. instrument

Processing method: Talal / 2023 / 20230816 / Low split

P-9

2023121 1

Electrolyte volume 120 ml. 30 mL

Propionic acid:
conc
pH
current density

PHS
Batch cell: 120 ml 1M PrA+NaPr
current density = 100 mA/cm²
WE: BDD = 3.89 cm²
CE: Pt/Ti
RE: Ag/AgCl.

He flow: 30 ml/min
O_2 before = 0.03%
injection 5 - 14

01_CV: 0 - 3 VRHE → -0.505 to 2.495
02_CA 7.983 Ω
03_CC = 100 mA/cm² = 387 mA
04_CV = 0 - 3 VRHE
05_CA = 7.253 Ω

Maybe a new gc calibration is needed; have to check it.

pH after same

	Rep 1	Rep 2
EtOH	103155	107794
EtPro	36366	31434
MeAc	3879	2145
Acetal	1913	2960

Pa repeat

Cell 2 electrode 2 : 120 ml electrolyte
for liquid products 100 mA/cm² PHS 1M

DOE : UT medrive: Talal : Propionic acid data

Propionic acid vary.

	Conc (M)	pH	Current density	
1	1	5	100	P9
2	0.55	8.5	62.5	P10
3	1	12	100	P11
4	0.1	5	25	P12
5	0.1	12	25	P13
6	0.1	5	100	P14
7	1.0	12	25	P15
8	0.1	12	100	P16
9	1.0		25	P17

Calibration co-efficient

MeAc: 4e-8
MeOH: 7e-8
EtOH: 4e-8
Et Pro: 2e-8
acetaldehyde: 3e-8

GC gas: → instrument method

(Chromeleon local / Instrument data / Talal / New method / Curves 024.seq
low-split method. instrument)

Processing method: Talal / 2023 / 20230816 / Low split

P-9

2023121 1

Electrolyte volume 120 ml. 30 mM

Propionic acid:
conc
pH
current density

He flow = 30 ml/min
O_2 before = 0.03%
injection 5 - 14

PH5
Batch cell: 120 ml 1M PrA+NaPr
current density = 100 mA/cm²
WE: BDD = 3.89 cm²
CE: Pt/Ti
RE: Ag/AgCl.

01_CV: 0 - 3 VRHE → -0.505 to 2.495
02_CI 7.983 Ω
03_CC = 100 mA/cm² = 387 mA
04_CV = 0 - 3 VRHE
05_CI = 7.253 Ω

Maybe a new gc calibration is needed; have to check it.

pH after same

	Rep1	Rep2
EtOH	103155	107794
EtPro	36366	31434
MeAc	3879	2145
Aceta	1913	2960

Pa repeat

Cell 2 edeltide 2 : 120 ml electrolyte
for liquid products 100 mA/cm² PH5 1M

P10

2023 12 11

120ml electrolyte

0.5 M PrAc/NaPropionate pH 8.5 (8.3 in reality) but will use 8.5 for CV

BDD : 3.87

Pt/Ti : mesh

RE : Ag/AgCl

He flow : 30 ml/min

O_2 before : 00493

injection : 5

01_ CV: 0 - 3 VRHE ⇒ -0.711 S to 2.2885 V Ag/AgCl

02_ CZ : 8.408 Ω

03_ CC : 62.5 mA/cm² = 241.875 mA

04_ CV : 0 - 3 VRHE

05_ CZ 4.437 Ω

(pressure in reactor was high could be due to blocking so gas analysis again

pH increase to 9.4

Acetal	58	1914
MeAc	152	368
EtOH	77148	75654
EtPro	8567	7955

P11

2023 12 11

120ml electrolyte 30 ml/min

1M PrAc/Napropionate pH 12 at 100 mA/cm² (original 11.7 but for calc using 12)

BDD : 3.87 cm²

Pt/Ti mesh

RE: Ag/AgCl

He flow: 30 ml/min

O_2 before: 00562

01_ CV: 0 - 3 VRHE ~~-0.711~~ -0.918 to 2.082 to 2.2885 injection: 5

02 : CZ 9.160 Ω

03_ CC = 100 mA/cm² = 387 mA

04_ CV: 0 - 3 VRHE

05_ CZ 6.340 Ω

Acetal	1897	2328
MeAc	6610	2972
EtOH	113013	116928
EtPr	13094	14514

~~pH overnight~~

pH 11_2 : overnight at 28 mA/cm² pH 12

0.1M

pH became 9 after overnight

	Acetal	meOH	EtOH	EtPr
Acetaldehyde	11871	30141	112055	28
	12546	26621	110665	74

↓ could be due to linear by baseline

P12

2023/12/11

0.1M Propionic acid/Na-propionate pH 5, current density 25 mA/cm²

BDD - 3 cm²

01_CV = 0-3 V RHE ⇒ -0.505 V to 2.495

He 30 ml/min

120 ml electrolyte

02 CI: ~~4.497 Ω~~ 48.165

03_CC = 25 mA/cm² = 96.750 mA for 1 hour

O₂ before: 0.0805

from injection

Clafte 44.419

	Acetal	EtOH	EtPr
Rep 1	3166	18071	2376
Rep 2	4717	18165	2105

P13

2023 12 13

0.1M Propionic acid/Na-propionate pH 12 at 25 mA/cm²

120 ml

He 30 ml/min

01_CV: 0-3 ⇒ -0.98 to 2.082 V

02_CI 21.129 Ω

03_CC: 25 mA/cm² ⇒ 96.750 mA for 1h

O₂ before = 0.0341 inject 1

04_CV

05_CI

electrolyte becomes translucent

P14

120 ml electrolyte
30 ml/min

202312

0.1M PHS 100 mA/cm²

01_CV: 0-3 V RHE = -0.505 to 2.495 V Ag/AgCl

02_CL: 37.659 Ω

03_CC: 100 mA/cm² = 387 mA
due to limitation by potentiostat
used a two electrode setup with
power supply

O_2 before: 00766
cell voltage ≈ 18 Volts
injection 9.

started 15:25
to 16:25

04_CV: 0-3 V RHE

05_CC: 24.242

P15

1M PHS at 25 mA/cm² 20231213

120 ml electrolyte
30 ml/hr

01_CV: 0-3 V RHE: -0.505 to 2.495 V Ag/AgCl

02_CL: 38.920 Ω

30 ml/hr

03_CC: 25 mA/cm² = 96.750 mA
O_2 before = 0.0504
cell voltage injection 7

04_CV

05_CL = 8.401

		3.019	Acetal	MeAc	MeOH	EtOH	EtPro
P15	Rep1	2656	3558	1190	681	86934	12108
	Rep	3150	4414	5966	5966	30660	10910

P16

0.1M pH12 at 100 mA/cm²

120 ml electrolyte
50 ml/min

01_CV: 0-3 VRHE :- 0.918 to 2.082 VAg/AgCl

02_CI = 25.66 Ω

- diffiault to electrolyze so use a divided cell

15.02
16.08

O₂ before = 0.0482

from injection

03 CC = by power supply = 100 mA/cm²

04_CV: 0-3 VRHE

05_CI = Ω

	3.01	Acetal	MeAc	MeOH	EtOH	EtPr
Rep1	2891	12914	3671	17409	69920	117
Rep2	2123	12848	1881	12936	70799	112

P17

1M pH12 at 25 mA/cm²

Velocity
190 ml

01_CV: 0-3 VRHE ⇒ -0.918 to 2.082 VAg/AgCl

02_CI = 8.388 Ω

03_CC = 25 mA/cm² ⇒

He flow = 30 ml/min

O₂ before = 0.0552 injection 5
time 1 hour

04_CV: 0-3 VRHE

05_CI = 6.172

	[3.01 9 ?]	[Acetal 3.36]	[MeAc 4.05]	[MeOH 5.101]	[EtOH 5.467]	[EtPr 5.72]
Rep1	1026	4010	1519	2518	32448	7737
Rep2	2743	211	2242	374	35298	8269

P18

~~20231212 - 1M NaPr pHS at 25 mA/cm²~~
~~flow cell: no purge no gas analysis~~

1M pHS 50mA/cm² = 193.5mA

continuous electroxidation of P17 w/out cleaned electrode from P17

1hr purge

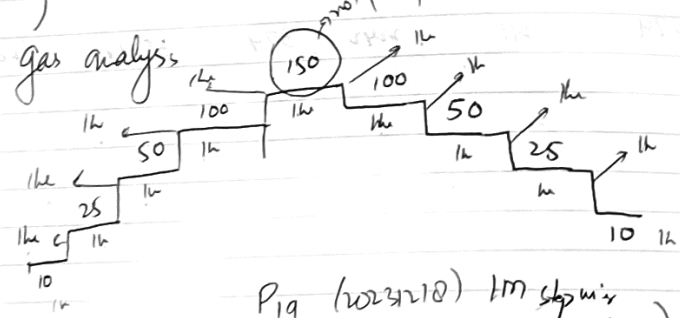
10hr CC: 50 mA/cm² : continuous monitoring of ethylene 41, CO2

P19 (20231215)

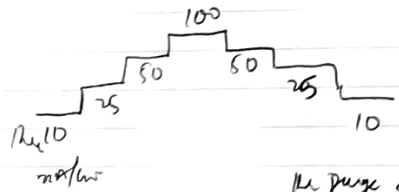
1M pH 5 ~~150 mA/cm²~~ 0.5M PrA, sodium gluconate

gc

gas analysis



P19 (20231218) 1M stepwise (1M)



→ it stopped due to buffer problem had to do it again

✓ P19_rep again 20231219 completed

P19_1.5M same experiment

P20

~~20231212 - 1M NaAcetate / 1M NaPr pHS at 25 mA/cm²~~

Repeat experiment in undivided two electrode cell → P20 to onwards

5.31 cm² : clearing 132.7mA P14 no gc electrolyte volume = 120ml

✓P20:	rep (P9)	CH1 (pHS)(100mA)(1)m = 531mA	1hr	11:59
✓P21	rep (P10)	CH2 (P10 8.5)(625)/0.55) = 331.875		11:59
✓P22	rep (P11)	CH1 (P11 8.5)(100)(1) = 531mA		13:39
✓P23	rep (P12)	CH2 (5)(25)(0.1) = 132.7mA		
✓P24	P13	CH1 = (12)(25)(0.1) ≠ 132.7mA	14:50	forgot shwig in Dly. 15:40
P25	P14	CH2 = (5)(100)(0.1) ≠ 531mA	15:45	
P26	P15	CH1 = (5)(25)(1/m) ≠ (132.7)	17:13	
P27	P16	CH2 = (12)(100)(0.1/m)(531.7)	10:13	
P28	P17	CH1 = (12)(25)(1)	11:16	
P29 rep	P25 rep	CH2 (5)(100)(0.1)	12:16	

To do P25, 28 & 29

The data in new folder. - -

P23 = no dilu
P21 (x5 dilu)
P24 (modi)
P27 (no dilution)
P29 (no dilution)

So, did a separate calibration so ethanol is $2e^{-8}$
now the data makes sense.

new results are stored in a new folder.

$(2e^{-8})(4e^{-0}), (2e^{-9}\ MeAc)$

Data (GC

		Acet	MeAc	MeOH	EtOH	EtPro
MX1	(x5 dil)	3880	5067	22751	50366	7205
		4945	7389	26752	50708	11952
MX2	(x5 dil)	70	8853	26182	49765	10854
		2681	8119	25948	49436	13833
MX3	(x5 dil)	3255	9355	48481	89188	12881
		5277	6794	46317	88525	15212

20240127

		Acet	MeAc	MeOH	EtOH	EtPro
lol MX15	(x10 dil)	5483	12640	93178	44779	32
		5062	13156	95993	46589	108

2024 H2O

203 MX13	(rep x10)	2166	8043	28529	20561	908
		52	6351	32453	16165	8118
				26351		

204 H2O

100 ~~mM~~ol. 120ml electrolyte.

Experiment: mixture of acids

main exp / Rep

MX1 4, 11 2

inflow out at 25:	32.5
50:	34
100:	36.7

⇉ ⊙pHS
⊙ 25 mA/cm²
⊙ 0.5M Acetic acid / 0.5M Propionic acid.

⇉ ⊙pHS
⊙ 50 mA/cm²
⊙ 0.5M acetic acid/0.5 Propionic acid
MX 3 4, 11 4

⇉ ⊙pHS
⊙ 100 mA/cm²
⊙ 0.5M acetic acid / 0.5 M propionic acid. MX 5 4, 11 6

⇉ pHS
⊙ 25 mA/cm²
⊙ 0.5 M acetic acid / 1M Propionic acid MX 7 - 8
(MS wrong liquid sample) so only MS analysis (liquid product)

⇉ pHS
⊙ 50 mA/cm²
⊙ 0.5 M acetic acid / 1M propionic acid MX 9 - 10

⇉ pHS
⊙ 100 mA/cm²
⊙ 0.5M acetic acid / 1M propionic acid. MX 11 - 12
installed new bubble cold trap
gas flow = 36.7 ml/min

⇉ pHS
⊙ 25 mA/cm²
⊙ 0.5 M acetic acid / 0.1M propionic acid MX 13
↳ rep again

⇉ pHS
⊙ 50 mA/cm²
⊙ 0.5 M acetic acid / 0.1M propionic acid MX 14

⇉ pHS
⊙ 100 mA/cm²
⊙ 0.5M acetic acid / 0.1M propionic acid MX 15
↳

mx1 $\frac{(\text{calib coeff} \times \text{HPLC Area})}{\text{conc.}} \times \frac{\text{volume of electrolyte}}{\text{mol.}} \times 6.02 \times 10^{23}$

FE = $\frac{\text{Electron req}}{\text{Electron with charge passed}} = \frac{\text{molec produced} \times 2}{\text{charge} \times 6.21 \times 10^{18}} = \frac{\text{moles found} \times 6.09 \times 10^{23} \times 2}{I \times t \times 6.2 \times 10^{18}}$

$= \frac{\text{conc} \times \text{volu} \times 6.02 \times 10^{23} \times 2}{I \times t \times 6.2 \times 10^{18}}$

$= \frac{\text{HPLC calan} \times \text{coeff} \times \text{volume} \times 6.09 \times 10^{23} \times 2}{I \times t \times 6.2 \times 10^{8}}$

mx1

Using Redox me electrode holder.

area = 3.87 cm²

	MeOH	MeAc	EtOH	EtPro	Acetal	Meth	EtAc	Ethyl	CO
	22.80	0.416	33.774	0	3.889	0.402	32.244		82.8
mx2	26.12	0.567	33.14	0	2.68	0.22	1.75	22.977	91.034
	Amp 24.40 1.66	8.0755	33.457 0.317	0					
mx3	23.75	0.269	29.64		2.130	0.156	1.14	2381	89.61
mx4	23.142	0.34	33.52	1.83	3.282	0.205	1.408	25.60	94.368
mx5	25.35	0.21	28.80	1.24	2.695	0.165	0.92	19.57	110.884
mx6	17.917	0.209	28.62	1.234	2.7	0.175	0.94	19.134	109.4
mx7	-	-	-	-	-	0.577	3.105	34.26	89.05
mx8	24.761 18.56	0.241	37.234	7.064	1.3158	0.55	4.408	35.359	87.06
mx9	21.43	0.46	33.87	3.840	2.03	0.3469	2.602	29.50	103.855
mx10	17.64	0.462	35.766	4.1566	4.03	0.4055	3.119	32.09	119.16
mx11	13.61	0.94	32.094	3.618	2.08	0.35	1.825	30.06	124.02

25 mA/cm² a SMAAPA

Cc (V)		CN	Before Peak	shoulder	C2	after peak	shoulder	C2
2.98		mx1	32	N	9	35	N	0.8
2.87	40	mx2	32	N	8.9	40	N	8.5
3.8	Et0	mx3	22	N	11.5	27	Y	9.5
3.5	Et0	mx4	40	N	8.5	47	N	8.5
4.4	Et0	mx5	33	N	9	42	Y	8.5
4.2	Et0	mx6	14	N	12	45	Y	8
3.1		mx7	24	N	11.5	29	Y	10
2.7		mx8	48	N	8	60	Y	7.5
2.4		mx9	32	N	9.5	40		8
3.2		mx10	44	N	8	58	Y	7.5
3.9		mx11	48	N	8	56	N	7

Propionic acid oxidation

		Et	EtPr	I	Acetal
		37.37	44.78	7.41	69%
		29	40.12	5.13	88.40
		28.23	43.48	4.974	122.4
		45.4	51.40	10.204	73%
		18.44	23	2.07	102 (two acetal)
		45.09	46.45	10.59	76.79
		23.177	35.06	6.60	1.21
		37.410	40.99	1.77	1.54
		34.72	38.41	1.78	6.069
		16.13	24.22	1.19	47% 7.90
P13 25 0.1m PH12		39.144	47.259	0	1.8 9.83
P14 100 0.1 PH5		5.93	10.36	0.361	92.257 5.44
P15 25 1m PH5		38.9	45	6.15	89.4
P16 100 0.1m PH12		17.61	23.47	0.01	6.69 6.44
P17 25 1m PH12		39.16	45.27	4.27	4.23 4.57
P20 100 1m 5		-	49.58	5.05	- 3.05
P21 0.5m 625 8.8		-	54	1.54	- 4.46
P22 100 1m 12		-	52.02	1.91	- 2.05
P23 25 0.1m PH5		-	54.109	7.67	- 1263
P24 25 0.1m PH12		-	45	1.09	- 4.01
P25 100 0.1m PH5		-	3.00	0.04	- 4.09
P26 25 1m PH5		-	57.86	8.20	- 958
P27 100 0.1 PH12		-	25.55	0.26	- -
P28 25 1m PH12		-	41.94	2.707	- 1.89
P29 100 0.1m PH5		-	6.44	0.67	5.03

Conc

P12	0.1	PH 5	25
P14		PH5	100
P13		PH12	25
P16		PH12	100
P2		PH5	25
P29		PH5	100
P24		PH 12	25
P27		PH12	100

P12 = P23
P14 = P29

Conc

P11	1m	PH5	100
P15	1m	PH5	25
P17	1m	12	25
P20	1m	5	100
P22	1m	12	100
P26	1m	5	25
P28	1m	12	25

Ethylene with increasing pH 41 j = ~~reduce~~ decrease

	Ethy	cetanol	Acetal
PH 12 1M 100 mAlc	~4.72	38.41	6.09
with jc		52.02	2.05
		↳ ctanol	acetaldehyde
PH12 1m 25	39.16	45.27	evapor
Ethy	Ethene	41.94	
PH 5 1m 100 23	49		
	38.5	45	

formaldehyde?

Mx1 Reaction condition 20240129

201 H_2O
202 Mx16 (x5 d.1) No liquid
203 H_2O
204 Mx17 (x5 d.1) MeAc 6901, 9955 MeOH 36639, 39958
205 H_2O
206 Mx18 (x5) 13265, 13160 74283, 71967
207 H_2O
208 Mx19 (x5) 18764S, 20088 139483, 144140
209 H_2O
210 100 mM MeOH in 0.1MPP. 3167975, 3177786

20240130

	Acetal	MeAc	MeOH	EtOH	EtH_2
201 H_2O					
202 Mx20 (x5 d.) =	4200	2683	23933	41355	9483
	2173	8893	22983	45333	10225
203 H_2O					
204 Mx14 rep (x5)	4449	14895	101316	48593	762
	4998	14925	98738	48267	70

Experiment mix acids

pH5 Mx17
@ 25 mA/cm²
0.5M acetic acid / 0.5 formic acid ✓

pH5 Mx18
@ 50 mA/cm²
0.5M acetic acid / 0.5M formic acid ✓

pH5 Mx19
@ 100 mA/cm²
0.5M acetic / 0.5M formic ✓

Mix all

pH5 Mx20
@ 25 mA/cm² 0.5M AA, 0.5M Formic, 0.5M Propionic acid.
→ CV before after

Mx16: @ 25 mA/cm²
0.5M formic acid ✓ pH after: 5.7

pH12 Mx21
@ 25mA/cm² → 0.5M AA, 0.5M Formic, 0.5M Propionic acid.

Mx14 rep

Presentation content

→ What is the influence of mix acid oxidation?
Can reaction condition alter the selectivity?
↳ pH, current density, concentration

→ What is the effect of combination of acid (directly oxidize and indirect oxidation)
formic acid, acetic acid.
→ does formic acid inhibits the oxidation of acid.

Triangle phase:
→ powder titanium

MX

To observe the effect of adsorption of acetate on BDD

MX 21 : CH5: 1M Kacetate pH 5

CV- C1
CC = 25 mA/cm² ⇒ 265.5 mA ✓
CV- C1
CC = 25 mA/cm² ⇒ 265.5 mA
CV- C1
CC 25 mA/cm² ⇒ 265.5 mA
CV-C1
CC 25 mA/cm² ⇒ 265.5 mA
CV-C1

EtOH after
0.100 M

Both stopped after 1hr

* Be careful: min acid all experimed has same
MX id: MX 21

So now doing separately

(2) CV- C1 - CC ✓

(3) CV - C1 - CC ✓

(4) ~~CV - C1 - CC~~ ✓ } CC first then CV and C2

(5) CV - C1

13:56 ~ 14:24

MX 21_EtOH

now acetate is adsorbed already so to see the effect of alcohol.
after 0.1M

MX 22

To observe the effect of adsorption of propionate on BDD

CH2: 1M Na-propionate.

MeOH after
0.08M

CV C1
CC = 25 mA/cm² ✓
CV- C1
CC = 25 mA/cm² ✓
CV- C1
CC = 25 mA/cm² ✓
CV- C1
~~CC = 25 mA/cm²~~ ✓ } CC first then CV- C1
CV- C1

= 0.08M.

Both stopped after 1 hour, from these experiments
MX 22_ MeOH
now propionate is adsorbed, so the effect of alcohol oxidation needed.

MX 23

0.5M AA , 0.5M Pr , 0.5M FA = 120ml (50 mA/cm²)

pH 8
01_CV_CC : 0.3VRHE : -0.505V to 2.495 V Ag/AgCl
02_CC : 50 mA/cm²
03_CV_CC : 0-3VRHE : -0.505V to 2.495V } column temperature slightly increase from 45 to 45.3 so some injection might be missing

MX 24

0.5M AA , 0.5M PrA, 0.5M FA = 120ml (100 mA/cm²)

01_CV 0- 3VRHE
CI
CC = 100 mA/cm²
CV 0 - 3VRHE
C1

P30

1m Propionic acid / Na Propionate

10, 25, 50, 100, 150 → Batch

pH 5

P30 = 10 mA/cm²
- CV: 0-3 VRHE
- Cl
- CC
- CV
- Cl

P31 = 25 mA/cm²
- CV: 0-3 VRHE
- Cl:

P32.

P33. 100 CV:

P34

1m Propionic acid / Na Propionate

flow rate = 20 100

pH 5

Zakres: #biohu2020

mx 25

mx 25 @ p# 05m AA, FA, PA

25, 50, 100 mM/cm²

mx 25 CH: 0.3 uA/cm²

CE

CC: 25 mM/cm²

CH

CE

mx 26

p# 12, 05m AA, FA, PA

P30 (20240221)

Flow cell
Analyte = 1M Propionic acid / Na-propionate . 120ml
pH: 5
Catholyte 1M H_2SO_4 = 100 ml.
Membrane: 324
flow rate: 60 ml/min

CC: 25 mA/cm² = 0.079 mA (3.16 cm² area

[FE towards ethylene was very low, maybe it is due to the pH gradient, but also FE towards CO_2 is low.

	Prot	Acid	EtOH: 29355	EtPro: 7041
Et[illegible]	300 7548	432	30947	6198
	6411	2802	28754	8337
Et[illegible]	6809	2823		

(something is formed at 3

P31

Same conditions as P30, different current density

CC: 50 mA/cm² =

20240221 p31_202

	Uptrum 3.013	EtOH	EtPro	Acetal
Rep1	4553	50869	12936	3289
Rep2	6126	49119	11275	[illegible]
Rep3	5537	52688	11446	3480

J: 2/3
N: 3/3

P32

He = 32 ml/m

20240311_P32_25 mA/cm²

Catholyte: Catholyte 1M H_2SO_4
Anolyte = 1M Na propionate pH 5

WE: BDD
CE SS
Membrane Nafion 324

CC: 25 mA/cm² = 0.079 mA

Very low ethylene & CO_2
found out catholyte was not flowing, pump problem
so doing it again:
with same conditions.

P33

Same conditions as P32 but electrode is not cleaned.

P34 ✓

He = 40 ml/min

20240312_P34_50 mA/cm²

Electrolyte: catholyte = 1M H_2SO_4
anolyte 1M Na-propionate pH 5

BDD: WE
CE
SS
324 Nafion: Membrane

CC = 50 mA/cm² = 0.158 mA

11:57 - 12:57

P35

He = 40 ml/min ✓

20240312_P35_100 mA/cm²

Electrolyte: Catholyte = 1M H_2SO_4

Analyte = 1M Na P_r PH: 5

WE = BDD
CE: SS
Membrane: Nafion 324

CC: 100 mA/cm² = 3.16 cm² area = 316 mA 13:53 to 14:55

P36

He flow 40ml/m

20240312 _ 1M NaPr pH5 _ 150 mA/cm²

Electrolyte: Catht: 1M H_2SO_4
Anolyte: 1M NaPr → changed to fresh because of high PA from previous catholyte.

BDD: WE
CE: SS
324 Nafion

CC = 150 mA/cm² = 474mA for 1hr

15:54 to 16:[illegible]

glycerol output 49.5.

Data: D: Total: 20240312 P34 35 36

		at 3.06	Acetal	EtOH	EtPrO
201	H_2O				
202	H_2O			48303	8375
203	P34	7851 4961 3513	3362 4608 5458	47920 49635	9881 13520
204	H_2O				
205	P35	9005 9713 12520	6969 4977 6937	101838 94578 98503	8277 7462 9967
206	H_2O				
207	P36	8168 9084 10701	4893 5528 5557	139534 129684 140830	22074 20477 25596
208	H_2O				

(Nafion membrane weired and dissolve brownish at cathode)
Pic

P37

He flow 40ml/m

effect of flow rate: 10 ml/min

20240313 _ 1M NaPr pH5 _ 100 mA/cm²

Electrolyte: Catht: 1M H_2SO_4
Anolyte: 1M (120 ml) NaPr

BDD: WE
CE: SS
324 Nafion

CC = 100 mA/cm² for 1hr = 316 mA

17:12-18:12 (Thu)

	A: 3:0 at 3:06	Acetal	EtOH	EtPro
P37	10606	42055	93969	18731
	9145	42540	91193	17087
	5269	42628	94066	19560

→ very high acetaldehyde & ethanol oxidation

P38

Effect of flow rate: 100 ml/min

20240318_1M Na Pr_pH5 _ 100 mA/cm²

Electrolyte: 1M Na-propionate pH5 : analyte

1M H_2SO_4 Catholyte

BDD: WE

CE: SS

Membrane: Nafion 324

CC = 100 mA/cm²

Electrolyte vol = 120ml

He flow 40+

P39 MX25 ✓

20240318_0.5M FA AA PrAc flow

Electrolyte: 0.5M FA/NaFr, 0.5M AA/NaAc, 0.5M Pr/NaPr → analyte

Catholyte → 1M H_2SO_4

WE: BDD

CE: SS

Membrane Nafion 324

CC = 25 mA/cm²

He flow 40ml/min

Electrolyte volume: 120ml

P40 MX26

: 20240318_0.5M FA AA PrA_flow_50mlpm

same conditions except current density:

CC = 50 mA/cm² : flow cell.

P41 MX27 ✓

: 20240318_0.5M FrA, AA, PrA_flow_50ml/pm

Same conditions except current density

CC = 100 mA/cm² : flow cell

→ P39 mix 26, 28

20240318 P38 mix 25 26

	at 3:0	Acetaldehyde	EtOH	EtPro
201 H2O				
202 P38	8967 ~~4~~ 9192 5632	45064 44288 44789	58713 57703 56858	14659 14190 13180
203 H2O				

	Acet	MeAc	MeOH	EtOH	
204 - mix 25	31380	886 ~~44740~~	28231	29533	1367
	32620	1781	24513	33846	6545
	31356	886	28231	29533	1367
205 H2O			32491	62886	6114
206 mix 26	31996	5730	30128	63289	7176
	30963	4221			
	31903	2930	32954	63261	6523

20240319 P39 mix 27 28

	at 3:0	Acetal	MeAc	MeOH	EtOH	EtPro
H2O	-	-	-	-	-	-
mix 27	6279 6040 8577	5789 7478 5601	8915 11198 9889	51705 51778 49511	114915 120826 115033	8980 6127 7222
H2O						
mix 28	7168 7297 6571	6578 6870 6861	10513 10938 7038	35009 34662 36889	137944 137635 142576	6580 6969 8885
H2O					102299	10197
P39		3442 5024 3448			161418 161865	10731 9240
H2O						

What is the effect of counter electrolyte

1M H_2 Acid: 100 mA/cm² } flow cell.

1M Mix acid: 100 mA/cm² }

P39

20240319_P39_100mA/cm²_60ml/min_both side propionate

Electrolyte: 1M Na propionate = both catholyte and analyte pH6

at 100 mA/cm²

100 mA/cm² @ 319 mA for 1hr.

~~mix 28~~ mix 28

20240319_~~mix 28~~ - 100 mA/cm² - 60 ml/min both sides all acids

Electrolyte: 0.5M FA AA PA: pH6: both sides

at 100 mA/cm² = 319 mA for 1 hr.

Mx29

20240329 - 0.5M all pH6 at 50 mA/cm²
both electrolyte 0.5M NaPi

He flow 30 ml/min

CC = 50 mA/cm² = 0.158 mA

Mx30

20240324 - 0.5M all acid pH6 at 25 mA/cm²
both electrolyte 0.5 M NaPi

He flow = 30 ml/min

CC = 0.080 mA

Mx31

20240328 - 0.5M all acid pH6 at 15 mA/cm²

He flow = 40

CC = 150 mA/cm² = 474 mA | electrode area = 3.16 cm²

10:20 - 11:18

20240328 Mx32

P40 mx32

2024 03 28 _ 0.5m all at 300mA/cm² →

CC- 300 mA/cm² ⇒ 948mA

over voltage due to counter electrode)

CC.
↳ 10:28 to 10:52 = 20min
10:56 to 10: 58 = 2min
11:00 to 11:07 = 7min
~ 30min total curves

mx33

repeat mx32

20240328_ 0.5m all at 300mA/cm²

out flux- 54

P40

1m propionic acid sodium propionate (both sides pH6)
at 25 mA/cm²

P41

1m propionic acid / sodium propionate (both sides pH6)
at 50 mA/cm²

20240328 MX29 30

	3.0	Acet	MeAc	MeOH	EtOH	EtPro
H2O 201	9549	4962	6220	24555	76459	80
	5555	5817	493	28174	71755	428
MX29 202	7714	6255	9227	25378	79026	6832
H2O 203						
	4179	2780	1896	19734	41404	5820
MX30 (204)	5257	3862	6055	21067	40670	242
	9809	1437	6706	13301	41657	2730
H2O 205						
	5954	6232	12580	51651	205074	8204
MX31 206	8670	7174	12422	48601	204362	7847
	6906	6796	12515	49487	207526	8934
H2O 207						
	12620	14673	13375	106602	368586	12474
MX33 208	10487	15543	13493	109916	371056	14156
	9341	14732	14482	107826	376939	11065
H2O 209						

	3.0	Acetal	EtOH	EtPro
P40 210				
H2O 211				
P41 212				

	EtOH	Acet	EtOH	EtPro
	5262	2116	29900	4173
P40	476	719	32570	4617
	6134	4694	36423	5662
H2O				4982
	6755	329	52084	8240
P41	6238	4665	56740	6642
	5312	397	52186	

Can high concentration of acids avoid overoxidation

2M Propionic acid at 150 mA/cm²

1M min all acids at 150 mA/cm²

1M acetic acid + 0.5M other acids at 150 mA/cm²

20240329 P42 : 2M Na Propionate at 150 mA/cm²

CC, 150

3.019	Acetaldehyde	EtOH	EtPro
5628	1354	73519	11459
9776	3316	69541	11991
5206	1613	72796	10944

20240329 P43 1M Na Propionate:

Can pH affect selectivity

pH 9, 7, 25, 50, 100, .

P43

20240329 1M Na Pr both sides pH6 at 150 mA/cm²

CC= 150

3.01	acetaldehyde	EtOH	EtPro
8509	3316	130161	19016
7648	4907	135896	19256

MX34

PHS 0.5M all acid flow divided analyte
Catholyte 1M H_2SO_4
at 150 mA/cm²

or 0.0566.

inject 11 to

15:34 to 14:34

20240409 MX34

201 - H_2O

	3.0	Acetal	MeAc	MeOH	EtOH	EtPro
-202	9854	9004	11883	68123	182135	6366
	11100	7916	8587	65604	183787	7183
	8713	8538	9748	64216	179043	6349

Electrolyzer big
BDD mesh (size) ~~stainless steel~~ electrolyzer.
gasket

solubility of products:
→ ethane
→ CO_2
→ Ethylene

? rate constant ethylene with OH radicals.

active electrode area
By BDD: 7Bcm x 9cm² = 70.98 cm²

$J_0 = \frac{I}{A}$

$I = J_0 \times A$

mA/cm²	A
25 =	1.7
50 =	3.54 A
100 =	7.098 A

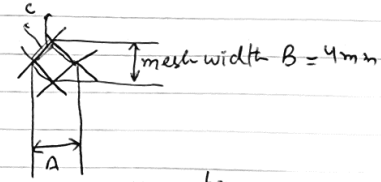
mA/cm² = 7.09 A

BDD mesh (30x30 mm) (thickness needed) 1.5mm & 0.5mm

Original mesh spec
50x100x1.4mm
2500ppm B
5 µm coating

9.6 cm²

mesh characteristics



A = mesh length = 6mm
C = strand width. 1mm
D = strand thickness 1mm

mx35

0.5 M all acid in batch cell two electrode at 150 mA/cm²

- power supply is causing problem. (data was not recorded)
- firmware update.

inject: 32, 33, 34, 35 ? 36 should be ignored because the flow stopped and accumulation of ethylene in the cell head.

ymx34 copy gc data

20240410-mx35

201 - H2O						
202 -	at 3:0	Acetaldehyde	MeAc	MeOH	EtOH	EtPro
Rep1	8101	8026	12186	78630	241046	9495
2	5002	7486	11071	73843	243995	9573
3	4717	8076	8795	79788	251904	11181

Put repeat for ethylene.

~~0.5, 0.85, 1.5~~

0.1M, at 25

20240418_mx36_pH 6 0.5MAA 0.5MPrA at 100mA/cm² flow

mx36

0.5M AA/0.5M PrA → Anolyte

1M H_2SO_4 → Catholyte

flow cell at 60 ml/min

Vol = 120 ml

CE = 100 mA/cm²

from injection 11

Data

201 - H_2O

300, Acetal, MeAc, MeOH, EtOH, EtPro, EtBu

mx36 202 {8296, 6325, 8345, 65779, 153507, 128}

{7592, 5785, 8087, 66912, 154342, 5644}

{3052, 2436, 11789, 65268, 147901, 188}

203 H_2O

mx37 {5944, 3635, 1156, 25372, 83723, 12 16}

204 {5994, 3108, 8488, 26543, 85402, 6896}

{5465, 4478, 6529, 24941, 86613, 7727}

205 H_2O

mx37

0.5M AA/1M PrA → Anolyte

1M H_2SO_4 → Catholyte

flow at 60 ml/min

Vol = 120 ml

CE = 100 mA/cm²

206 {6474, 6276, 17319, 150414, 67902, 2280}

mx38 {6937, 5931, 18594, 149898, 68859, 4346}

{7498, 5781, 18163, 146439, 67097, 3425}

inj = 8.

mx38

0.5M AA/0.1M PrA → anolyte

1M H_2SO_4 → catholyte

flow at 60 ml/min

Vol = 120 ml

CE = 100 mA/cm²

inject 9

20240 flow cell both sides

MX39

0.5M AA/0.5M PrA → both catholyte anolyte
flow cell = 60 ml/min
Vol = 120 ml
CC = 100 mA/cm²

from injection 7

MX40

0.5M AA/0.1M PrA → both catholyte anolyte
flow cell: 60 ml/min
Vol. 120 ml
CC = 100 mA/cm²

MX41

0.5M AA/0.1M PrA → both sides same anolyte
flow 60 ml/min
Vol. 120 ml
CC = 100.

Data

GC-FID headspace 20240419_MX39 40 41 PvL

		3:00	Acetal	MeAc	MeOH	EtOH	EtPrO
201	H_2O						
202	MX39	7717	5899	7900	65783	138211	22
		8089	6624	12284	68521	151242	5348
		7045	6429	13613	64502	146906	4148
203	H_2O						
204	MX40	4433	5863	116	23470	80571	8071
		~~5885~~ 6127	4210	1964	16586	80316	7830
		6657	2964	1408	19835	83323	7139
205	H_2O						
206	MX41	9974	7431	18030	143817	70146	6896
		7121	6723	17804	139642	69991	2536
		6841	6676	17611	144654	71055	2920
207	H_2O						
208	PvL 1		2852			94281	11245
			2071			92465	11415
			3206			91567	11700

Doing the pulse experiment if we can alter the selectivity

100mA ⎍ 5sec

Pulse frequency: 1 min, 30 sec, 5 sec for one hour experiment.

One experiment to do impedance : before & after impedance
one hour acetic acid
propionic acid

by Raman (with new electrode)
Boron band position (Lorentz fitting)
by could it be insitu
first by excite

Research title could be paired electrolysis
with H_2 generation.

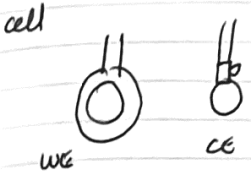
Pulse 1

1M propionic acid / Na propionate pH6

100 mA/cm²

He flow 30ml/min
electrolyte = 120ml

Batch cell

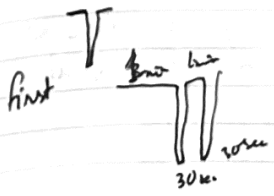


(two electrode cell)

electrode area = 3.87

100 mA/cm² = 387 mA = 0.387A

5 mA/cm² = 19.35 = 0.01935A



Previous cell broken, now new cell but small insize.

go to list: add parameters

Start 0
group id
end cycle
cycle: 99999
End state: last

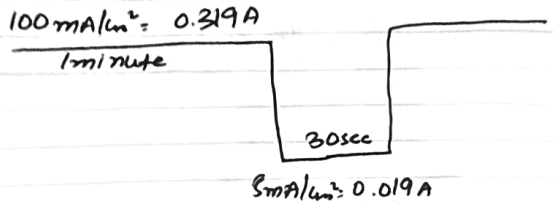
start no : 000	NO	Volt	Curr	Time(s)
Group : 2048	0000	-	-	-
cycle : 0000	0001	-	-	-
End state : Out off	0002	-	-	-
	0003	-		
	0004			

Basic | Parameter | Temp | memory | startup

1200 c/s = Pre-set of cycles

Pul 2

apply same conditions to Pul 1 but different electrolyte (combination 0.5AA + 0.5MP.A)



Vol = 120 ml
He flow. 30 ml/mins.

Batch cell two electrodes

* Problem with pulse data
* the pulse were applied at CH2 but recording was done at CH1, so it need to be done again Pul1 & Pul2

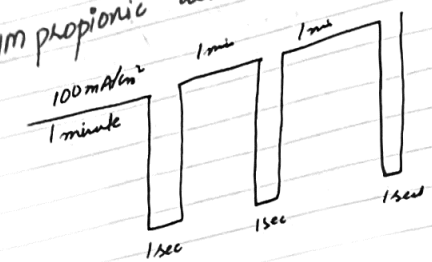
Pul 3

apply same conditions to P1 but different electrolyte (combination: 0.5AA + 0.5MP.A + 0.5F.A)

PUL 4

50.83.
50 minutes for 952C
.83.

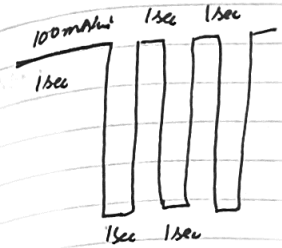
im propionic acid



PUL 5

93.97 mins

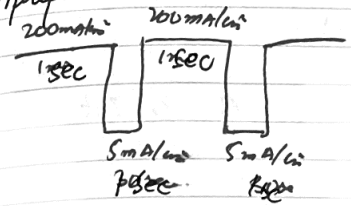
im propion

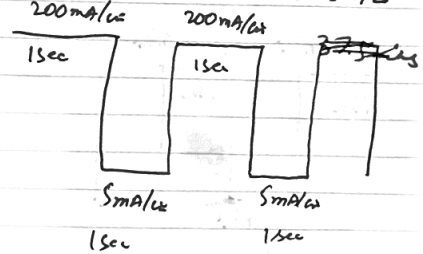


PUL 6

48.72

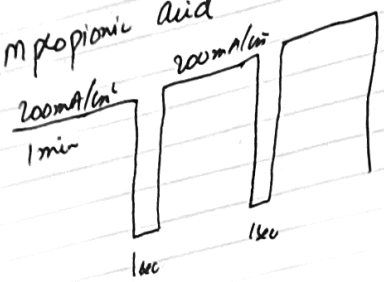
Im propionic acid:





PUL 7

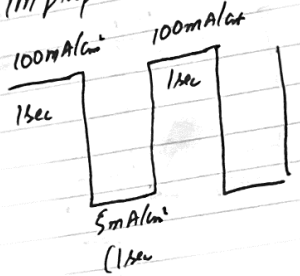
1M propionic acid



25.24 minutes

PUL 8

1M propionic acid



(similar to PUL5) but for 78 minutes.

$A = Q = I \times t$

Folder: 2024-04-23 PUL 2 3 4 5

GC area	at 3:0	Acetaldehyde	MeAc	MeOH	EtOH	EtPrO
201 H_2O	3586	4454	7502	54669	132420	7820
202 PUL2	1586	6079	11183	55019	132149	7593
	~~3580~~ 7110	~~7110~~ 4858	~~4658~~ 11184	56175	133033	7295
203 H_2O						
204 PUL3	6307	7331	9449	42142	106907	109
	4463	4455	11738	44800	112750	8396
	4463 6380	5200	8145	44964	116203	8725
205 H_2O						
206 PUL4			~~102293~~ 3		102293	12246
					95844	12656
					104110	12276
207 H_2O						
208 PUL5					104104	11489
					101049	9785
					100449	9321

minutes

no acetaldehyde

Folder: 20240423 PUL 6 7

	at 3:0	Acetald	EtOH	EtPr
201 H_2O	5308		85941	9632
202 Pul 6			82722	10199
			85656	13707
203 H_2O				
204 PuL			83248	14480
			84311	13549
			86442	10448

Folder 20240423 PUL 8 Z1

	at 30	Acetald	EtOH	EtPrO
201 H_2O			85941 75888	9632 11852
202 PUL8	7541		82722 75643	10199 11121
			85656 76883	13707 11028
203 H_2O				
204 Z1	5306		~~83248~~ 45108	14480 7768
			84311 45937	13549 5005
			86442 40205	10448 5763

Zero gap BDD mesh

7 x 2 / 18

area = 18 cm² mesh 3×3cm :

Z1

Catholyte: 1M Na propionate

20240424_Z1_1M Propionate pH5
both sides 25 mA/cm²

Analyte = same

Vol: 120 ml each, flow rate = 60 ml/min

CC: 25 mA/cm² = 0.450 A 1hour

He flow 40 ml pmin

Problem (due to wrong area)

repeat again

Z2

area = 7 cm²

Vol = 120 ml each propionate both sides flow rate 60 ml/h
He flow 40 ml/min 1hr

CC = 25 mA/cm² = 0.175 A for 1hr.

Z3

area = 7 cm²
Vol = 120 ml each

CC = 100 mA/cm² = 0.7A for 1hr

1M Propionate

Z4

zero gap
0.5 M AA + 0.5 M PrA ✓
at 100 mA/cm²

Z5

zero gap
0.5M AA + 0.5 M FrA + 0.5 M PrA ✓
at 100 mA/cm²

Do the experiment in big cell
active area = 70.98 cm²

B1

1M PrA / sodium propionate

Vol: 120 ml both
flow rate: 60 ml/min
He flow: ~~30~~ 0 ml/min → due to possibly high gas evolution ↑, gc protection

Current density - 100 mA/cm² = ~~70.98~~ 7.1 amps

→ here the parallel connection is used to increase the current limit of channel 14 2.

the pressure reached to 0.39 barg, limit is 0.49 so for B2, B3, I will use 20 ml/min

The observed FE is very low, this could be due to excessive bubble formation, mass transfer limitations, current density distribution, temperate due to joule heating, surface area to volume ratio,

started at 11:46

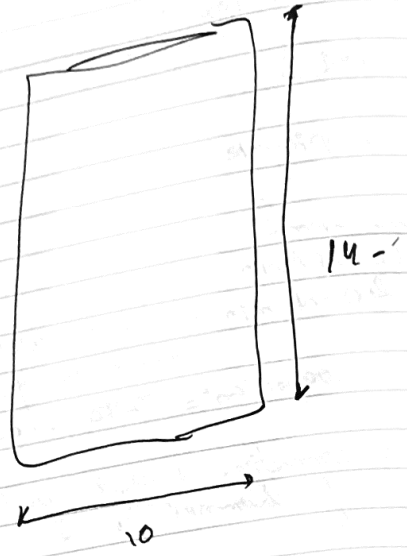
Potential was increasing to limit so stopped at 11:12 (26 mins)

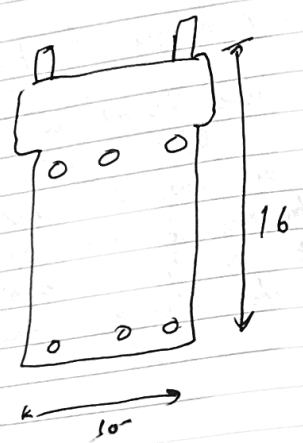
temperature is like ~~60~~ C

~~etc~~

Data:

Actal	EtOH	EtPrO
31818	468352	22757
32384	463465	21760
31768	505426	218656





Raman BDD

diff integration time

power 0.512

wavelength 785 nm

integration time = 30 sec

averaging = 4 or 1 could also be enough

dark measurement

Spec name

① blank sample after dark (BDD chip.) — 01

② BDD on tantalum (black) after electrolysis 02 → very dark
↳ signal problem low signal power changed to 0.65

③ Another used BDD 03? (least dark)

④ BDD on tan (mid black

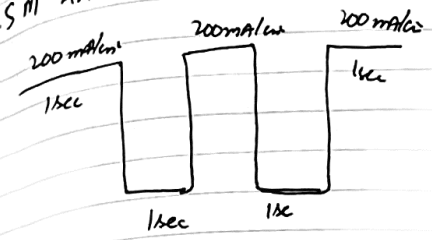
mid dark after flow cell

⑤ Flat BDD on Nb

20240429

PUL 9 ✓

0.5M AA + 0.5M P. A at 200 mA/cm² = 48.72 mins



Vol = 120ml

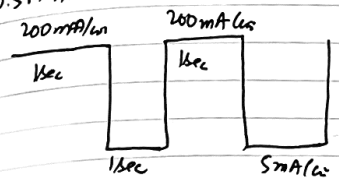
He flow = 30 ml/min

5mA/cm²: 0.01935A

200 mA/cm²: 0.638A

PUL 10 ✓

0.5M AA + 0.5M P. A + 0.5 M Fr A at 200 mA/cm² - 48.72 mi



20240429 - PUL9, 10

		at 3:00	Acetal	MeA.	MeOH	EtOH	EtOH/H₂O
201	H₂O						
		6017	6152	7246	58045	126485	6267
202	PUL9	5830	4572	8255	5525	127830	7811
		3412	6626	10689	53028	127264	8419
203	H₂O						
		4315	5179	9256	42818	111744	7856
204	PUL 10	6917	5264	9690	47241	105145	10720
		6126	5277	6171	47585	109617	9127

P45

20240329_p45_200 mA/cm² batch 1m propionate (cathode BDD

CC = 200 mA/cm² ⇒ 0.774 A for 1L.

P46 (repeat of P45 last diff cathode (Ti/Pt mesh)

20240329_P46_200 mA/cm² batch

CC: 200 mA/cm² ⇒ 0.774A for 1L

data: 20240802 P46

vol- H₂O

vol- P46 :

	at 7:00	Ace	EtOH	EtPr
	11954	29943	2523913	135838
	8834	30055	2676013	144846
	8542	36578	2538737	134958

data processing

design of experiments

let's check if it fits batch cell results

		Exp	Chro
1m	25	30.3	40.4
	50		
	100	33.07	40.22

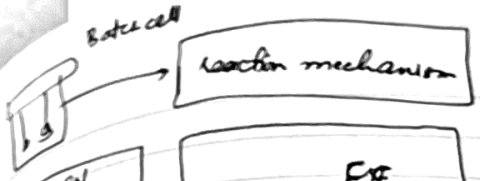


Fig 1

Fig 2

Fig 3

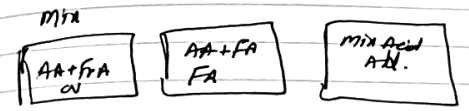
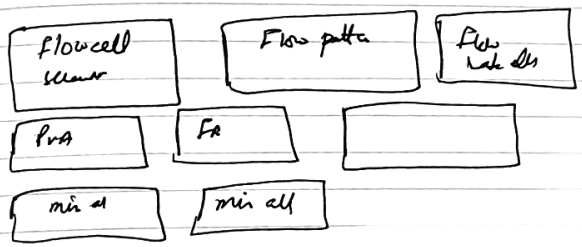


Fig 4



d.

le

im

Introduction: 1500 words → (1.5 hour)
materials & methods: 700 words. ✓
Propionic acid oxidation: 1000 words ✓ (1hr)
Propionic/acetic acid oxidation: 1000 words (model included)
Acetic formic acid = 500 words. ✓
All adds = 300 words.

Flow cell: 1000 words : (500) (40 mins) ✓
pulse = ~~500~~ words. (40 min) ✓

Conclusion = 100 words.
Outlook same
Reference: 60

1500
700
1000
1000
500
300
1000
500
100
6600

Supplementary information

① ali express batch cell ✓
② condias cell. ✓
③ calibration curve ✓

④ FE w.r.t (25, 50, 100, 150) Propionic acid
WE potential -- same
→ concentration effect + prolonged experiment

5. DOE (plot)
↳ faradic efficiency
→ voltage all runs ✓

⑥ ethanol CV methanol oxidation.
CV (ethanol, acetate, propionate adsorption)

⑦→ CV (acetic acid only) blank ✓
⑧→ Formic acid oxidation CV (potential + faradaic efficiency) —
⑨→ FE + cell voltage all current density (min acid)
0.1 M PrA + 0.5 M AA, 0.5 M AA + 0.5 M PrA, 0.5 MA + 1M PrA
0.5, 0.5 ~~MSA~~ AA + PrA + AA

→ divided cell propionic acid with both catht, FE & cell voltage

→ divided cell min all acid with both catht, FE & voltage

→ Pulse plot - pulse 1, pulse 2, Pul 4
current plot, potential plot
FE plot (propionic acid, at 100 & 200)
PrA + AA at 200, PrA + AA at 200

20240125 Talal

MX13 - MX14

201 - H_2O Act		MeAc	MeOH	EtOH	EtPro
MX13 Rep1	3882	9951	48629	26335	1137
Rep2	3161	8758	52734	28707	7717
Rep3	3939	10476	43397	26683	1603
203 H_2O					
204 MX14	2205	7549	32713	18429	-
	5833	4768	28586	19328	278
	9686	5681	30005	18951	-
205 - H_2O					

graph

Mix all acids

Faradaic efficiency (Batch) 25, 50, 100, 150

Faradaic efficiency (flow) = 25, 50, 100, 150 (H_2SO_4 catholyte)

Faradaic efficiency (propional calth) flow: 25, 50, 100, 150

Ratio AA+PrA

0.1M PrA + 0.5M AA
0.5M AA + 0.5M PrA
0.5M AA + 1M PrA
} Batch 25, 50, 100

PrA

faradaic efficiency (Batch) = 25, 50, 100, 150

" flow H_2SO_4 calth. " "

" flow (propionate calth) = " "

design (conc effect pH " current density)

Batch (CV)

Modelling

Alcohol oxidation:

Flow electrolyzer

Small cmdias, zero gap, big electrolyzer

at 100 mA/cm² = 60 ml/min

1M Pr acid =

0.5M AA + PrA =

0.5M all acid =

computational effect: to ~~~
hydration part goes to CN part.
CN-phenanc...

H_2O_2 in previous...

formaldehyde to ethylene glycol.

acetic acid
propionic acid
mix acid.
} reaction condition
pH
current density
acid ratio

effect of counter reaction
↳ formaldehyde to ethylene glucol.
↳ alcohols from aldehyde

effect of purged/non purged electrolyte
membrane ...

simulation: conc of OH radicals 2d to 3d. comsol, agnieszka
economic aspect BDD v Platinum

OH radical concentration profile
by DMPO

		20230815 wiktor	
201	~~H_2O~~	MeOH	~~MeOH~~
202	O_3	3696,4731,4131	17334,15837,18649
203	O_5	5298,6377,5146	17743,20112,17592
204	H_2O	-	
205	O_4	27703,26316,21254	139349,139385,114733
206			
207			