Understanding of CO_2 electrolysis from a device perspective

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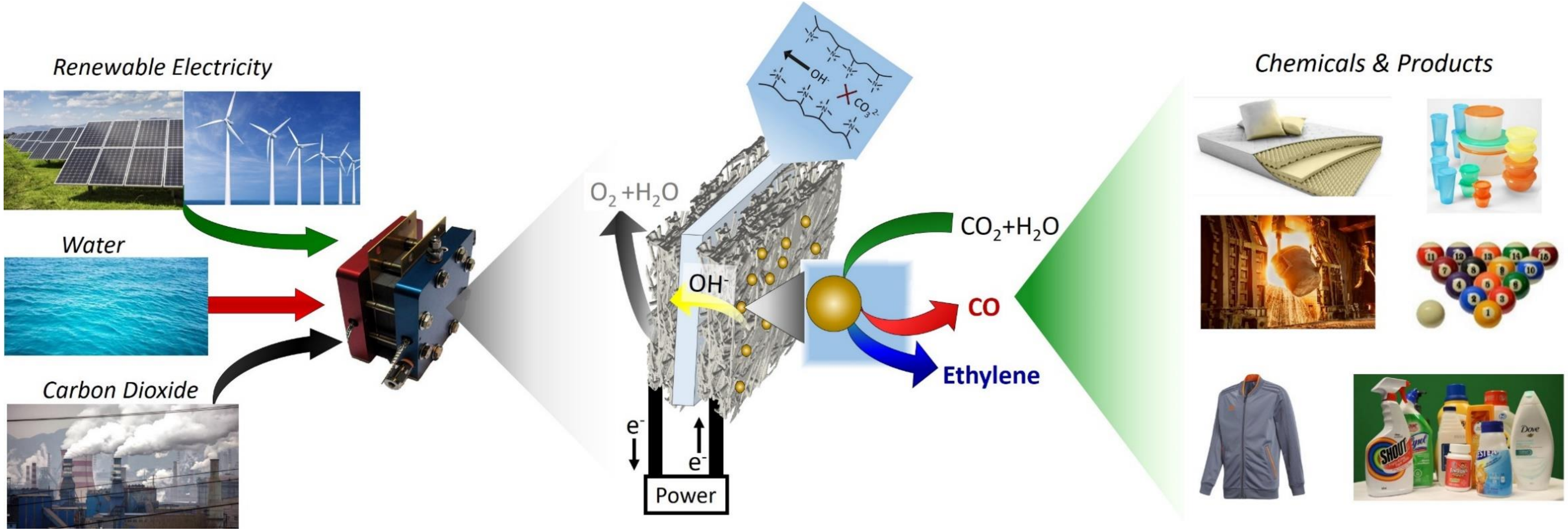
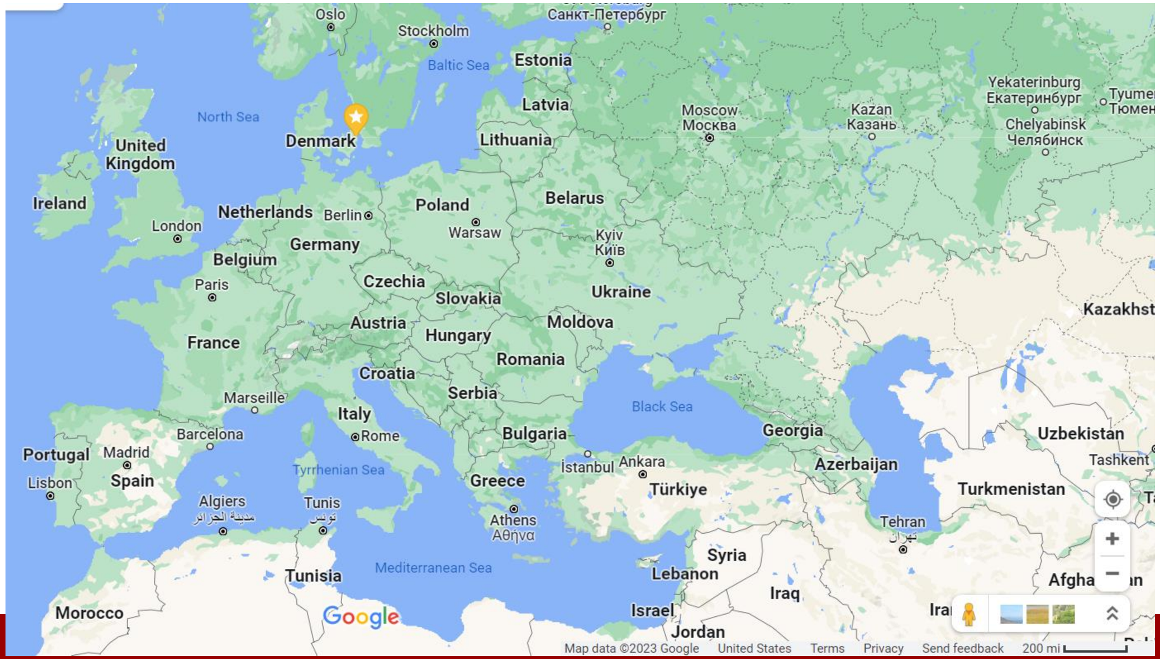


Technical University of Denmark (DTU)

- Hans Christian Ørsted founded the university in 1829.
  - Also discovered electro-magnetism and metallic aluminum
- 11,000 Bachelor& Master Students
- 1300 PhD students
- One Bachelor study line in English, all Masters and PhD courses in English

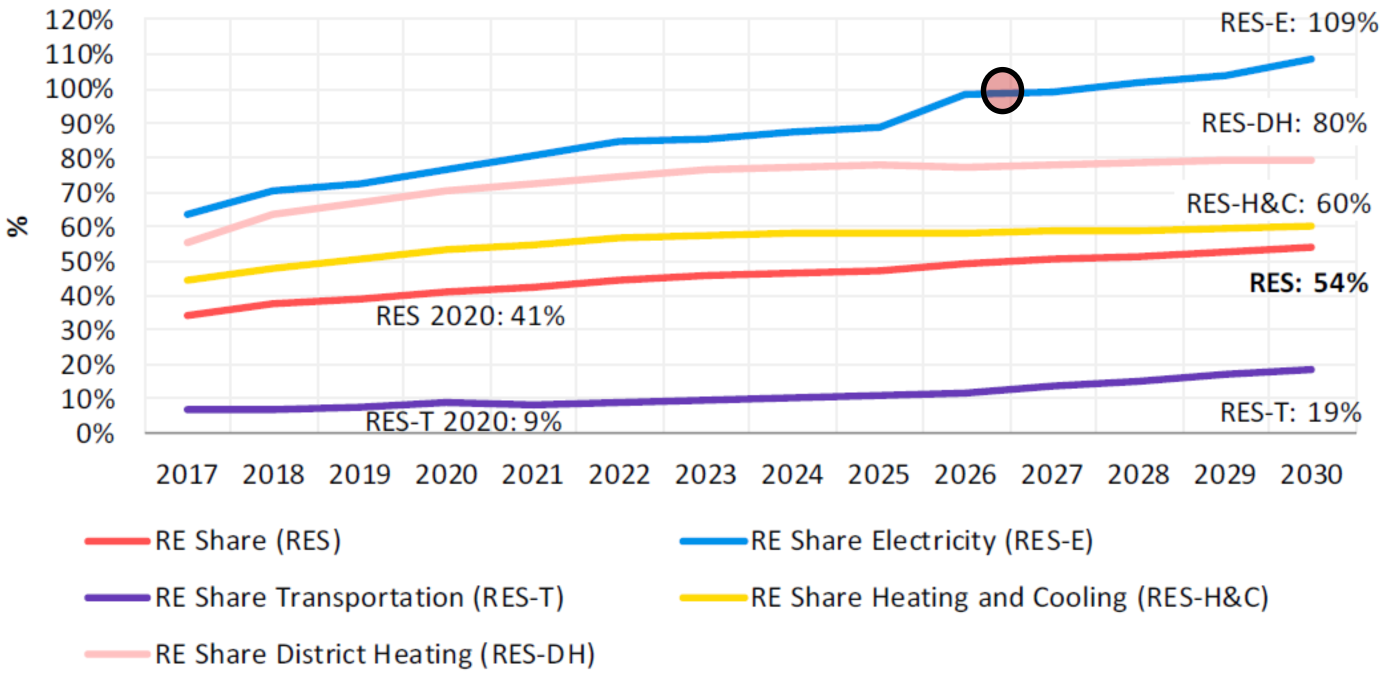


Rankings

- US News: #165
- World University Research Rankings: #2

The power of electrochemicals

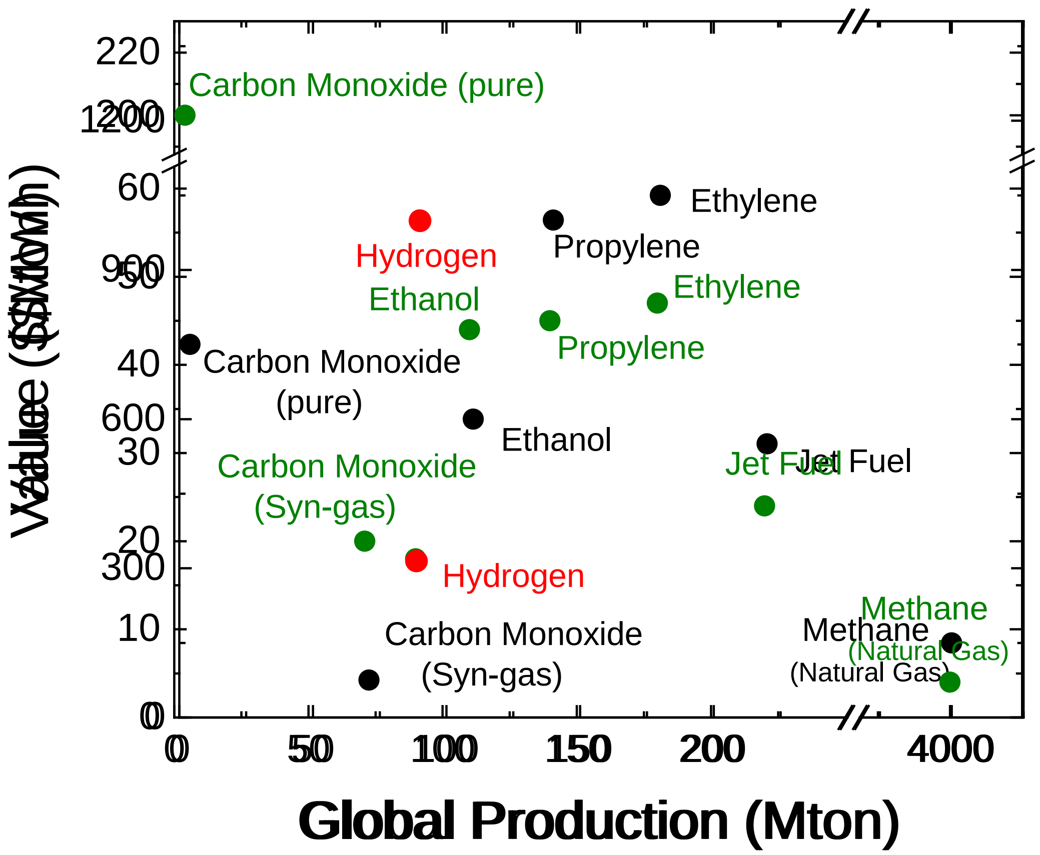
- Denmark will reach 100% renewables by 2027



- Should we use excess electricity to make hydrocarbons?

Overall: $H_2O + CO_2 \rightarrow C_xO_yH_z + O_2$

What are we trying to do it



Applications of chemicals

- CO → Chemicals
- Ethylene → Plastics
- Propylene → Plastics
- Ethanol → Fuel, Solvent
- Methane (Natural gas) → Burning

- *If all of Europes's electricity went to ethylene production (@ 2V electrolysis), we would only produce 67% of world's ethylene.*

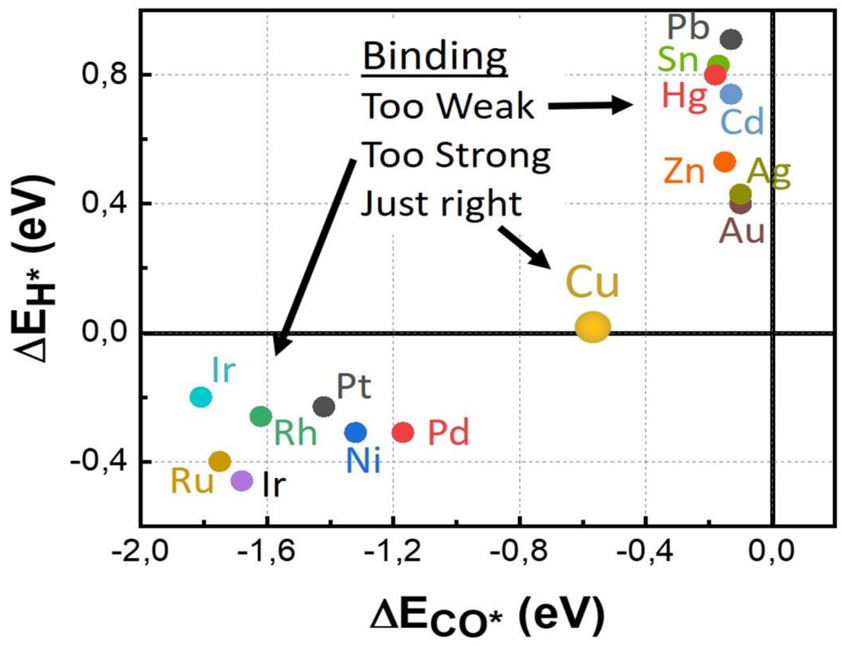
What catalyst should we use?

Table 1. Various products from the electroreduction of CO_2

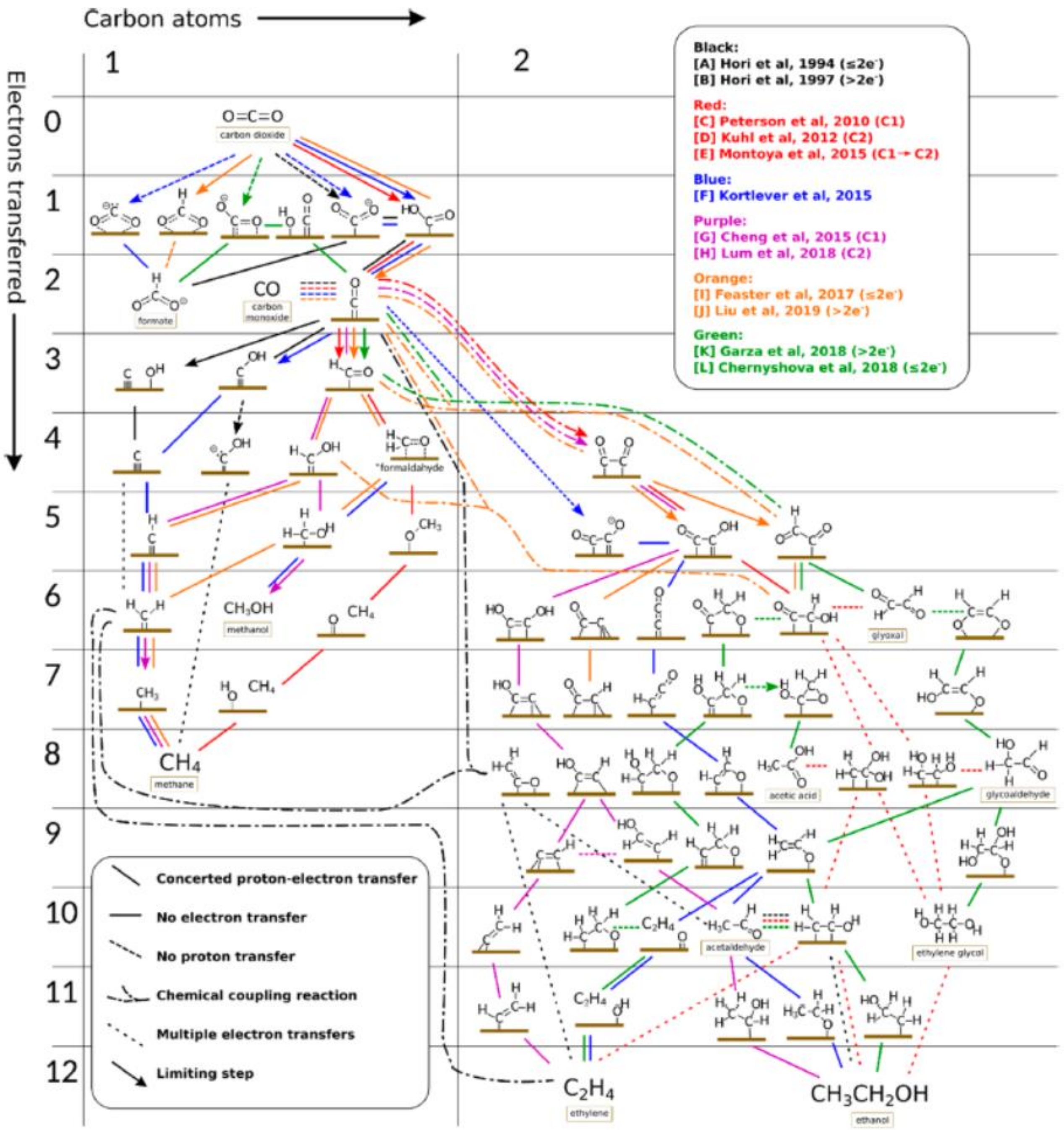
Electrode	Potential (V) vs. *nhe*	Current density (mA cm^{-2})	CH_4	C_2H_4	EtOH	PrOH	CO	$HCOO^-$	H_2	Total
			Faradaic efficiency/%							
Cu	−1.44	5.0	33.3	25.5	5.7	3.0	1.3	9.4	20.5	103.5*
Au	−1.14	5.0	0.0	0.0	0.0	0.0	87.1	0.7	10.2	98.0
Ag	−1.37	5.0	0.0	0.0	0.0	0.0	81.5	0.8	12.4	94.6
Zn	−1.54	5.0	0.0	0.0	0.0	0.0	79.4	6.1	9.9	95.4
Pd	−1.20	5.0	2.9	0.0	0.0	0.0	28.3	2.8	26.2	60.2
Ga	−1.24	5.0	0.0	0.0	0.0	0.0	23.2	0.0	79.0	102.0
Pb	−1.63	5.0	0.0	0.0	0.0	0.0	0.0	97.4	5.0	102.4
Hg	−1.51	0.5	0.0	0.0	0.0	0.0	0.0	99.5	0.0	99.5
In	−1.55	5.0	0.0	0.0	0.0	0.0	2.1	94.9	3.3	100.3
Sn	−1.48	5.0	0.0	0.0	0.0	0.0	7.1	88.4	4.6	100.1
Cd	−1.63	5.0	1.3	0.0	0.0	0.0	13.9	78.4	9.4	103.0
Tl	−1.60	5.0	0.0	0.0	0.0	0.0	0.0	95.1	6.2	101.3
Ni	−1.48	5.0	1.8	0.1	0.0	0.0	0.0	1.4	88.9	92.4†
Fe	−0.91	5.0	0.0	0.0	0.0	0.0	0.0	0.0	94.8	94.8
Pt	−1.07	5.0	0.0	0.0	0.0	0.0	0.0	0.1	95.7	95.8
Ti	−1.60	5.0	0.0	0.0	0.0	0.0	tr.	0.0	99.7	99.7

Electrolyte: 0.1 M $KHCO_3$; temperature: 18.5 ± 0.5°C.
* The total value contains C_3H_5OH (1.4%), CH_3CHO (1.1%) and C_2H_5CHO (2.3%) in addition to the tabulated substances.
† The total value contains C_2H_6 (0.2%).

Hori, Electrochim Act, 1994



Bagger et al. *Chem-PhysChem* 2017

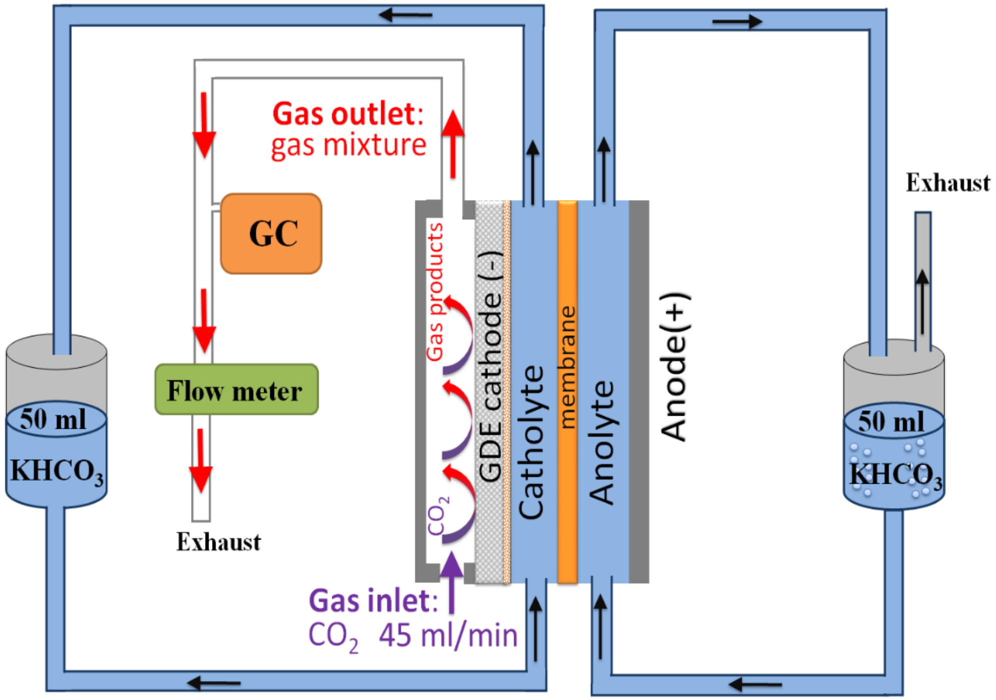


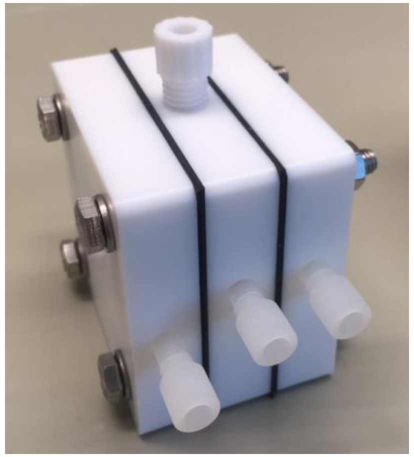
Nitopi et al., 2019

Chem Reviews

Analyzing copper for CO_2 reduction

- With copper producing liquid products, we decided to go with a flowing liquid on the cathode approach.
- The liquid catholyte allows us to vary pH





Cathodic reactions

$CO_2 + H_2O + 2\,e^- \rightarrow CO + 2\,OH^-$

$2CO_2 + 8H_2O + 12\,e^- \rightarrow C_2H_4 + 12\,OH^-$

$2\,H_2O + 2\,e^- \rightarrow 2\,H_2 + 2\,OH^-$

$CO_2 + OH^- \rightarrow HCO_3^-$

$HCO_3^- + OH^- \rightarrow CO_3^{2-}$

Anodic reactions

$2\,H_2O \rightarrow O_2 + 4\,e^- + 4\,H^+$

$OH^- \rightarrow$ $OH^- + H^+ \rightarrow H_2O$

$HCO_3^- \rightarrow$ $HCO_3^- + H^+ \rightarrow CO_2 + H_2O$

$CO_3^{2-} \rightarrow$ $CO_3^{2-} + 2\,H{+} \rightarrow CO_2 + H_2O$

Anion exchange membrane

The Carbon/Charge Coefficient (CCC) is as followed

$OH^- \Rightarrow$ CCC=0

$CO_3^{2-} \Rightarrow$ CCC=1/2

$HCO_3^- \Rightarrow$ CCC=1

Function of current

Function of carbon/charge ratio

$$Gas\ out = Gas\ in \pm Reaction - Crossover$$

Testing different electrolytes

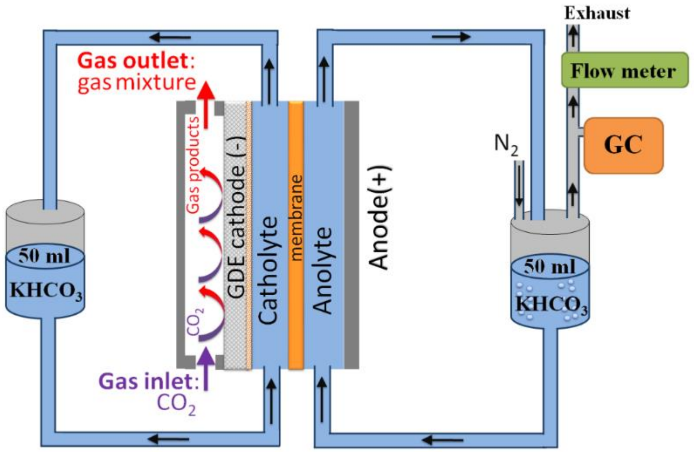
- We tested in both neutral and basic electrolytes.
  - Basic electrolytes are effectively ‘ CO_2 scrubbers’

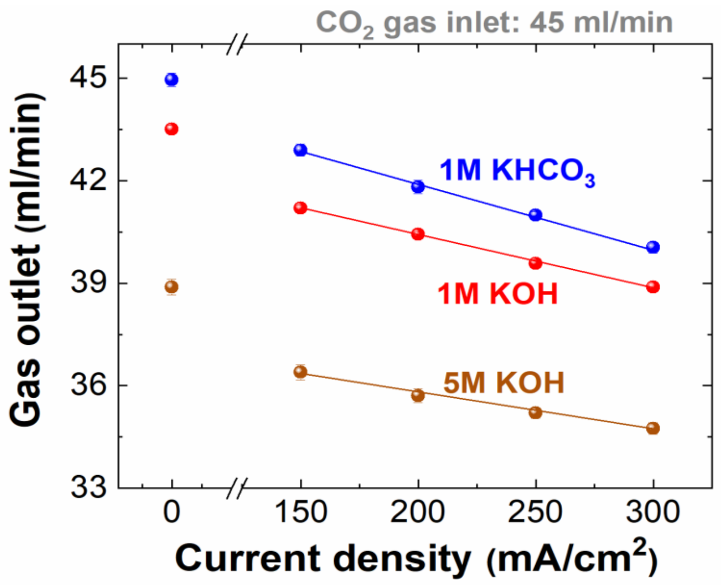
$$\mathrm{CO_2} + OH^- \rightarrow HCO_3{}^-$$

$$HCO_3{}^- + 2OH^- \rightarrow CO_3{}^{2-} + H_2O$$

- Even at open-circuit, significant CO_2 is consumed.

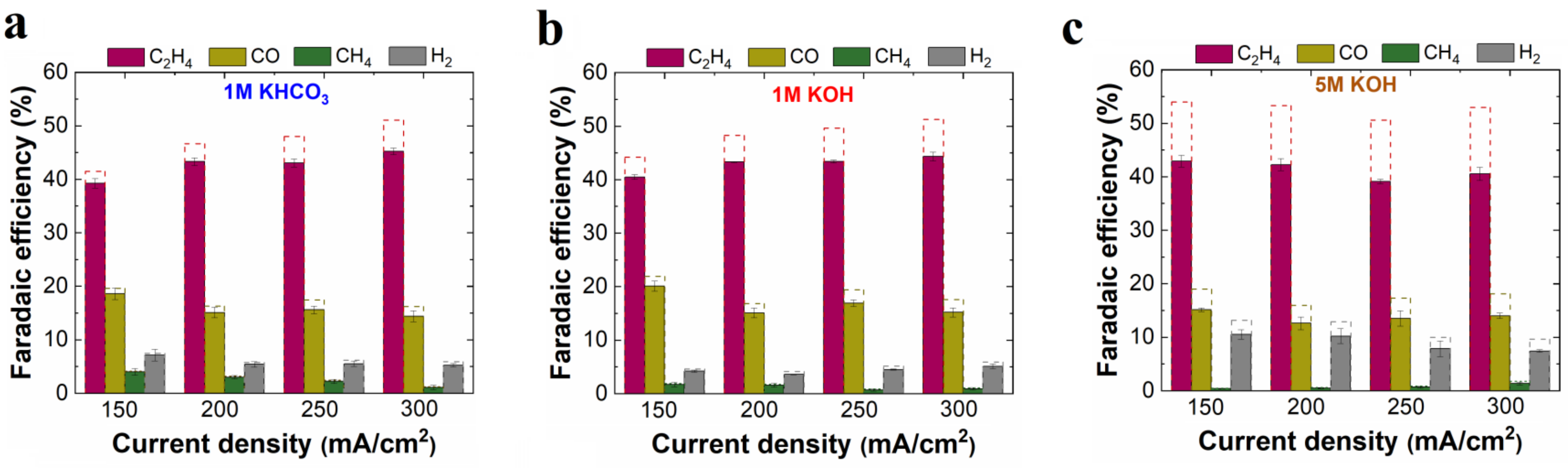
$$Gas\ out = Gas\ in \pm Reaction - Crossover - \color{red}{Scrubbed}$$



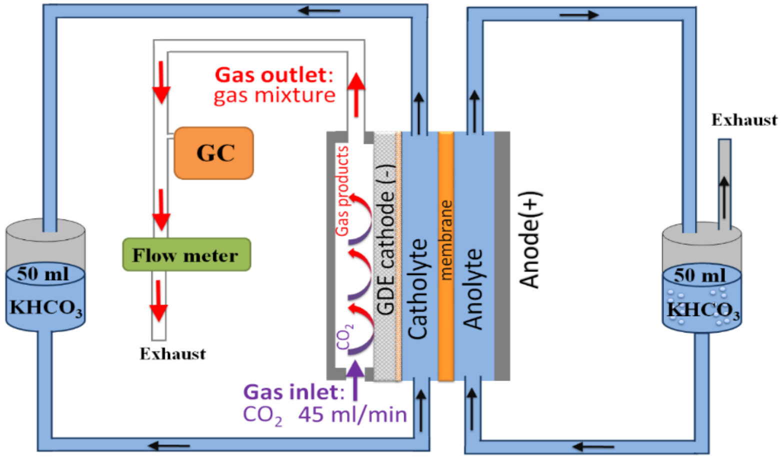


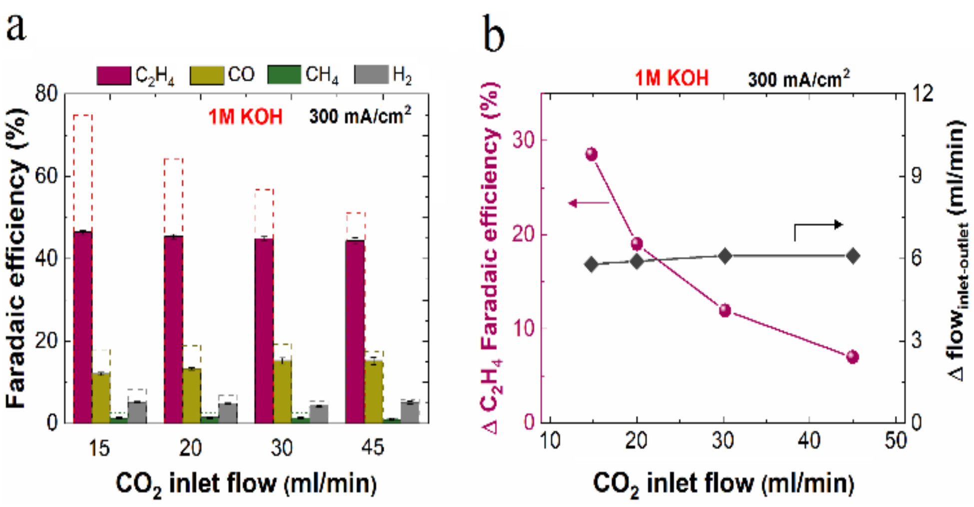
Ma, M., et al E&ES 2020

Comparison of selectivites in different electrolytes



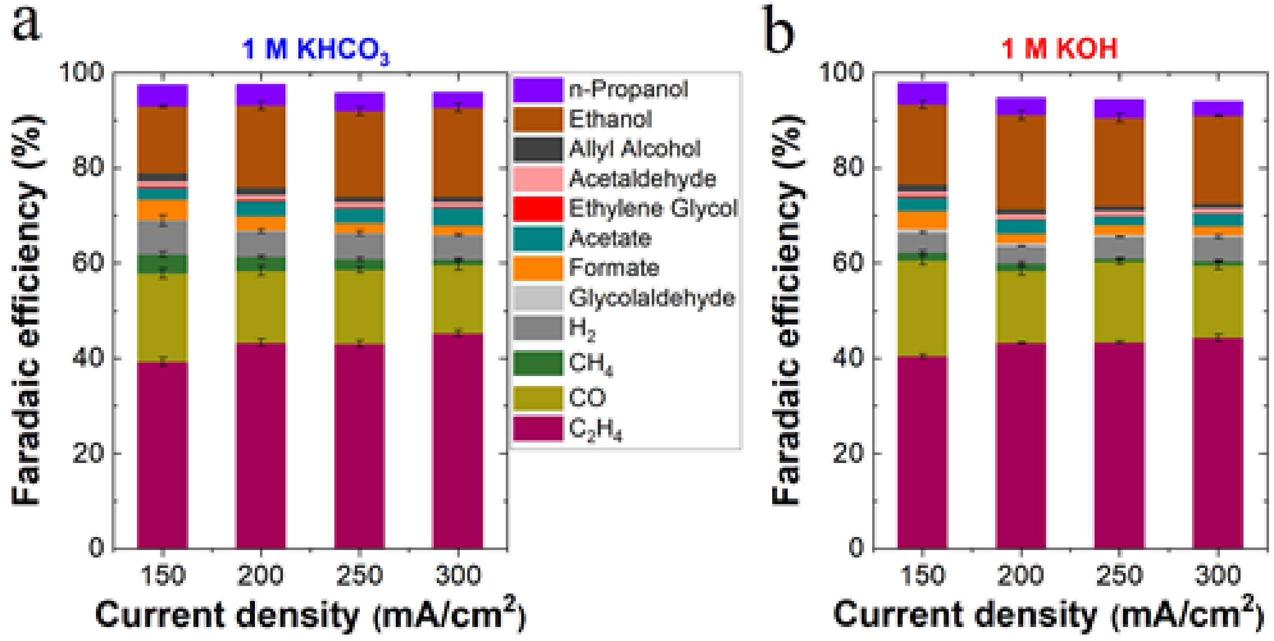
- How important is it to take into consideration actual gas flow rate leaving reactor?





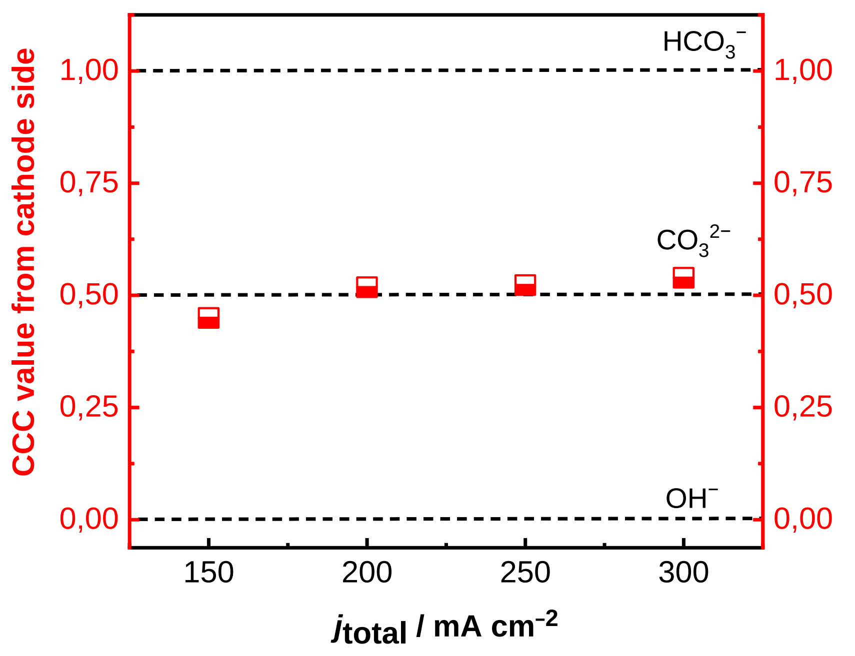
Liquid selectivites

- When we add liquid products we get 100% selectivity of products
- Minimal variation at different current regimes.



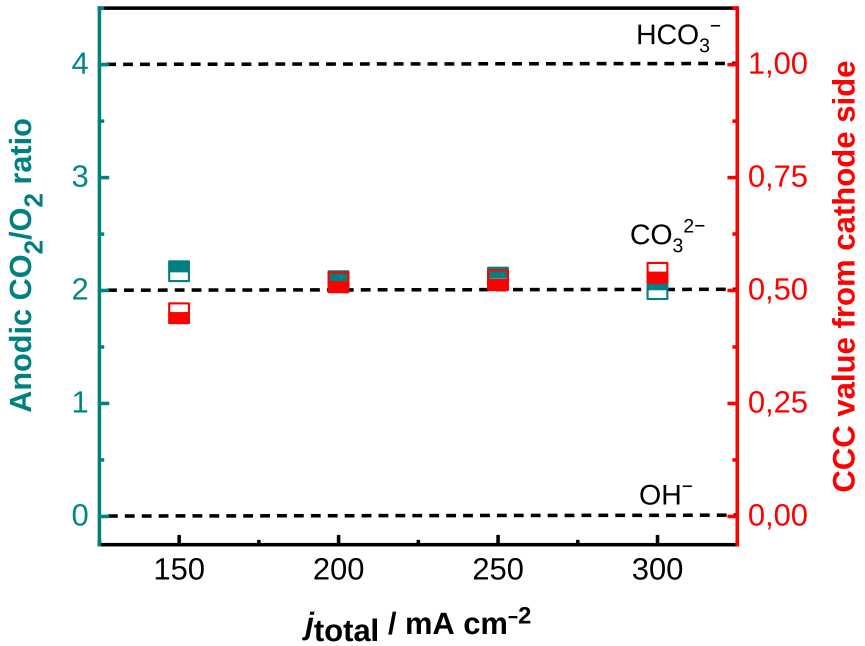
Ma, M., et al E&ES 2020

Tests in 1M $KHCO_3$

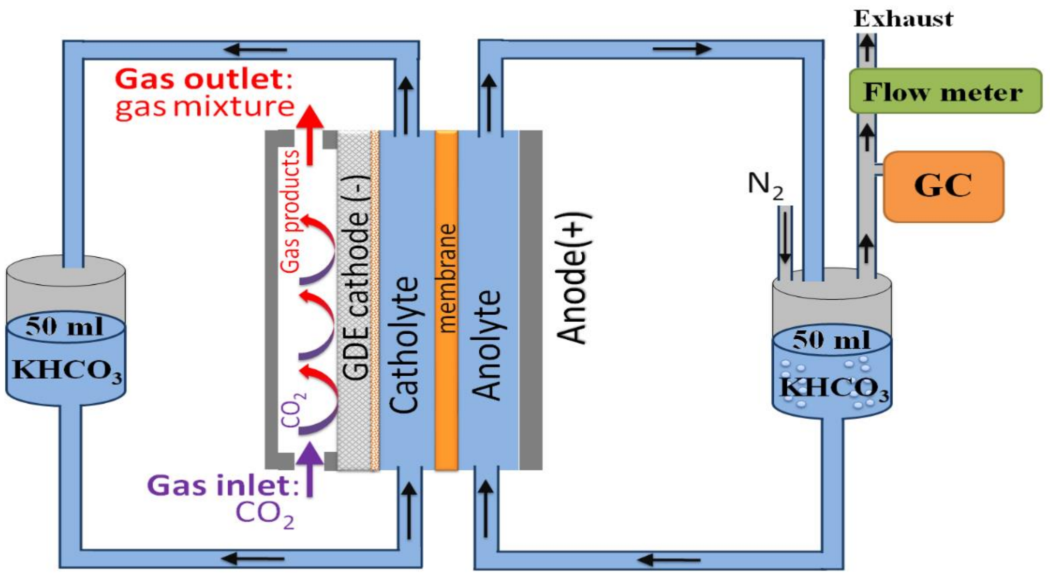


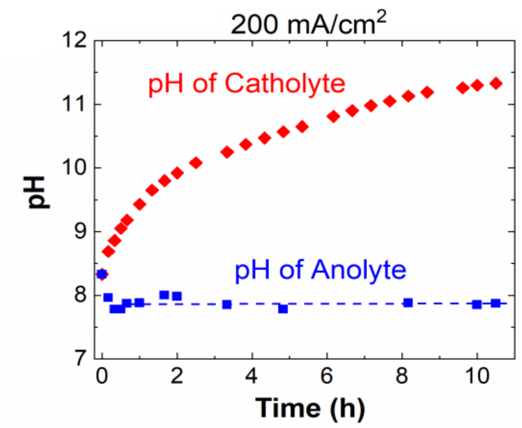
Larrazabal, G., et al., *Account. Mat. Res., 2021*

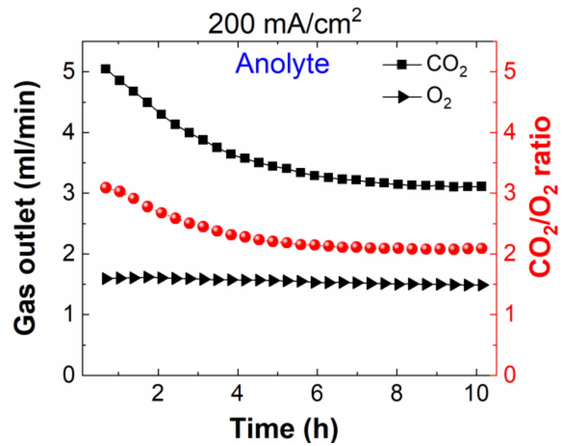
Understanding membrane crossover



Larrazabal, G., et al., *Account. Mat. Res., 2021*





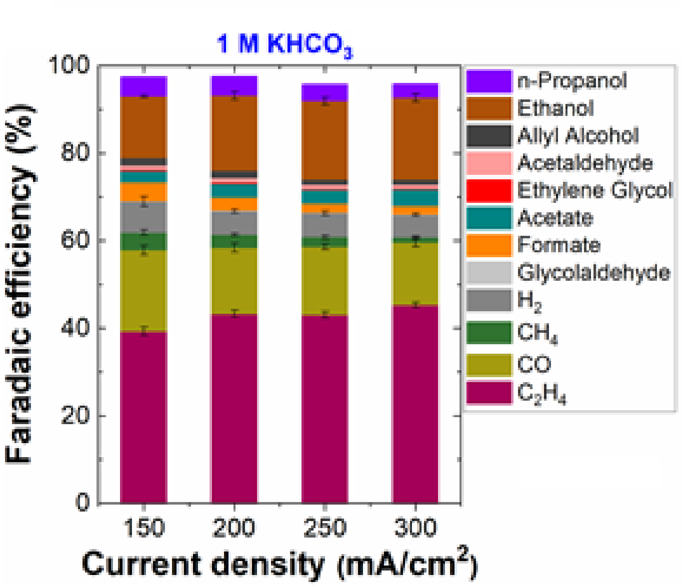


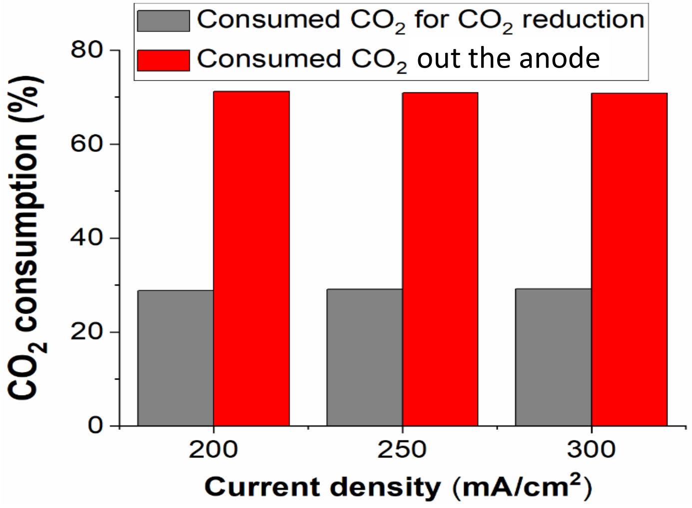
Ma, M., et al., *E&ES, 2020*

Anode reactions:	CO_2/O_2 ratio	CCC
$4HCO_3^- \rightarrow 4\,CO_2 + O_2 + 2H_2O + 4e^-$	4	1
$2CO_3^{2-} \rightarrow 2CO_2 + O_2 + 4e^-$	2	1/2
$4OH^- \rightarrow 2H_2O + O_2 + 4e^-$	0	0

Device analysis

- Account for 100% of our electrons
- Full carbon balance





Ma, M., et al., *E&ES, 2020*

$$\emptyset_{inlet\ CO_2} = \emptyset_{unused\ CO_2} + \emptyset_{CO_2\ to\ gas} + \emptyset_{CO_2\ to\ liquid} + \emptyset_{out\ the\ anode}$$

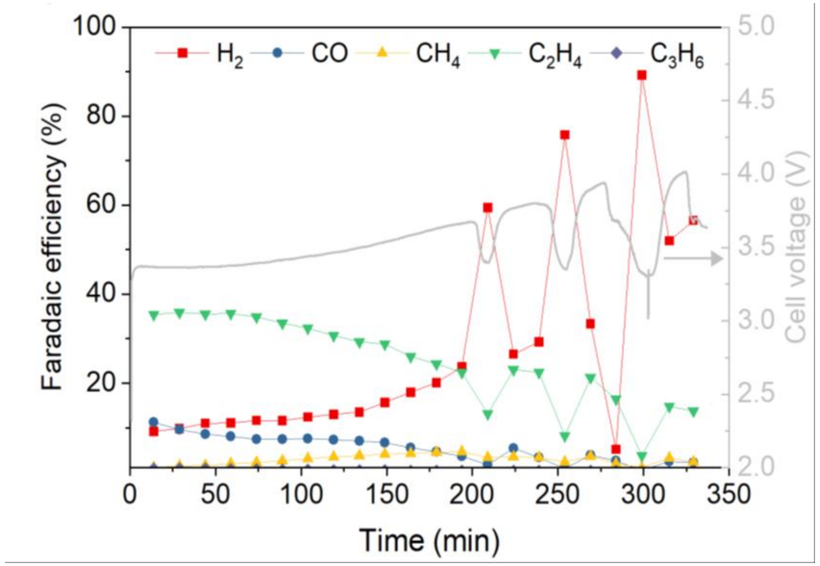
J (mA/cm^2)	$\emptyset_{unused\ CO_2}$ (ml/min)	$\emptyset_{CO_2\ to\ gas}$ (ml/min)	$\emptyset_{CO_2\ to\ liquid}$ (ml/min)	$\emptyset_{Anode}$ (ml/min)	$\emptyset_{total\ CO_2}$ (ml/min)
200	40.8	0.92	0.34	3.1	**45.2**
250	39.7	1.17	0.39	3.8	**45.1**
300	38.6	1.38	0.48	4.5	**45.0**

Using 1 M $KHCO_3$ as initial electrolyte

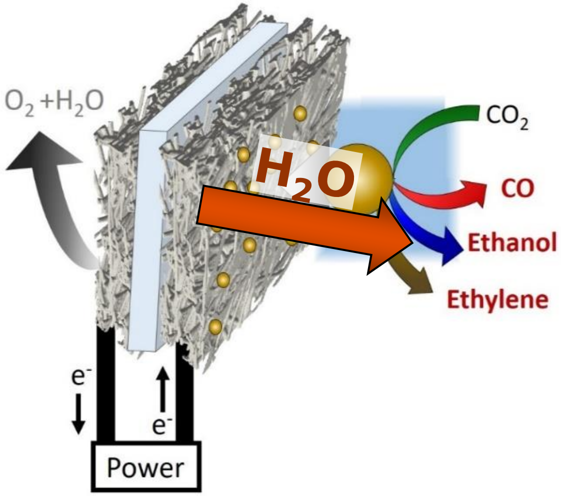
Inlet CO_2 flow: 45 ml/min

More problems: Oscillations

- It is well known in the field that H_2 evolution increases over time
- It is thought that this is due to water 'flooding' into the cathode preventing CO_2 mass transfer.
- Sometimes oscillations come with this.



Is water 'flooding' our catalyst ?

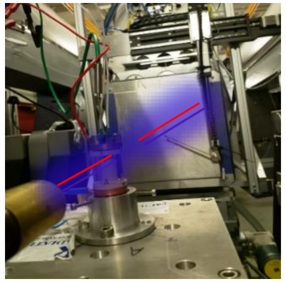


Designing a synchrotron experiment

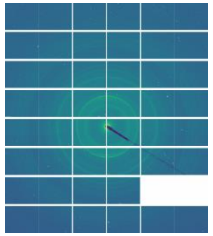
- We thought excess water may prevent efficient CO_2 mass transfer to the catalyst
- We used synchrotron X-ray scattering at ESRF to analyse this.

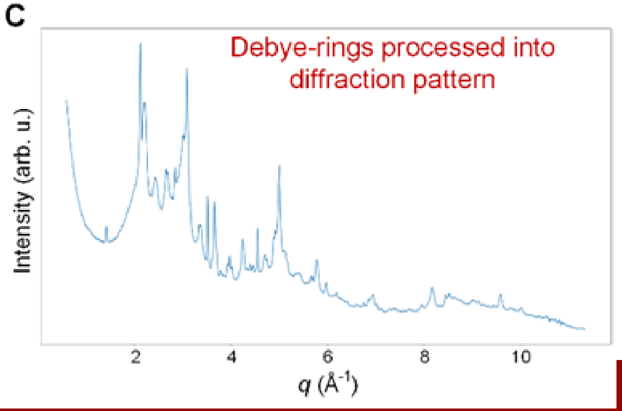
Synchrotron

Experiments

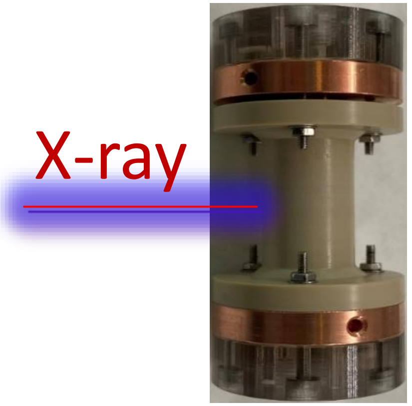


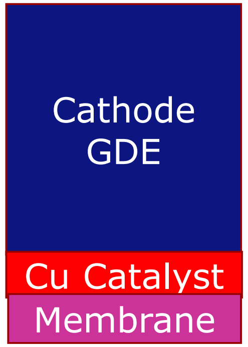
Raw X-ray results





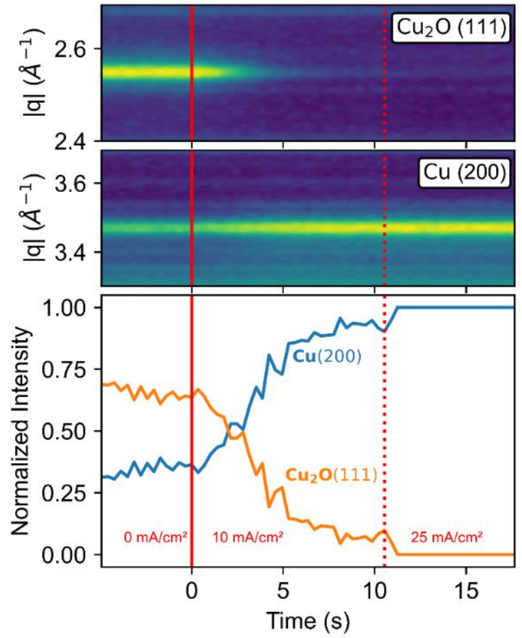
CO_2 Reactor

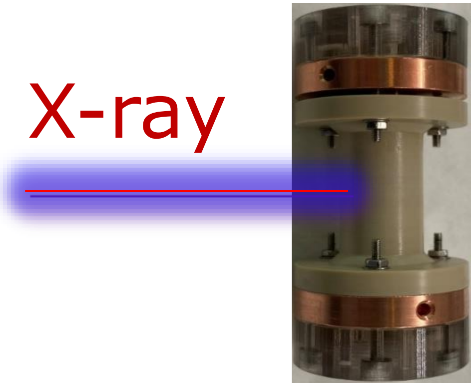


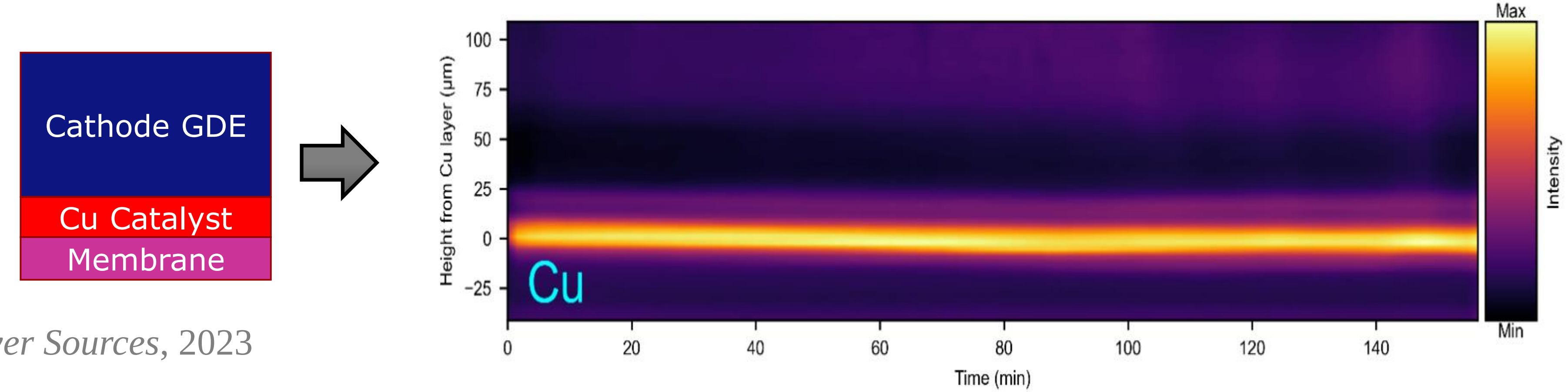


Analysing copper in our device

- We can easily see the change in the surface oxide in Cu being reduced.
- We can also monitor Cu as a function of height within the gas diffusion layer







Moss., et al., *J of Power Sources*, 2023

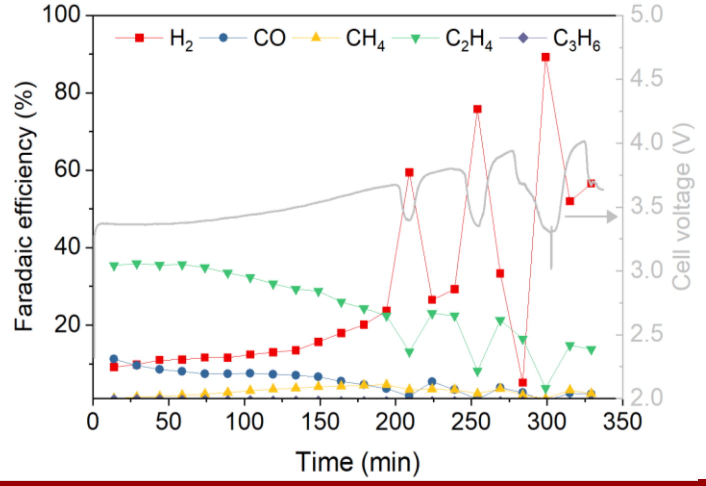
Analysing water

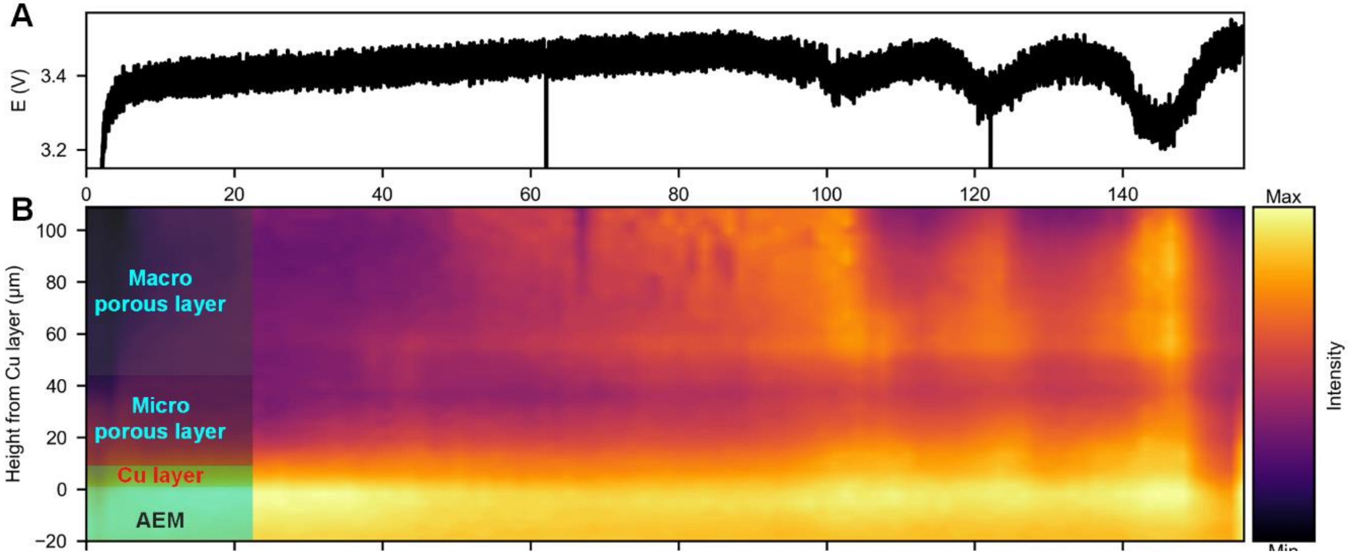
- By using variations in background signal in q-space where there are no Bragg peaks, we can use this as a proxy for water content.

- We can relate water content to potential variations.

- Lower potential, more water, more hydrogen.

From earlier

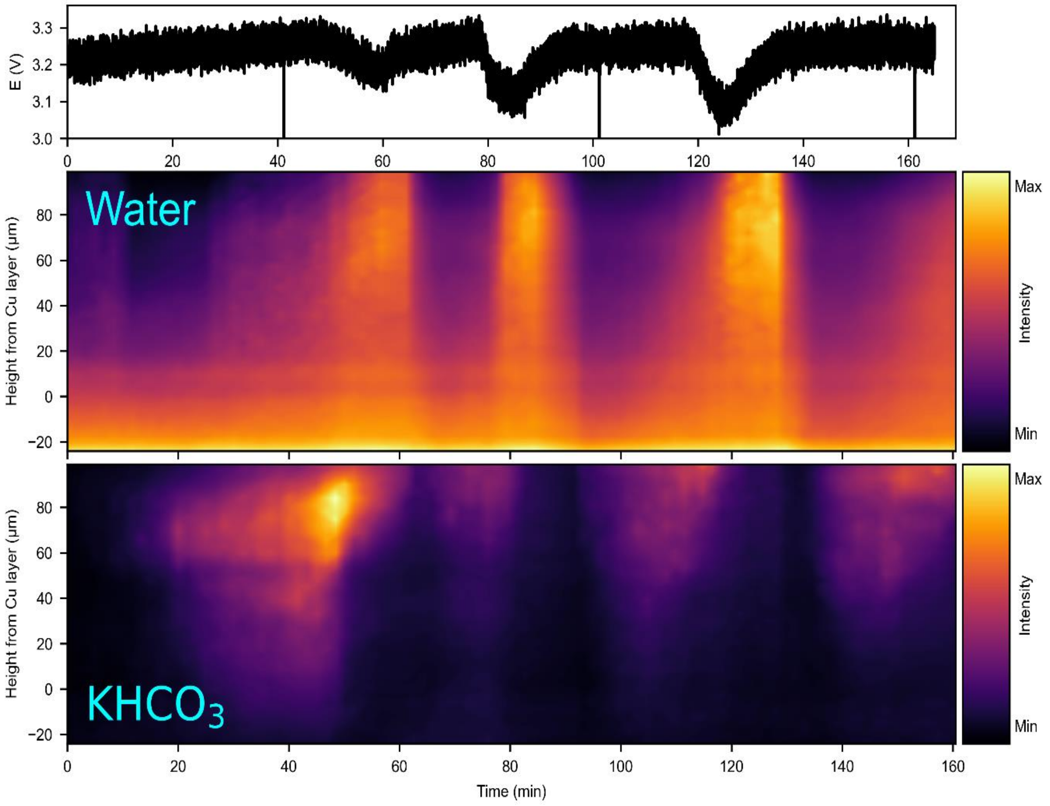


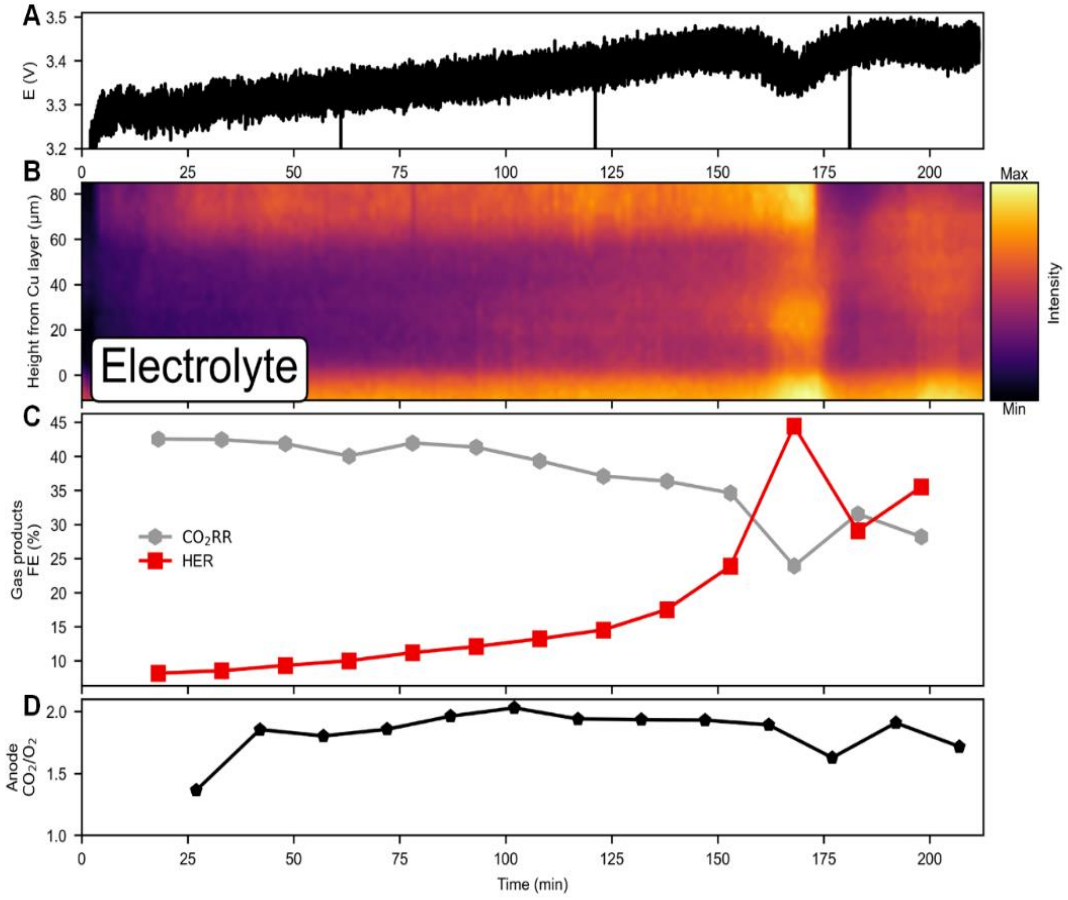


Moss., et al., *Joule*, 2023

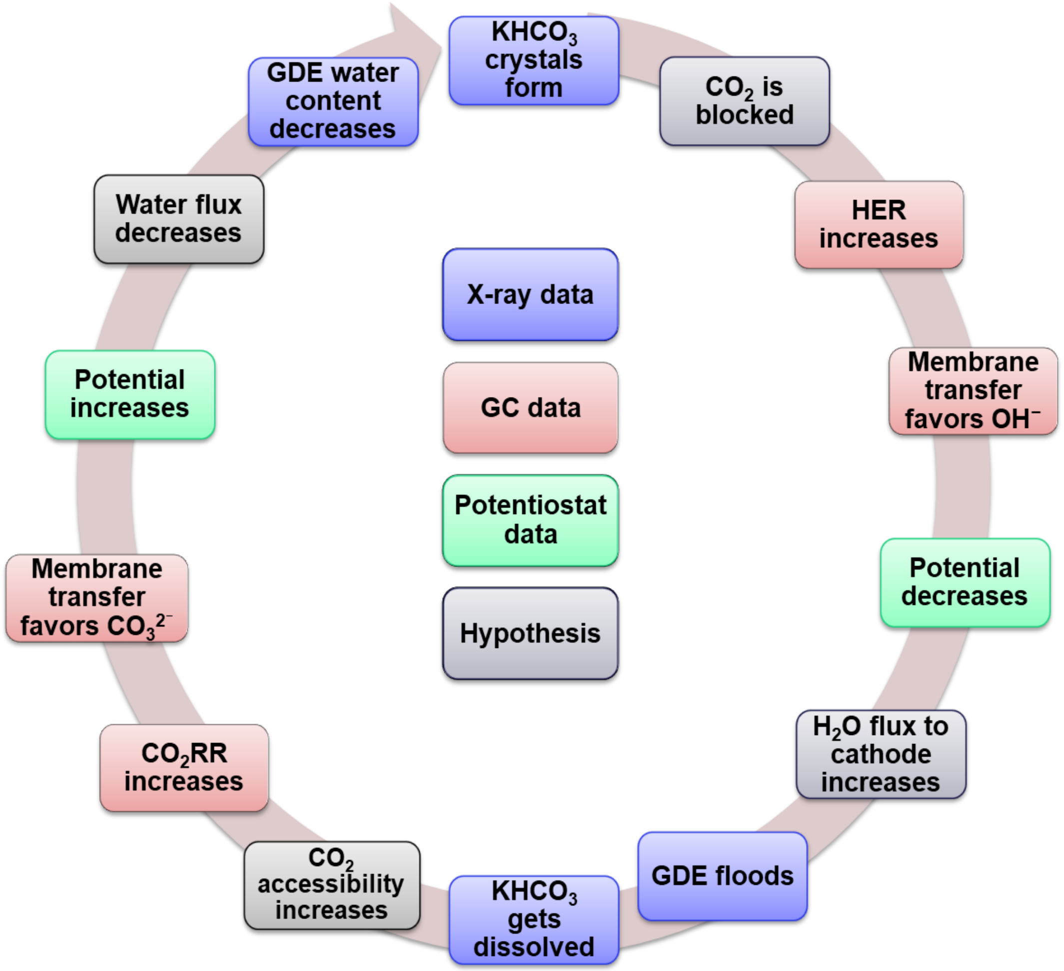
Mass transfer issues

- When looking at salts we see $KHCO_3$, but no K_2CO_3
- We see the salt deposition before water floods the cell

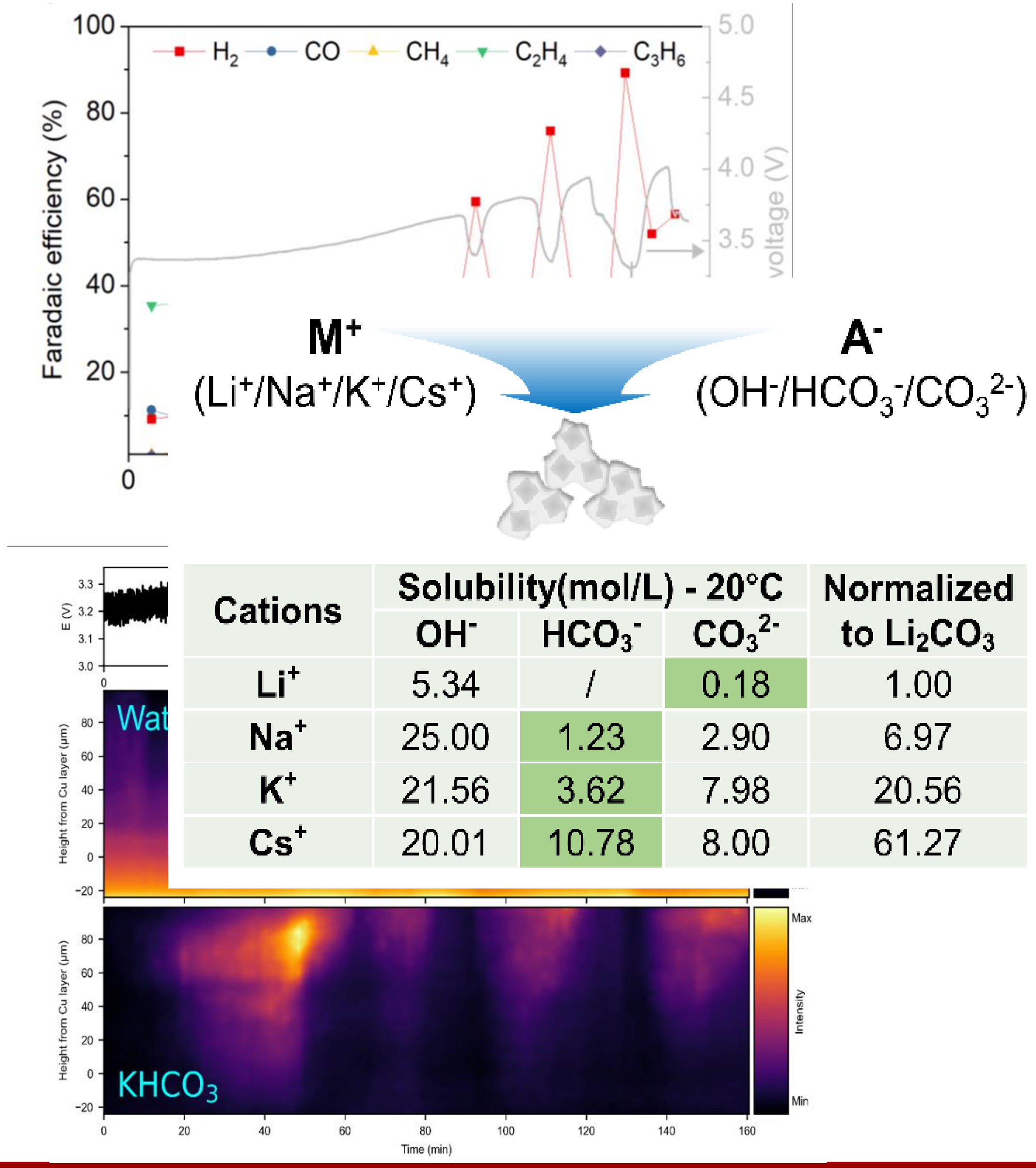




Oscillation hypothesis

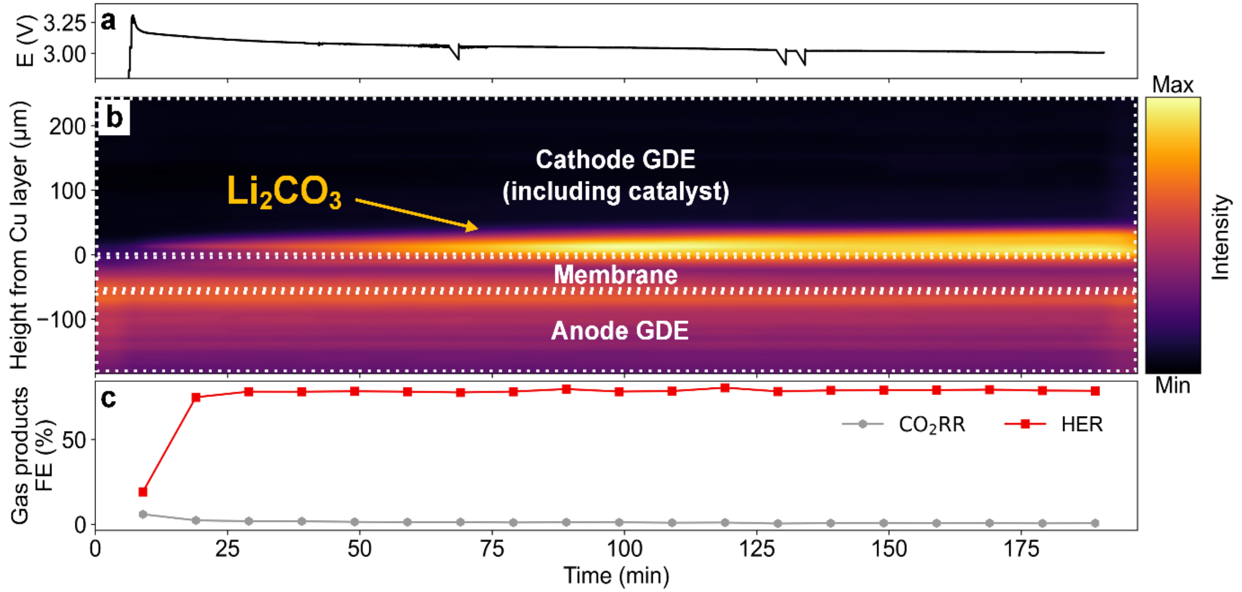


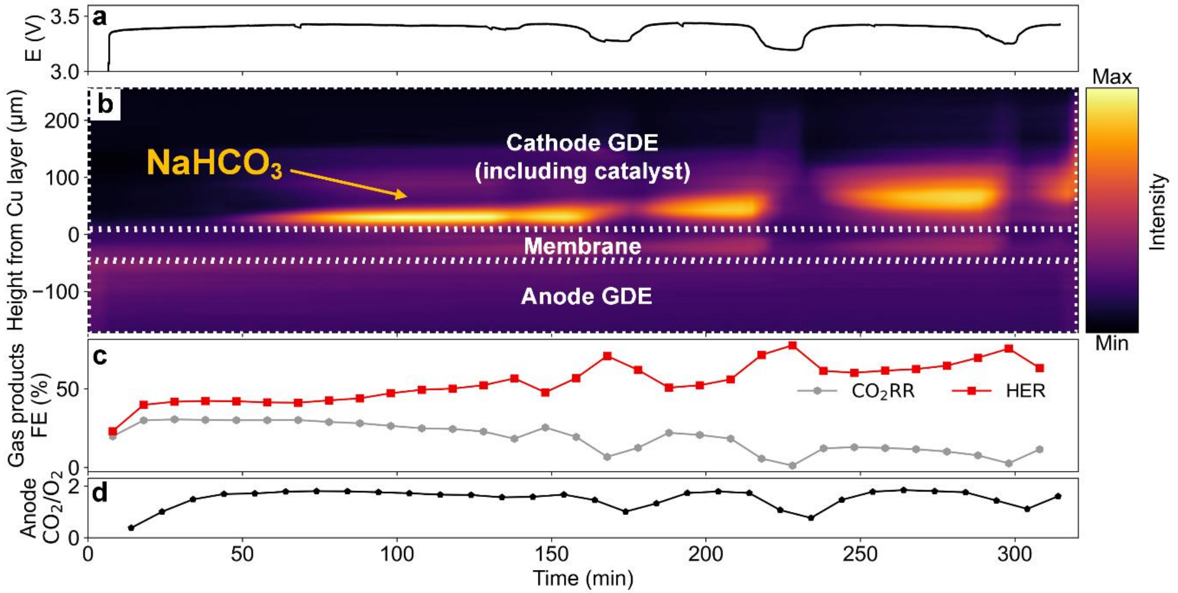
Moss., et al., *Joule*, 2023

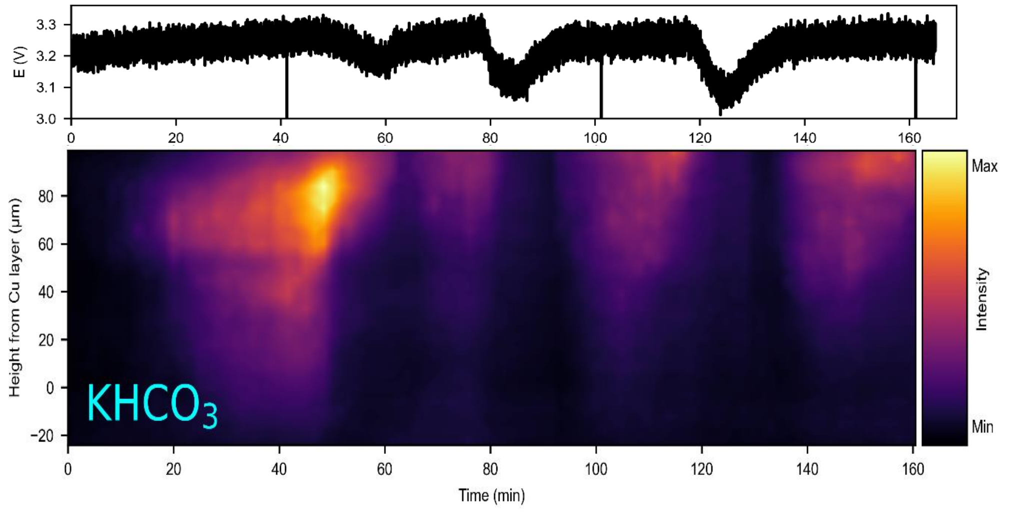


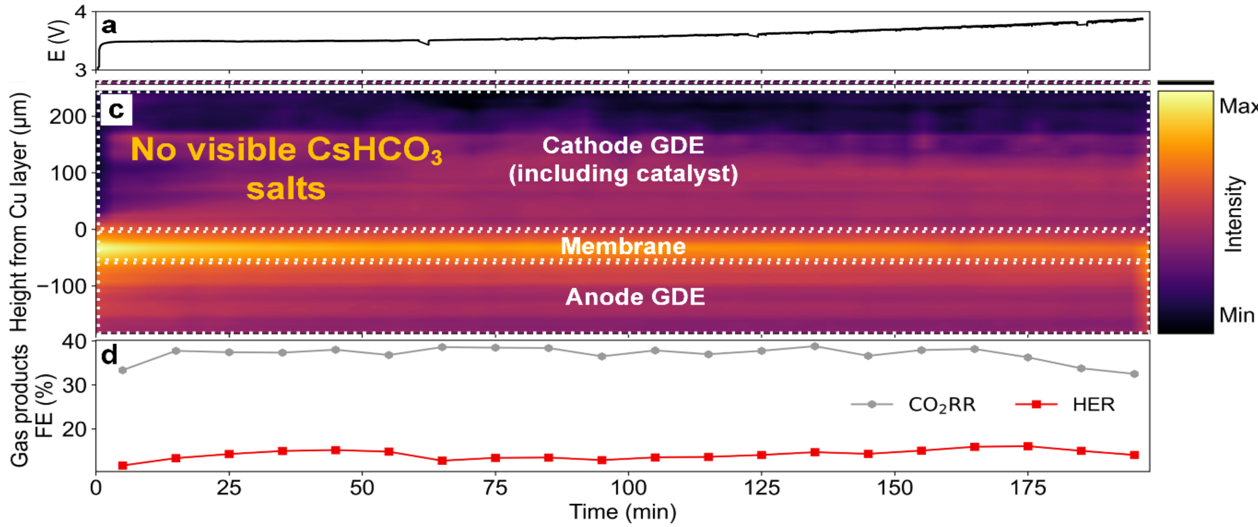
Cations	Solubility(mol/L) - 20°C			Normalized to Li_2CO_3
	OH^-	HCO_3^-	CO_3^{2-}	
Li^+	5.34	/	0.18	1.00
Na^+	25.00	1.23	2.90	6.97
K^+	21.56	3.62	7.98	20.56
Cs^+	20.01	10.78	8.00	61.27

Salt precipitation of various cations



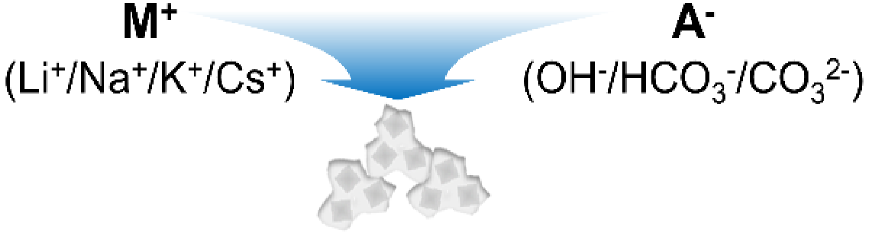




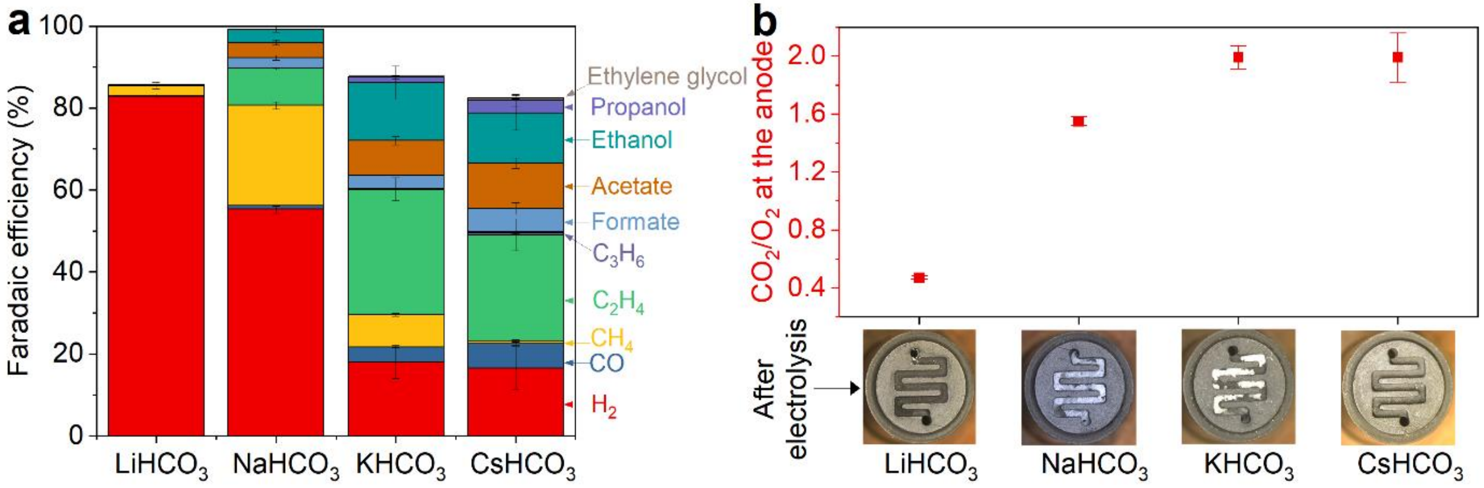


Salt precipitation of various cations

- Normalizing scattering between experiments shows the influence of water
- We show that Cs not only increases electric field, it’s high solubility also prevents salt build-up.



Cations	Solubility(mol/L) - 20°C			Normalized to Li_2CO_3
	OH^-	HCO_3^-	CO_3^{2-}	
Li^+	5.34	/	0.18	1.00
Na^+	25.00	1.23	2.90	6.97
K^+	21.56	3.62	7.98	20.56
Cs^+	20.01	10.78	8.00	61.27



Garg, et al., *E&ES*, 2023

A Solution !!- CO Electrolysis

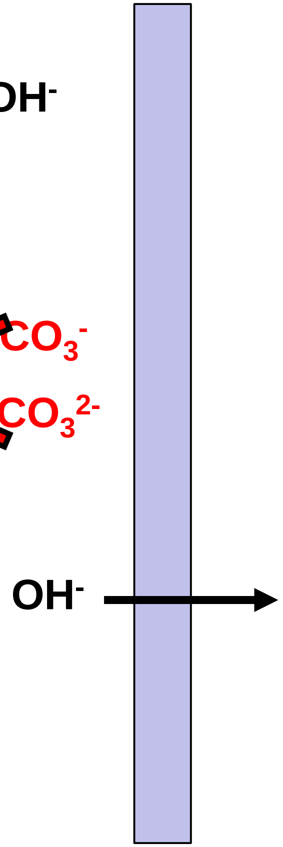
<u>Cathodic reactions</u>

$CO + H_2O + X\ e^- \rightarrow C_iH_jO_k + X\ OH^-$

$2\ H_2O + 2\ e^- \rightarrow 2\ H_2 + 2\ OH^-$

$\cancel{CO_2 + OH^- \rightarrow HCO_3^-}$

$\cancel{HCO_3^- + OH^- \rightarrow CO_3^{2-}}$



Anion exchange membrane

- CO does not form carbonates, thus no issues with CO_2 coming out the anode
- CO does not buffer the pH, thus more efficient alkaline pH can be used
- CO is not hard to produce.

Fundamenal Analysis on CO Reduction

- Using an EC-MS, we can see many products in-situ.
- These devices operate at ~1 mA/cm^2
- From these results we discover acetaldehyde is the precursor to ethanol

Spectro Inlets – *DTU Spinoff*

Varying alkalinity for CO electrolysis

- Acetate increases whereas other C_2 products decrease as alkalinity increases
- Ethanol seems to decrease faster than ethylene

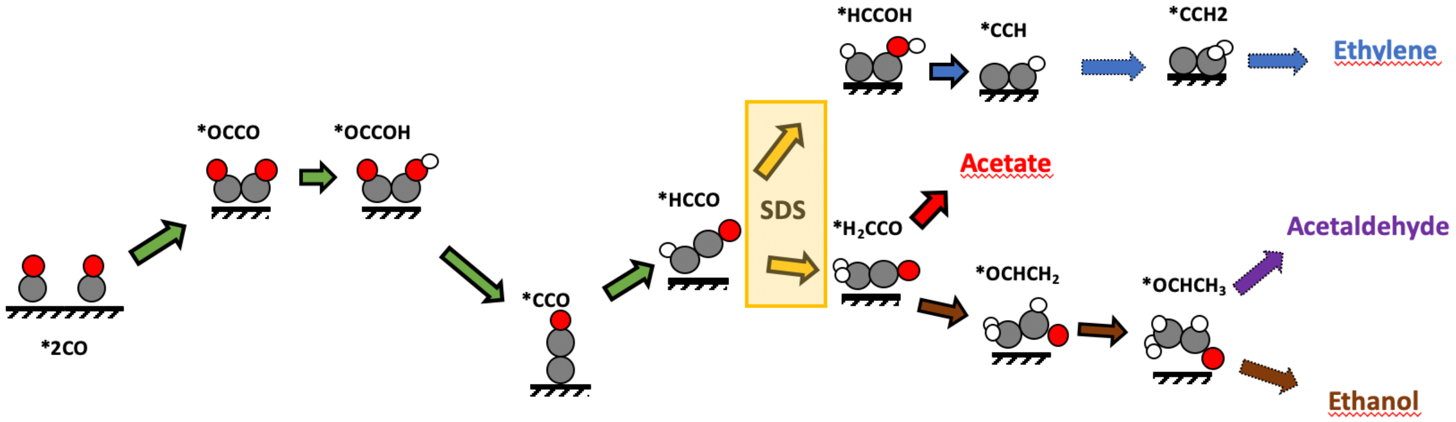
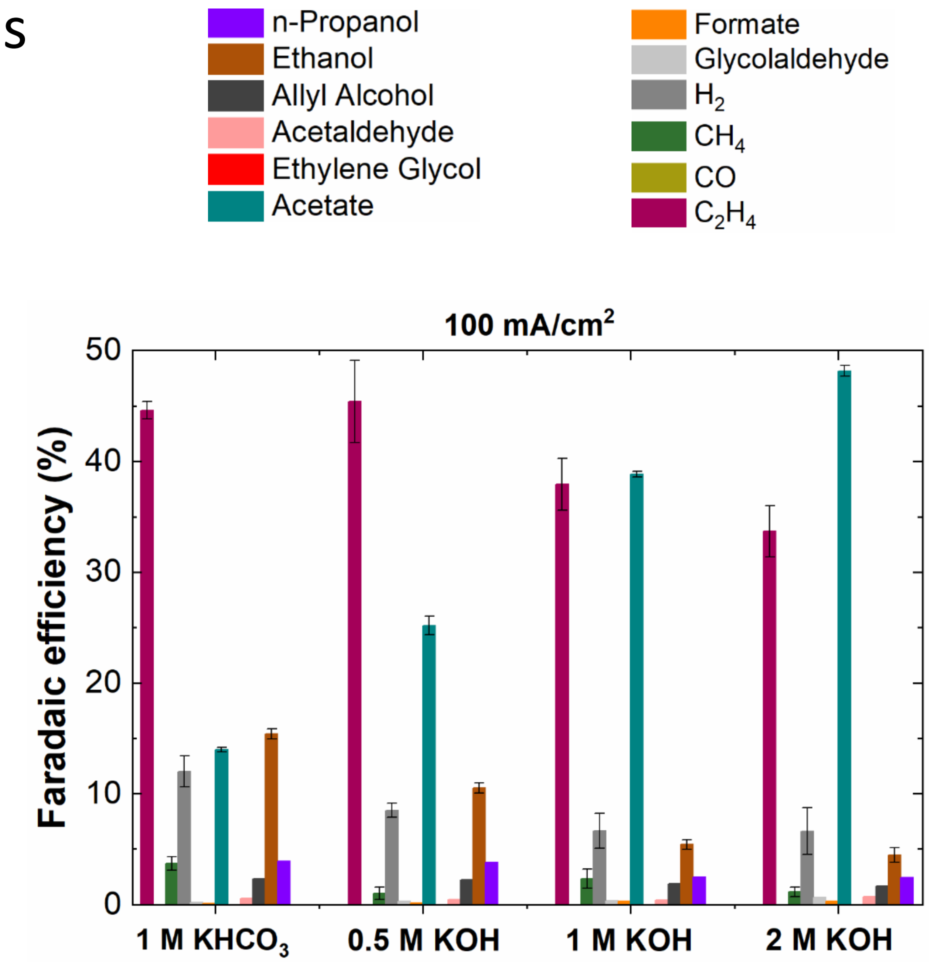
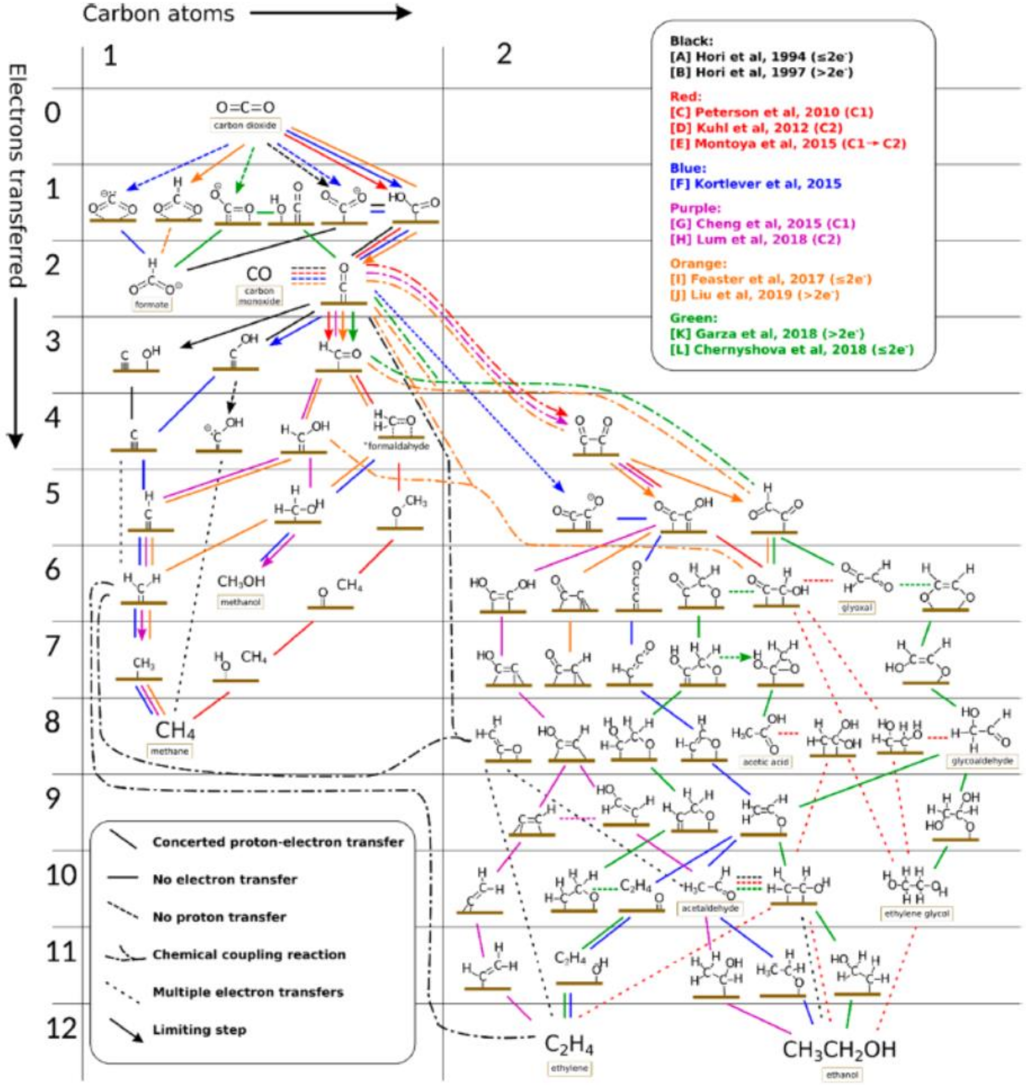


Image by Georg Kastlunger



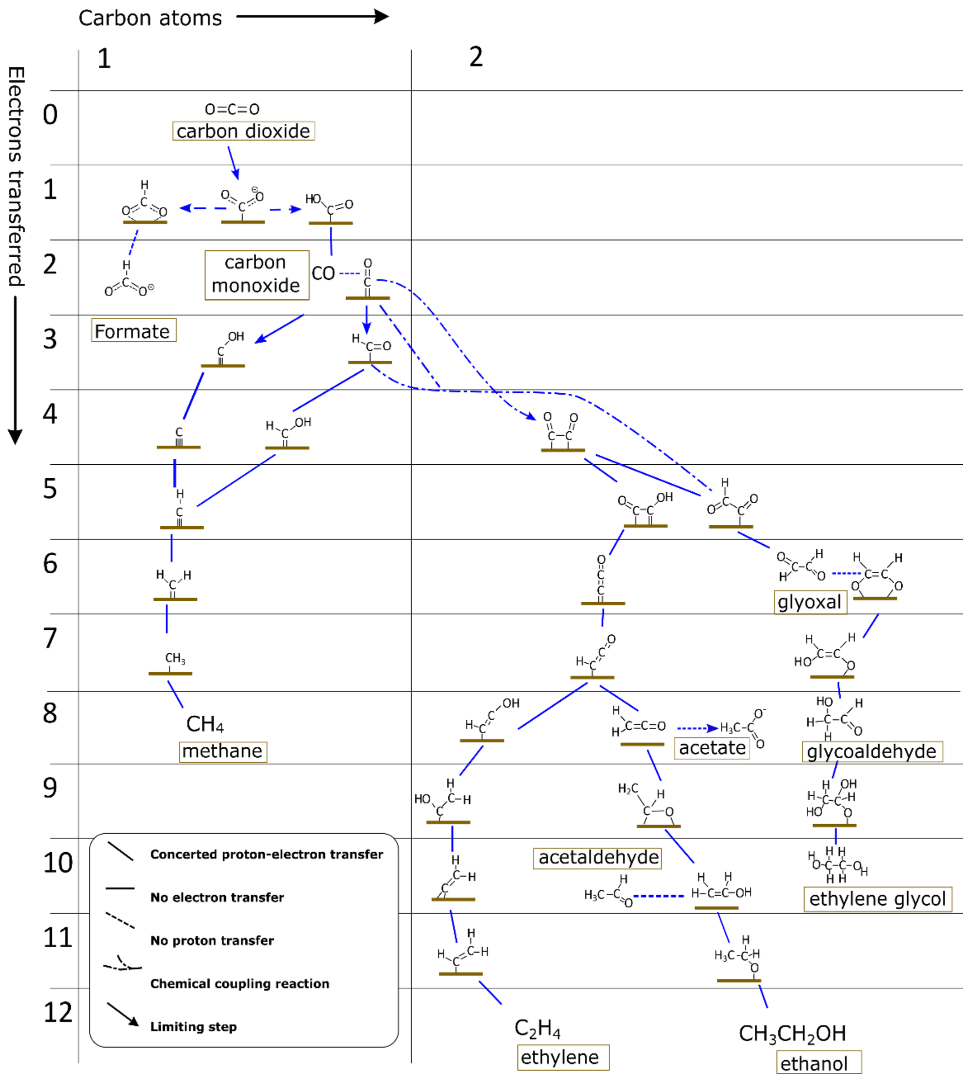
Ma, et al. E&ES. 2022 15, 2470-2478

2018



Carbon atoms
Electrons transferred
Black:
[A] Hori et al, 1994 (≤2e⁻)
[B] Hori et al, 1997 (>2e⁻)
Red:
[C] Peterson et al, 2010 (C1)
[D] Kuhl et al, 2012 (C2)
[E] Montoya et al, 2015 (C1→C2)
Blue:
[F] Kortlever et al, 2015
Purple:
[G] Cheng et al, 2015 (C1)
[H] Lum et al, 2018 (C2)
Orange:
[I] Feaster et al, 2017 (≤2e⁻)
[J] Liu et al, 2019 (>2e⁻)
Green:
[K] Garza et al, 2018 (>2e⁻)
[L] Chernyshova et al, 2018 (≤2e⁻)
O=C=O
carbon dioxide
CO
carbon monoxide
formate
formaldehyde
CH3OH
methanol
CH4
methane
glyoxal
acetic acid
glycoaldehyde
acetaldehyde
ethylene glycol
C2H4
ethylene
CH3CH2OH
ethanol
Concerted proton-electron transfer
No electron transfer
No proton transfer
Chemical coupling reaction
Multiple electron transfers
Limiting step

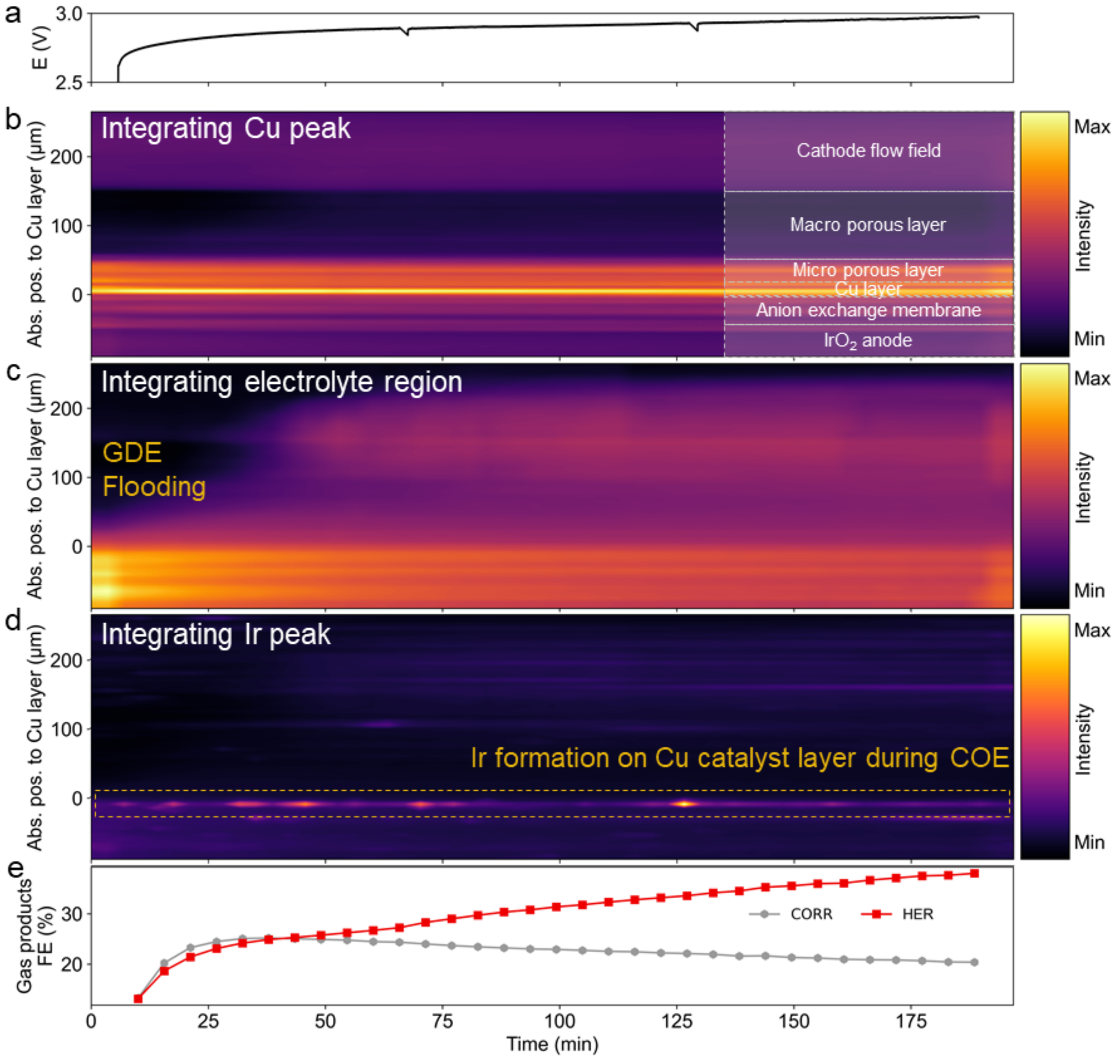
2022



Carbon atoms
Electrons transferred
O=C=O
carbon dioxide
carbon monoxide
CO
Formate
CH4
methane
glyoxal
acetate
glycoaldehyde
acetaldehyde
ethylene glycol
C2H4
ethylene
CH3CH2OH
ethanol
Concerted proton-electron transfer
No electron transfer
No proton transfer
Chemical coupling reaction
Limiting step

Issues with CO electrolysis

- The flooding is not a major issue with CO electrolysis.
- Ir crossover is an issue, though for CO_2 electrolysis this was not an issue.
- We believe this is a pH issue (CO, pH=13), CO_2 (pH=8)
- Switching to a Ni anode basically resolved this.



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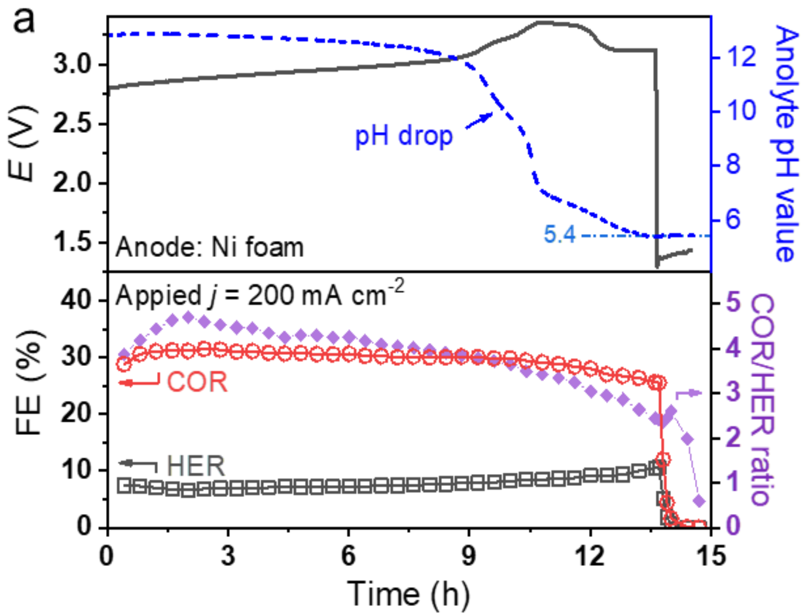
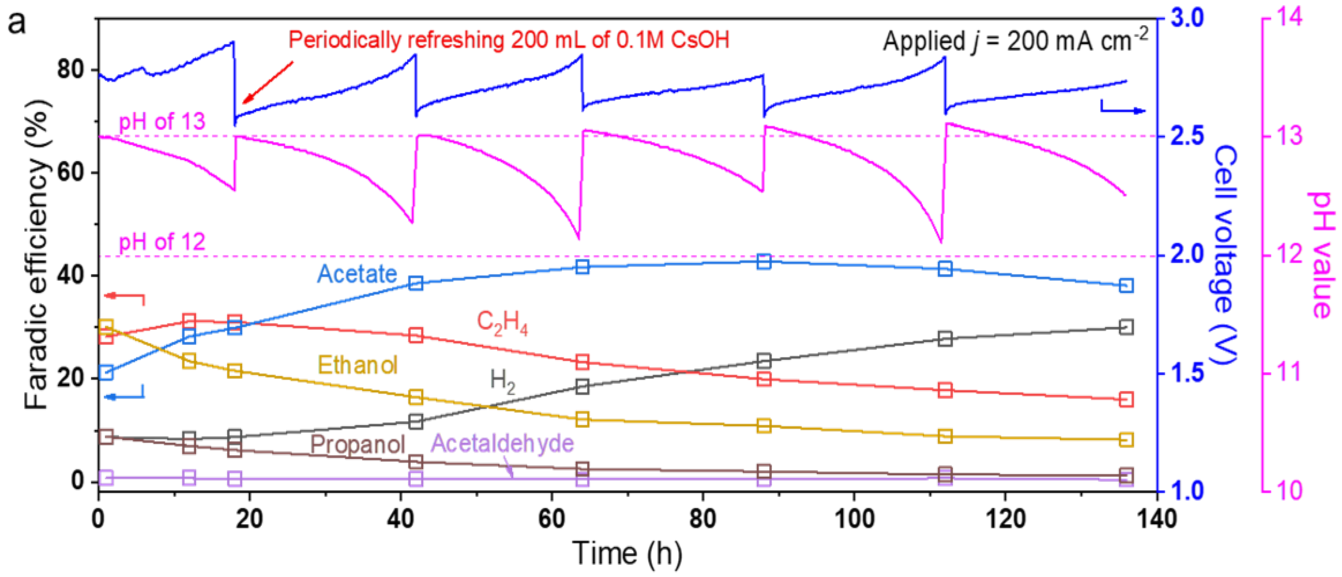
Varying alkalinity for CO electrolysis

- Acetate goes through our membrane and starts acidifying our anode
- More acidic pH corrodes our anode
- By removing the acetate at the anode, we can operate over 100 hours.





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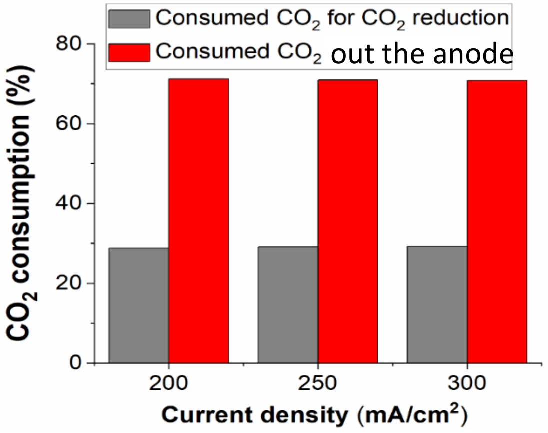
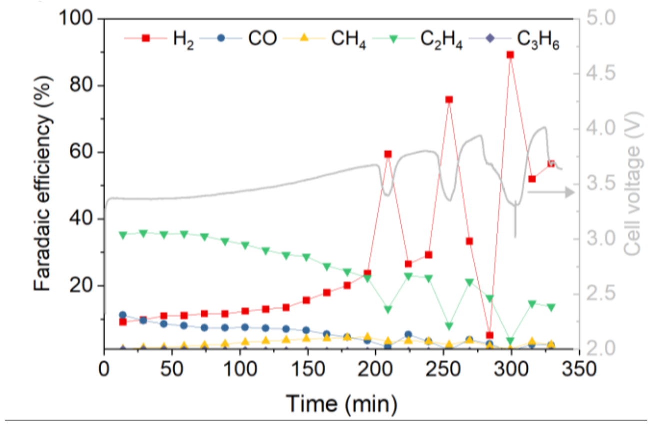
Conclusions

- We need to be smart in our scientific progression.
- CO_2 crossover is a huge issue, which I am not sure we can resolve.
- CO electrolysis has substantial potential and we are looking to engage with companies now.

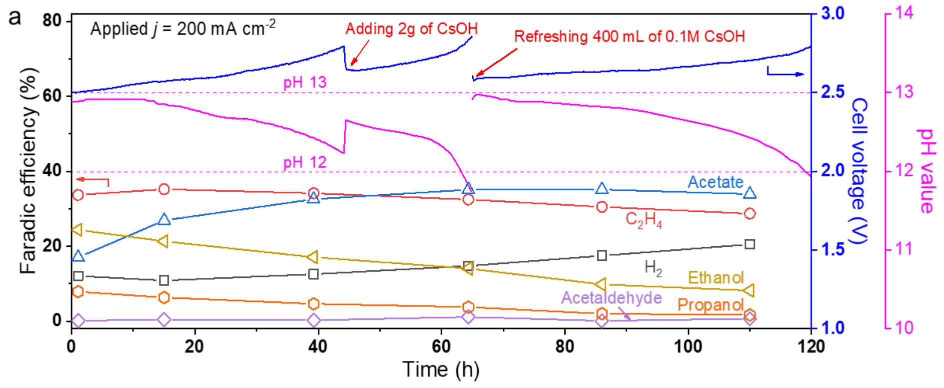
Problem



Problem



Solution



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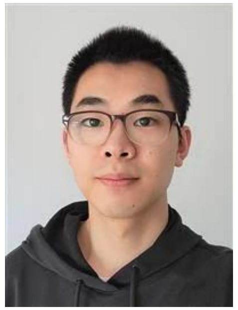
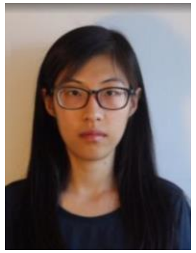
Asger Moss

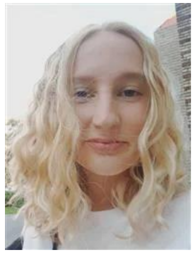

Sahil Garg


Carlos Rodriguez


Qiucheng Xu


Yu Qiao


Bjørt Joensen


Clara Jensen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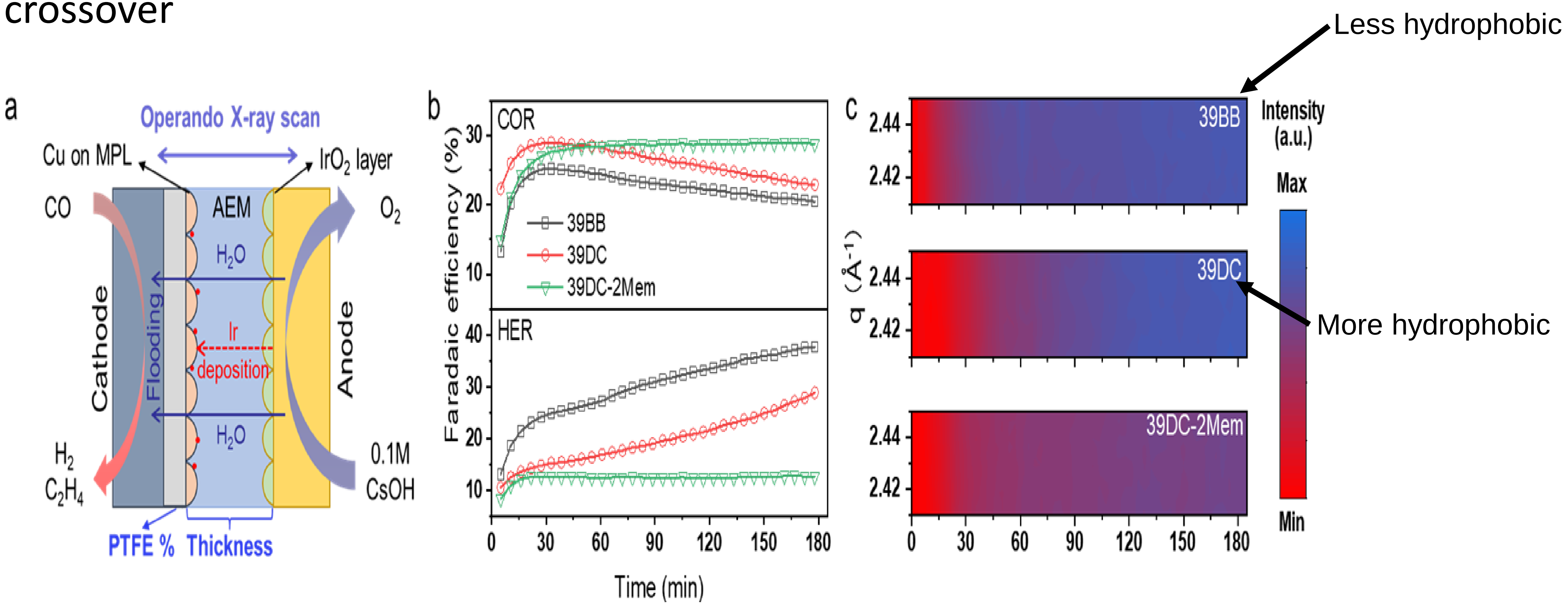
Collaborators

Ib Chorkendorff
Kasper Therkildsen

More Synchrotron Data

- We also varied GDL hydrophobicity and membrane thickness to monitor water crossover



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