Book 6
Talal

Propionic acid oxidation on BDD electrodes

→ at pH5 different current density

P1 : 25 mA/cm² } Batch
P2 : 50 mA/cm²
P3
P4 : 10 mA/cm²
P5 = 150 mA/cm²
P6 = 10 mA/cm²

P7 : in flow cell 50 mA/cm²

P8 : same as P7 w/o purging ↳ no gas analysis

P9 : 100 mA/cm² } Batch

P10 : 0.5 M PA pH 8.5

P11 = 1M : pH 12 → 100 mA/cm²

m Faradaic efficiency

	Conc	PH	current	FE Ethylene	error	FE Ethanol	error	FE EtPro	error	Acetal	error	CO_2	[illegible]
P_1	1	5	25	38.30	1.02	52.49	0.67	6.11	1.4			90.6	6.8
P_2	1	5	50	34.23	0.84	40.127	1.36	5.13	0.96			160.70	4.61
P_3	1	5	100	33.077	0.479	42.8	1.55	5.09	1.49			153.7	5.2
P_4	1	5	10	42.57	1.83	51.48	2.5	9.7	4.4			70.7	7.41
P_5	1	5	150	24.60	1.52	35.79	1.92	2.07	1.6			1363	3.6
P_6	1	5	10	42.74 ~~[illegible]~~ 43.74	~~[illegible]~~ 1.96	~~[illegible]~~ 46.46	1.4 ~~[illegible]~~	11.25	0.962			716	6.19
P_7	1	5	50	22.64	2.81	~~[illegible]~~ 43.4	3.71	3.41	~~[illegible]~~ 0.19			4787	5.10
P_8	1	5	50			39.6	1.03	2.52	1.88				
P_9	1	5	100	28.84	3.805	35.06	2.2	5.681	2.1	1.2		141.0	6%
P_{10}	0.55	8.5	62.5	43.13	0.2	40.99	0.7	1.773	0.8	1.54		177.4	6.3
P_{11}	1	12	100	5.7	1.8	38.41	1.7	1.84	0.51	6.06	1.9	9.52	5.1
P_{12}	0.1	5	25	17.71 ✓	0.93	24.2 ✓	0.25	1.19 ✓	0.6	7.90	1.5	57.8	1.03
P_{13}	0.1	12	25	~~61.00~~ 38.5	0.41	47.25	1.15	:	1.	9.8	1.09	204	0.10
P_{14}	0.1	5	100	7.51	2.8	10.36	0.31	0.361	0.1	5.4	1.1	66.5	1.9
P_{15}	1	5	25	40.79	0.84	45.1	0.3	6.15	0.3	7.99	0.85	98.3	2.9
P_{16}	0.1	12	100	21.22	2.49	23.4	0.6	0		6.4	0.2	7.08	1.0
P_{17}	1	12	25	42.40	0.43	45.2 ~~[illegible]~~	4.2 ~~0.3~~	4.27	1.9	4.23	1.04	6.5	0.3
P_{18}	1	5	50			~~[illegible]~~	~~[illegible]~~	~~[illegible]~~	~~[illegible]~~	~~[illegible]~~	~~[illegible]~~		
P_{19}	0.5		~~0.5~~			~~[illegible]~~	~~[illegible]~~	~~[illegible]~~	~~[illegible]~~	~~[illegible]~~	~~[illegible]~~		
P_{20}	1	5	100			49.2	1.16	5.50	1.2	3.5	1.1		
P_{21}	0.55	8.5	62.5			54.6	1.3	1.57	0.7	5.26	2.48		
P_{22}	1	12	100			52.0	1.37	1.91	0.8	2.65	0.1		
P_{23}	0.1	5	25			54.109	0.6	7.6	1.1	11.42	1.2		
P_{24}	0.1	12	25										
P_{25}	0.1	5	100			~~[illegible]~~		~~[illegible]~~		~~[illegible]~~			
P_{26}	1	5	25			57		8.10		9.5			
P_{27}	0.1	12	100			25.55		0.26					
P_{28}	1	12	25			41.94		2.707		1.899			
P_{29}	0.1	5	100			6.04		0.67		5.07			

fixed alcohol concentration

EtOH in Acid.

Conc	J mA/cm²	Conversion
0.1	50	8.36
0.1	100	19.04
0.1	150	20.3
0.1		
0.5	50	8.2
0.5	100	8.9
0.5	150	5.63
1	50	1.82
1	100	0.87
1	150	0.67

MeOH in Pr Ac

Mix acid oxidation.

Conc ratio
0.5 m AA / 0.1 m PrA
"
"

0.5 m AA / 0.5 m PrA

0.5 m AA / 1 m PrA

		FE Ethane	Ethylene	Acetan	MeOH	MeAc	EtOH	AR	Ach
I_x	0.5 mAA								
25	FE %								
50	FE Er								
100	Fr Gr								
25									
50									
100									
25									
50									
100									

Flow by:
- nanostructure
- enhance mass transfer
- enhance the active area
- → different doping

0.5 m AA / 0.1 m PrA	25 ✓	m13
0.5	35 ✓	m1
1 m	25 ✓	m8
0.5 m / 0.5 mPr	50	– mx 14 ✓
0.5	50	~~mx9~~ mx 3 ✓
1	50	mx 9 ✓
0.5 / 0.1 m^{Pr}	100	– mx15 ✓
0.5 m^{Pr}	100	→ mx 5-6 ✓
1 m^{Pr}	100	→ mx 12 ✓

formic acid

25 mx17
mx18
mx19

fraction

$$\text{Fraction formic acid} = \frac{K_{formic} \times C_{formic}}{K_{formic} \times C_{formic} + K_{acetic} \times C_{acetate}}$$

$$\text{fraction acetic acid} = \frac{K_{acetic\ acid} \times C_{acetic\ acid}}{K_{acetic\ acid} \times C_{acetic\ acid} + K_{formic} \times C_{formic}}.$$

$C_{formic} > C_{acetate}$: OH radicals are preferably scavanged by formate

Content:

1- introduction slide
2- ~~Chapt~~ Previous plan
3- New plan
4- Chapter 2
5- Chapter 3
6- Chapter 4
6 - Chapter 5
7 Activities.

Try putting

Pillar electrodes

DOE

acetate

propionate

H_2O_2

Fist, i think it the problem of ethylene electron transfer
so revise all the data.

Flow experiment:

25, 50, 100, 150 mA/cm²

	mA/cm²	FE Ethylene	error	FE EtOH	error	EtPrO	error	AceAl	error
P30	25								
31	50								
32	25								
33	25	39	3.5	40.43	1.29	5.9	0.6	6.3	1.4
✓34	50	40.50	1.32	39.79	1.5	2.576	0.33	4.892	1.6
✓35	100	43.802	3.2	40.23	1.2	1.280	0.169	6.1053	0.346
✓36	150	~~36.81%~~ 36.2%	3.4%	36.65	1.5	2.32	0.25	4.26	0.249

~~44.69~~ 43.92.7
25

Effect of flow rate (10, 60, 100) at 100 mA/cm²

Can pulse save the ethanol oxidation at high current density ~~150 mA/cm²~~ in batch cell:

100 mA/cm² — electrolysis time (1hr)

1 mA/cm²

→ pulse duration
2 sec, 30 sec, 1 minute,

Flow cell undivided BDD both cathode & anode.

100 mM
→ propanol oxidation in 0.5 M acetic, 0.5 M Propionic acid
→ Mix acid oxidation in flow cell. at 25, 50, 100 mA/cm² 1M pH5 all

Carboxylic acid oxidations (min)

17/04/24 : materials & methods + Propionic acid (CV, FE, DOE) Batch + ~~model~~

18/04/24 : ~~Mix all acids~~ electrooxidation Propionic ~~acid~~ flow ~~Batch~~, (~~H₂SO₄, Propionate~~)

19/04/24 Acid ratio batch (Propionic & acetic acid)

20/04/24 showing how acetic acid prevented alcohol oxidation

acetic + formic acid batch

all acid (acetic formic, propionic acid)

flow results flowcell: Propionic acid (diff catholyte)

Acid ratio (batch) (diff catholyte)

effect of flow rate (FE) + Comsol simulation

all acid (diff catholyte)

effect of cell:

zero gap all acid + big cell

all acid catholyte all acid catholyte

Current high pulse: ~~[illegible]~~ C_H (A)

" low " : C_L (A)

Time high pulse = t_H (sec)

time low pulse = t_L (sec)

Charge high pulse: Q_H

" low: Q_L

time full cycle: $t_F = t_H + t_L$

total charge high Pulse: T_{Q_H}

" low: T_{Q_L}

Cycle needed per hour $C = 3600/t_F$

Total Charge all $T_{CA} = T_{Q_H} + T_{Q_L}$

Propionic acid oxidation

CVs: ~~D~~ FE at pH5 Batch, ~~Concentration~~ DOE (conc, pH, & current den

Product oxidation possibility, pulse

Mixture of acetic & propionic acid oxid

Ratio ☐ 0.1 M PrA 0.5 M AA (at diff current density)

0.5 M PrA 0.5 M AA (at diff current density

0.1 M PrA + 0.5 AA (at diff current density)

→ Model results

Mixture of other carboxylic acids.

AA FA PrA at pH diff current density

~~Batch~~ Flow cell investigation

Propionic acid with H_2SO_4, propionate catholyte : impact of flow rate rate / conc

Mix acid 0.5 M Pr + 0.5 AA (with H_2SO_4 cath, propionate catholyte)

Mix acid all (0.5 M Pr + 0.5 AA + 0.5 M FrA) with H_2SO_4 cath, all acids cath

Different flow configuration

Zero gap cell = BDD mesh (Propionic acid, mix of acetic & propionic acid) + mix of all

Big cell : (Propionic acid, mix of acetic acid, mix of all)

Status:

Propionic acid oxidation:

- CV (missing)
- FE batch
- design
- Flow (both catholyte)
- effect of flow rate (missing)

Total electron flow:

$Q = I \times t$

$I = Q/t$

$$\frac{A}{F\,(C/mol)} = \frac{Q/t}{F} =$$

$$\text{Total electron flow} = \frac{Q/t}{F} = \frac{Q}{t} \div F = \frac{Q}{F \times t} = \frac{C}{C/mol \times s}$$

$$= \frac{C}{C/mol \times s} = \frac{C}{C/mol} = C \times \frac{mol}{C}$$

$$\left(\frac{\text{GC area} \times \text{Cal coefficient}}{1000000}\right) \times \text{gasflow velocity (mol/s)} \times Z$$

$$\text{gas flow} = \left(\frac{ml/min}{1000}\right)/60 \quad (L/sec)$$

$$\text{gas flow velocity} = \frac{(L/sec)}{22.4}$$

Cal liquid

Conc = area x dil x Cal coff mol/L

moles of product = Conc (mol/L) x (Velocity) (L)

molecules of product = 6.02×10^{23} x moles

electrons consumed = z x molecules of products

electrons with charge passed = Q x 6.21×10^{18}

$$\frac{nFz}{Q} =$$

moles:

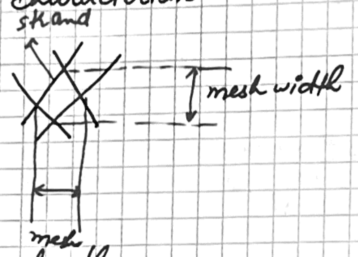
BDD mesh

30×30mm

doping = 2500ppm B

coating 5 µm on Niobium

mesh characteristic



Mesh length = 6mm

mesh width = 4mm

strand width = 1mm

strand thickness = 1mm

Total area covered by mesh = l×W = 30×30 = 900 mm²

Area covered by each strand

Total meshes along length = length of full mesh / length of one mesh = 30mm/6mm = 5

" " width = 30mm/4mm = 7.5 ≈ 8

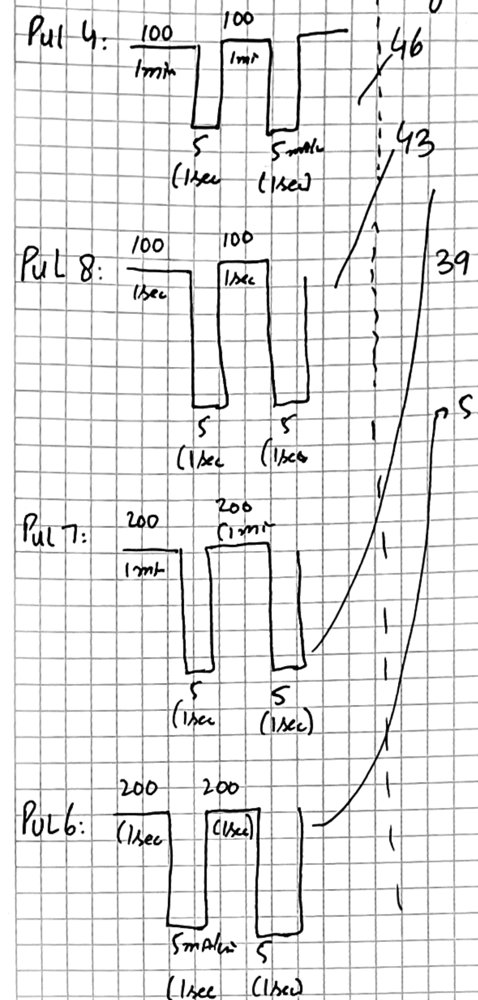
Total area covered = 5×8×(6mm × 4mm) = ~~160~~ mm² 960

Total area both sides = 1920 mm²

900 mm² Total area covered by strand = 30×1 + 30×1 = 60 mm² × 2 = 120 mm²

area (1920 − 120) = 1800 mm² = 18 cm²

Pulses



	1M Propionicard	FE Ethylene	EtOH	Et Pro
Pul 4		46	49	2
Pul 8		43	41	2
Pul 7		39	41	2
Pul 6		52	41	

Propionic acid oxidation.

Batch: FE decreases by increasing

→ Propionic acid

in batch.

CV show, no direct oxidation takes places —

current density shows at low current density high FE

DOE shows

ethanol:

PH5 (25, 100)

	Ethanol,	Ethylene
25	40.4	38.8
100	36.5	24.6

DOE

Conc (M)	PH	J =	FE ethyl	FE ethanol
0.1	5	25		
1	5	25		
0.1	5	100		
1	5	100		
0.1	12	25		
1	12	25		
0.1	12	100		
1	12	100		
0.55	0.85	62.5		

(10) IMP. A flow H_2SO_4

IMP. A	flow H_2SO_4	25	P_{32}
		50	P_{34}
		100	P_{35}
		150	P_{36}
IMP.	flow PrA	25	P_{40}
		50	P_{41}
		100	P_{39}
		150	P_{43}

All acid mix	H_2SO_4	25	mx25
		50	mx26
		100	mx27
all acid mix	all acid	25	mx30
		50	mx29
		100	mx28

~~150~~ →

Pulse

Pulse 1: 100 mA/cm² 1min; 5m 1sec (150min) (Pul 4)

Pulse 2: 100 mA/cm² 1sec; 5mA/s 1sec (70min) (Pul 8)

(2) 200mA 1min; 5mA. 1sec (1h) (Pul 7) Pulse 3

200 mA/cm² 1sec; 5mA/cm² 1sec (50min) (Pul 6) Pulse 4

(1) Electrochemical hydrogenation of benzyldehyde, furanaldehyde.

- → Product selectivity based on reaction conditions
- → divided vs undivided
- → cation effect
- → substrate specificity : Ni foam, copper foil, copper mesh, graphite felt, BDD

Research showed addition of phenol can tune selectivity of furfural.

- → catalyst property

(2) Magneli Phase:

Effect of electrolyte: CW: $KHCO_3$, $NaHCO_3$, K_2CO_3, $NaHCO_3$ + 2M at CC {50, 10, 150, 200, 250, 300} FE%, conc.