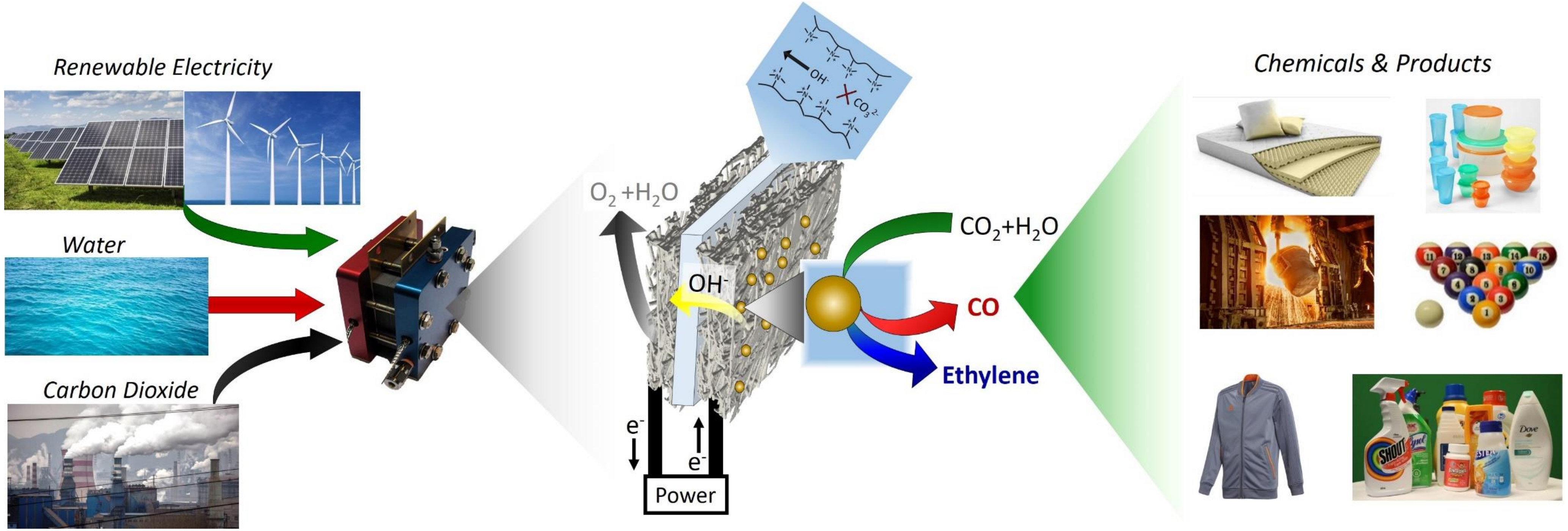
Analysis of CO_2 electrolysis devices via a carbon balance and in-situ synchrotron based approaches.

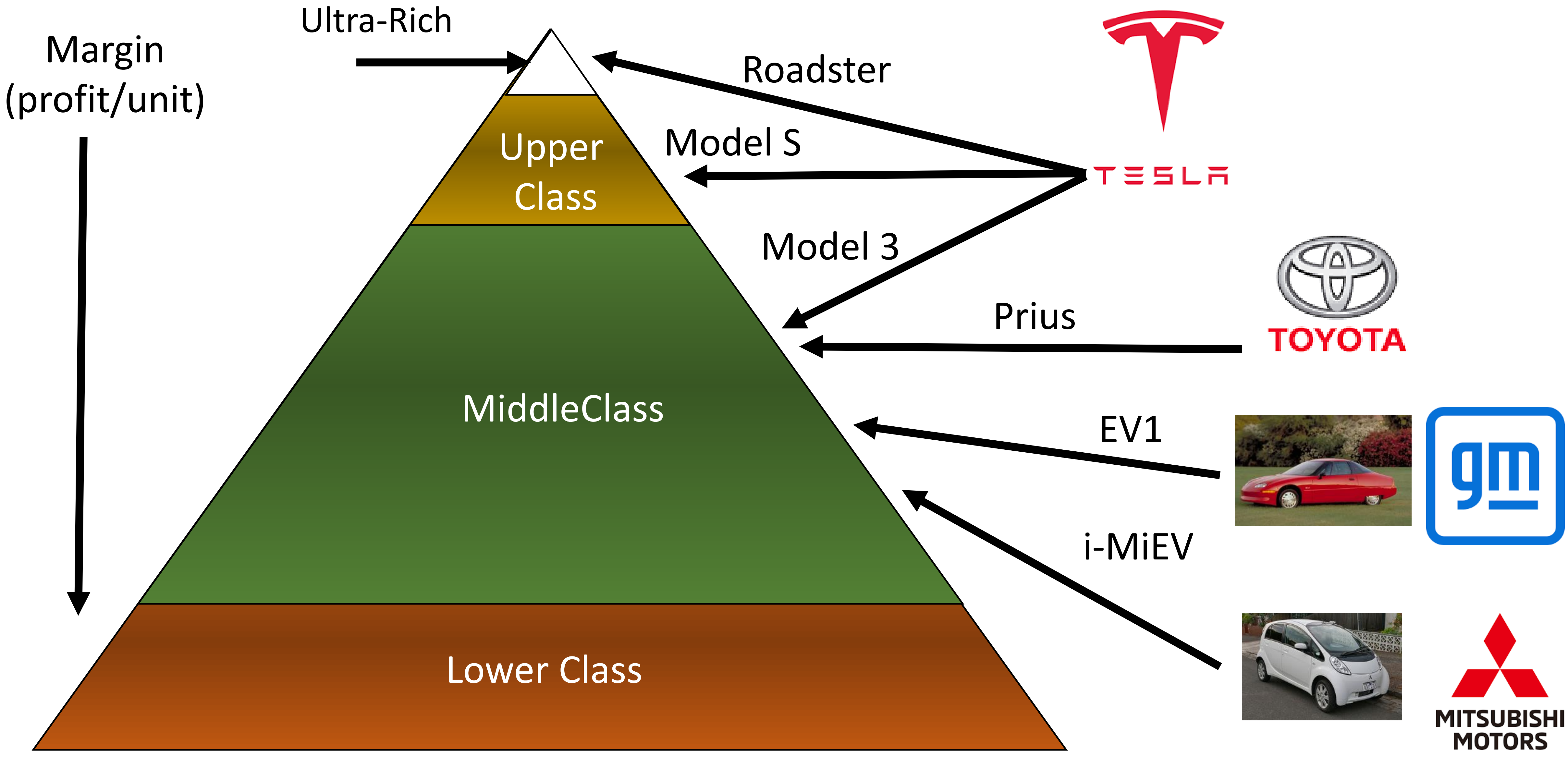
Brian Seger

SurfCat Summer School

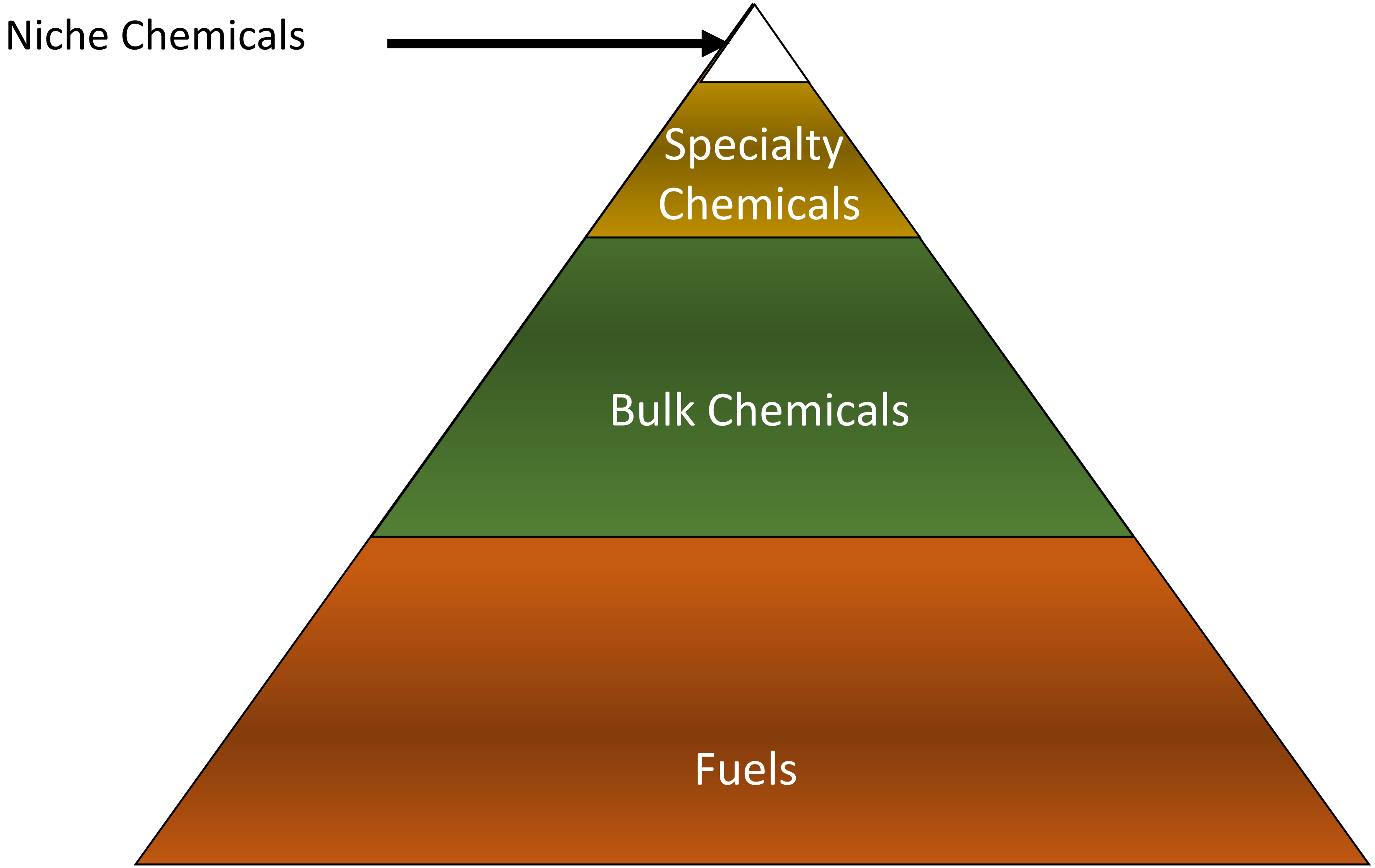
August 11, 2022, right before lunch



Electric Cars

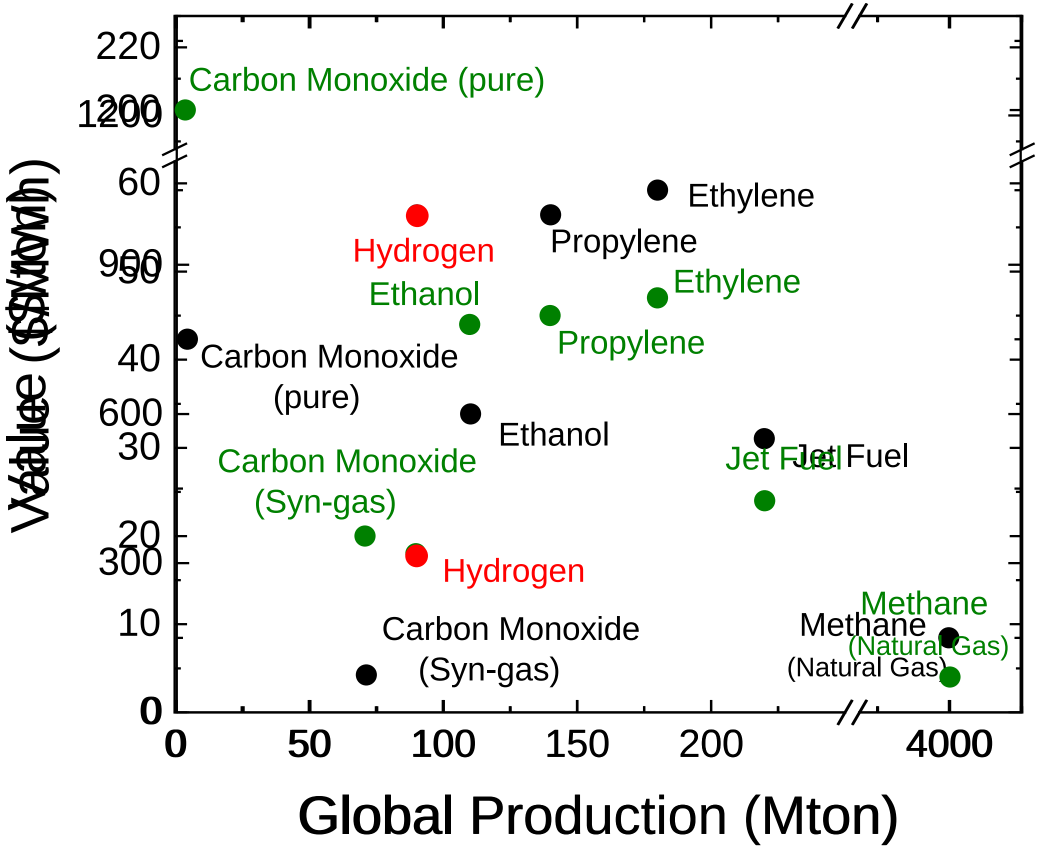


Carbon Based Products



What are we trying to do it

- Chemicals are 7% of EU's greenhouse gasses emissions



Applications of chemicals

Ethylene → Plastics

Propylene → Plastics

Ethanol → Fuel, Solvent

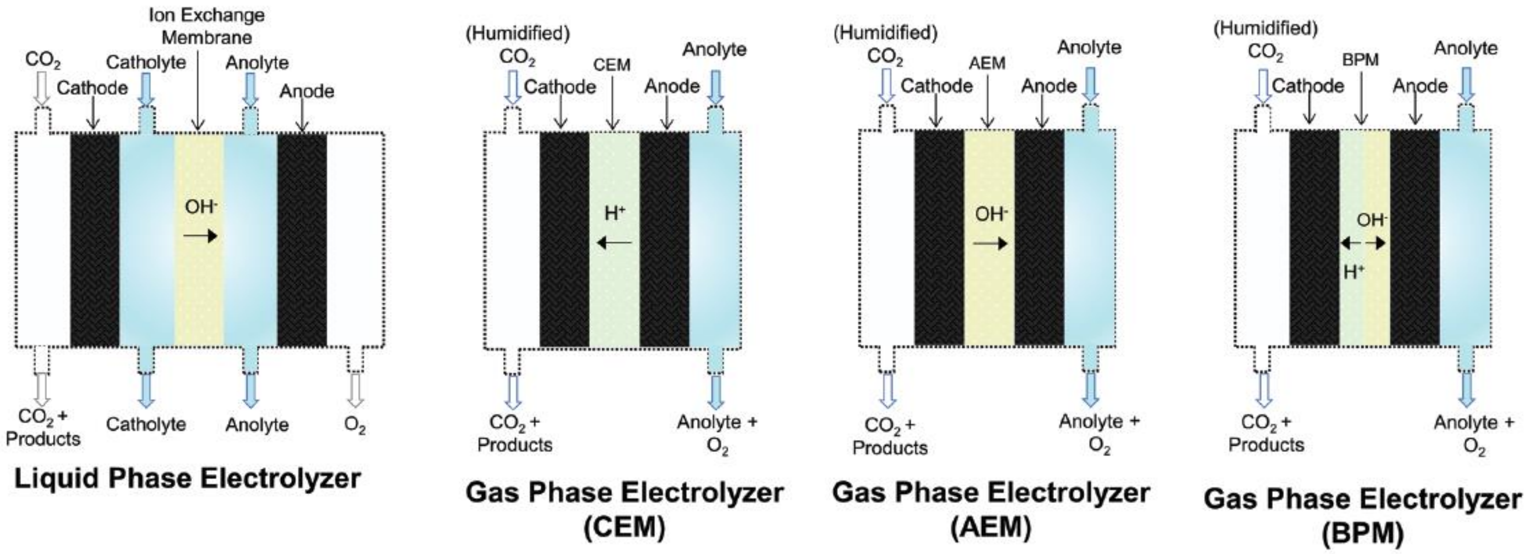
Methane (Natural gas) → Burning

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

Industrial relevant approaches to CO_2 electrolysis

Advantages:

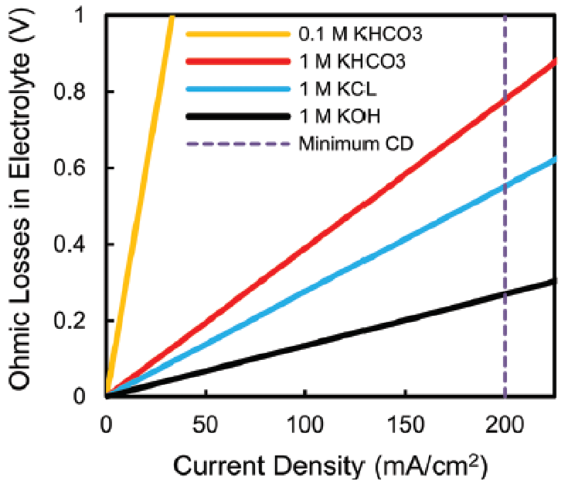
Liquid Product Extraction | Low ohmic loss, stable | Helps selectivity | Cheaper anode



High ohmic losses | Non-H^+ crossing over membrane | CO_2 crossover | Mechanical stability issues

Disadvantages:

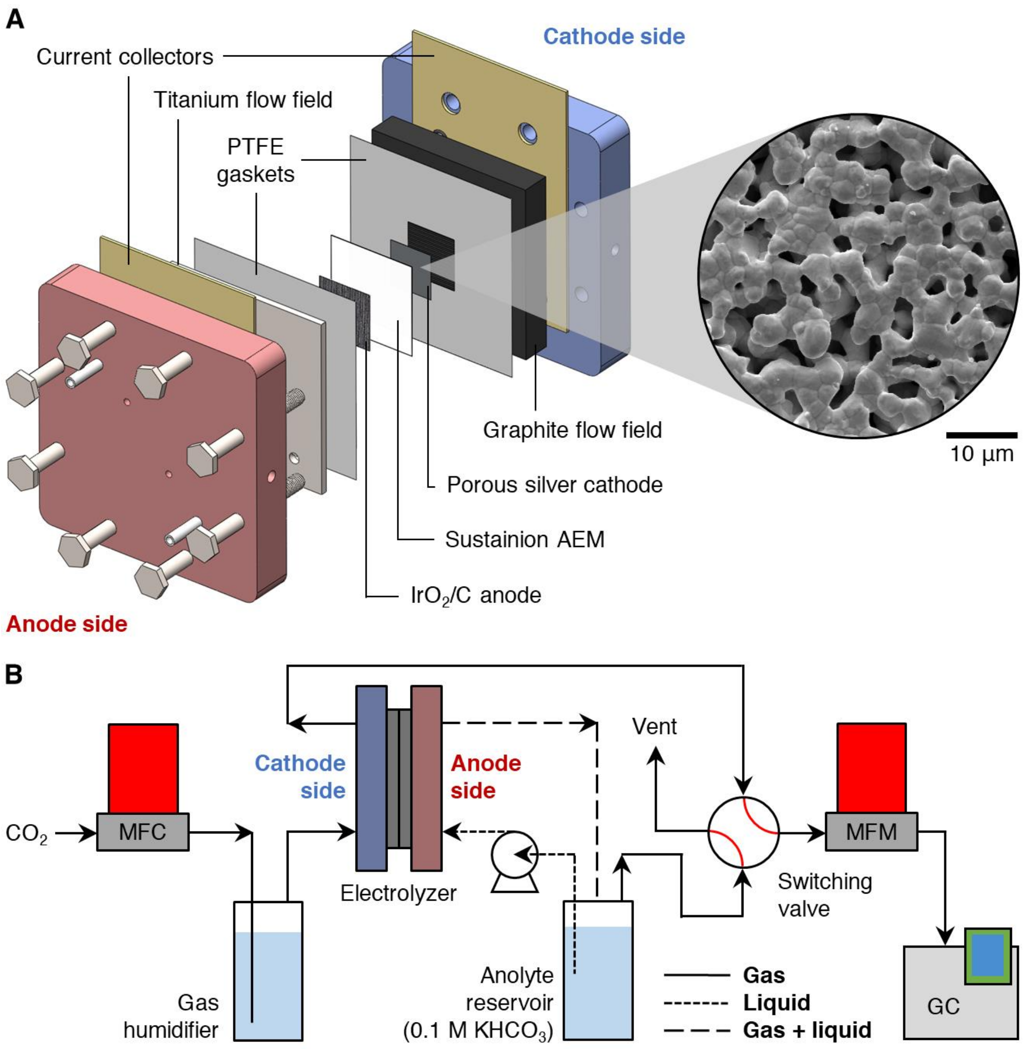
Kibria, et. al, Adv. Mat. , 1807166, (2019)

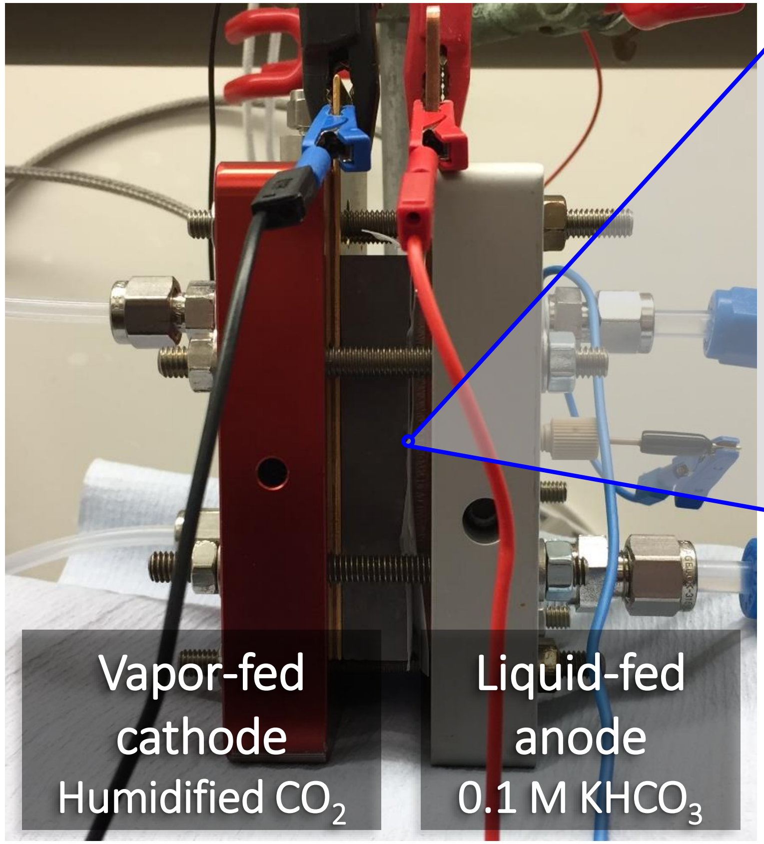


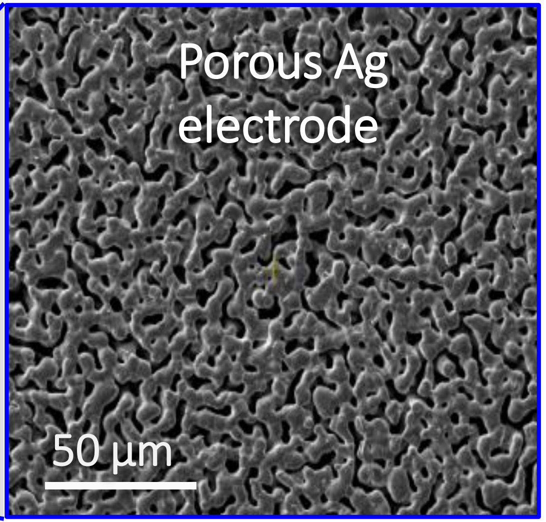
3 mm anolyte & catholye

Burdyny and Smith, E&ES, 12, 1442—1453, (2019)

Electrochemical set-up







Cathode: silver membranes of 50 μm thickness

Anode: IrO_2 on carbon paper

Membrane: Sustainion 37-50 AEM

Temperature: 30 C

Issues with outlet flow rate

- It is not straightforward to measure outlet flow rate

Inaccurate

(? Δ in conductivity)

Gas	Thermal Conductivity (W/m K)
CO_2	0.017
CO	0.025
H_2	0.18

Inaccurate

(? Δ in viscoscity)

Gas	Viscosity (10^{-5} Pa s)
CO_2	1.47
CO	1.74
H_2	0.88

Issues with outlet flow rate

- It is not straightforward to measure outlet flow rate

Soap bubble
(positive displacement)

Accurate
(Positive Displacement)
MESA Labs- Defender 530

Accurate (Buoyancy)
Bioprocess Control µFlow

Product Line

N_2 Bleed line
(known flowrate)

Cathodic reactions

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

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

$CO_2 + H_2O + 2e^- \rightarrow HCOO^- + OH^-$

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

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

Anodic reactions

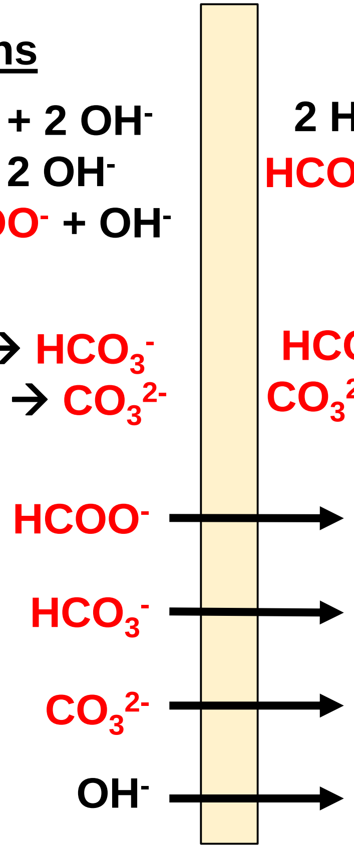
$2H_2O \rightarrow O_2 + 4e^- + 4H^+$

$HCOO^- \rightarrow CO_2 + 2e^- + H^+$

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

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

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



Anion exchange membrane

- We define an ‘A’ value is the number of CO_2 crossover per e^- transferred

$A=0 \rightarrow OH^-$

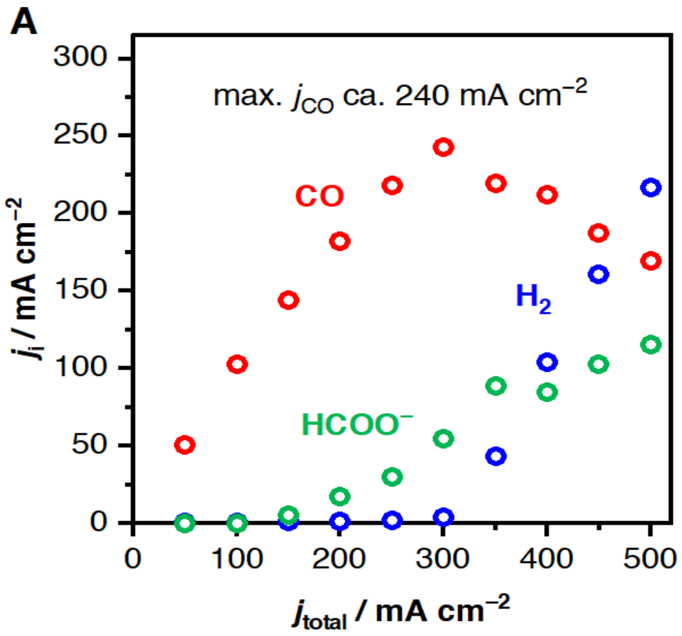
$A=1/2 \rightarrow CO_3^{2-}$

$A=1 \rightarrow HCO_3^-$

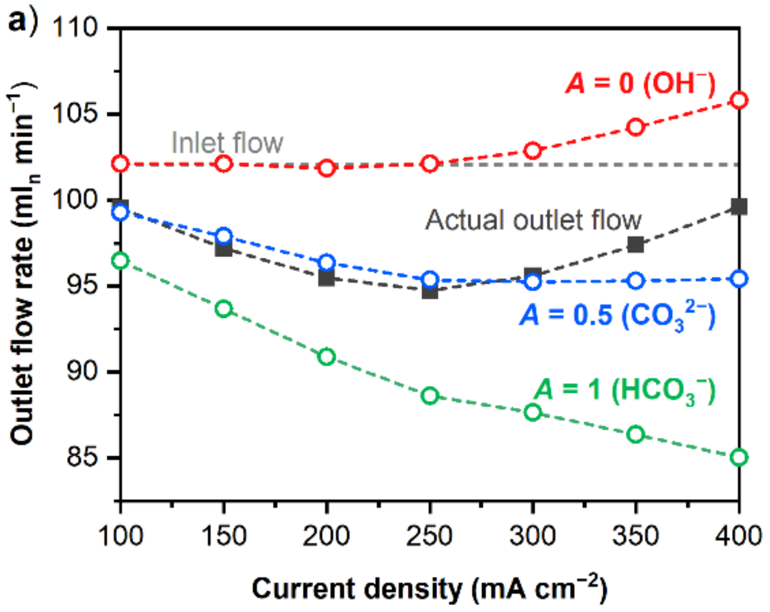
$$Q_{gas,out} = Q_{gas,in} - \frac{RT}{PF}\left[\sum_0^i I_i \frac{\#C_{liq,i}}{\#e^-_{liq,i}} + \sum_0^j I_j\left(\frac{\#C_{gas,j} - 1}{\#e^-_{gas,j}}\right) + A\left(I_{Total} - {}^1\!/_2\, I_{Formate} - {}^1\!/_8\, I_{acetate}\right)\right]$$

Measuring cathodic products

- Using Ag membranes as catalysts gave good, but not great performance.
- We attributed unknown partial current density to formate.
- By measuring our cathodic outlet flow, we were able to determine an ‘A’ value.



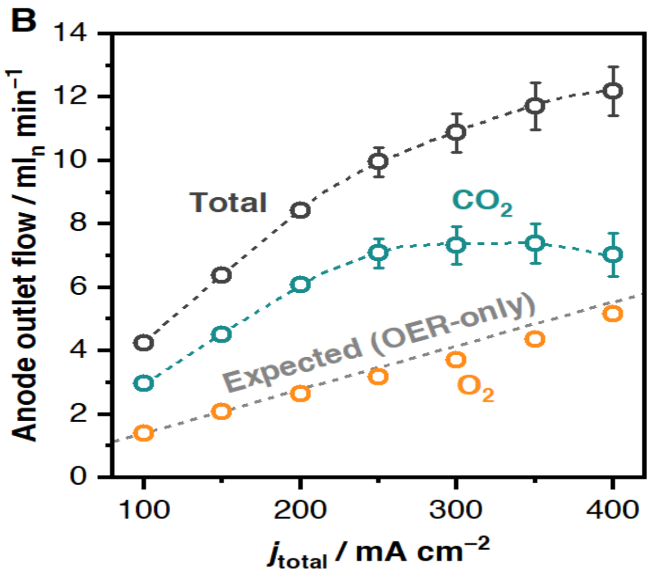
Larrazabal, G., et al., *Appl. Mat. & Int., 2019*



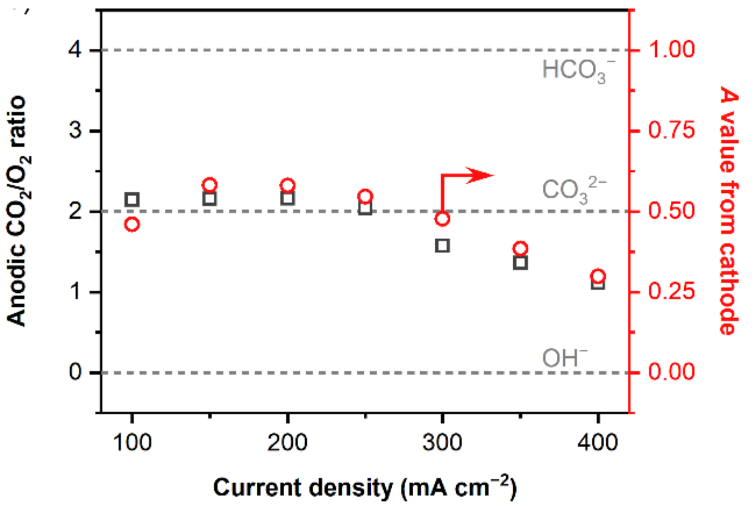
Larrazabal, G., et al., *Account. Mat. Res., 2021*

Measuring anodic products

- By measuring our anodic outlet flow we can get the amount of oxygen produced.
- We can correlate our CO_2/O_2 ratio to what species is predominately going through the membrane.



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

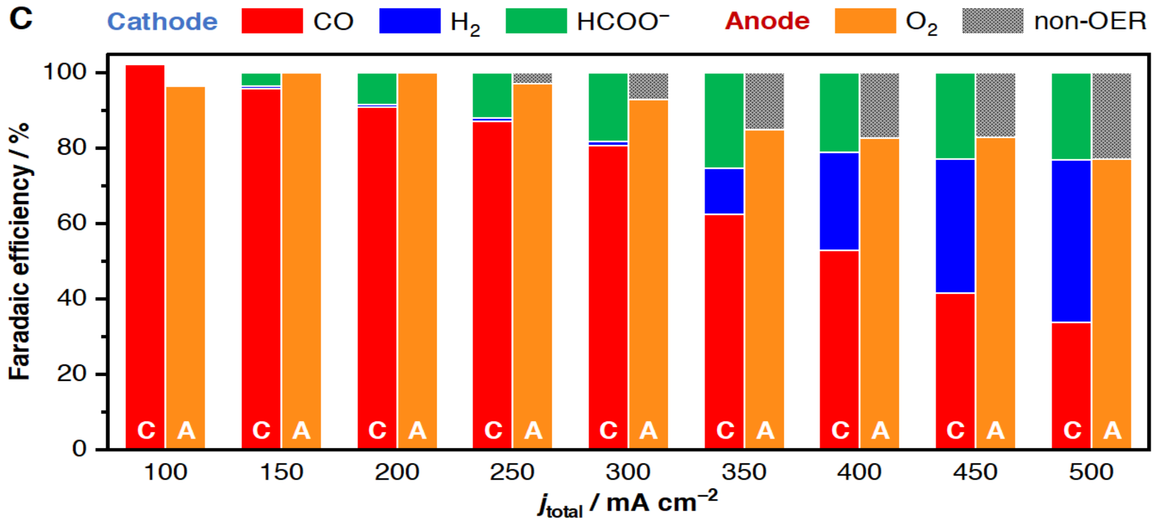


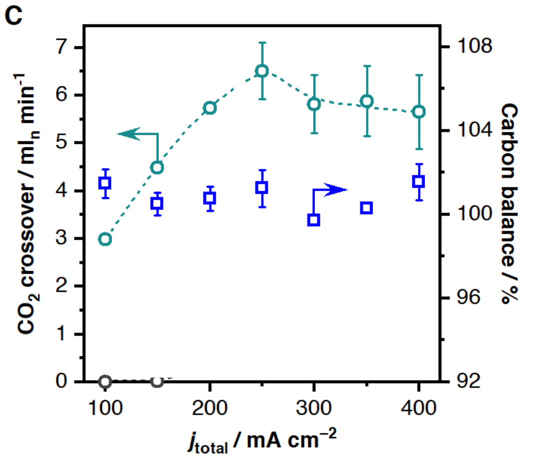
Larrazabal, G., et al., *Account. Mat. Res., 2021*

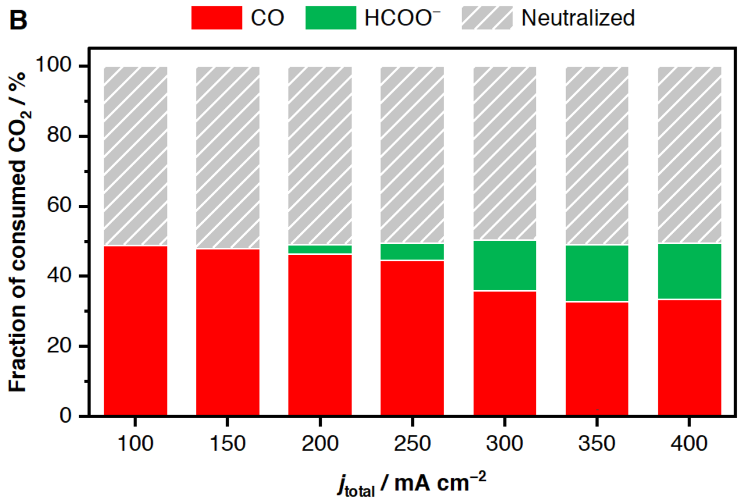
Total system analysis

- 100% faradaic efficiency is great to see

- Full carbon balance is just as important to see.







Larrazabal, G., et al., *ACS Appl. Mat & Int., 2019*

Formate: Not a wanted product

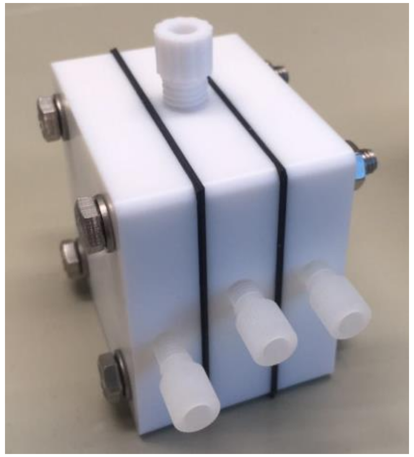
- We never produce formate, but rather postassium formate
- Where does the K^+ come from?
- $KHCO_3$ is usually the source.

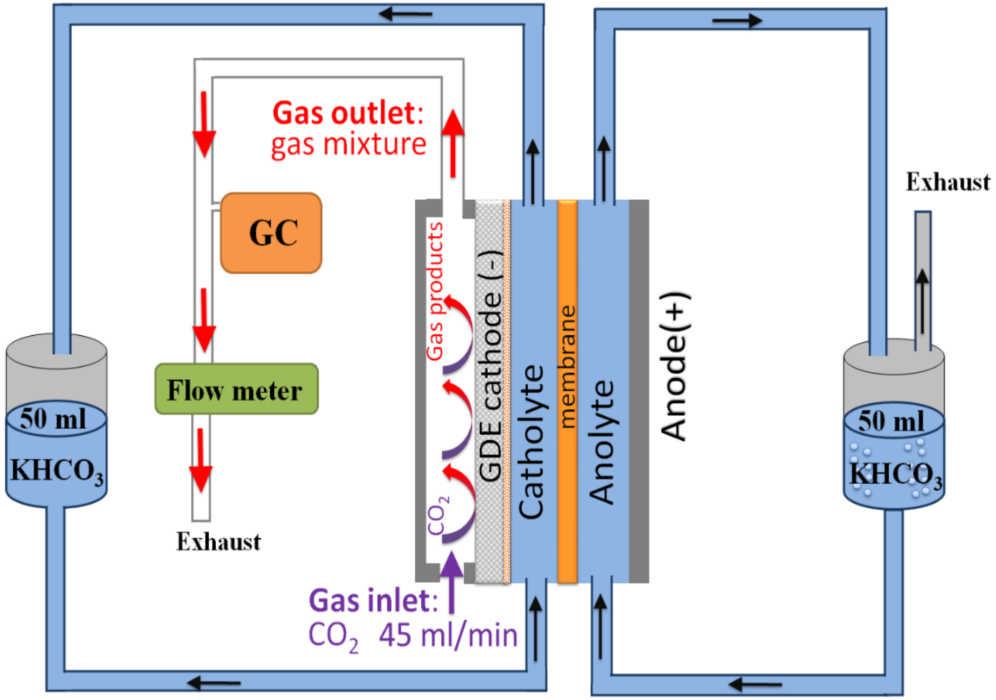
$$KHCO_3 + CO_2 \rightarrow KCOOH + {}^{1}/_{2}\, O_2 + CO_2$$

Name	**Value ($/Kg) Aldrich**	**Value ($/kmole)**
Potassium bicarbonate	120	1.20
Potassium formate	100	1.19

Analyzing copper for CO_2 reduction

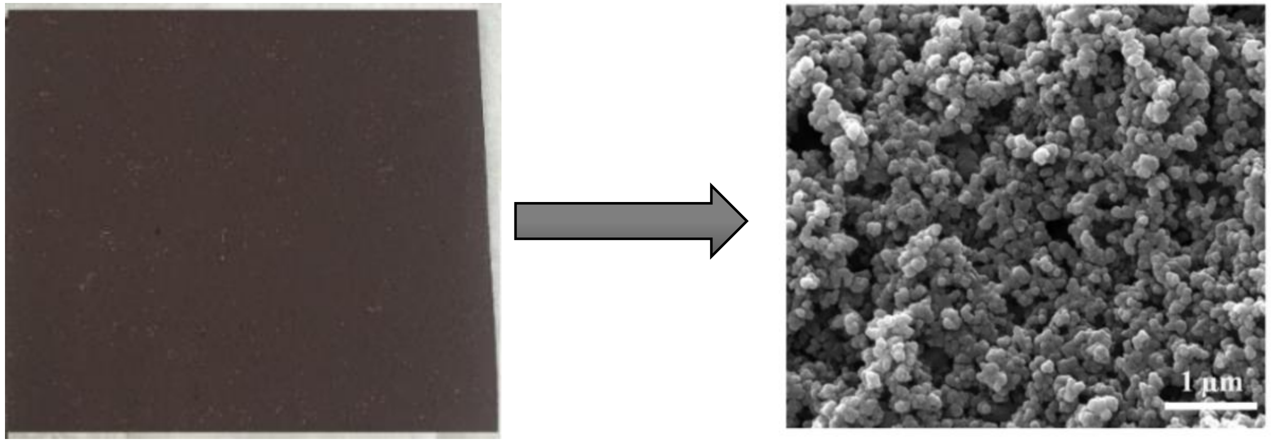
- With copper producing liquid products, we decided to go with a GDE approach.
- 70 nm sputtered Cu on a gas diffusion layer.





Electrode

SEM



Testing different electrolytes

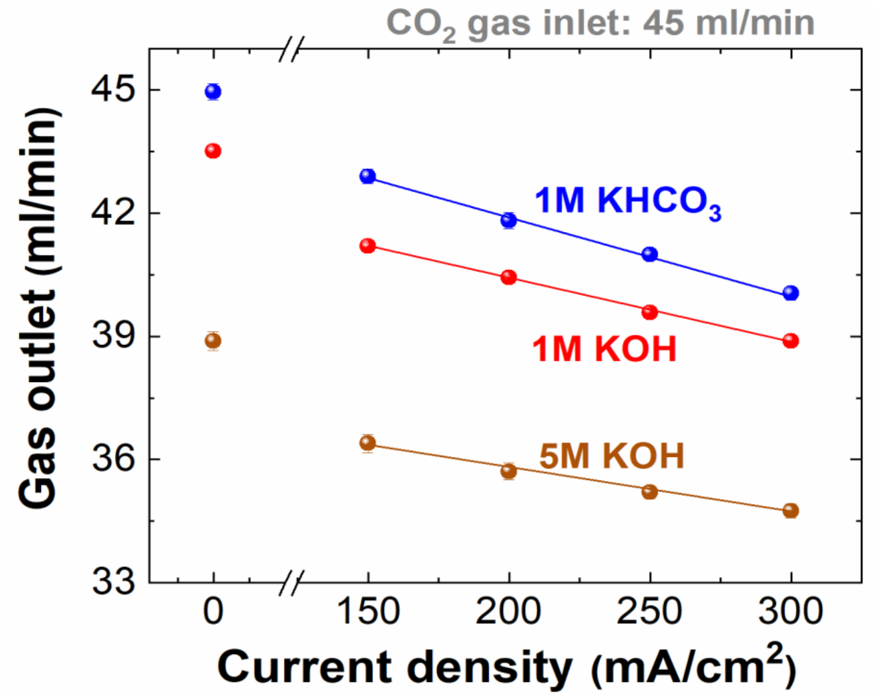
- We tested in both neutral and basic electrolytes.
- Basic electrolytes are effectively ‘ CO_2 scrubbers’

$$CO_2 + OH^- \rightarrow HCO_3^-$$ pKa (effective)=7.8

$$HCO_3^- + 2OH^- \rightarrow CO_3^{2-} + H_2O$$ pKa = 10.3

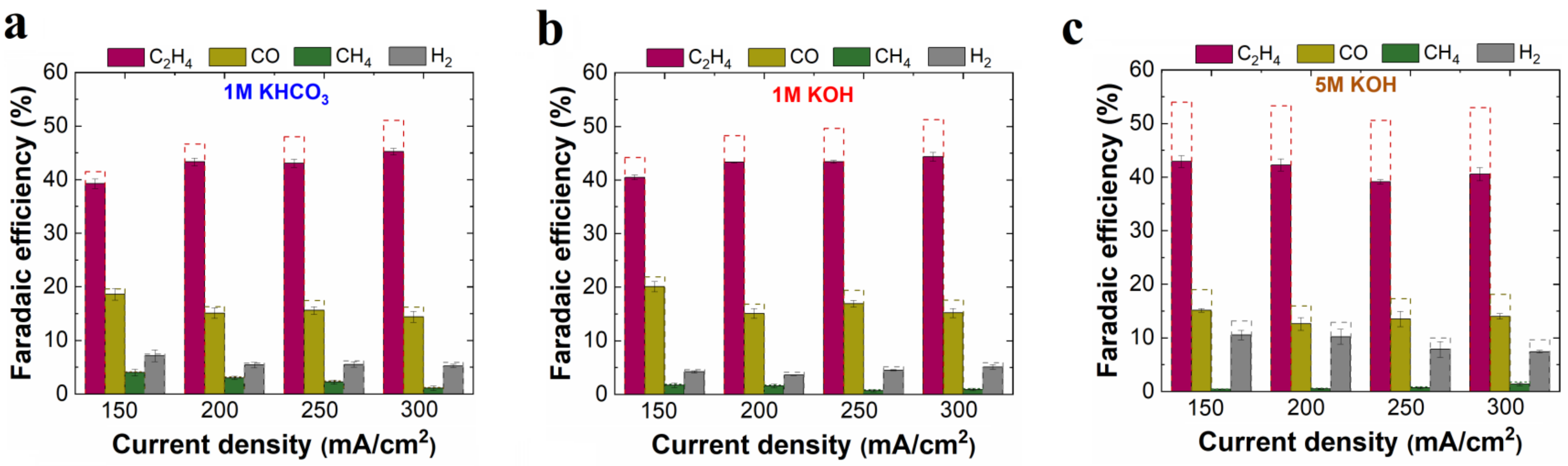
- Even at open-circuit, significant CO_2 is consumed.
- CO_2 reduction naturally produces OH^-, thus increasing ‘scrubbing’ capability of catholyte gas

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



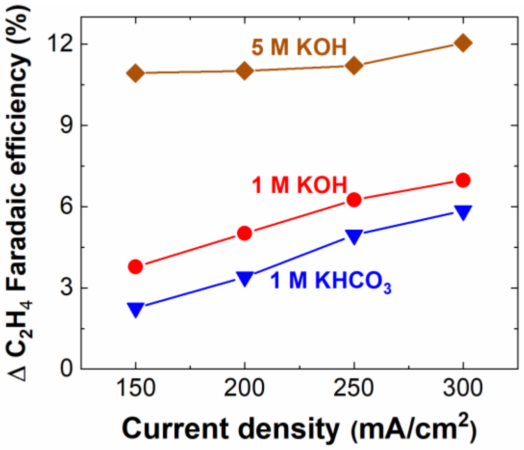
Ma, M., et al E&ES 2020
Doi:10.1039/D0EE00047G

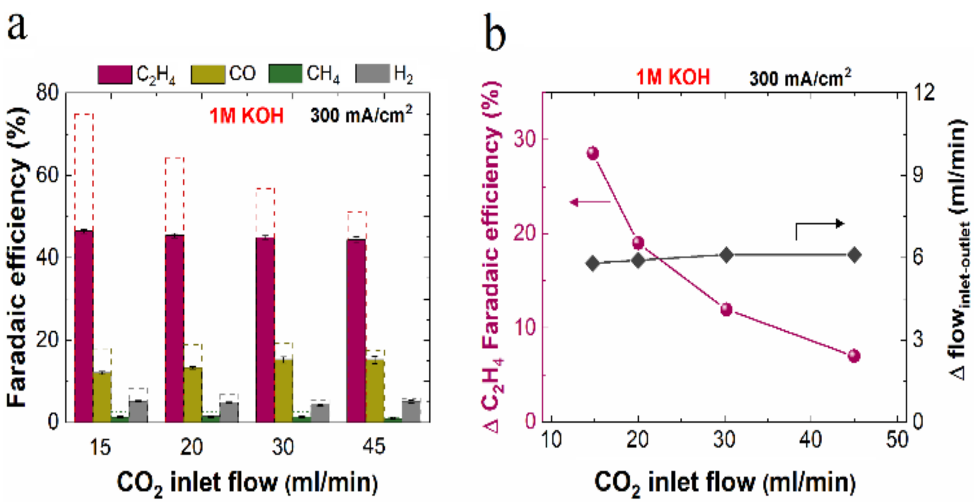
Comparison of selectivites in different electrolytes



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

Compared to uncorrected for outlet flow rate

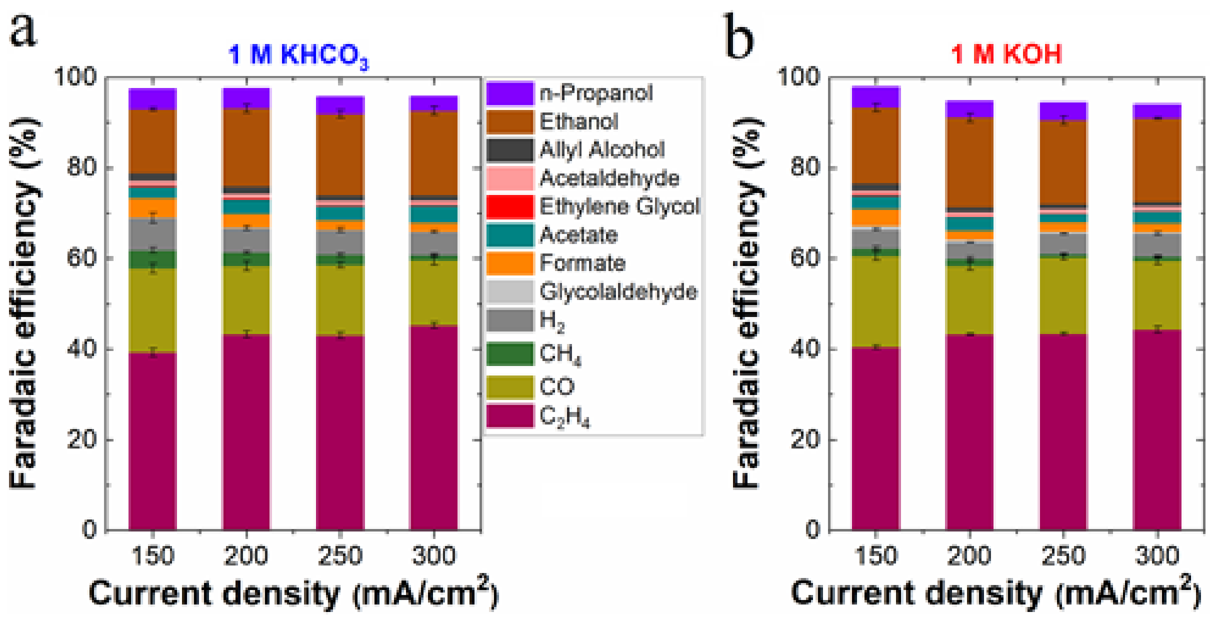


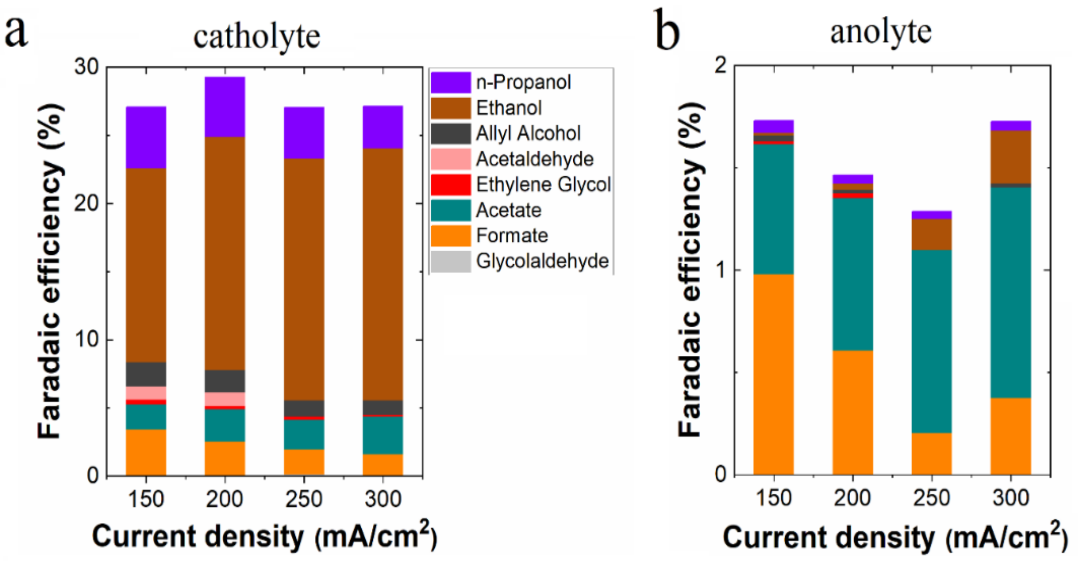


Ma, M., et al., *E&ES,2020*

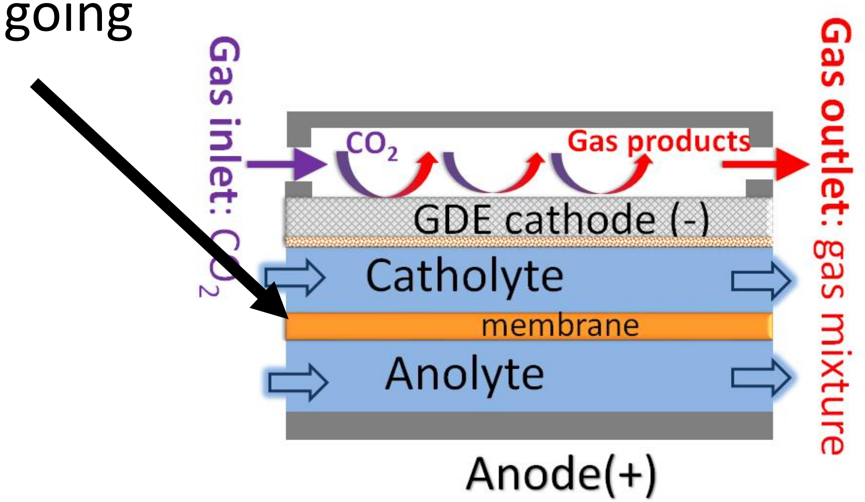
Liquid selectivites

- We see 8 different liquid products
- Minimal variation at different current regimes.
- We see significant products coming out the anode.



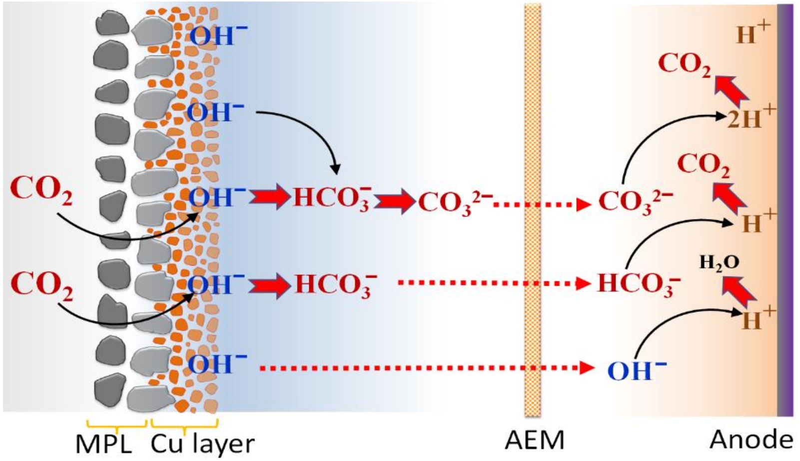


What is going on here

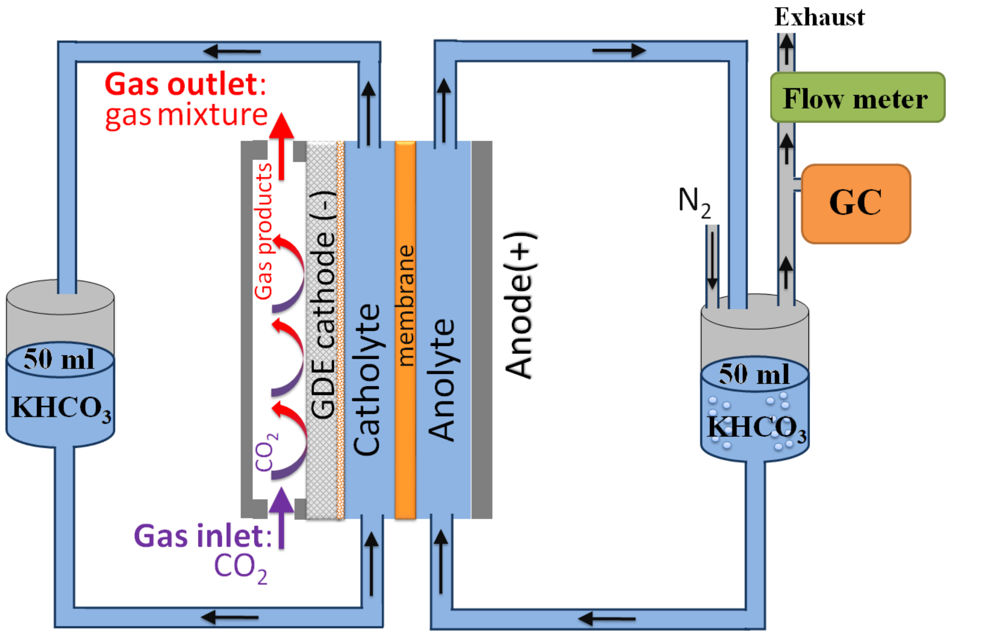


Ma, M., et al., *E&ES,2020*

Understanding membrane crossover



Proposed carbon balance paths via CO_3^{2-} or HCO_3^- formation from CO_2 and a subsequent CO_2 production from CO_3^{2-} or HCO_3^-



Anode reactions:

CO₂/O₂ ratio

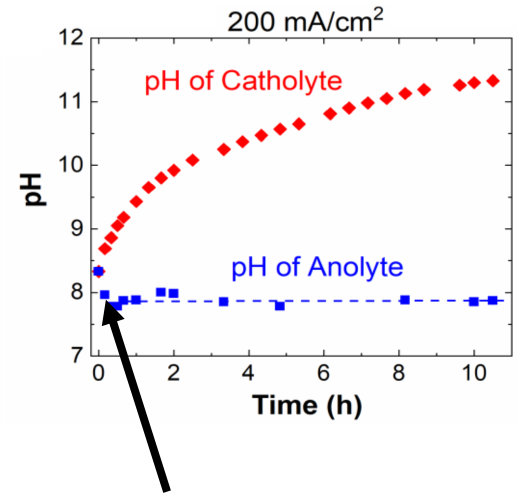
$$4HCO_3^- \rightarrow 4\,CO_2 + O_2 + 2H_2O + 4e^- \longrightarrow 4$$

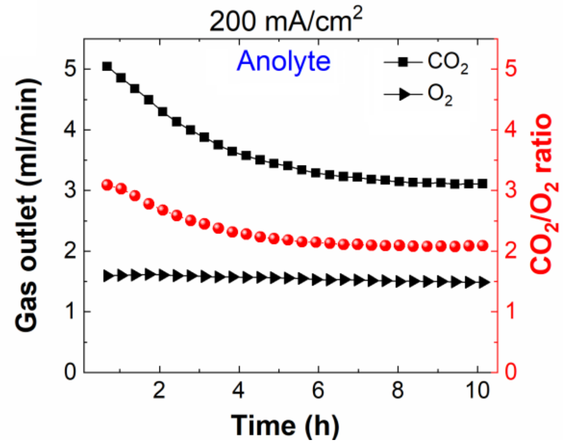
$$2CO_3^{2-} \rightarrow 2CO_2 + O_2 + 4e^- \longrightarrow 2$$

$$4OH^- \rightarrow 2H_2O + O_2 + 4e^- \longrightarrow 0$$

$$4COOH^- \rightarrow 4HCOOH + O_2 + 4e^- \longrightarrow 0$$

$$4CH_3COO^- \rightarrow 4CH_3COOH + O_2 + 4e^- \longrightarrow 0$$

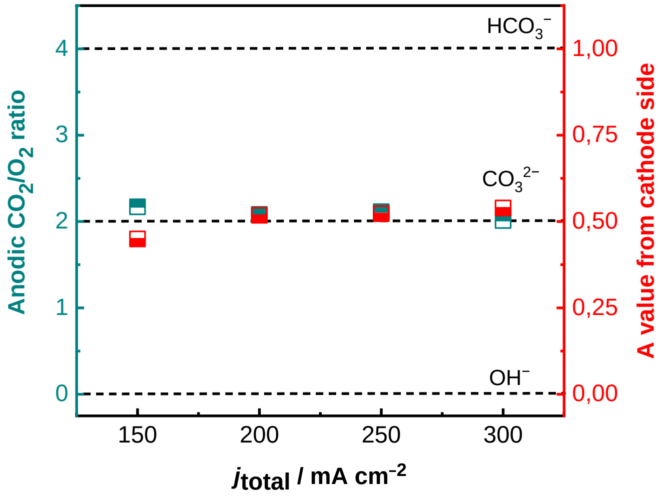




pKa of HCO_3/CO_2 = 7.8

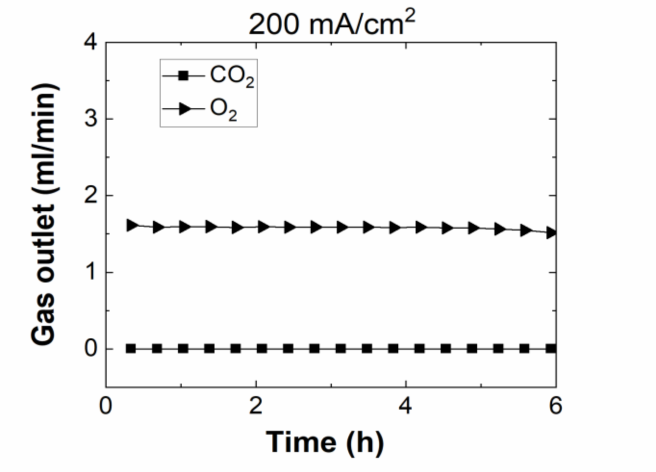
Ma, M., et al., *E&ES, 2020*

- Did our 'A' value line up with our CO_2/O_2 ratio

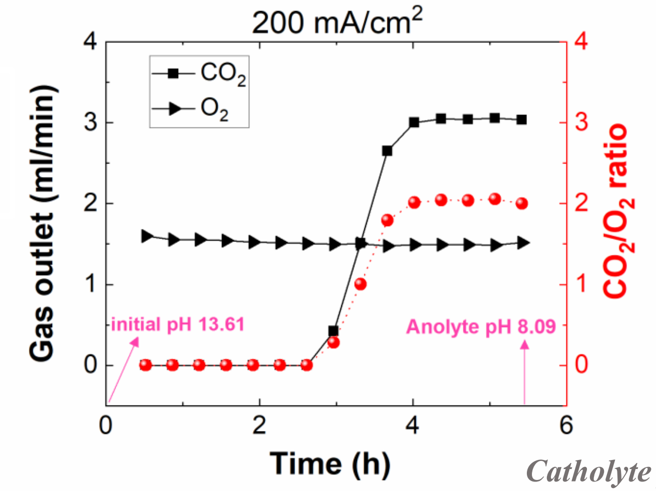


- With basic electrolytes there is no CO_2 emitting from anolyte.
- A smaller reservoir shows CO_2 just needs to satruate the solution.

Initial solutions:
50 ml 1 M KOH catholyte
50 ml 1 M KOH anolyte



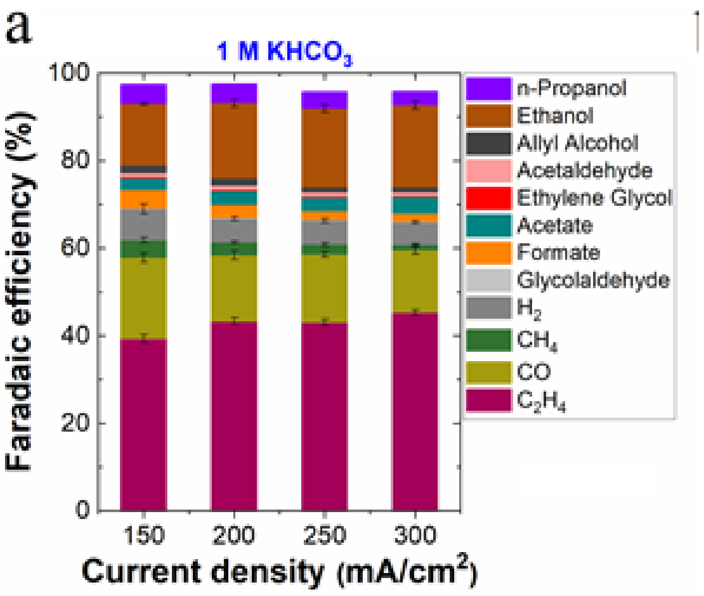
Initial solutions:
20 ml 1 M KOH catholyte
20 ml 1 M KOH anolyte

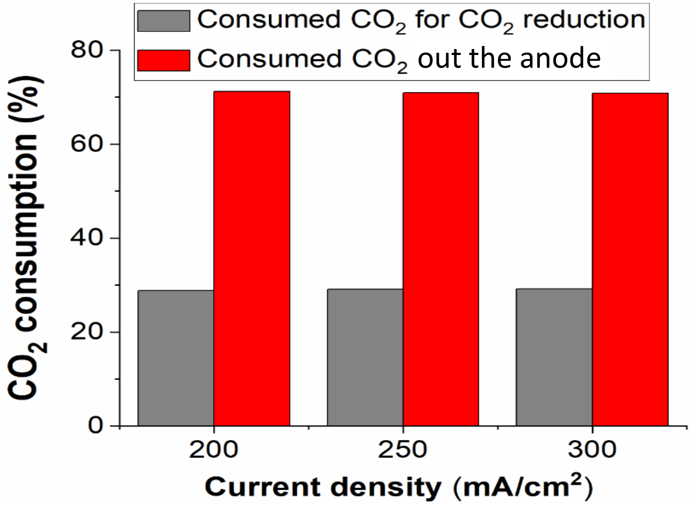


Catholyte pH reduced to 11.6

Device analysis

- 100% faradaic efficiency
- Full carbon balance





Inlet CO_2 flow:
45 ml/min

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

J (mA/cm^2)	$\emptyset_{\text{unused}\ CO_2}$ (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	40.806	0.922	0.3387	3.11156	**45.178**
250	39.735	1.169	0.3928	3.80596	**45.103**
300	38.616	1.379	0.4779	4.50385	**44.977**

Using 1 M $KHCO_3$ as initial electrolyte

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

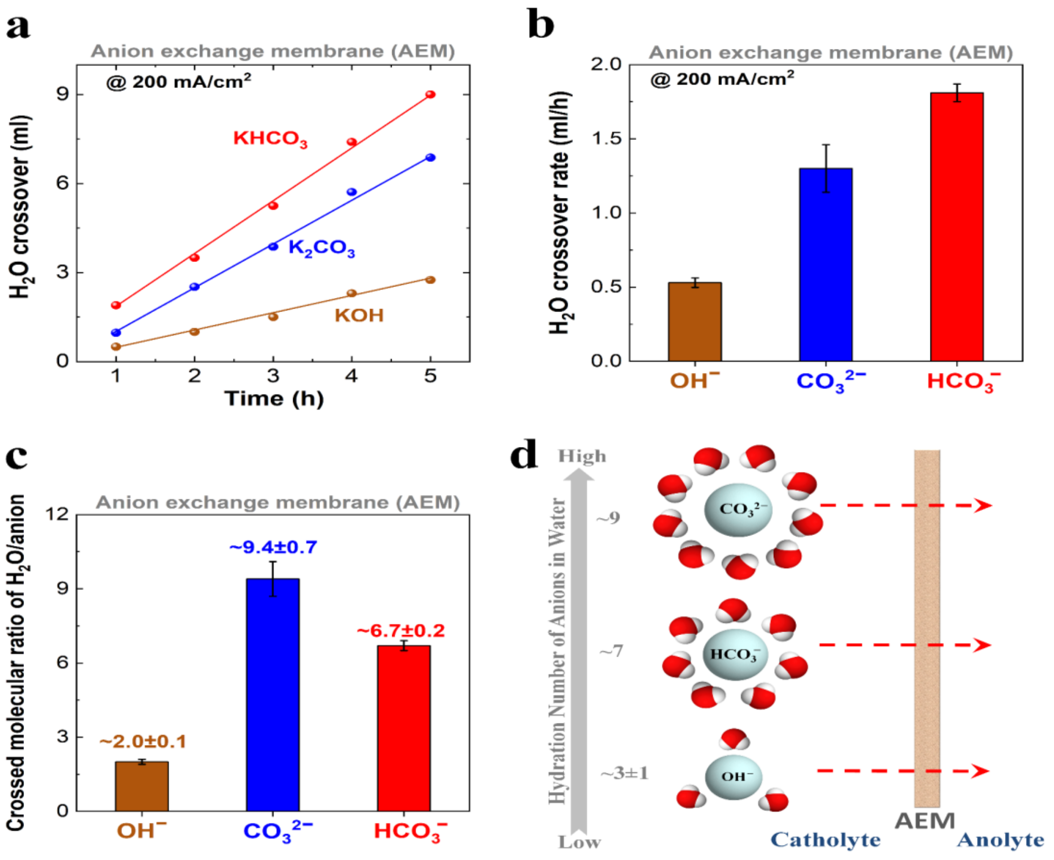
We still screwed up our analysis ?

- If we have a cell with 50 mL catholyte when we start, when we finish can we multiply our HPLC/NMR liquid product data on a final water volume of 50 mL?

- When carbonates transfer across the membrane it brings with it a lot of water

- We found the water crossover matches the free ion hydration number

- In other words, water transfer is membrane independent.

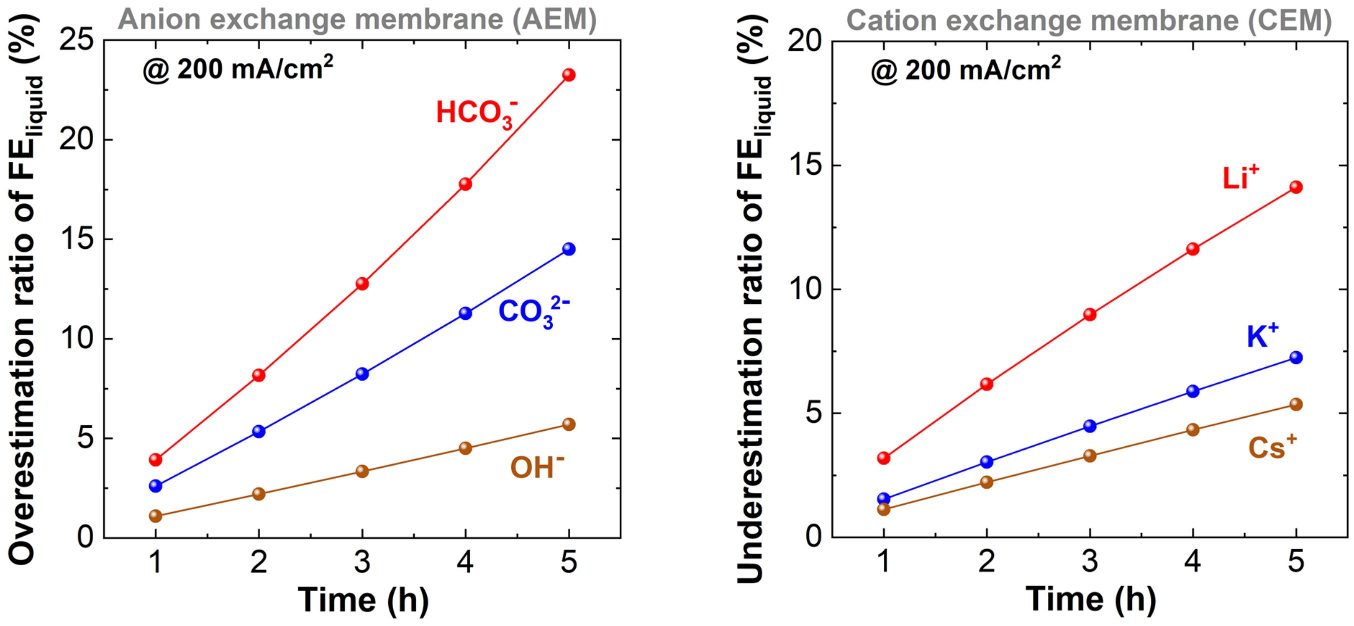


Ma, et al. ACS Energy Letters, 2022

How big of a screw up is this?

- The overestimation is not that big for shorter time period operations

- If a cation exchange membrane is used, non-compensated membranes will lead to an underestimation of produts

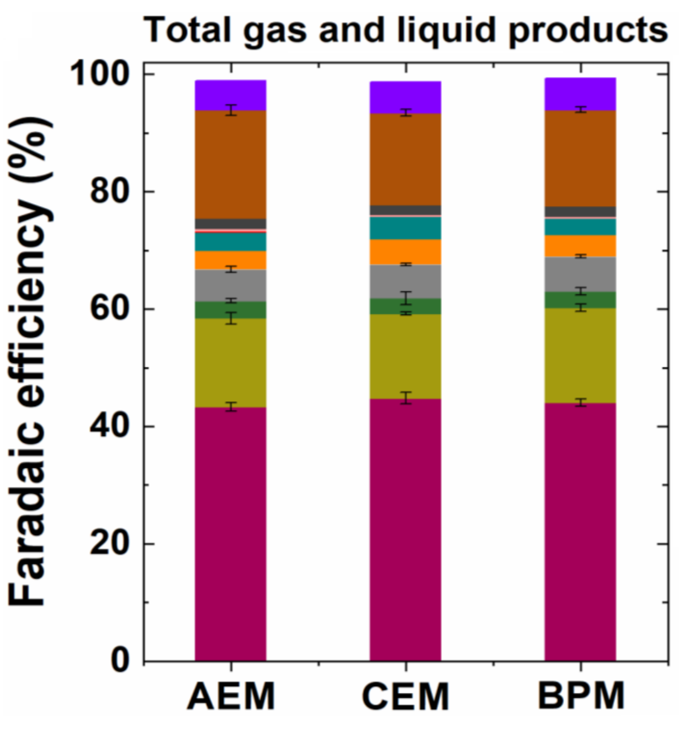


For 50 mL reservoirs and operating at 400 mA

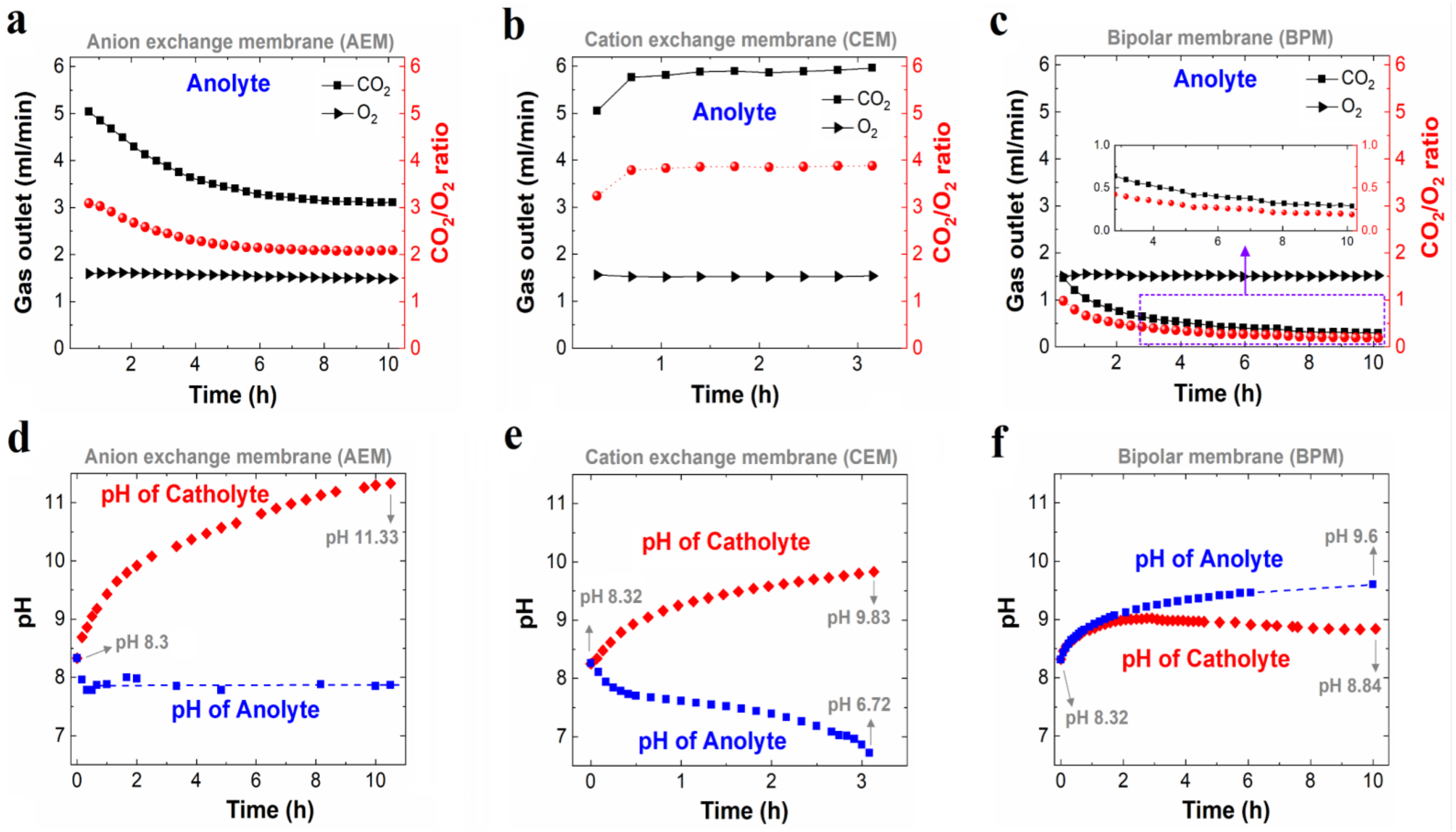
Ma, et al. ACS Energy Letters, 2022

How do CEM & Bipolar membranes compare ?

- Selectivity does not vary as long as you have a gapped cell (1cm for us).
- The CO_2 crossover is quite different.

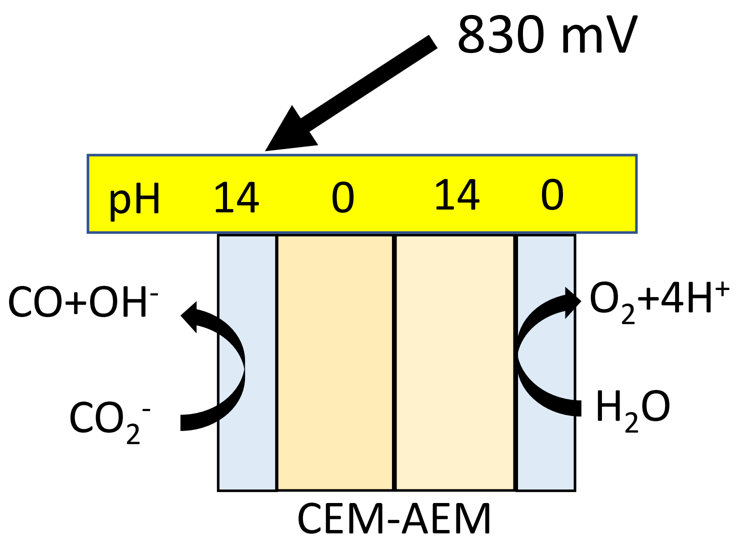


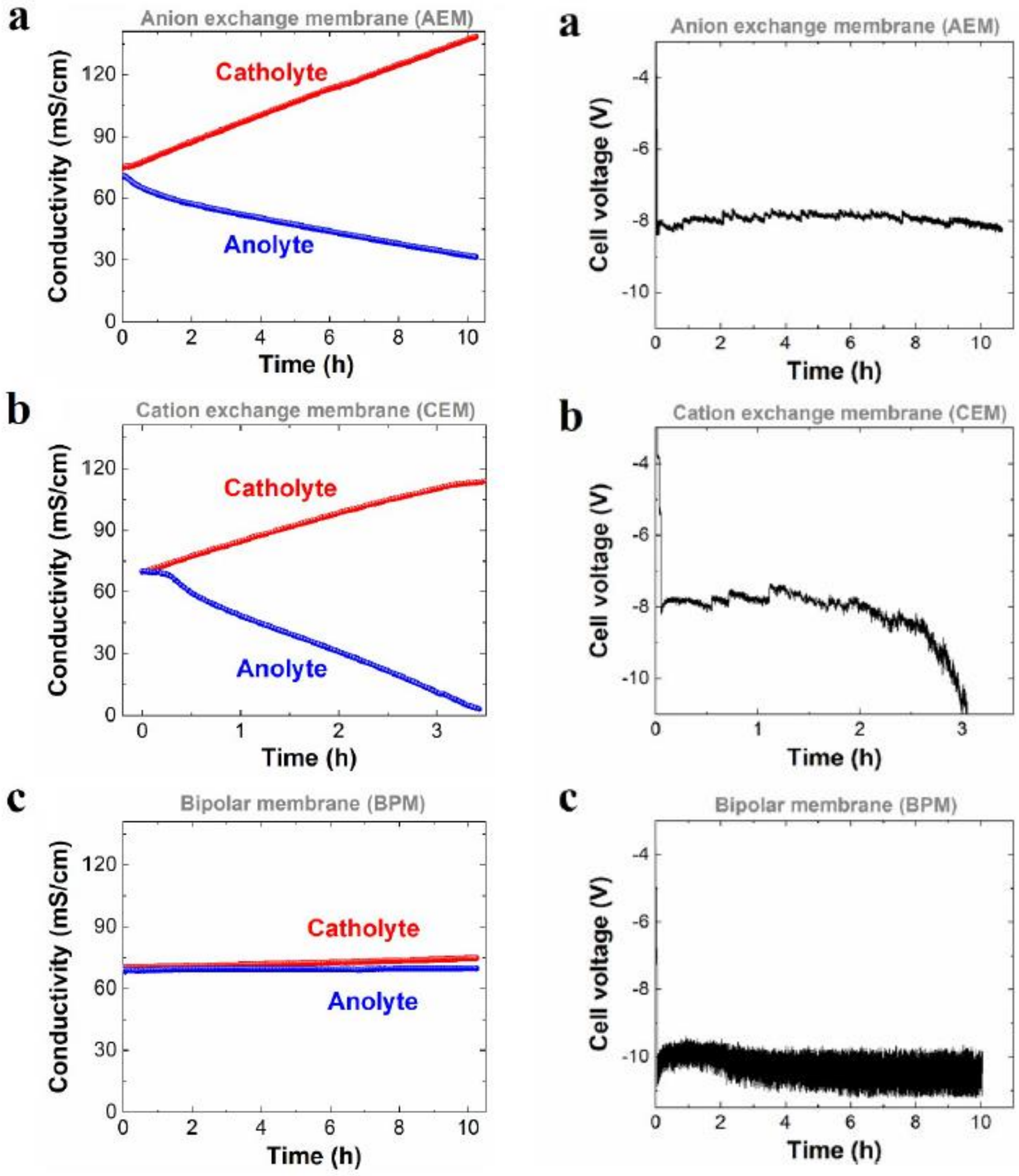
Ma, M., et al., *Chem. Sci., 2020*



Total cell voltage

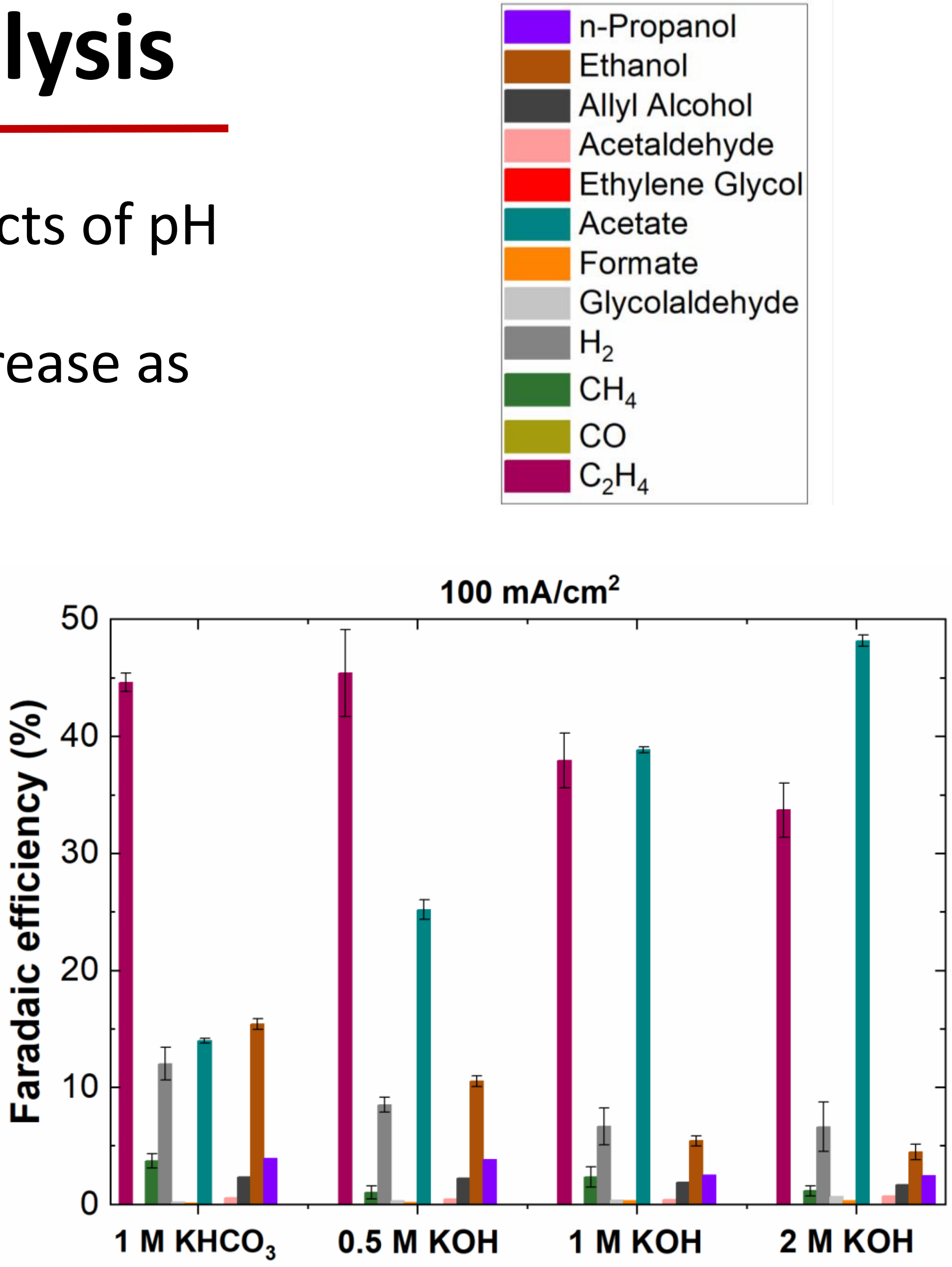
- Ohmic resistance in electrolytes dominate cell voltage.
- Conductivity does not account for water-splitting in BPM.
- CO electrolysis does not have these issues.



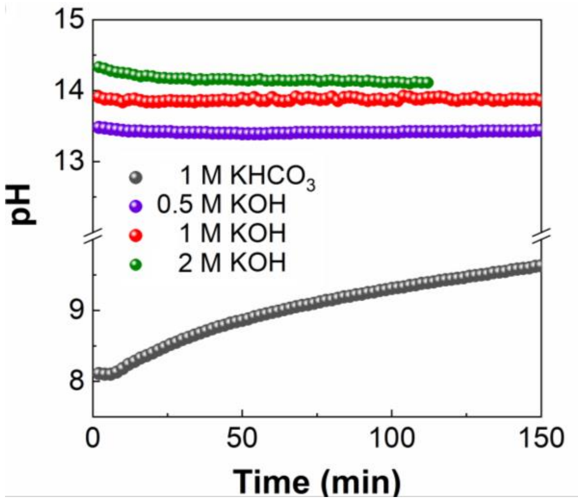


Varying alkalinity for CO electrolysis

- Transient tests (1 hour) allowed us to see the effects of pH
- Acetate increases whereas other C_2 products decrease as alkalinity increses
- Ethanol seems to decrease faster than ethylene
- Trends seem to be related to linear shift (rather than logarithmic) with alkaline concentrations.



@-1.42 V @-1.44 V @-1.44 V @-1.47 V

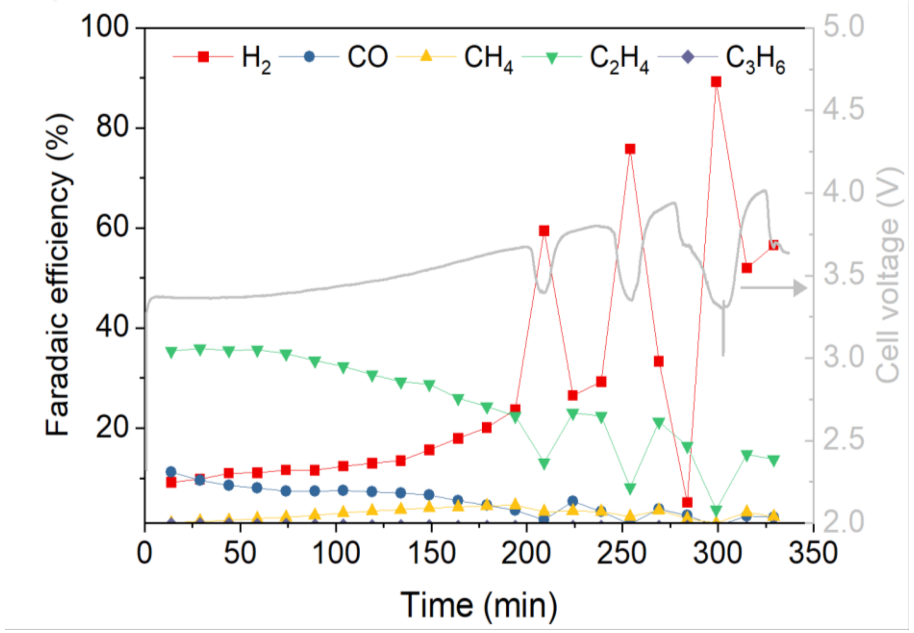


Ma et al., E&ES, 2022

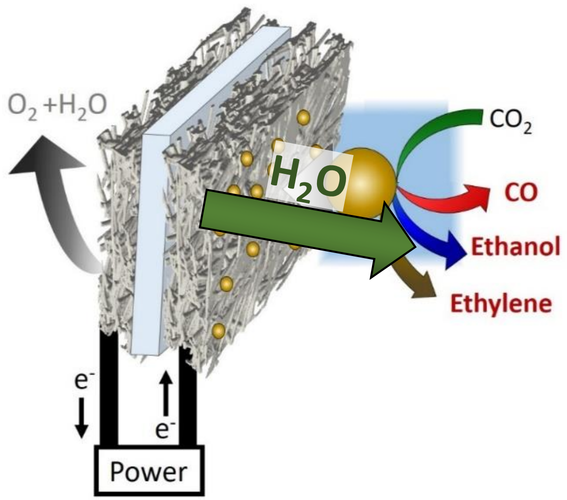
Understanding Degradation Mechanisms

Understanding 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 ?

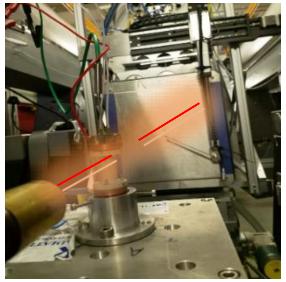


Designing a synchrotron experiment

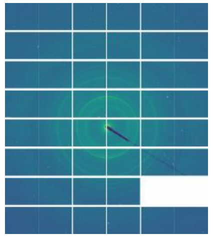
- We thought excess water may prevent efficient CO_2 mass transfer to the catalyst
- We used synchrotron X-ray scattering at ESRF to analyse this.

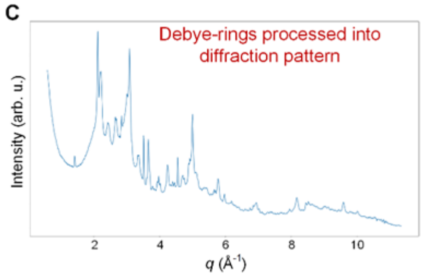
Synchrotron

Experiments

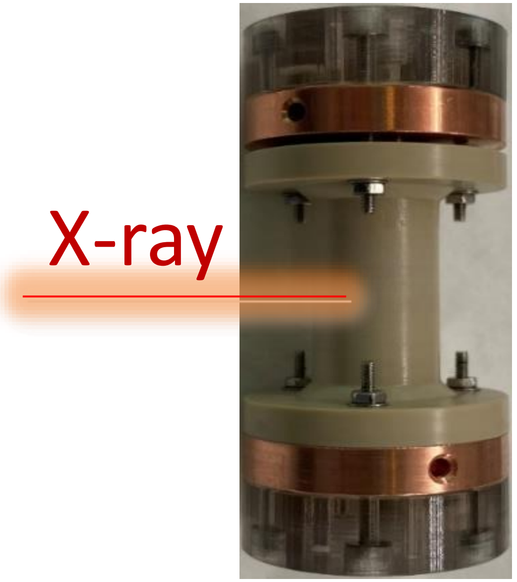


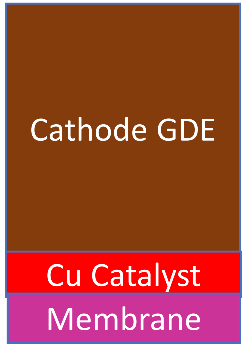
Raw X-ray results





CO_2 Reactor

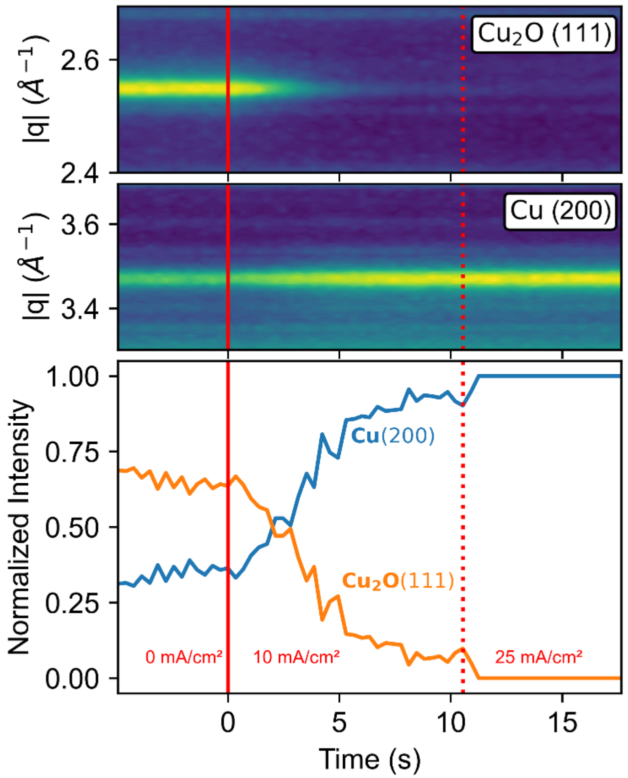


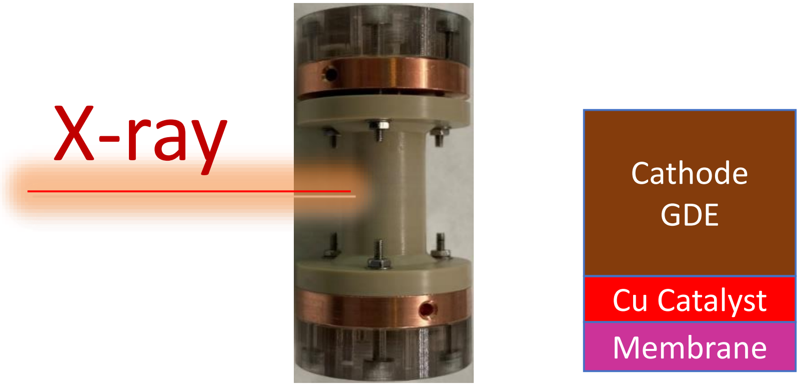


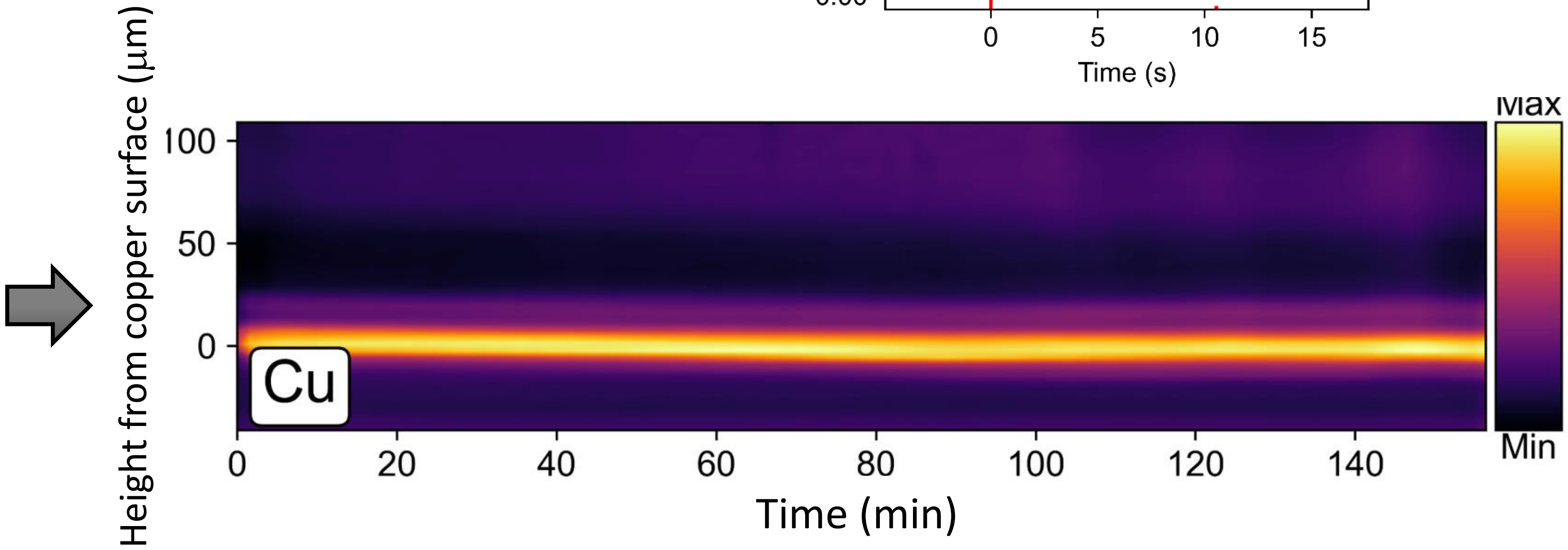
Analysing copper in our device

- 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







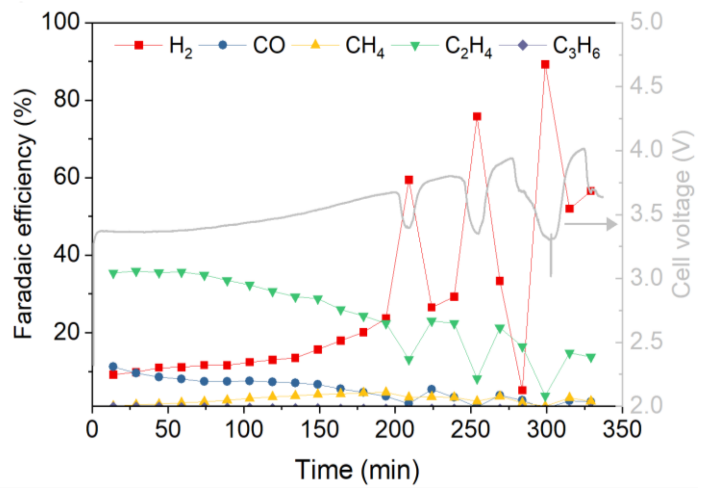
Analysing water

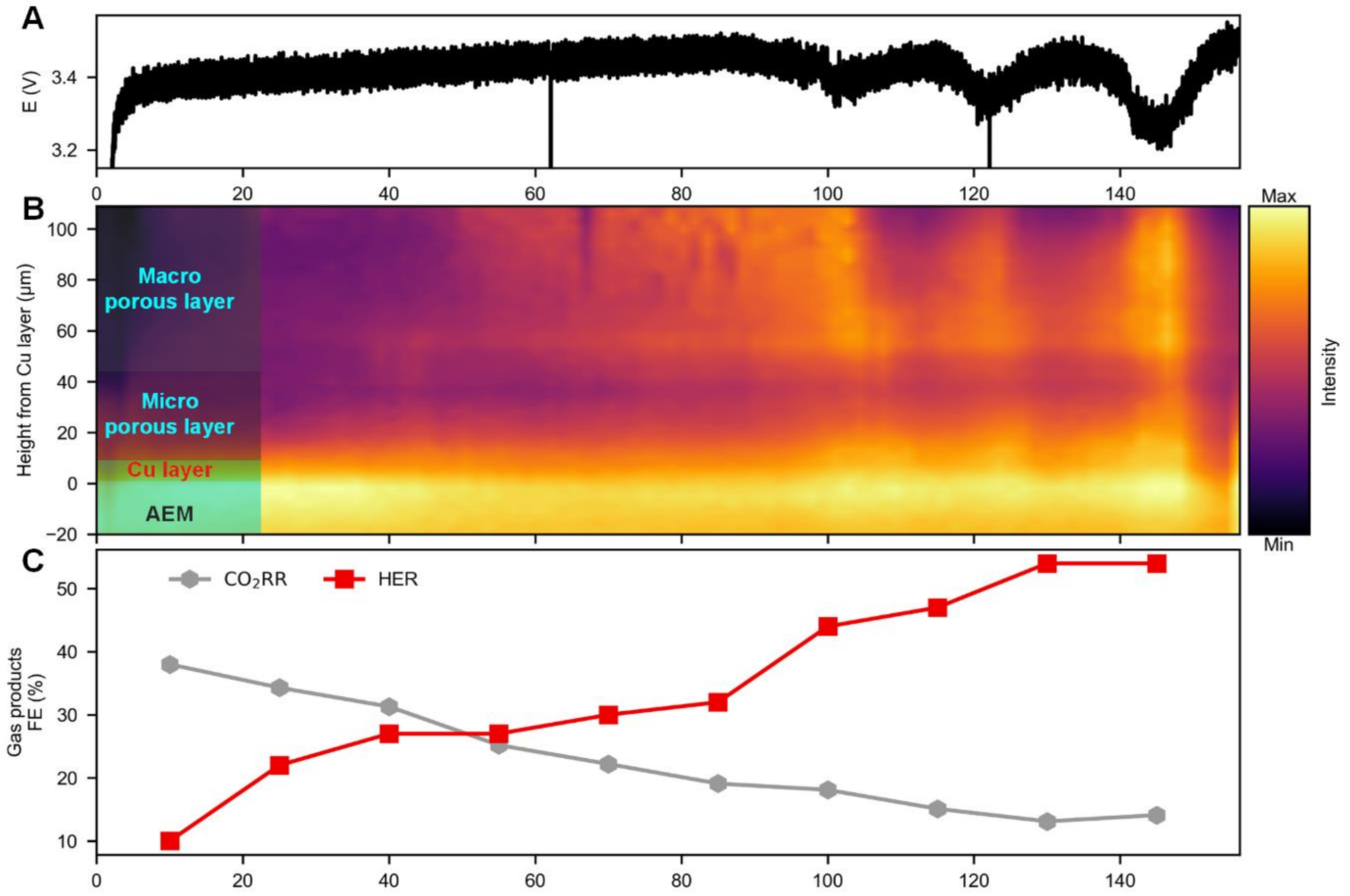
- By using variations in background signal in q-space where there are no Bragg peaks, we can use this as a proxy for water content.

- We can relate water content to potential variations.

- Lower potential, more water, more hydrogen.

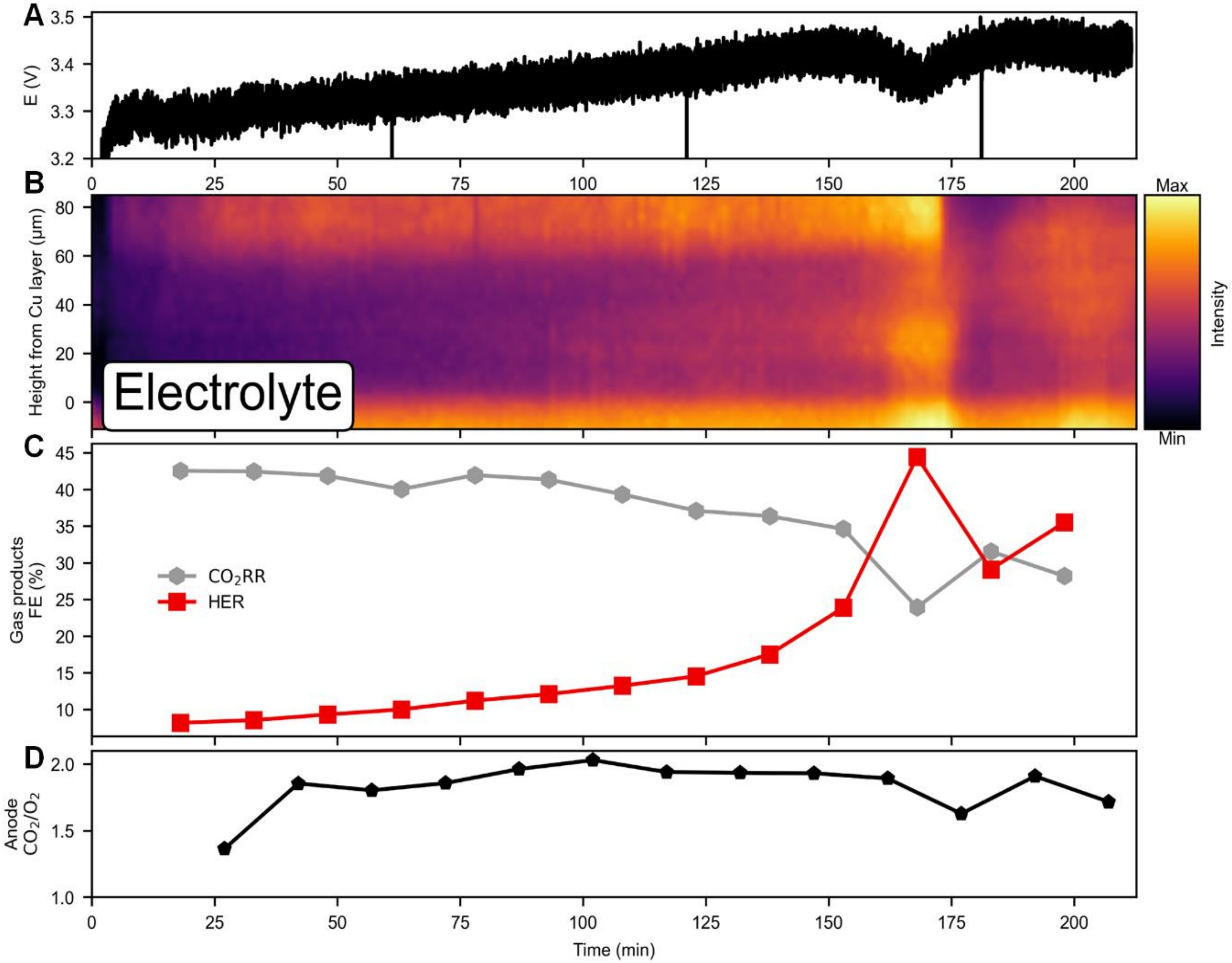
From earlier





Analysing CO_2 to O_2 ratio

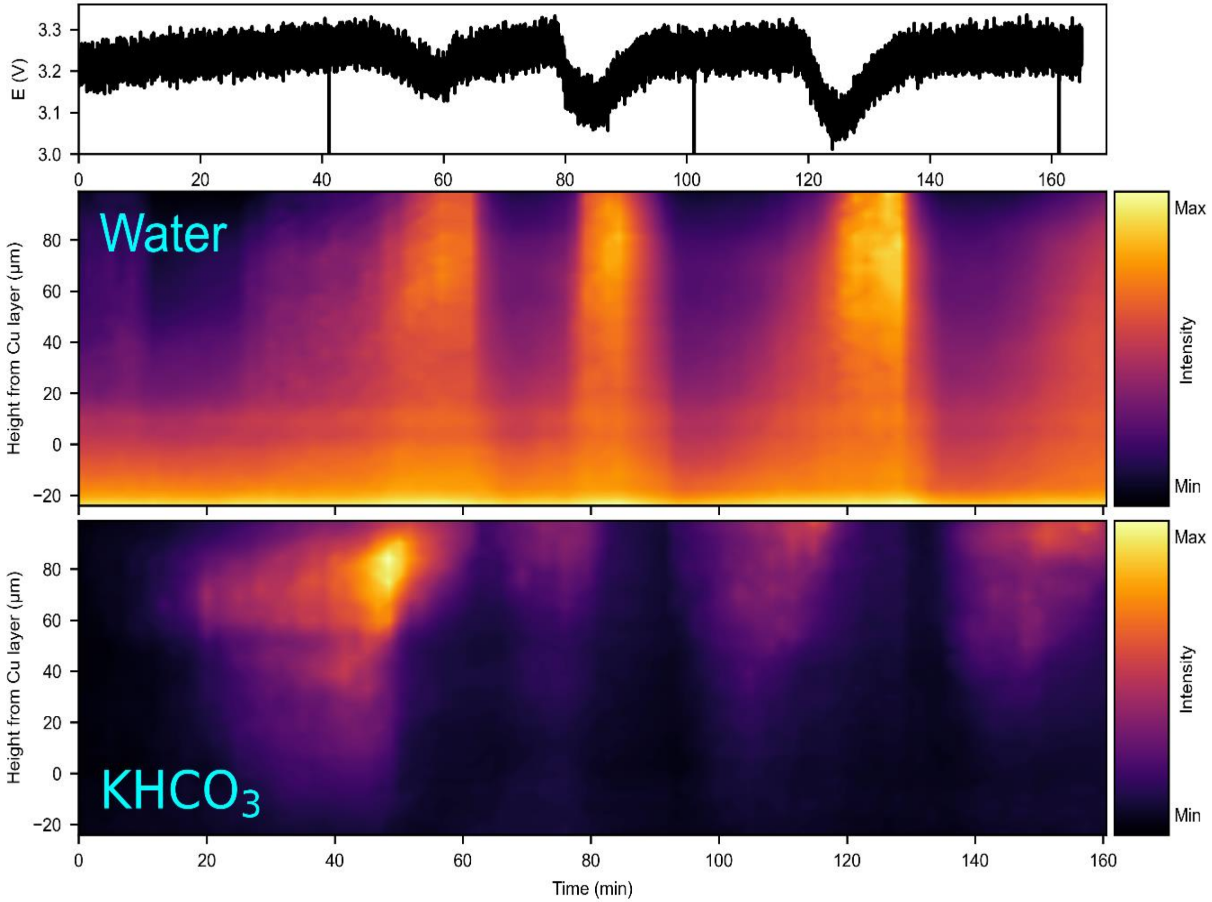
- In a different experiment we measured CO_2 to O_2 ratio
- We notice the CO_2 to O_2 ratio decreases as the potential decreases
- Membranes are 2.5x more conductive with OH^- compared to CO_3^{2-} transferring.
- This also means are cathode is being starved of CO_2.

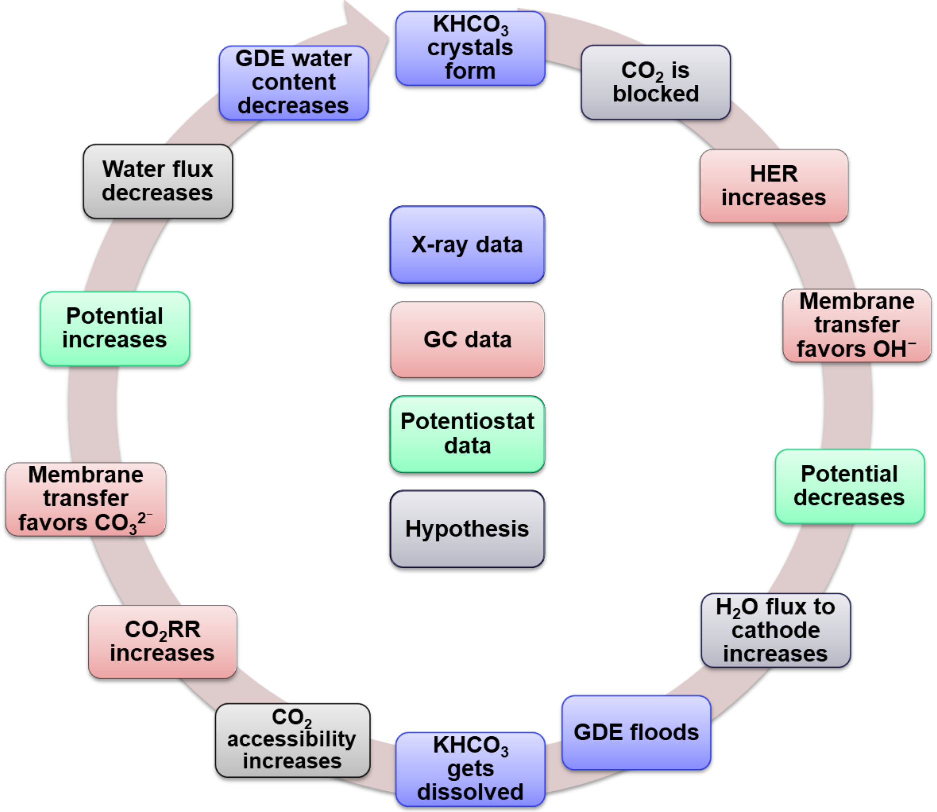


Mass transfer issues

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

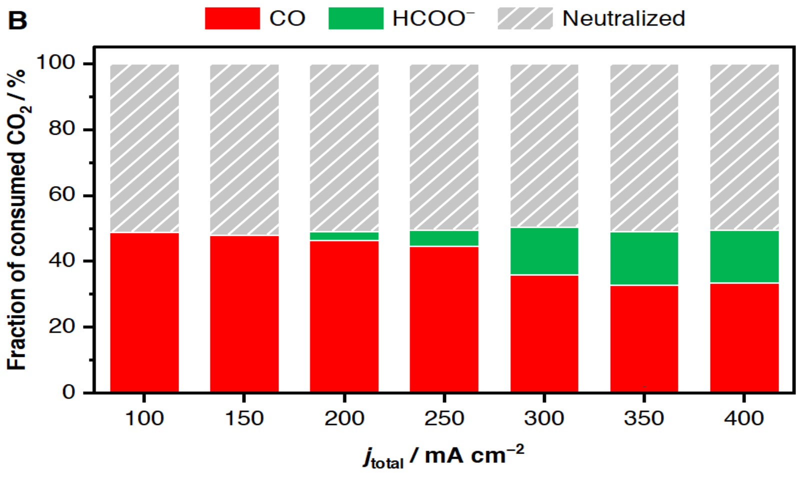
100 mA/cm²



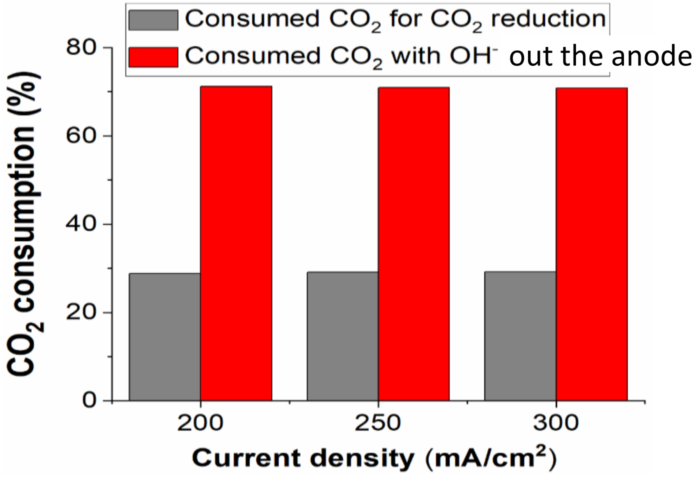


Conclusions

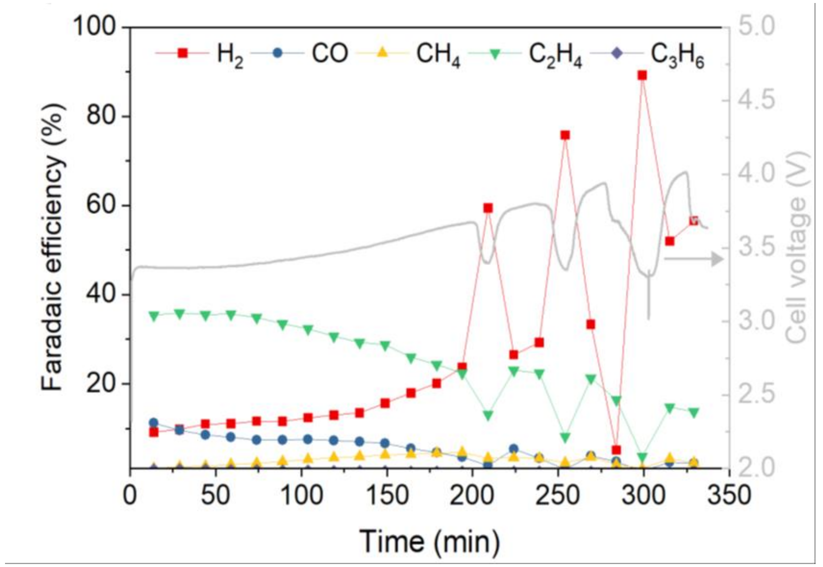
- Engineering CO_2 electrolysis will be much more complex than water electrolysis.
- The field is understanding and adapting quite quickly.



Larrazabal, G., et al., *Appl. Mat. & Int., 2019*



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



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HORIZON 2020

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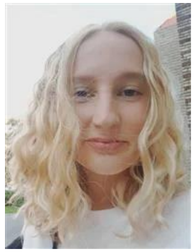
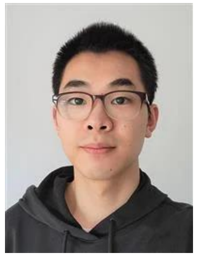

Clara Jensen


Wanyu Deng


Qiucheng Xu

Collaborators

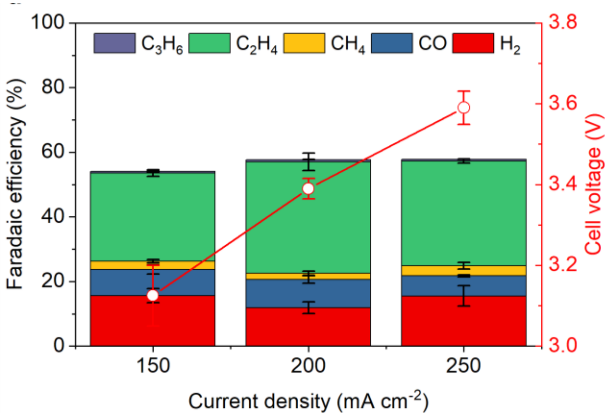
Ib Chorkendorff
Kasper Therkildsen

X-ray impact

- The X-rays had no noticeable impact on our selectivity.

- We also did some experiments at DTU and some at ESRF with no noticeable change.

Without X-rays.



With X-rays.