Synchrotron based analysis on zero-gap CO_2 and CO electrolysis devices

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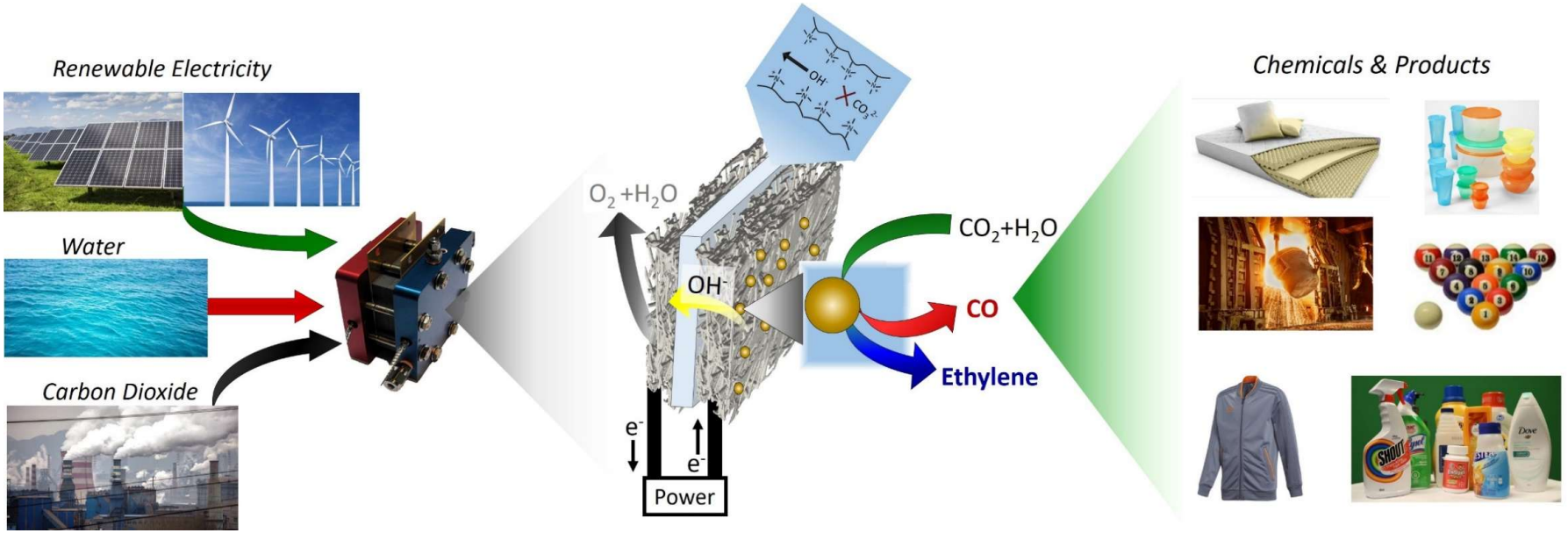


Cathodic reactions

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

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

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

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

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

Anodic reactions

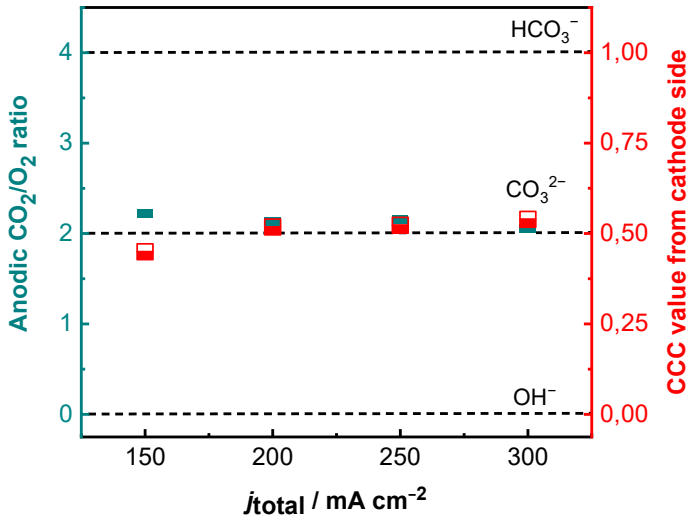
$2\,H_2O \rightarrow O_2 + 4\,e^- + 4\,H^+$

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

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

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

Anion exchange membrane



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

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

Cathode Mass Balance

The Carbon/Charge Coefficient (CCC) =

OH^- → CCC=0

CO_3^{2-} → CCC=1/2

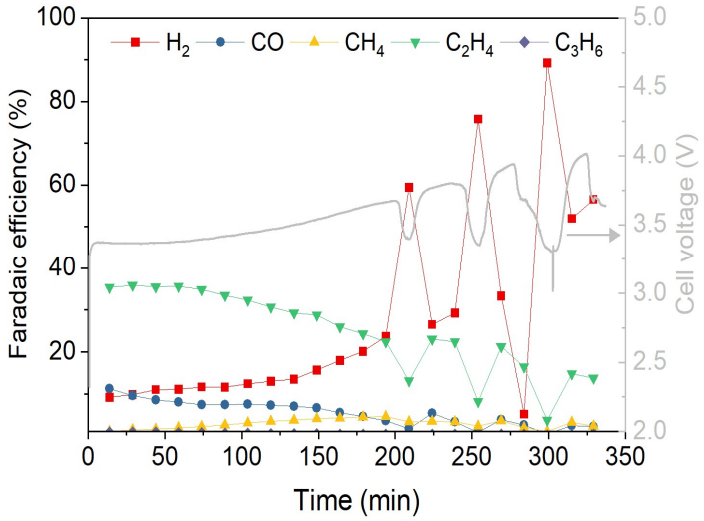
HCO_3^- → CCC=1

Anode reactions:

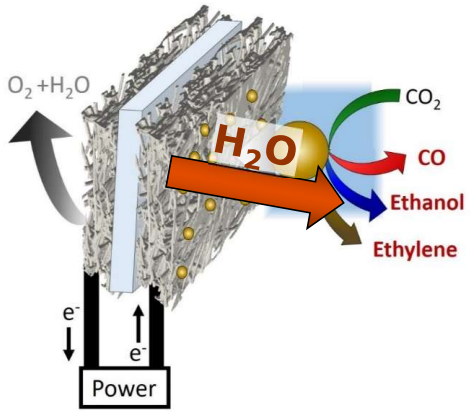
	CO_2/O_2 ratio
$4OH^- \rightarrow 2H_2O + O_2 + 4e^-$	4
$2CO_3^{2-} \rightarrow 2CO_2 + O_2 + 4e^-$	2
$4HCO_3^- \rightarrow 4\,CO_2 + O_2 + 2H_2O + 4e^-$	0

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.

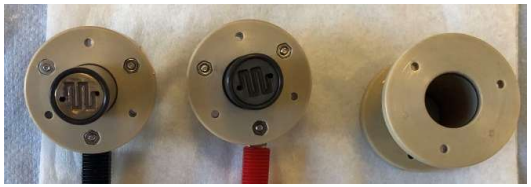


Is water 'flooding' our catalyst ?



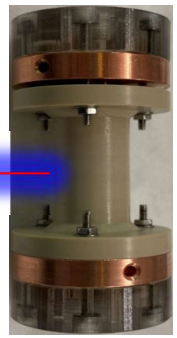
Designing a synchrotron experiment

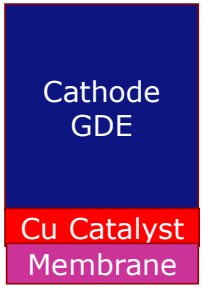
- We thought excess water may prevent efficient CO_2 mass transfer to the catalyst
- We used synchrotron X-ray scattering at ESRF to analyse this.

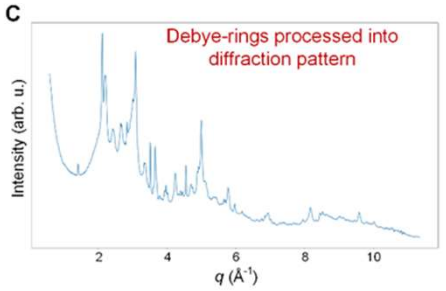


CO_2 Reactor

X-ray



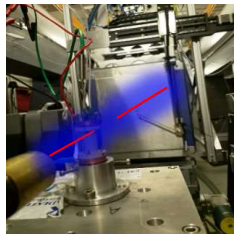




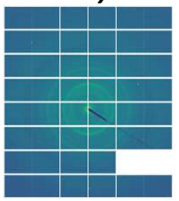
Moss., et al., *J of Power Sources*, 2023

Synchrotron

Experiments

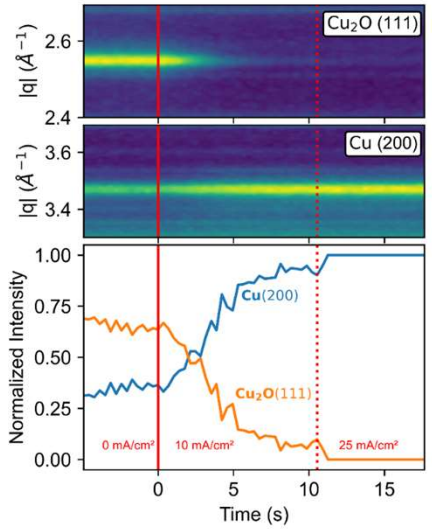


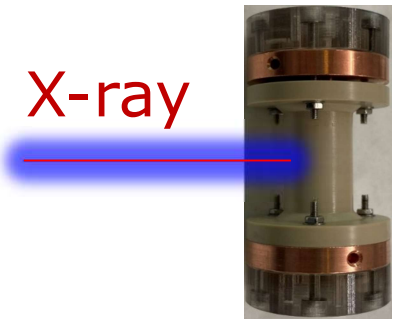
Raw X-ray results

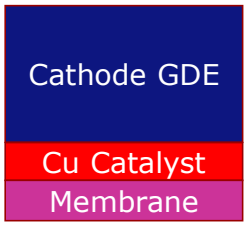


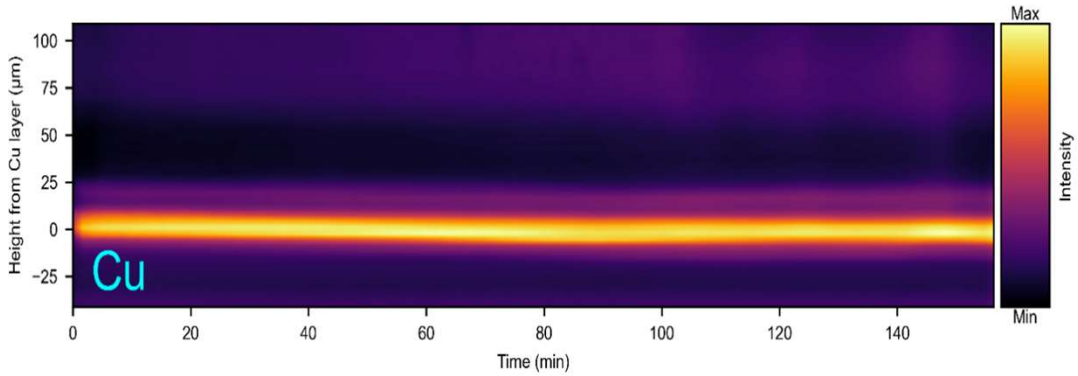
Analysing copper in our device

- 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





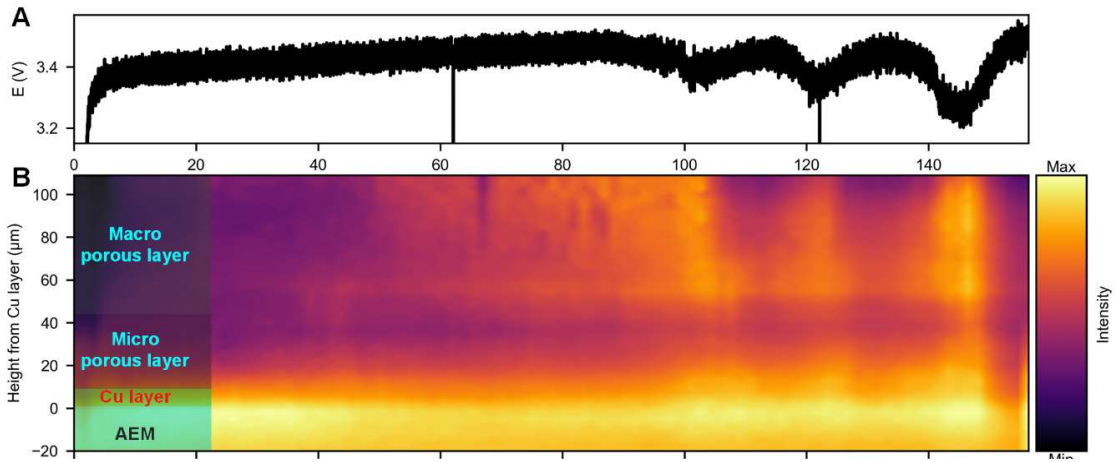




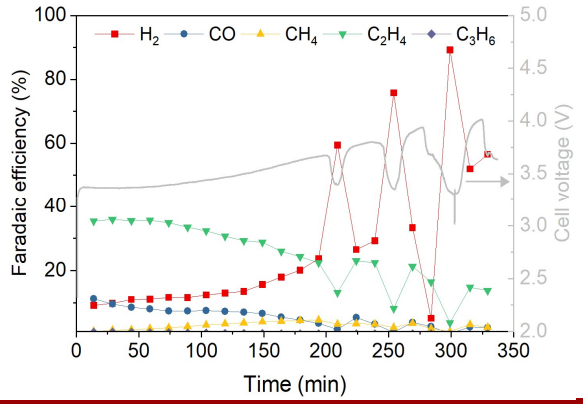
Moss., et al., *J of Power Sources*, 2023

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.



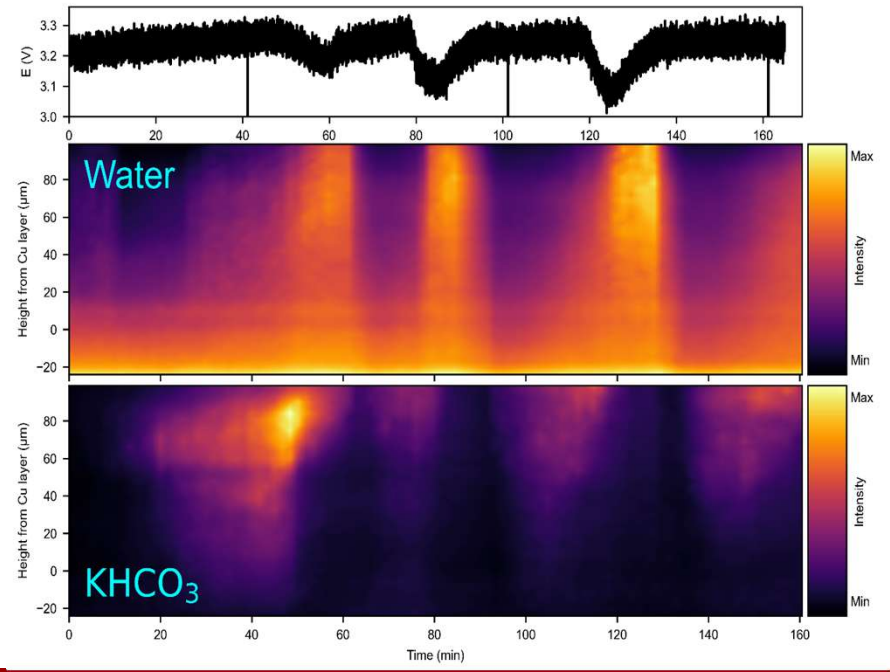
From earlier

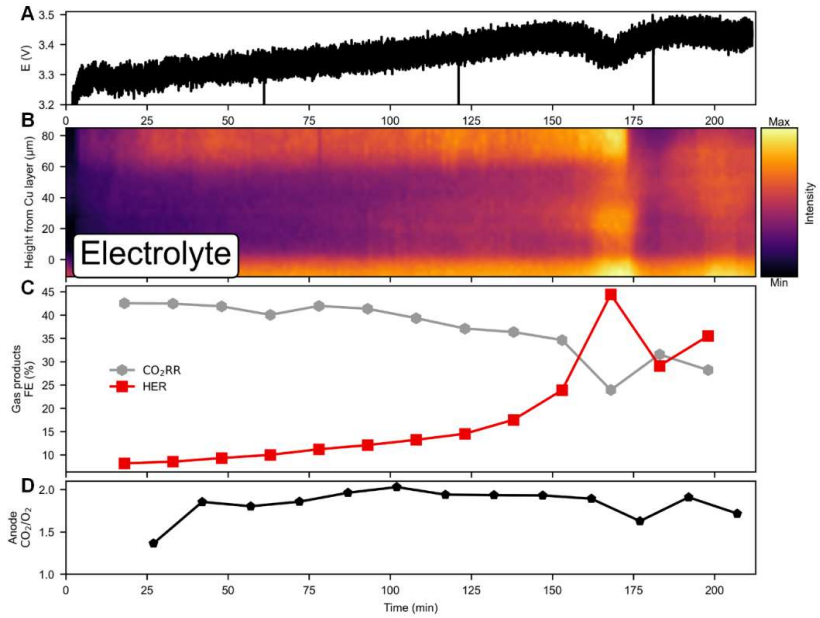


Moss., et al., *Joule*, 2023

Mass transfer issues

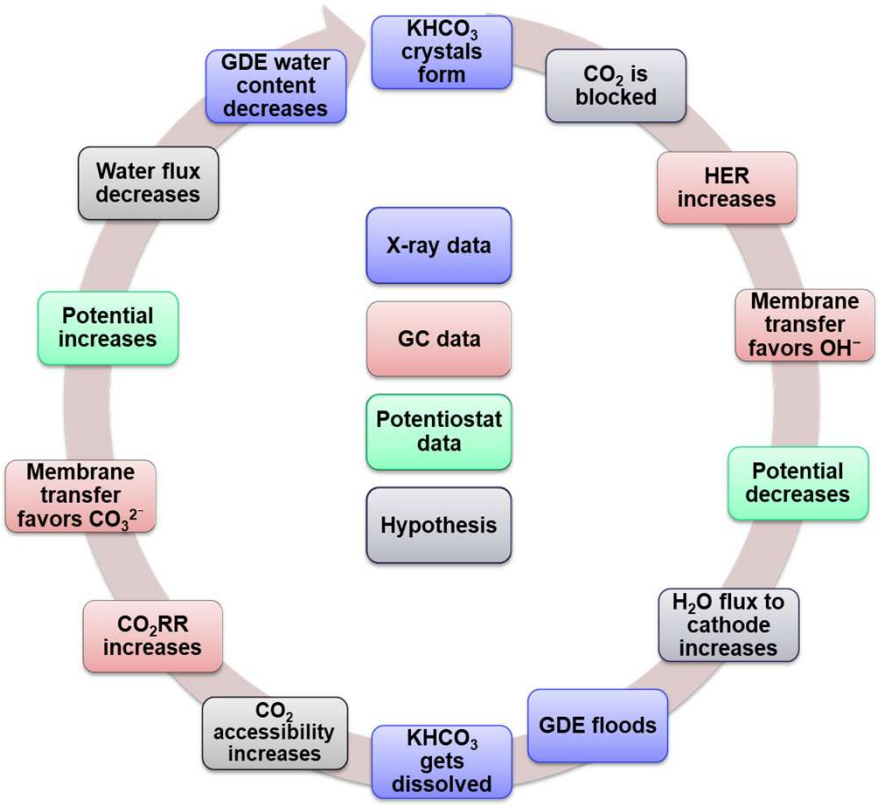
- When looking at salts we see $KHCO_3$, but no K_2CO_3
- We see the salt deposition before water floods the cell





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

Oscillation hypothesis



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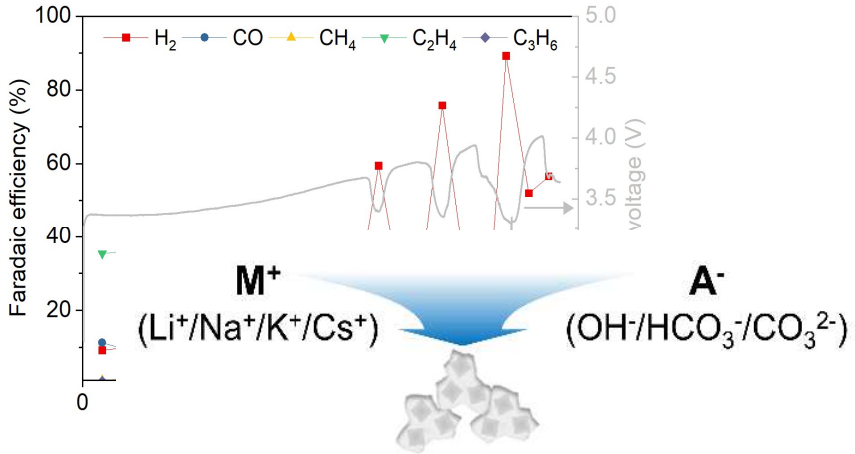
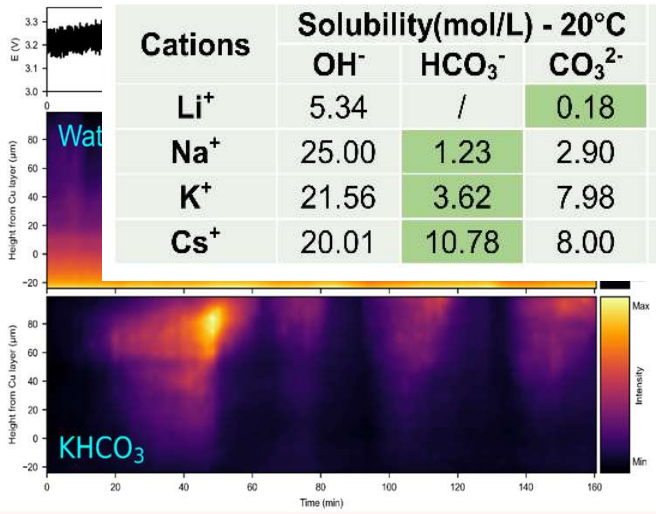
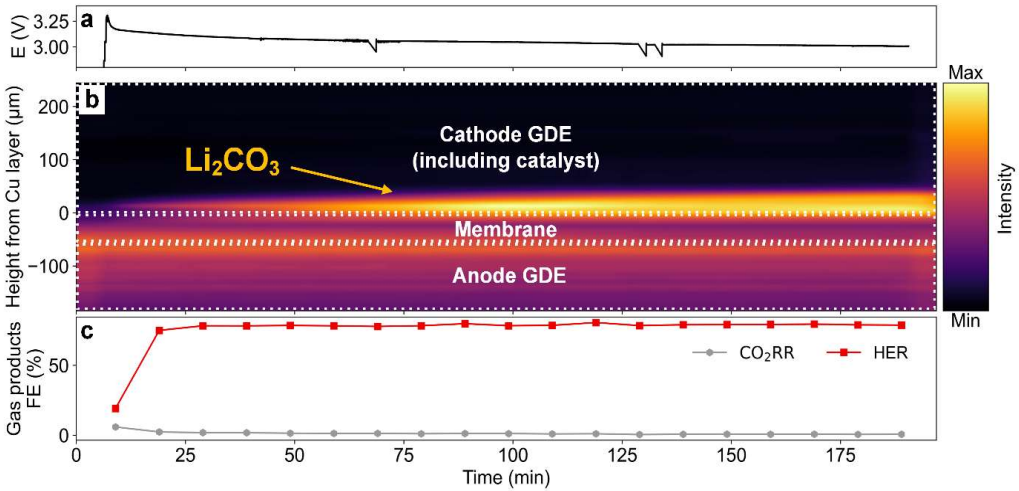
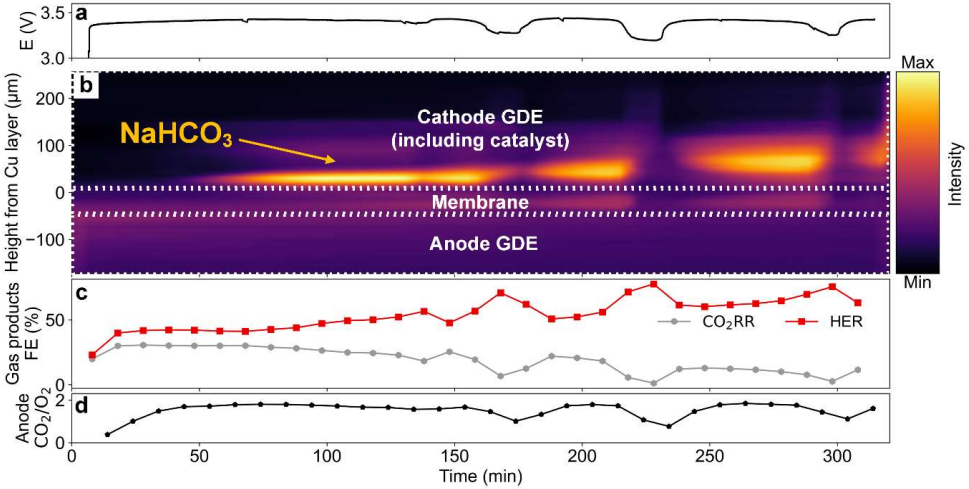


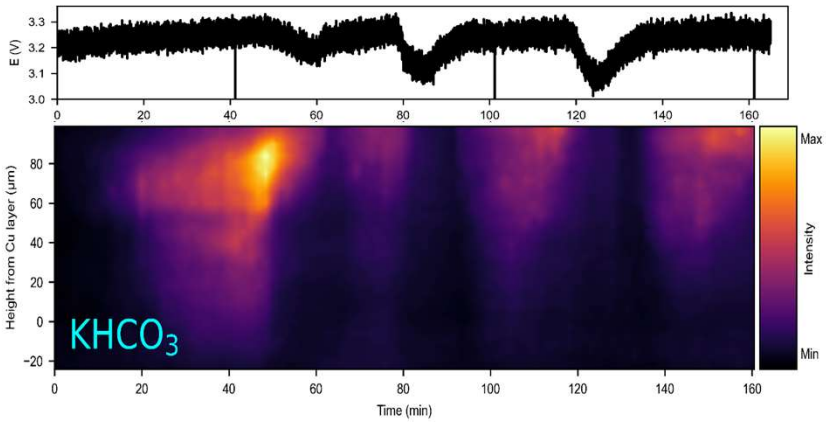


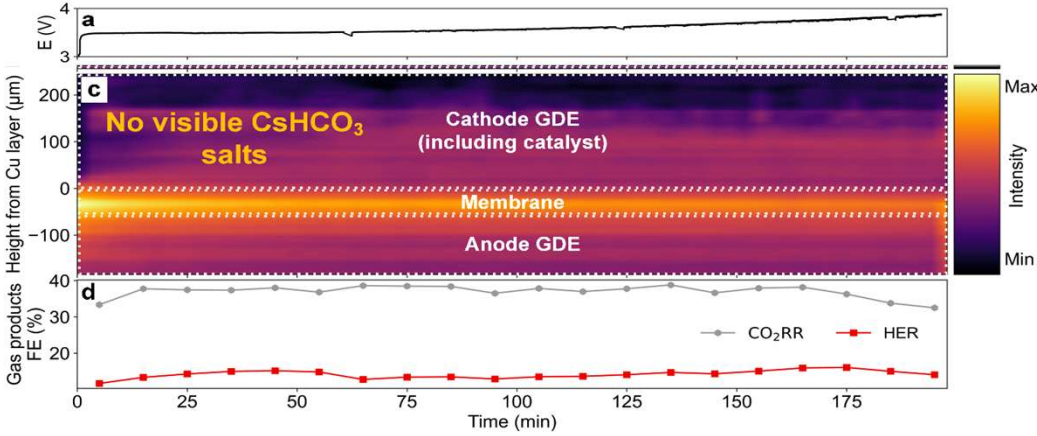
Cations	Solubility(mol/L) - 20°C			Normalized to Li_2CO_3
	OH^-	HCO_3^-	CO_3^{2-}	
Li^+	5.34	/	0.18	1.00
Na^+	25.00	1.23	2.90	6.97
K^+	21.56	3.62	7.98	20.56
Cs^+	20.01	10.78	8.00	61.27

Salt precipitation of various cations







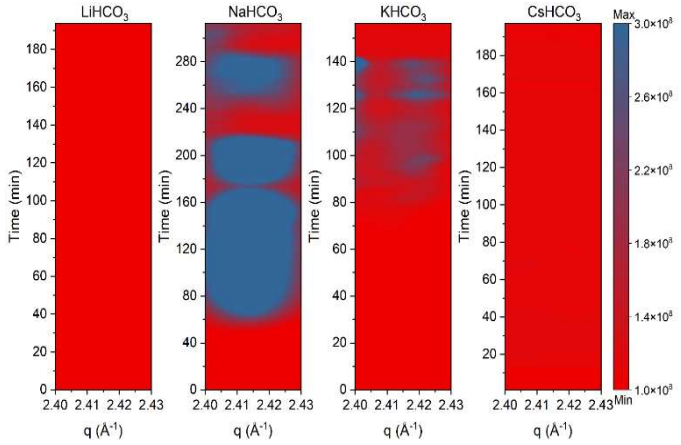


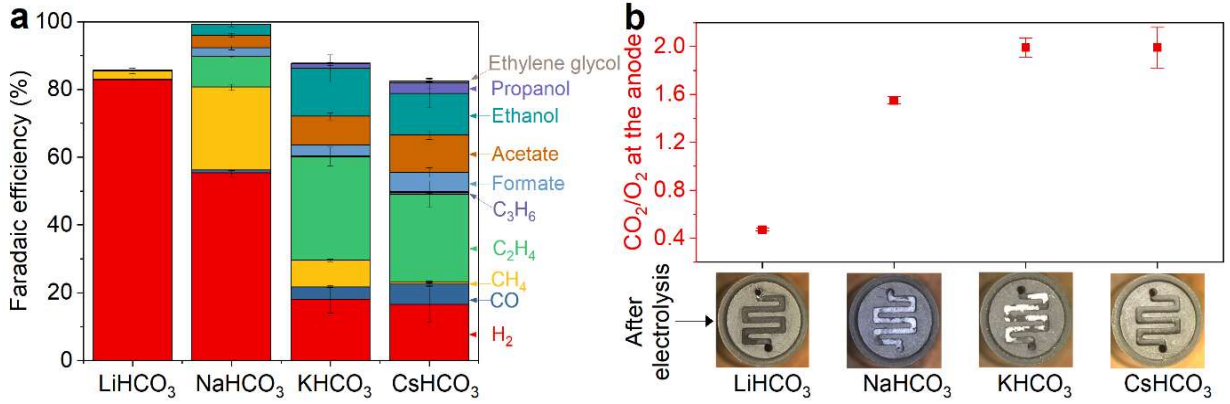
Garg, et al., *E&ES*, 2023

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.

Normalized electrolyte build-up





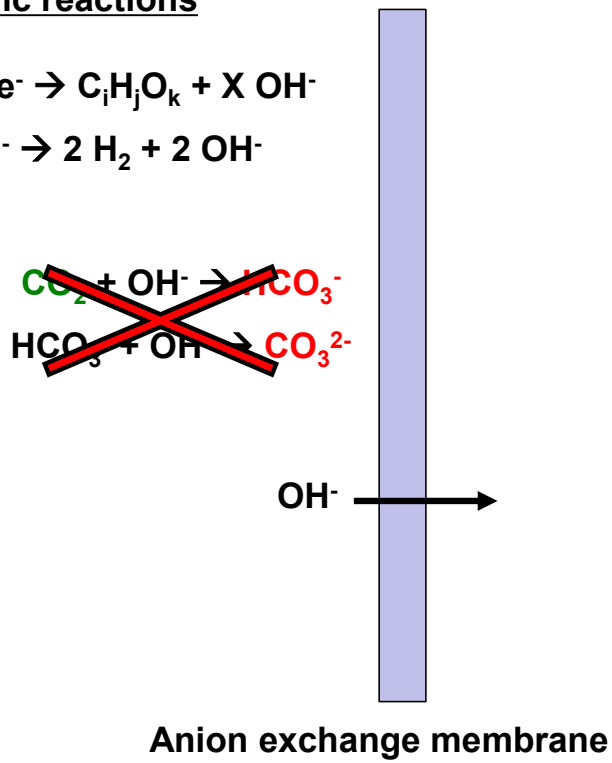
Garg, et al., *E&ES*, 2023

Resolving the carbonate issue: CO Electrolysis

Cathodic reactions

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

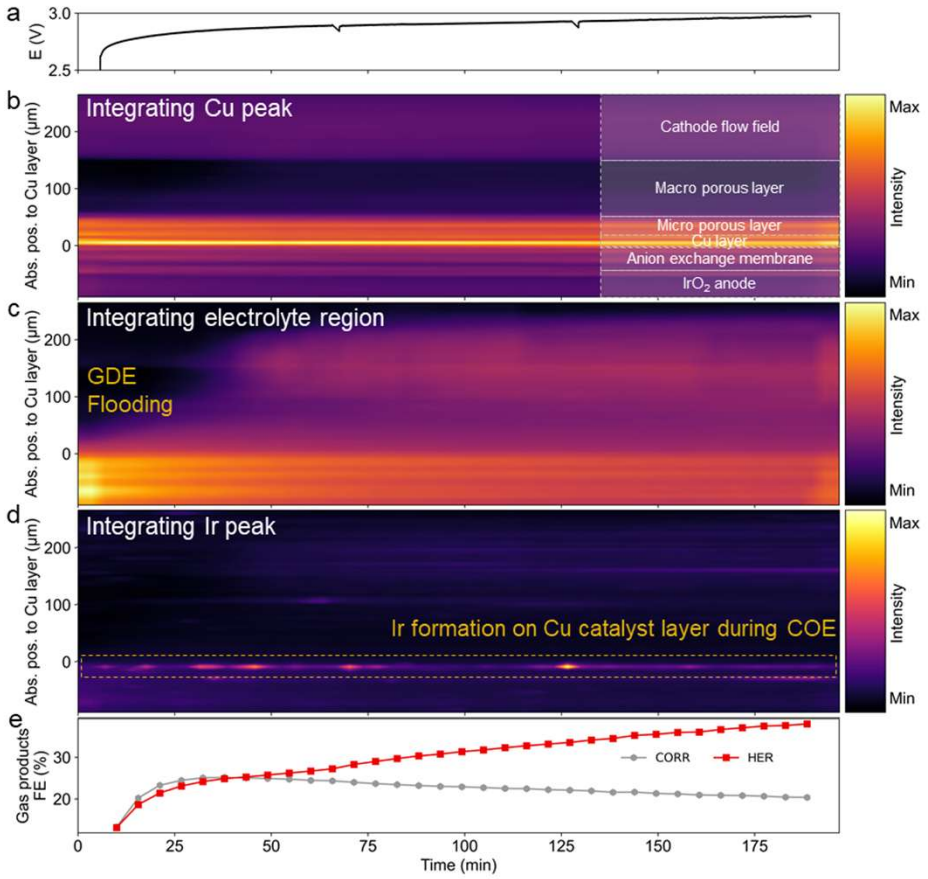
$2\ H_2O + 2\ e^- \rightarrow 2\ H_2 + 2\ OH^-$



- 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.

Issues with CO electrolysis

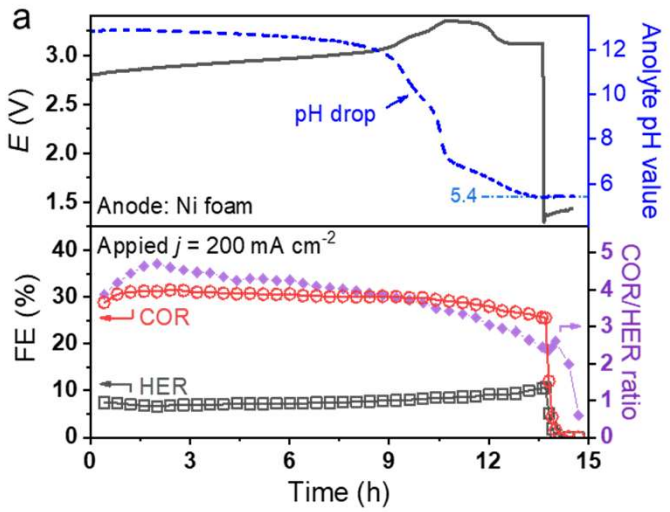
- The flooding is not a major issue with CO electrolysis.
- Ir crossover is an issue, though for CO_2 electrolysis this was not an issue.
- We believe this is a pH issue (CO, pH=13), CO_2 (pH=8)
- Switching to a Ni anode basically resolved this.

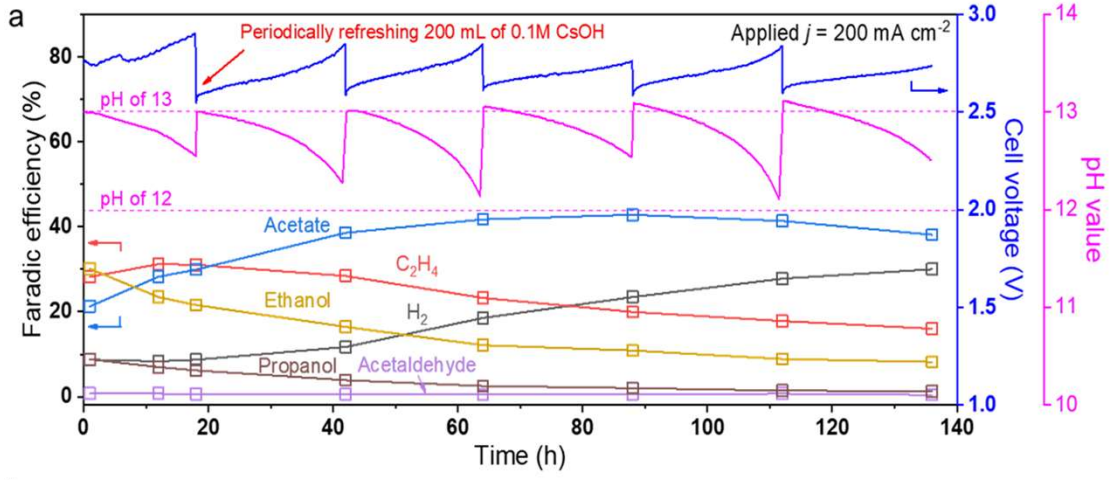


Xu. et al., Submitted, *Preprint on Research Square*

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.



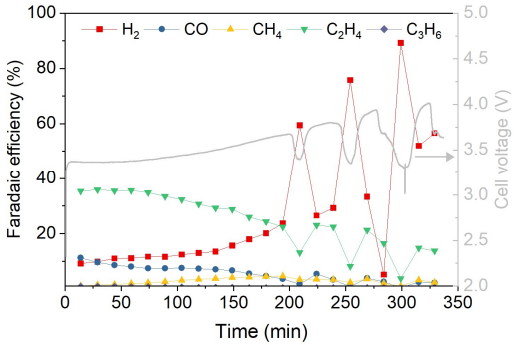


Xu. et al., Submitted, *Preprint on Research Square*

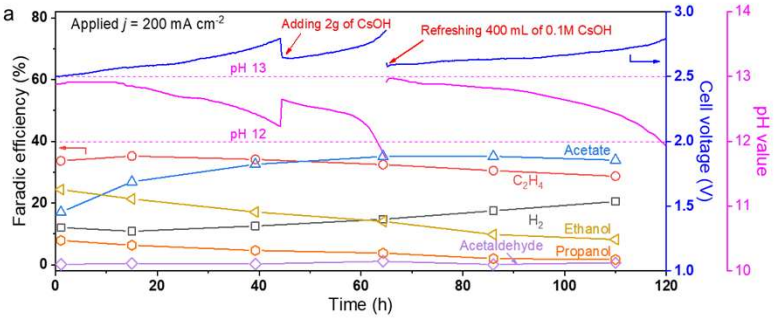
Conclusions

- Applied electrolysis entails there are many factors effecting performance.
- Synchrotron work allows us to clearly see salt deposition
- Salt solubility really effects durability

Problem



Solution



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Marta Mirolo


Roosa Ilvonen


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Qiucheng Xu

MARIE CURIE ACTIONS

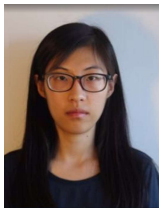
HORIZON 2020

SELECT CO_2

EuroTech Universities
Excellence in Science and Technology


Asger Moss


Carlos Rodriguez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Francesco Longhin

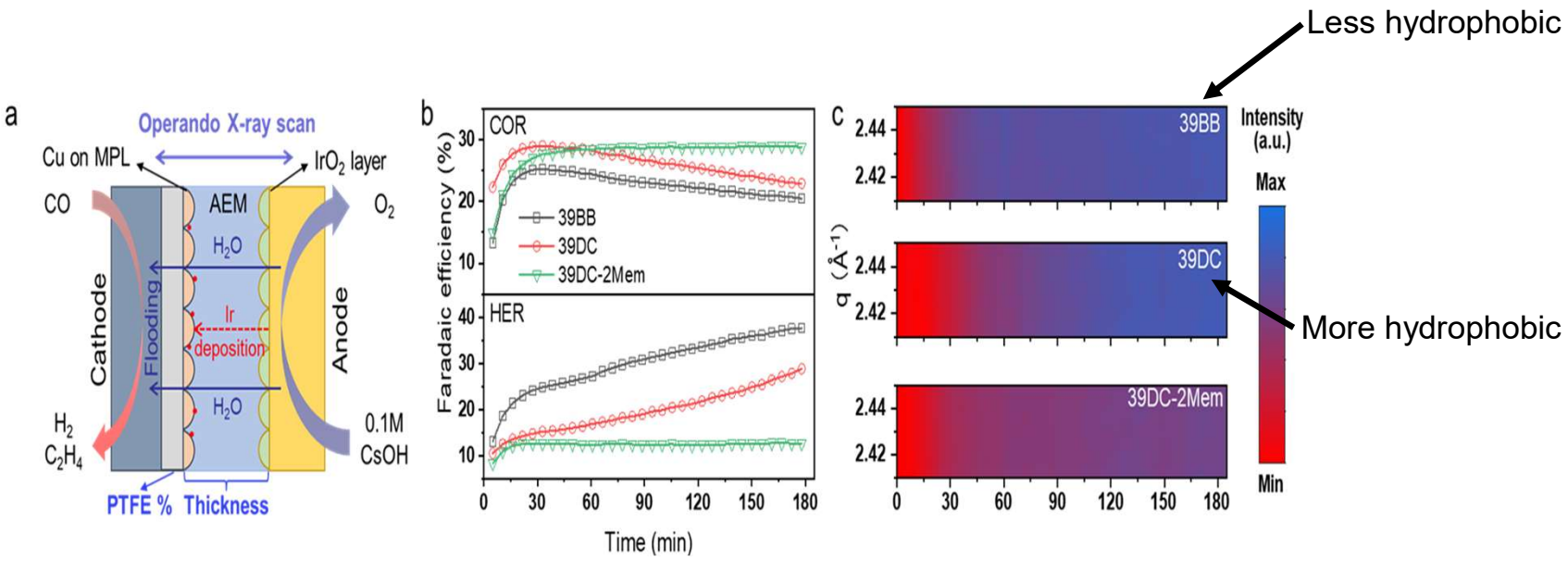

Tugce Yilmaz

DTU Collaborators

Ib Chorkendorff

More Synchrotron Data

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



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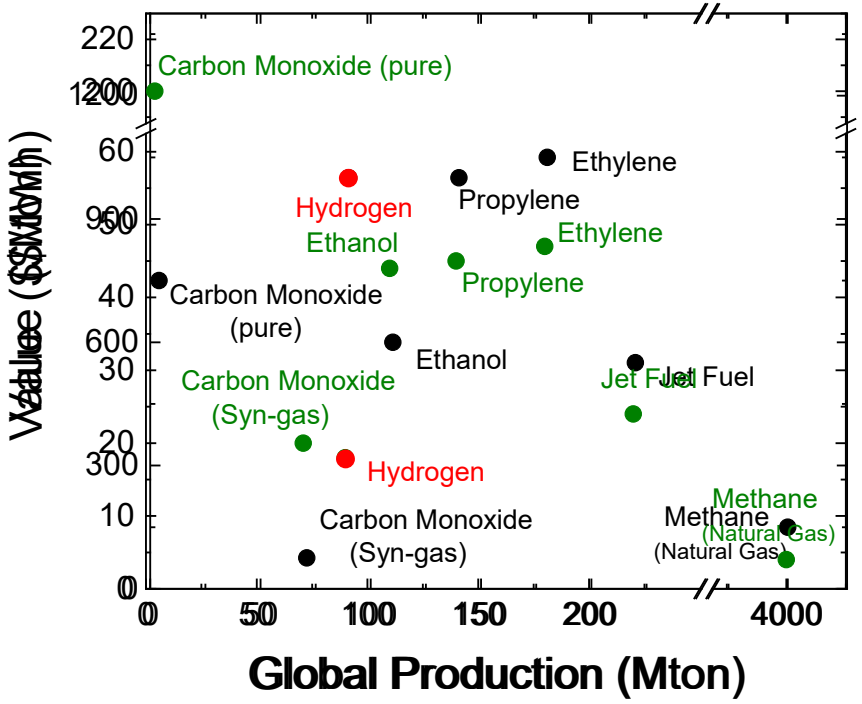
What are we trying to do it



Applications of chemicals

CO → Chemicals

Ethylene → Plastics

Propylene → Plastics

Ethanol → Fuel, Solvent

Methane → Burning

(Natural gas)

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