BOOKS
Talal

Aim

Goal: Aldehydes, phenols and ketones hydrogenation in conjunction with anodic decarboxylation or OER or other compounds of interest.

aldehydes: Furfural, Benzyldehyde, crotonaldehyde, Butyraldehyde

Phenol: Phenol, cresol or eugenol

Product portfolio

Furfural: furfural alcohol, Tetrahydrofurfural alcohol, 2-methyl furan.

Benzyldehyde: Benzyl alcohol, Toluene, cyclohexylmethanol cyclohexane

Phenol: cyclohexanone, cyclohexanol, cyclohexane

Butyraldehyde: Butanol, butane

Crotonaldehyde: Butyraldehyde, Butanol, Butane

Cresol: (position of methyl group change composition) 2-methyl cyclohexanol, methyl cyclohexanone, cyclohexanol, cyclohexane

1 lit (0.5 M H_2SO_4) = 27.78 ml : pH 0
1 lit (0.5 M Na_2SO_4) = 71.03g → need to order more: pH 7
1 lit (0.5 M KOH) = 28.06g : pH 14

1L (0.5 M H_2SO_4) = 27.78 ml
1L (0.5 M Na_2SO_4) = 71.03g
1L (0.5 M KOH) = 28.06g
(10 ml H_2SO_4 (0.5 M) could adjust pH of Na_2SO_4 (1L) 0.5 M pH to 5

16/08/2024)

Goal: Electrochemical reduction potential onset / CVs

First component: Furfural (conc 50mM)

CV scan in H_2SO_4, Na_2SO_4, KOH (0.5)M

Blank CV first 150, 100, 150 mV/sec)

First use copper foil as working electrode
→ to observe the effect of conc (10, 20, 30, 40, 50mM)

then use materials for (50mM conc) for other electrode material.
Copper mesh, graphite, BDD, Magneti, Nickle, Titanium, platinum

Same will be performed for Benzyldehyde, mix of Furf 4:1 Benzald (25:75, 50:50, 75:25)

Then effect of phenol will be determined (10, 20, 30, 40, 50mM)
then all are mined.

the experimental id for furfural experiments are ECH

20/08/2024

ECH1

CVs of furfural hydrogenation in 0.5 M H_2SO_4

electrode area = 9.42 cm^2 cm^2

01_ blank Copper foil
02_ furfural copper foil

02_ blank BDD
02_ furfural BDD
} Electrode area = 15.74 cm^2

03_ blank graphik
03_ furfural graphite
} Electrode area = 10.40 cm^2

04_ blank Pt
04_ furfural Pt
} Electrode area = 4.43321 cm^2

05_ blank Ni
05_ furfural Ni
} Electrode area = 6.1773 cm^2

06_ blank magneli
06_ furfural magneli
} Electrode area = 14 cm^2

07_ blank carbon paper
07_ furfural carbon paper
} Electrode area = 15.08 cm^2

08_ blank Ti
08_ furfaral Ti
} Electrode area 4.199 cm^2

Cell configuration: 3 electrode cell
- CE: Pt mesh
- RE: Ag/Ag Cl

CV at 100 mV/sec
from 0.2 V RHE
to − 0.8 V RHE

Blank = only 0.5 M
Furfural = 100 mM in 0.5 M H_2SO_4 (588 ml of furfural in 65 ml of H_2SO_4)

ECH2 : 0.5M KOH CH_4 plus furfural

01- blank copper
01- furfural copper

02- blank BDD
02- furfural BDD

03- blank graphite
03- furfural graphite

04- blank platinum
04- furfural platinum

05- blank nickle
05- furfural nickle

06- blank magneli
06- furfural magneli

07- blank carbon paper
07- furfural carbon paper

08- blank Ti
08- furfural titanium

ECH3: 0.5 M H_2SO_4 CH_4 plus benzyldehyde

The blank CH_4 are already taken in "ECH1" so only experimentation will be done in 100 Benzhld + H_2SO_4

01- benzyldehyde copper
02- benzyldehyde BDD
03- benzyldehyde graphite
04- benzyldehyde platinum
05- benzyldehyde magneli nickle
06- benzyldehyde magneli
07- benzyldehyde carbon paper
08- benzyldehyde titanium
09- benzyldehyde silver (16.702 cm^2)

65ml of 100mM Benzylaldehyde: (661µl in 65ml)

ECH4: 0.5M KOH CVs benzyldelyde (100mM)

Since blank CVs were conducted in 'ECH 2', therefore on CVs with benzyldelyde takes place

01_ benzyldelyde copper

02_ benzyldelyde BDD

03_ benzyldelyde graphite

04_ benzyldelyde platinum

05_ benzyldelyde nickle

06_ benzyldelyde magneli

07_ benzyldelyde carbon paper

08_ benzyldelyde titanium

09_ Benzyldelyde silver

Plan.

Furfural oxidation on BDD electrode in undivided, divided (batch) and flow cell

impact of pH, current density, electrolyte concentration, doping

Benzyldelyde oxidation on BDD electrode in batch, divided, undivide, flow cell (zero gap)

Mix electrolysis based on optimal conditions from above experiment

Factors: pH : 3, 14
current density 25, 50, 100, 200
Concentration 0.1, 0.5, 1M
~~Catholyte: NaOH, KOH~~
~~doping: low doped, high doped~~
} for KOH & H_2SO_4
fixed coulombs (300)

eliminate doping

Response: Conversion
: voltage
: F.E

Experiments:

Benzyldehyde reduction on BDD

acetate on anodic side

BDD as anode

Benzyldehyde 100mM on cathodic side, BDD cathode

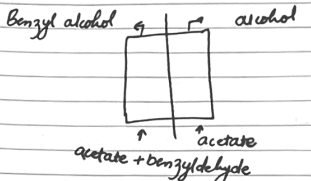
Effect of pH & current density

pH, 3, 6, 14

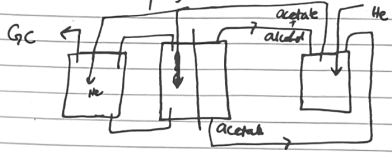
I. 20, 25, 50, 100, 200 mA/cm²

Electrolysis time: 30 mins

Cation exchange membrane



What if CO_2 is purge from ~~cathode~~ anodic to cathodic compartment



What if we recirculate anolyte into catholyte.

Preliminary experiment

Catholyte: 0.5 M potassium acetate

Anolyte: 0.5

DOE: benz

divided batch cell
BDD cathode
BDD anode
Benzyldehyde conc: 100 mM
anolyte acetate pH 5

factors pH = 5, 14
current density = 10, 25, 50, 100, 200 mA/cm²
Electrolysis time = 30 min
Cation exchange membrane

Run order	pH	J mA/cm²	DOE Id
1	14	50	BN1
2	5	200	BN2
3	14	25	BN3
4	14	10	BN4
5	14	100	BN5
6	5	25	BN6
7	5	100	BN7
8	5	50	BN8
9	14	200	BN9
10	5	10	BN10

Cathode area: 23 mm(dia) = 4.15 cm²
anode area: 26 mm(dia) = 5.31 cm²

Anolyte volume 100 ml : pH6: 0.5 M (160 ul acetic acid, 11.82 ul acetate K)
Catholyte volume 100 ml : (1.02 ml Bn_3Al in 100 ml) to 100 mM

Both cath & anolyte pH6, 0.5 M acetates

Plus addition of 100 ml of Bn_2AlK in catholyte

mA 25, 100, 200 — flow rate 50 / 150 / 350

pH 5

[illegible] 400

Area of each electrode: 15.74 cm^2 each [illegible]

volume: 160 ml

electrolyte [illegible] : 0.5 M [illegible] (H^+) catholyte

anolyte 0.5 M [illegible]

FR 1

[illegible]

25 mA/cm^2, 50 ml/min, 30 mins — pH before: 5

→ 0.394 A — pH after: 13

Electrolyte volume: 80 ml each — Anolyte: [illegible]

FR 2

100 mA/cm^2, 50 ml/min, 30 mins — pH before = 5

→ 1.574 A — pH after = 14

Electrolyte volume = 80 ml each — Forgot anolyte sample!

FR 3

200 mA/cm^2, 50 ml/min, 30 mins — pH before = 5

→ 3.148 A — pH after = 14

Electrolyte volume 80 ml each.

anolyte pH 3.1

temp 37

All samples diluted x5

x5 ÷ 5

Data 20240920_FR1-3

201	H_2O Fid tint	9.00	4.7	8.807	11.278	13.786
202	FR1C	0			986270 1046625	90282 95360
203	H_2O					
204	FR1A		15740 15892	178415 180008		
205	H_2O		–	–		
206	FR2C	2363 21740			692608 682424	93920 86432
207	H_2O					
208	FR3C	3734 of 3030 43			494987 453547	99590 89177
209	H_2O					
210	FR3A		58489 59660	307423 302140		
211	H_2O					
212	Acetate + Fe 100ppm (0.5)				2519124 2263810	
213	HO					
214	Acetate					

Minor acetate peak comes at 11.1 before furfural which starts at 11.8

FR4 25 mA/cm² 150 ml/min 30 min
0.394 A
Electrolyte vol 80 ml each

FR5 100 mA/cm² 150 ml/min 30 min
1.574 A
Elect vol = 80 ml each

FR6 200 mA/cm² 150 ml/min 30 min
3.148 A
Electrolyte vol = 80 ml each

20240930_FR456 Cal montage

		MeAc	MeOH
201	H_2O	3.2e4	3.804
202	5mM MeOH+MeAc	174937, 175133	118333, 120151
203	10mM MeOH+MeAc	456045, 446965	241580, 236200
204	50mM MeOH+MeAc	2309439, 2309026	1306443, 1310426
205	H_2O		
		FrF	FrA
206	FR_4 Calt	568990, 572537	36120, 36299
207	H_2O		
		MeAc	MeOH
208	Fr_4 Am	19018, 19069	171220, 168076
209	H_2O		
210	FR_5 Calt	380715, 374353	28375, 25318
211	H_2O		
		MeAc	MeOH
212	FR_5 Am	42068, 41615	355981, 357402
213	H_2O		
214	H_2O		
215	H_2O		
216	H_2O		

Paired electrolysis

Batch / flow
Cathode copper mesh: 33.3 x 41.2 mm = 27.192 cm²
Anode BDD

Catholyte: furfural (0.5 M), benzylidelyde (0.5 M), furf + benzald (0.25 + 0.25 M)
Anolyte: acetate (0.5 M), eugenol (0.5 M), acetate + eugenol (0.25 & 0.25 M)
Current density: 25, 100, 200 mA/cm²
pH 5, 12

Exp: ① 0.5 M F | 0.5 M acetate
0.5 M F | 0.5 M eugenol
0.5 M F | 0.5 M Ac + Eug
} 25, 100, 200 / 5, 12

Electrolysis time: 30 mins

Electrolyte volume 60 ml each.

Eugenol
Furf + Benz

S010

PH 5
Conc 25

33	31	1	1	Eugenol	Furfural+Benzaldehyde	100	5	S012
29	32	1	1	Eugenol	Benzaldehyde	200	5	S013
16	33	1	1	Acetate	Furfural+Benzaldehyde	100	12	
46	34	1	1	Acetate and Eugenol	Benzaldehyde	100	12	
5	35	1	1	Acetate	Furfural	200	5	S014
51	36	1	1	Acetate and Eugenol	Furfural+Benzaldehyde	100	5	S015
13	37	1	1	Acetate	Furfural+Benzaldehyde	25	5	S016
43	38	1	1	Acetate and Eugenol	Benzaldehyde	25	5	S017
21	39	1	1	Eugenol	Furfural	100	5	S018
10	40	1	1	Acetate	Benzaldehyde	100	12	
8	41	1	1	Acetate	Benzaldehyde	25	12	
37	42	1	1	Acetate and Eugenol	Furfural	25	5	S019
23	43	1	1	Eugenol	Furfural	200	5	S020
17	44	1	1	Acetate	Furfural+Benzaldehyde	200	5	S021
6	45	1	1	Acetate	Furfural	200	12	
38	46	1	1	Acetate and Eugenol	Furfural	25	12	
50	47	1	1	Acetate and Eugenol	Furfural+Benzaldehyde	25	12	
19	48	1	1	Eugenol	Furfural	25	5	S022
25	49	1	1	Eugenol	Benzaldehyde	25	5	S023
28	50	1	1	Eugenol	Benzaldehyde	100	12	
49	51	1	1	Acetate and Eugenol	Furfural+Benzaldehyde	25	5	S024
45	52	1	1	Acetate and Eugenol	Benzaldehyde	100	5	S025
3	53	1	1	Acetate	Furfural	100	5	S026
11	54	1	1	Acetate	Benzaldehyde	200	5	S027

StdOrder	RunOrder	PtType	Blocks	Anolyte type	Catholyte type	Current density	pH	
26	1	1	1	Eugenol	Benzaldehyde	25	12	
34	2	1	1	Eugenol	Furfural+Benzaldehyde	100	12	
53	3	1	1	Acetate and Eugenol	Furfural+Benzaldehyde	200	5	SO1
40	4	1	1	Acetate and Eugenol	Furfural	100	12	
9	5	1	1	Acetate	Benzaldehyde	100	5	SO2
54	6	1	1	Acetate and Eugenol	Furfural+Benzaldehyde	200	12	
1	7	1	1	Acetate	Furfural	25	5	SO3
20	8	1	1	Eugenol	Furfural	25	12	
4	9	1	1	Acetate	Furfural	100	12	
48	10	1	1	Acetate and Eugenol	Benzaldehyde	200	12	
36	11	1	1	Eugenol	Furfural+Benzaldehyde	200	12	
7	12	1	1	Acetate	Benzaldehyde	25	5	SO4
30	13	1	1	Eugenol	Benzaldehyde	200	12	
39	14	1	1	Acetate and Eugenol	Furfural	100	5	SO5
41	15	1	1	Acetate and Eugenol	Furfural	200	5	SO6
2	16	1	1	Acetate	Furfural	25	12	
12	17	1	1	Acetate	Benzaldehyde	200	12	
18	18	1	1	Acetate	Furfural+Benzaldehyde	200	12	
32	19	1	1	Eugenol	Furfural+Benzaldehyde	25	12	
27	20	1	1	Eugenol	Benzaldehyde	100	5	SO7
47	21	1	1	Acetate and Eugenol	Benzaldehyde	200	5	SO8
15	22	1	1	Acetate	Furfural+Benzaldehyde	100	5	SO9
14	23	1	1	Acetate	Furfural+Benzaldehyde	25	12	
22	24	1	1	Eugenol	Furfural	100	12	
44	25	1	1	Acetate and Eugenol	Benzaldehyde	25	12	
52	26	1	1	Acetate and Eugenol	Furfural+Benzaldehyde	100	12	
24	27	1	1	Eugenol	Furfural	200	12	
42	28	1	1	Acetate and Eugenol	Furfural	200	12	
31	29	1	1	Eugenol	Furfural+Benzaldehyde	25	5	SO10
35	30	1	1	Eugenol	Furfural+Benzaldehyde	200	5	SO11

Eug
Fur + Ben

SO11

pH 5
cur 200

PA1. ①

~~divided tested~~. undivided.

PH 5 , 1R
I= 25 , 100
Acetate 1M
Eugenol. 100 mM
Benzaldehy = 100 mM
Furfural 100 mM

~~PH5 , 1R~~
~~I~~

PH5 , I= 25 , Acetate 1M

PH5 , I= 25 Acetate 1M , Benzaldehy 100 mM,

PH5 , I= 25 Acetate 1M , Furfural 100 mM

PH5 , I= 25 Acetate 1M , Eugenol = 100 mM

PH5 , I= 25 = Acetate 1M + Benz 100 mM , Furfural 100 mM & Euge 100 mM

Run Order	PH	J	AM
1	5	100	AA+Eug
2	5	25	AA+Benz
3	5	100	AA
4	12	100	AA+Benz
5	5	25	AA
6	12	25	AA
7	12	25	AA+Benz
8	5	100	AA+Fu[illegible]
9	12	25	AA+Fu F
10	12	100	AA+Eug
11	5	25	AA+EUG+Fu ATB a2
12	12	25	A+E+F+B
13	12	100	AA+F
14	5	25	AA+F
15	5	100	AA+B
16	5	25	AA+Eu+Fu A+Ben
17	[illegible]	25	AA+Eug
18	12	100	AA
19	12	100	AA+Eug
20	12	100	AA+EUG+Fu D+Bnz

Effect of eugenol

Exp1 pH 5 , 25 mM/L 100 acetate , 100 mM Eugenol
Exp2 pH 5 , 100 mM/L 1M acetate 100 mM Eugenol

Exp3 pH 5 , 25 mM/L 100 acetate , 100 mM Furfural
Exp4 pH 5 , 100 mM/L 100 acetate 100 mM Benzaldehyde.

Flat low doped 3.54 cm²
high doped 3.88 cm²
SAP4 3.66 cm²
SAP16 3.44
SAP8 3.45 → Pillar gone Pil 5 to change to sap 8 ✓
SAP10 3.3806

Electrolyte vol: 25 ml
0.1 M K_2CO_3 & 2 M K acetate

Pil 1 : high doped flat: no stir 100 mA/cm² : too high voltage

Pil 2: high doped flat: stir

Pil 3 low doped flat no stir ✓

Pil 4 low doped flat stir ✓

Pil 5 SAP 8 9 no stir ✓

Pil 6 SAP 8 9 stir ✓

Pil 7 SAP 10 no stir ✓

Pil 8 SAP 10 stir ✓

Pil 9 SAP 14 no stir ✓

Pil 10 SAP 14 stir ✓

Pil 11 SAP 16 no stir ✓

Pil 12 SAP 16 stir

PUL1	0.156
PUL2	0.150
PUL3	0.197
PUL4	0.195
PUL5	0.043
PUL6	0.088
PUL7	0.132
PUL8	0.007
PUL9	0.006
PUL10	0.120
PUL11	0.082
PUL12	0.099

Acetate decarboxylation in pillars undivided. 0.5M acetate

15 mins electrolysis 50 mA/cm² 50 ml 15 mins

Flat low doped	Pul14	177 mA
Flat high doped	Pul13 (Pillars)	.164 mA ✓
SAP 9	Pul15	172.5 mA ✓
SAP 10	Pul16	165.3 ✓
SAP 14	Pul17	183 mA ✓
SAP16	Pul18	172 mA

30ml 20mM MeOH = 24.4 µl of MeOH in H_2O.

30ml of 20mM MeAc = 47.7 µl of MeAc in H_2O

20230206_15mm MeOH ACETONITRILE

		MeAc	MeOD
	H_2O		
	Poly 13	15319, 19059	55865, 65973
	H_2O		
4	Poly 14	~~19059~~ 16000, 13108	418023, 64305
5	H_2O		
6	H_2O		
7	H_2O		29742, 25998
8	Poly 15 (may Peaks)	17929, 17999	~~46718, 26893~~ (two other peaks
9	Poly 16	2 other peaks ~~18483, 18135~~ ~~17662~~, 18738	~~28431, 32182~~ 389290, 314231
10	Poly 17	18903, ~~60~~ 17667	~~48483~~, 337574 30574, ~~35~~ 35270
11	H_2O		
12	Poly 18	19431, 17805	~~73776, 71901~~ 35608, 33939
13	H_2O	-	-
14	MeOD 20mM	546187, 543605	
15	H_2O		
16	MeOD 20mM	1371656, 1309158	(Rat 3.903

MeOH (4.65 , 5.00)

MeOH 20mm 4.758 512702, 512702

MeAc (3.9 - 4.2) 3.982

MeAc 20mm = ~~848889~~ 849997, 862907

		MeAc	MeOH
203	Puli 13	3172, 4307	16204, 13150
204	Puli 14	438, 313	12852, 12268
208	Puli 15	4806, 8202	15084, 17999
209	Puli 16	6102, 6446	13373, 13257
210	Puli 17	7353, 3516	15699, 16018
212	Puli 18	482, 907	16727, 18295