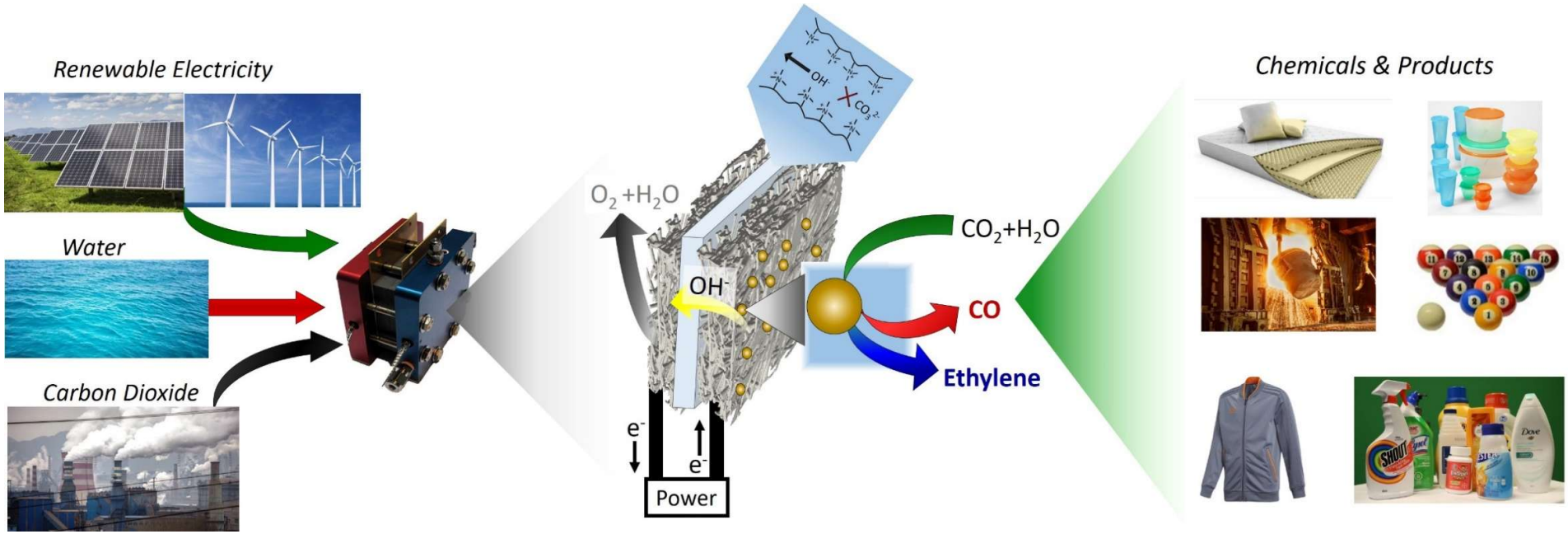
A synchrotron analysis of high current density CO_2 electrolysis devices

Brian Seger

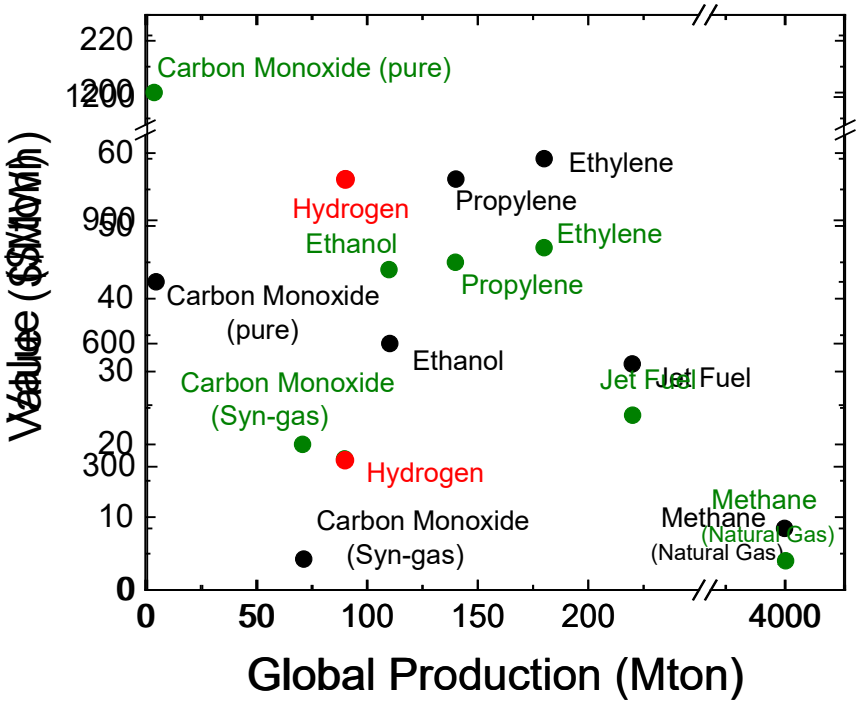
ICCCU24 Symposium

Dec 10th , 2024



What are we trying to do it

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



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

Literature review- point #1

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

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

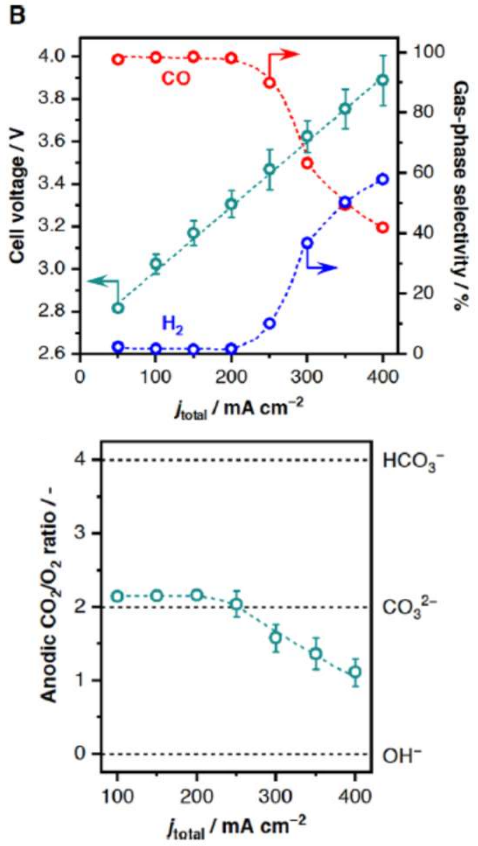
$CO_2{:}O_2$ ratio = 2

$2CO_3^{2-}$ → $2\,CO_3^{2-} + 4\,H^+ \rightarrow 2CO_2 + H_2O$

$4HCO_3^-$ → $4\,HCO_3^- + 4H^+ \rightarrow 4CO_2 + H_2O$

OH^- → $OH^- + H^+ \rightarrow 0CO_2 + H_2O$

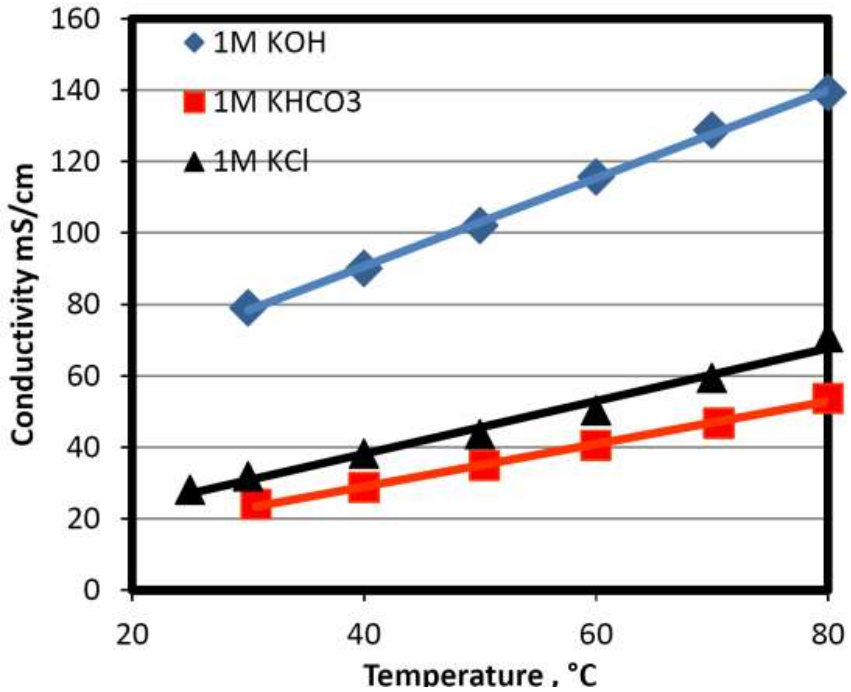
Anion exchange membrane (AEM)



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

Literature review- point #2

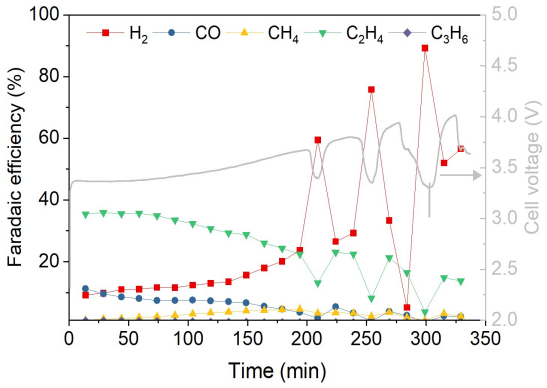
- In an AEM conductivity in OH^- is 3 times more conductive than HCO_3^-.
- Double negative CO_3^{2-} should be even less conductive.



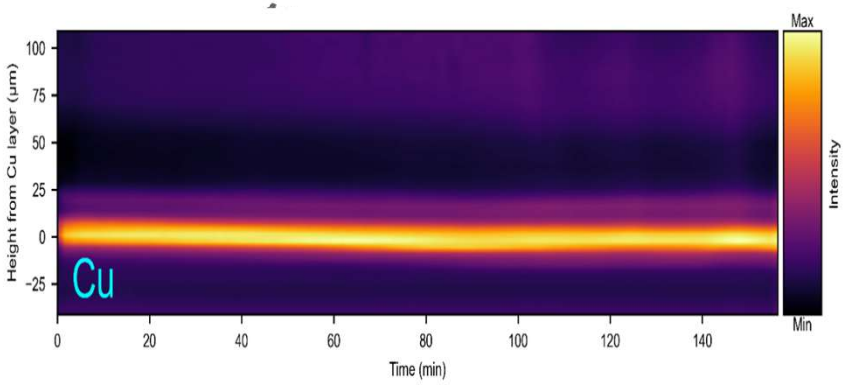
Dioxide Materials website

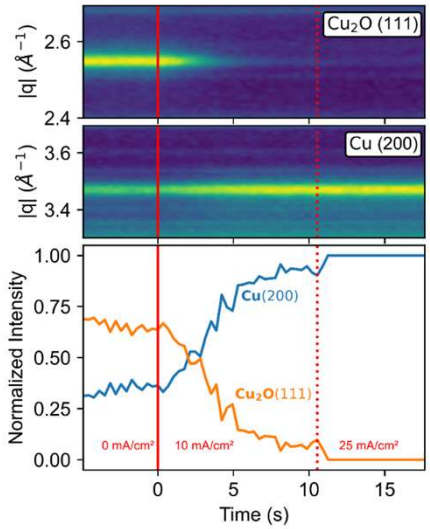
Energy Technology, Kutz et. al, 2017, DOI:10.1002/ente.201600636

Oscillations and analysis via synchrotron

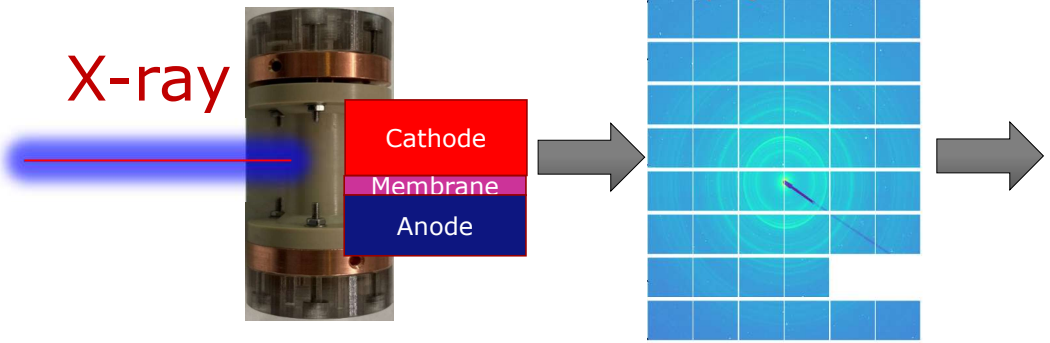


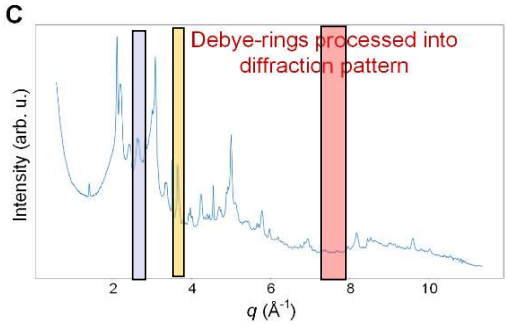
Moss et. al., Joule, 2023





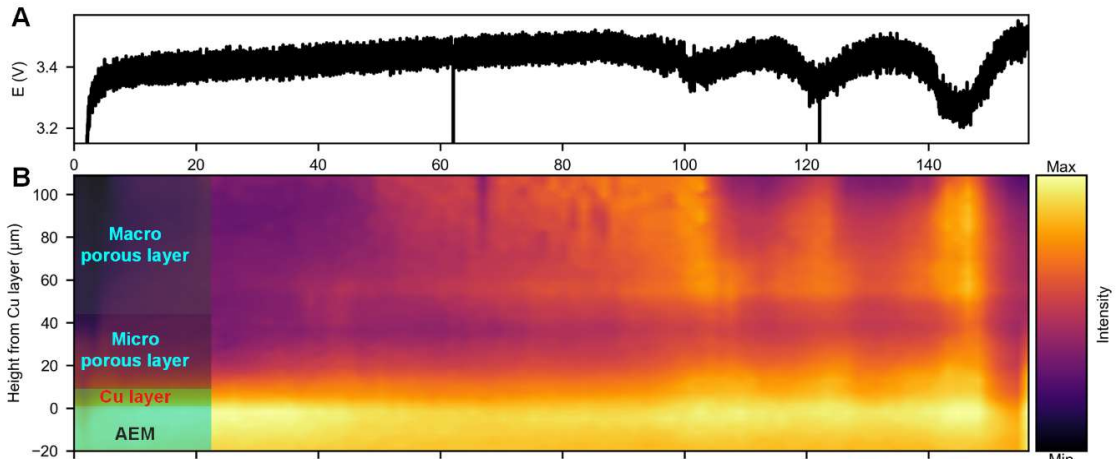
ESRF Synchrotron



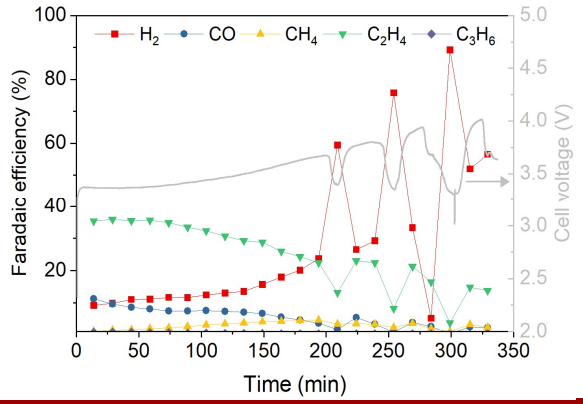


Analysing water

- 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.



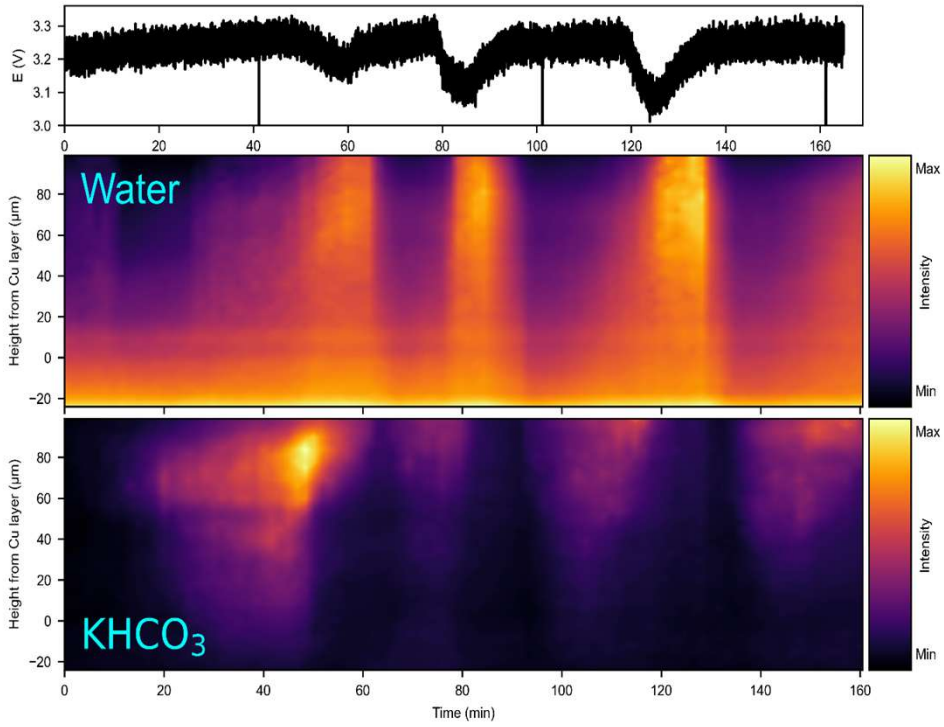
From earlier

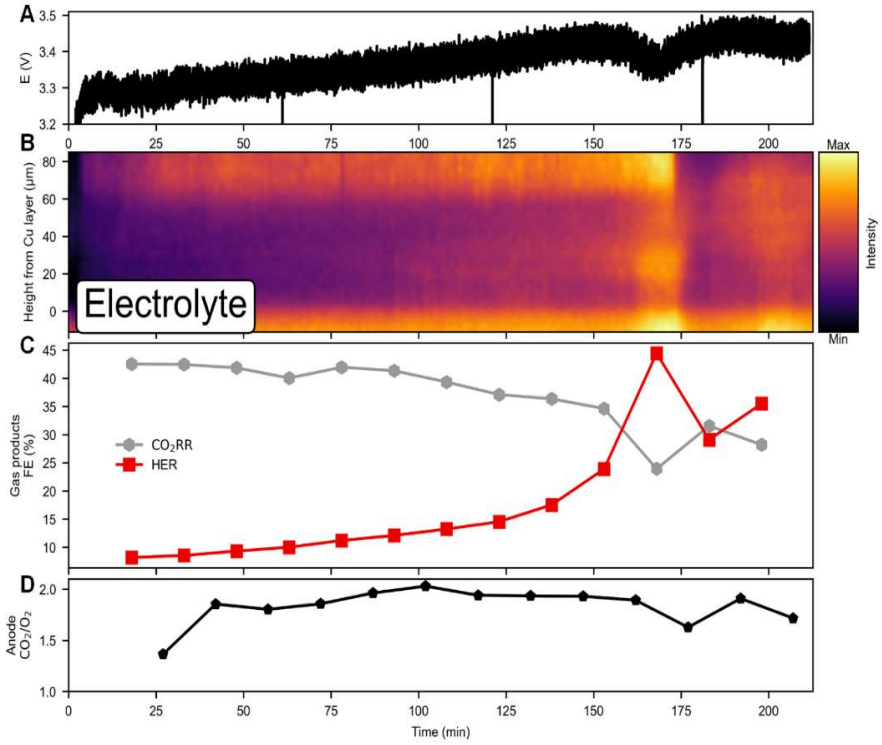


Moss., et al., *Joule*, 2023

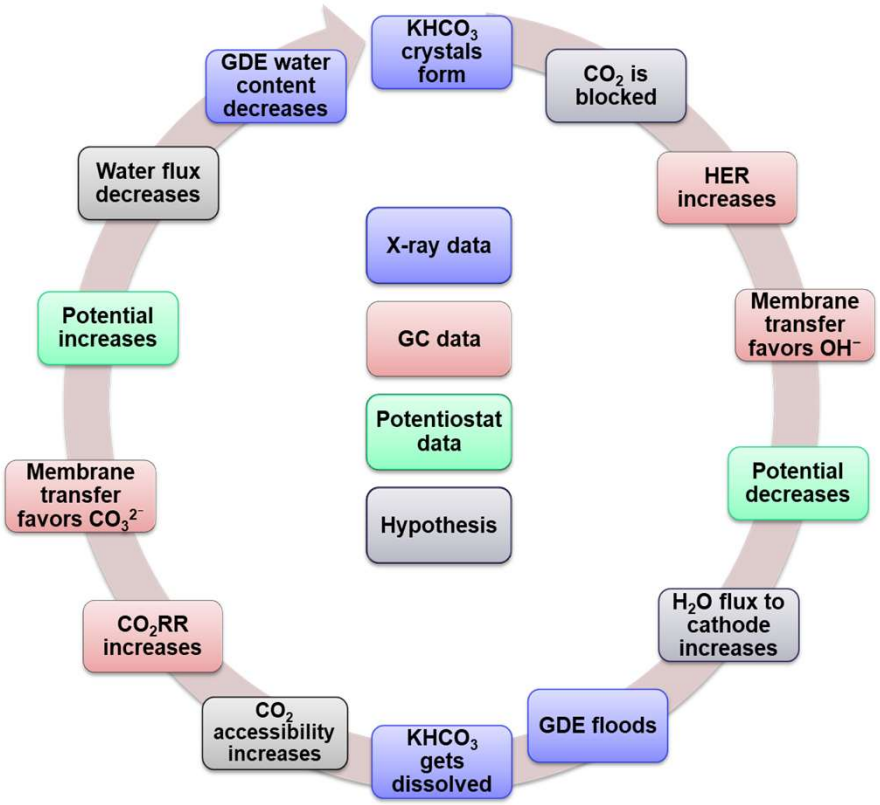
Mass transfer issues

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

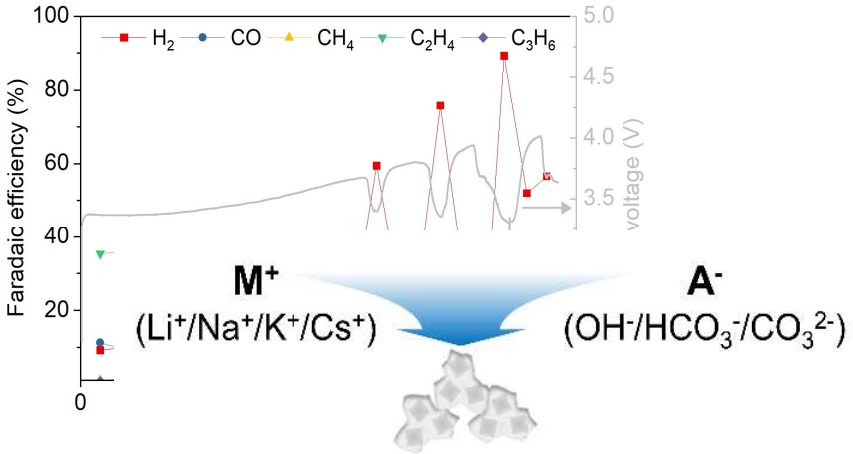




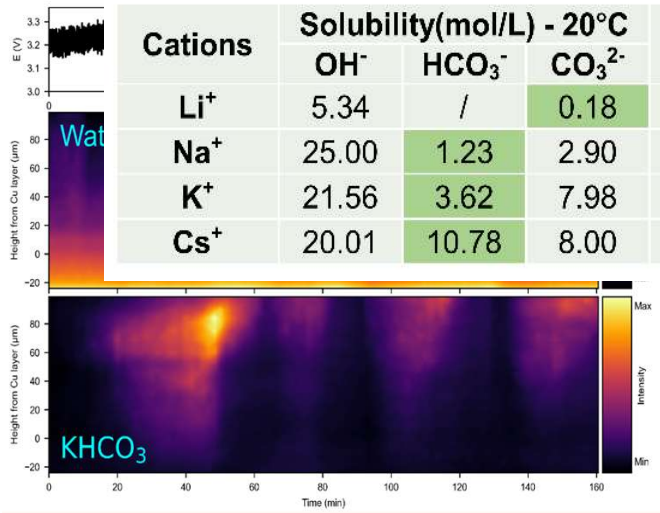
Oscillation hypothesis



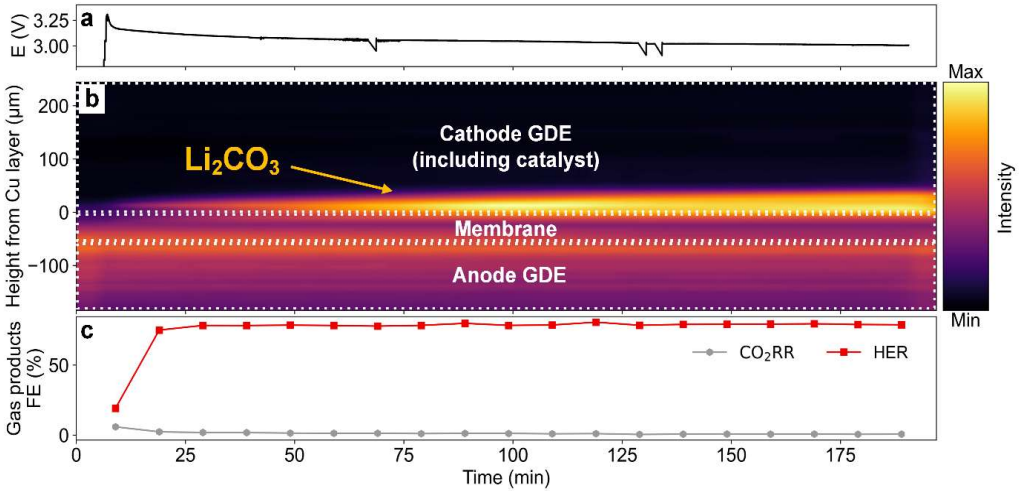
Moss., et al., *Joule*, 2023

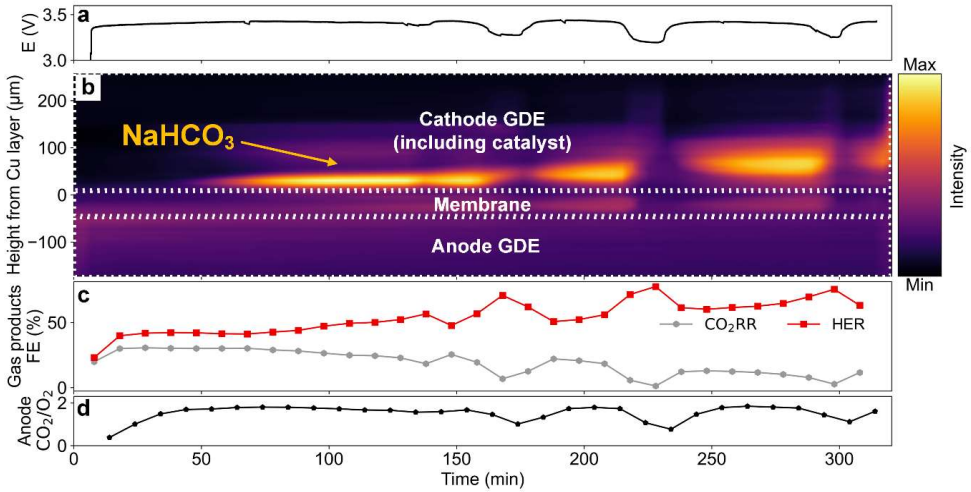


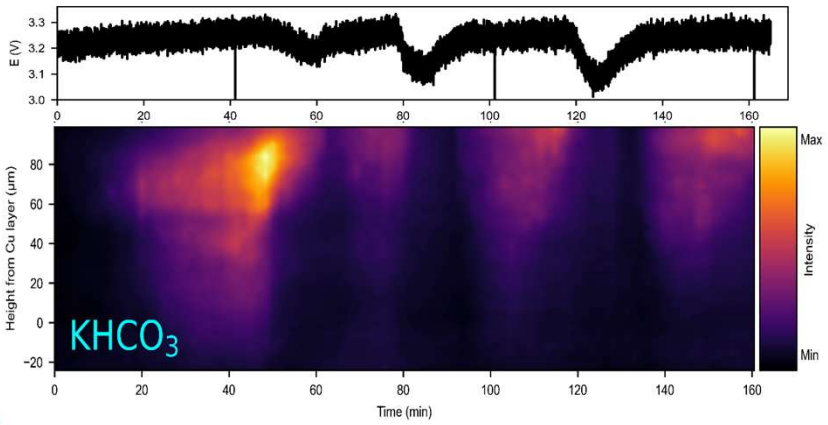
Cations	Solubility(mol/L) - 20°C			Normalized to Li_2CO_3
	OH^-	HCO_3^-	CO_3^{2-}	
Li^+	5.34	/	0.18	1.00
Na^+	25.00	1.23	2.90	6.97
K^+	21.56	3.62	7.98	20.56
Cs^+	20.01	10.78	8.00	61.27

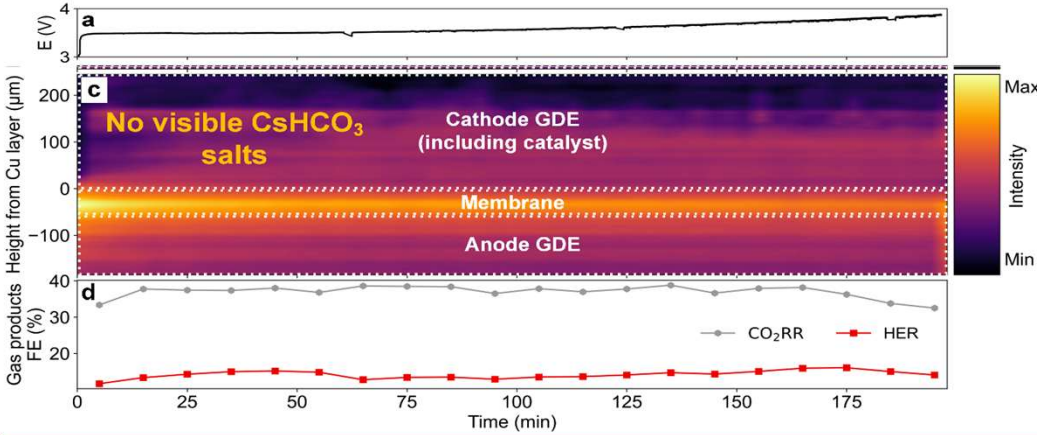


Salt precipitation of various cations





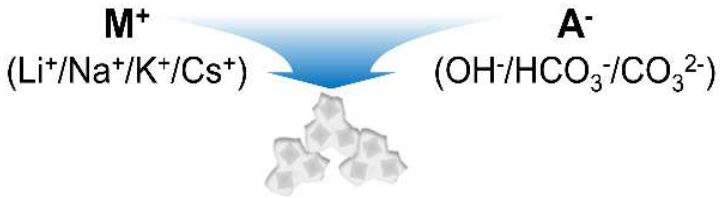




Garg., et al., E&ES, 2023

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.



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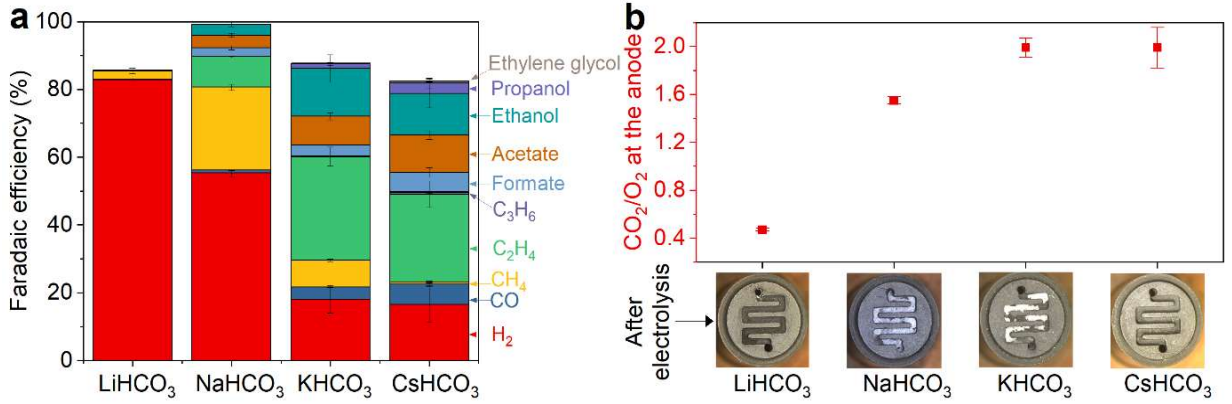
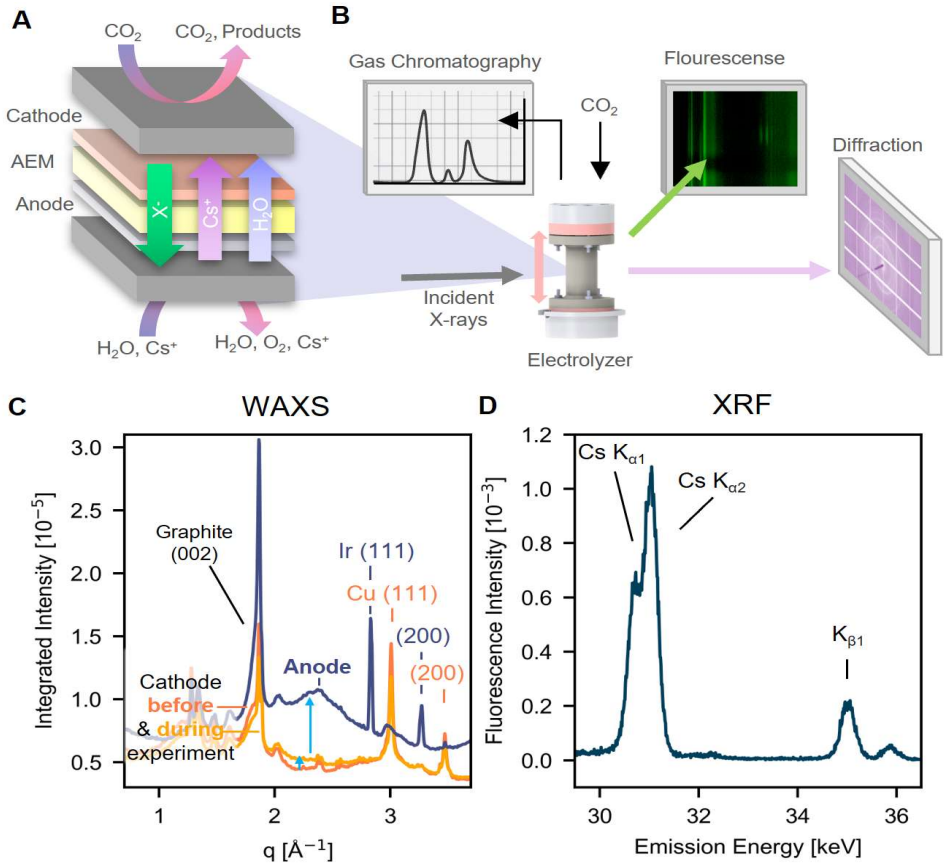
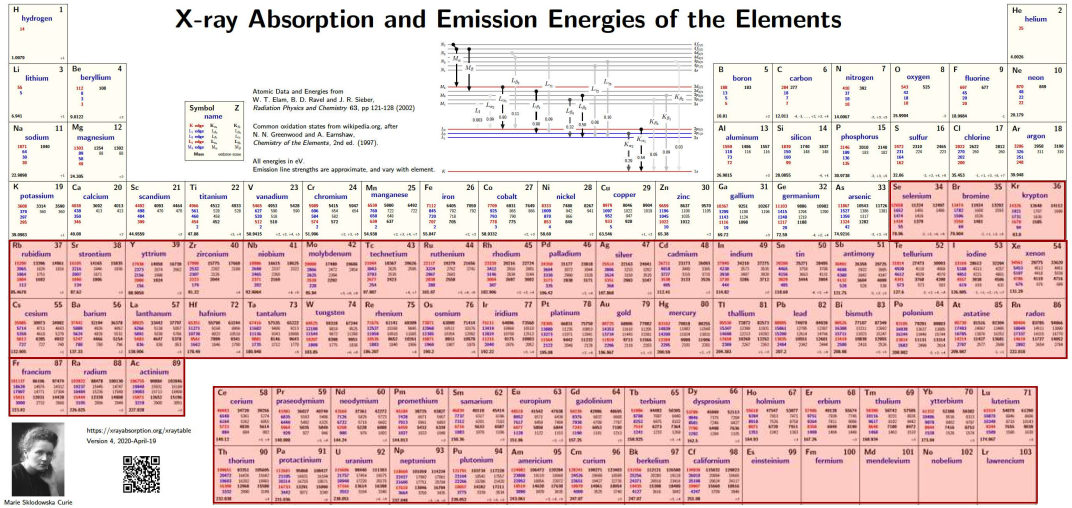


Garg, et al., *E&ES*, 2023

Adding fluorescence to X-ray analysis



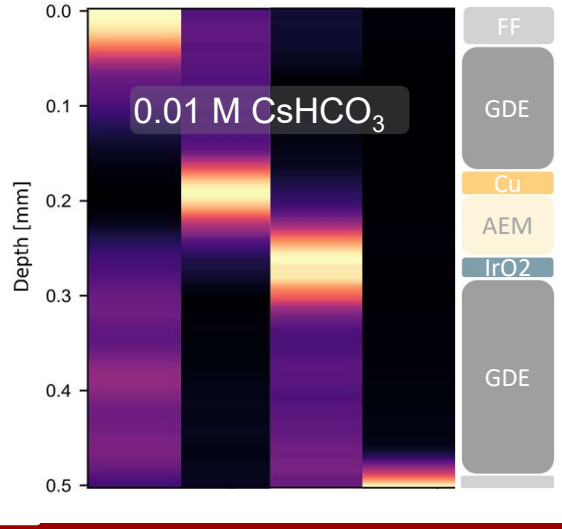


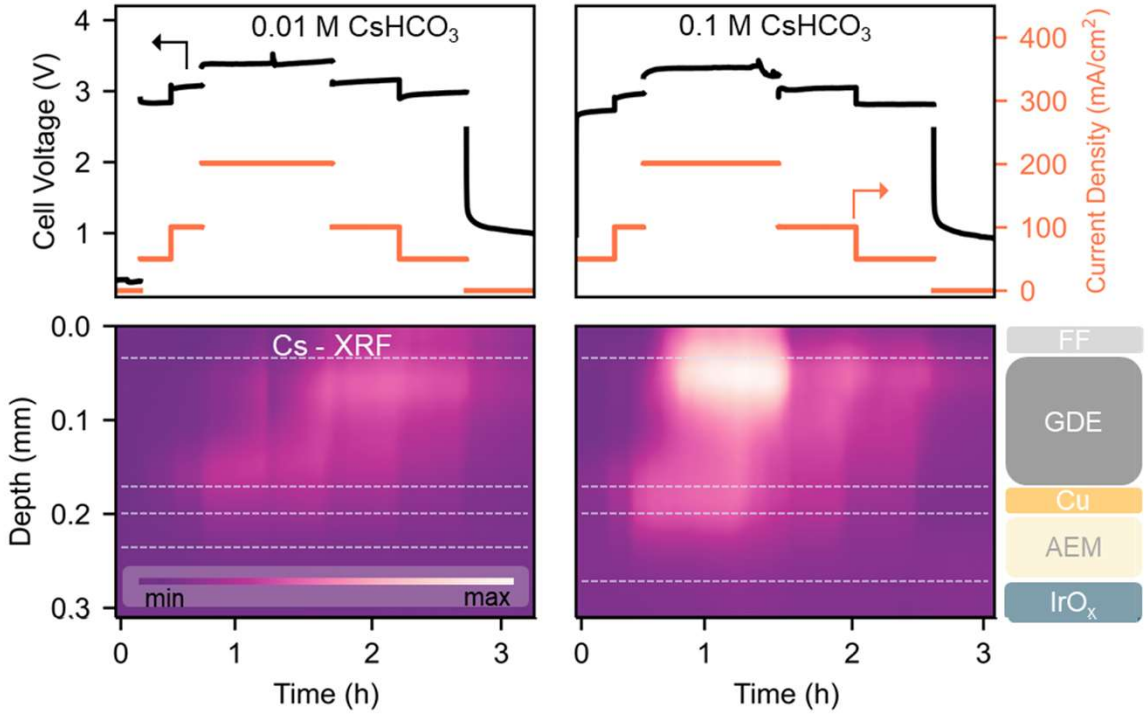
- Only photon emission > ~12 keV can escape the reactor cell.

Joensen., et al., Joule, 2024

Operando CO_2 Electrolysis

- Constant current density steps
- XFR Cs K_α peak
- WAXS for mapping
- Strong relation between potential and Cs^+
- Strong relation between concentration and Cs^+





Joensen., et al., Joule, 2024

Breaking down the Transport Mechanisms

OCV

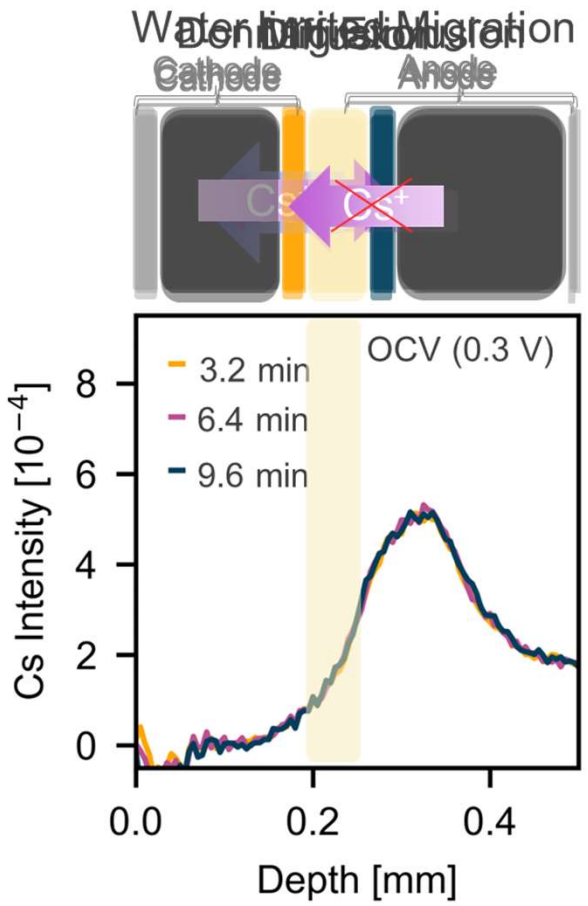
- Diffusion dominated
- Accumulate at CEM interface
- Small E-field

SCV

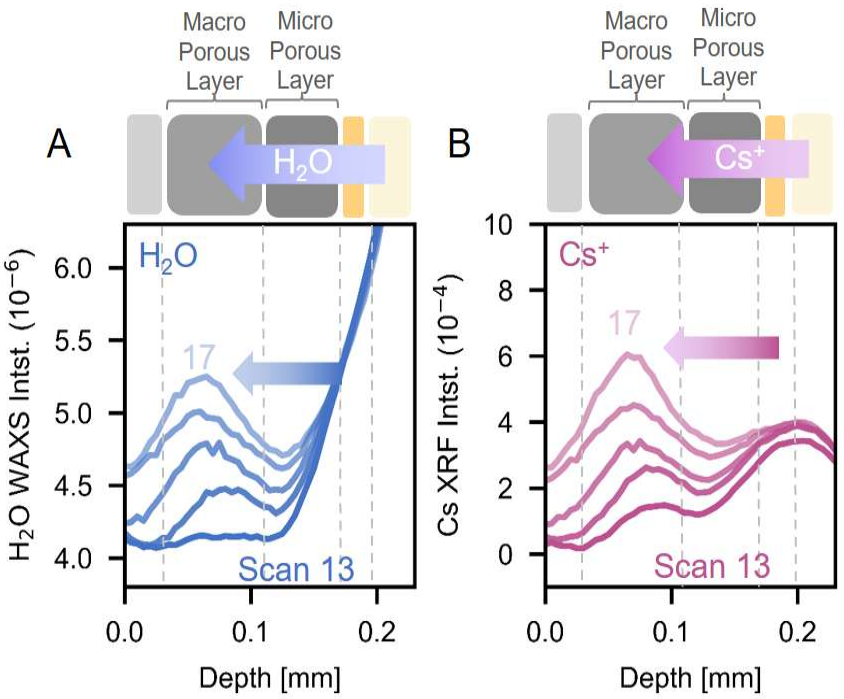
- Migration dominated
- Move slowly in dry media
- Low diffusivity in CEM
- Dependent on water
- Functional/Carboxy groups

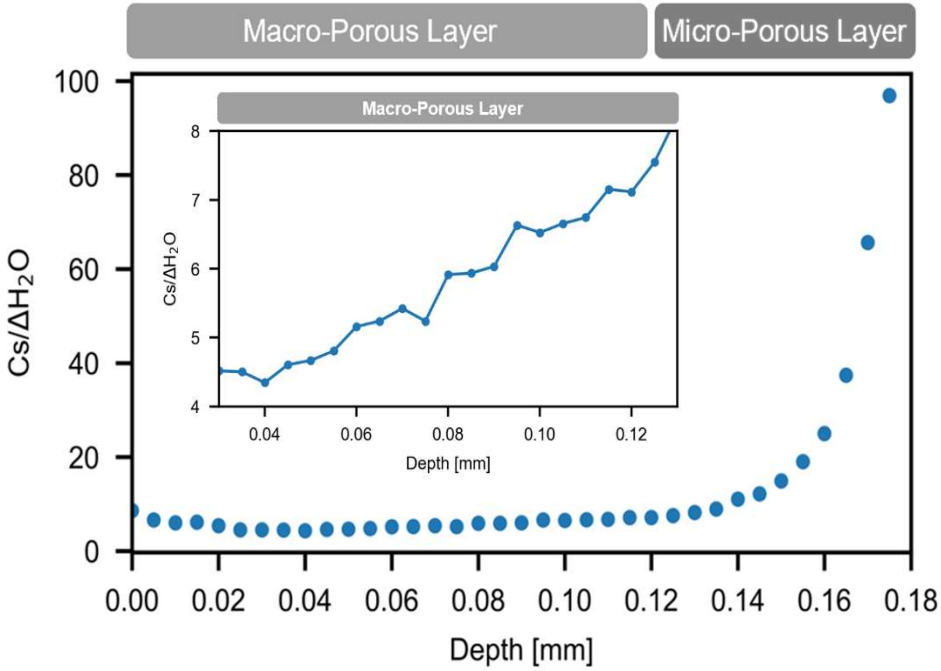
Nernst-Planck Equation

$$\boldsymbol{J} = \underbrace{-D\nabla c}_{\text{Diffusion}} + \underbrace{\frac{Dze}{k_B T} cE}_{\text{Electric Field}}$$



Micro/Macro-porous layer analysis





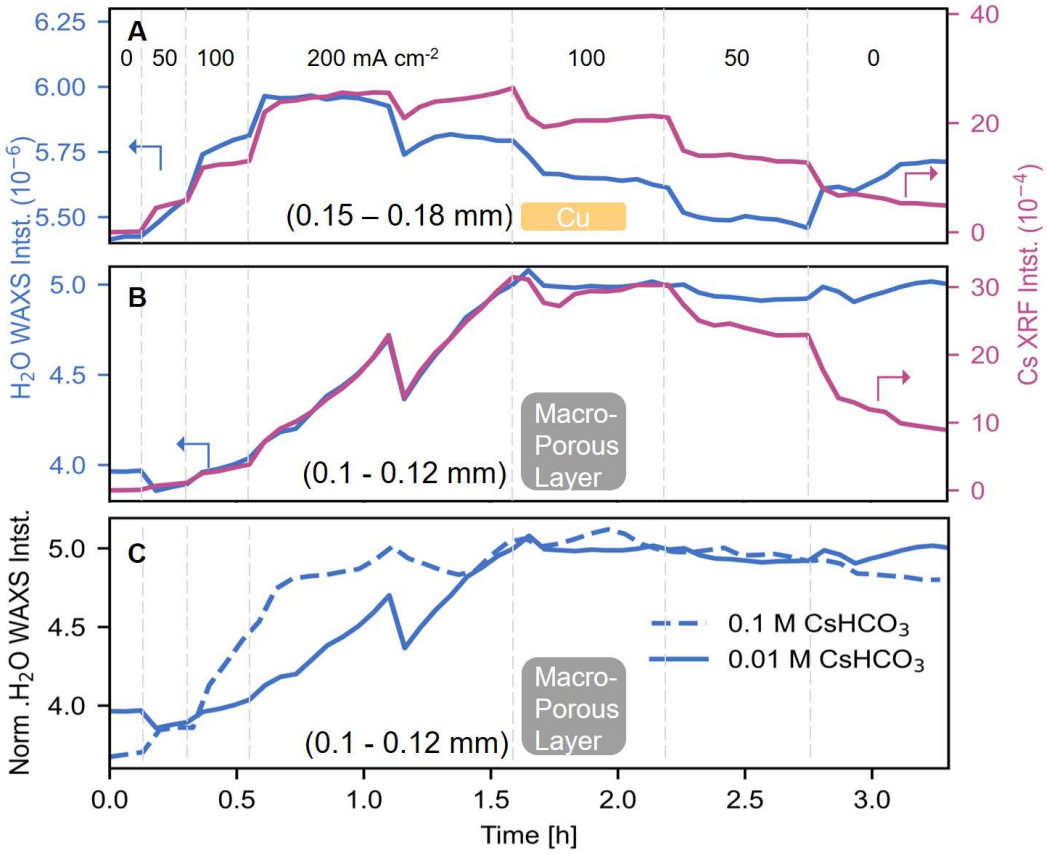
- As 'water' is just background, different depths has different backgrounds, thus Cs concentration can not be compared as a function of depth.

Micro/Macro-porous layer analysis

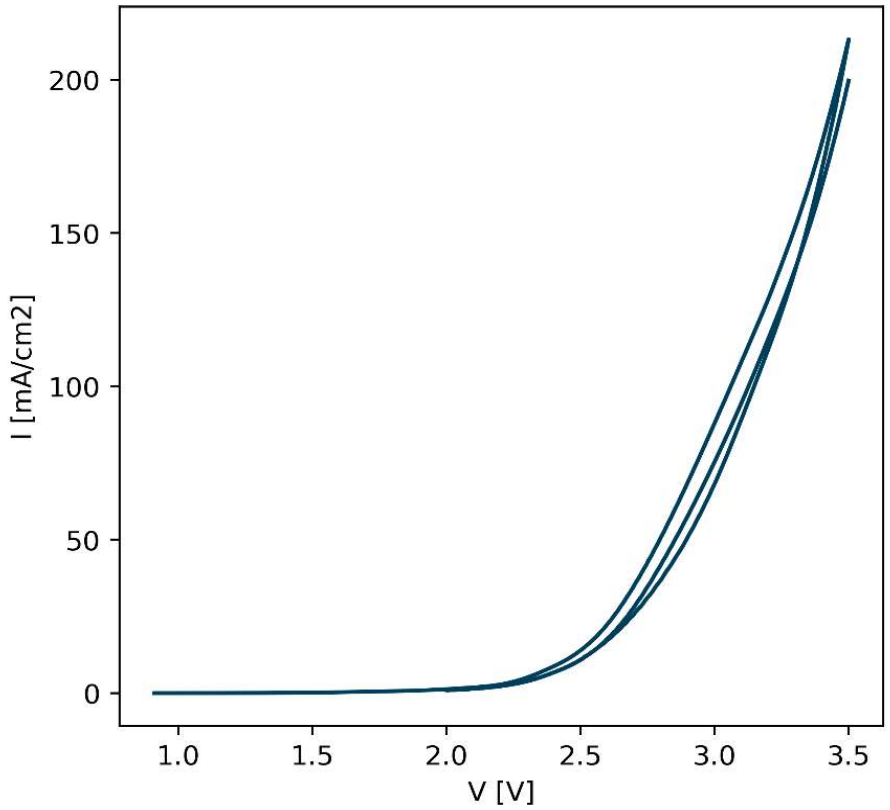
- As we decrease current the Cs diffuses back to the anode, thus all Cs decreases

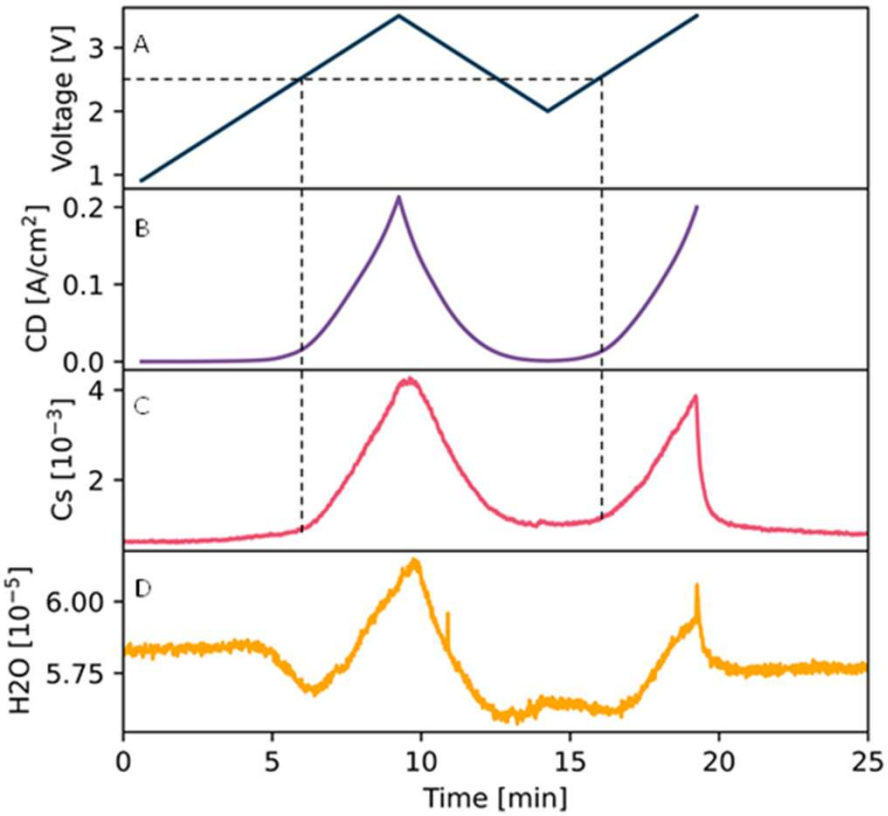
- The water has no driving force to go to the anode thus stays put.

- The microporous layer water decreases as it diffuses to the macroporous layer.



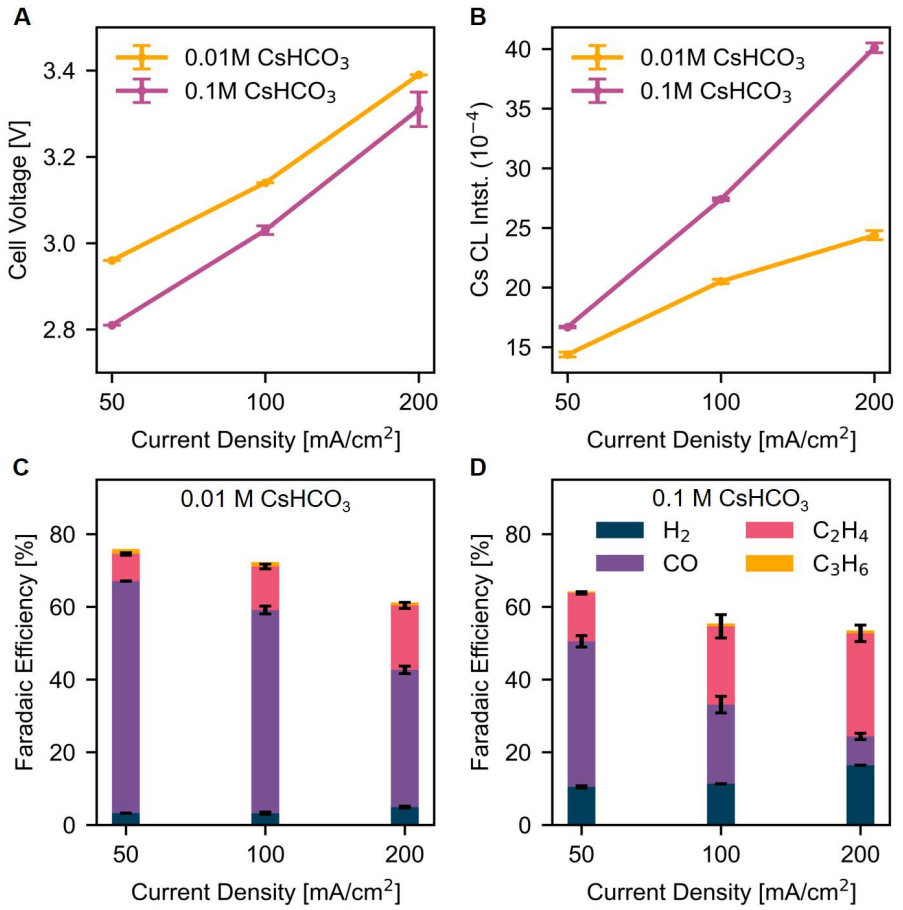
Analyzing a CV with Cs^+ cations





Voltage and Selectivity

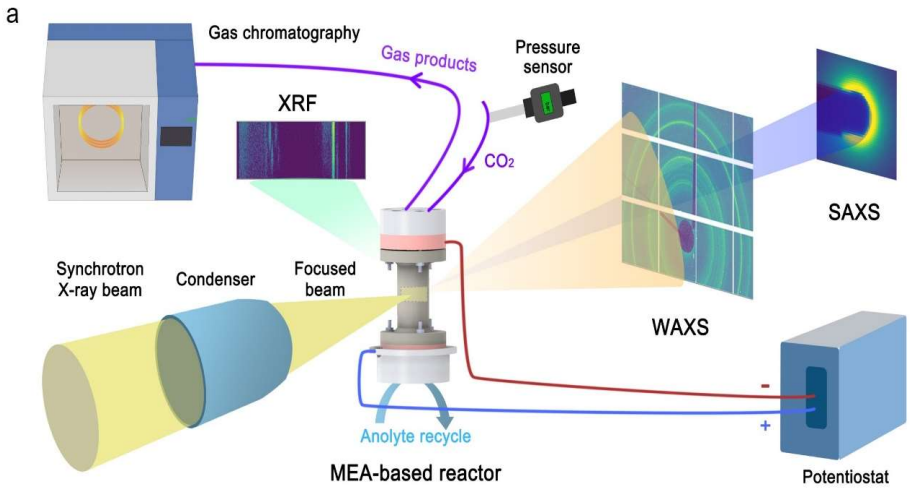
- Low Cs concentration gave us higher voltages and more CO
- High Cs concentrations gave us more Cs crossover and slightly more H_2.
- We did measure liquid products ex-synchrotron and the filled the Faradaic efficiency gap.



Small angle X-ray scattering (SAXS)

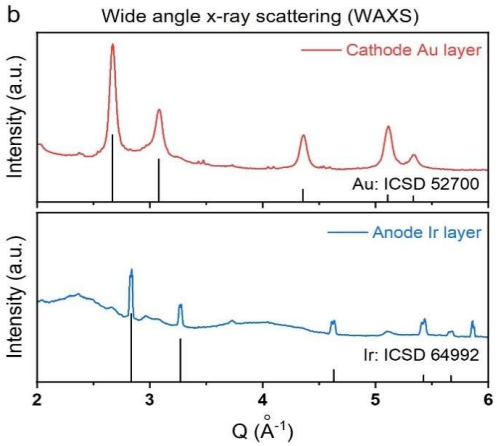
Set-up

Rotating between SAXS & WAXS every 30 seconds



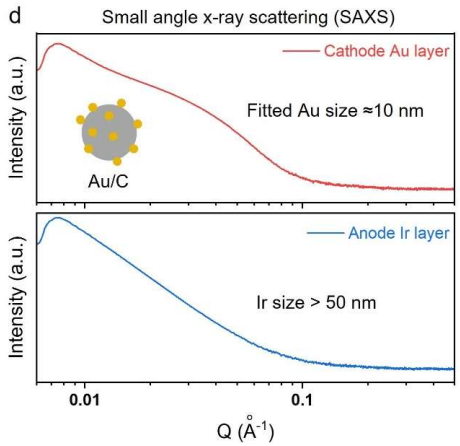
WAXS

- Scherrer Equation
- Corrosion
- Ripening



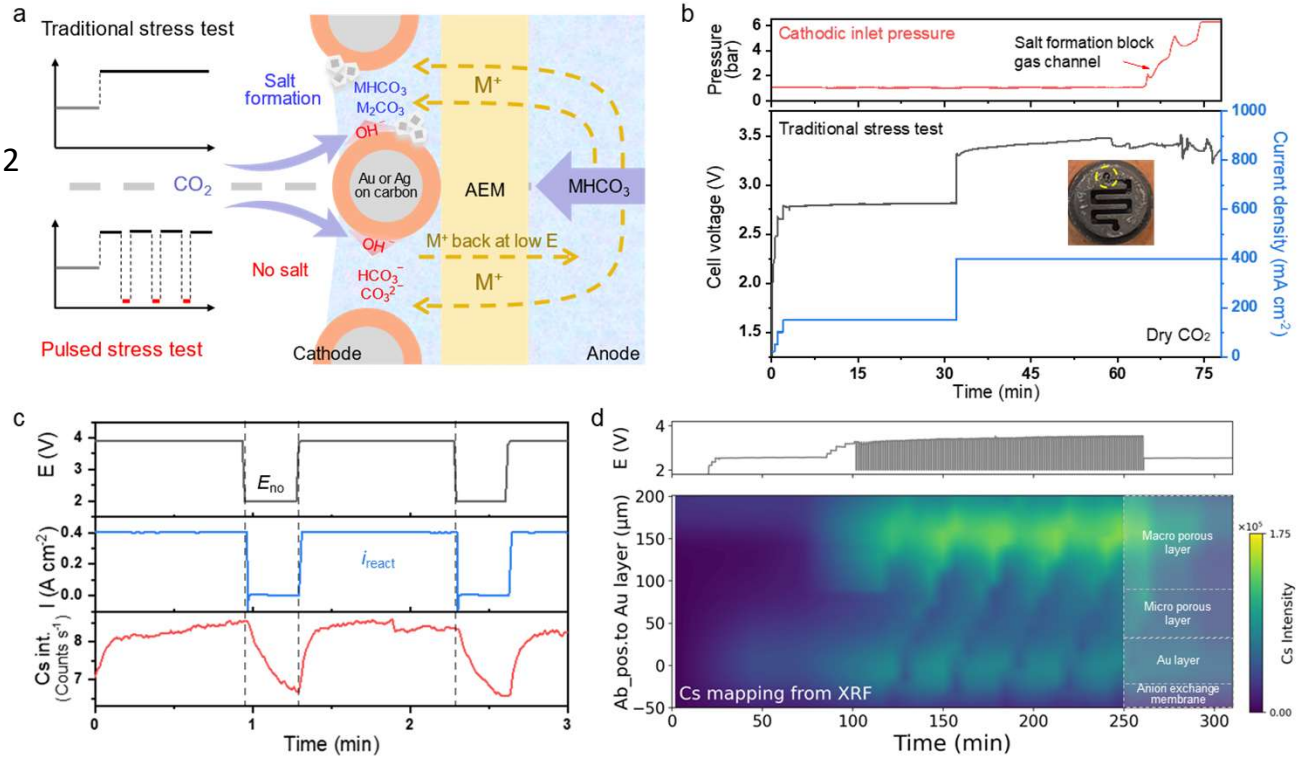
SAXS

- Complex Model
- Detachment
- Aggregation

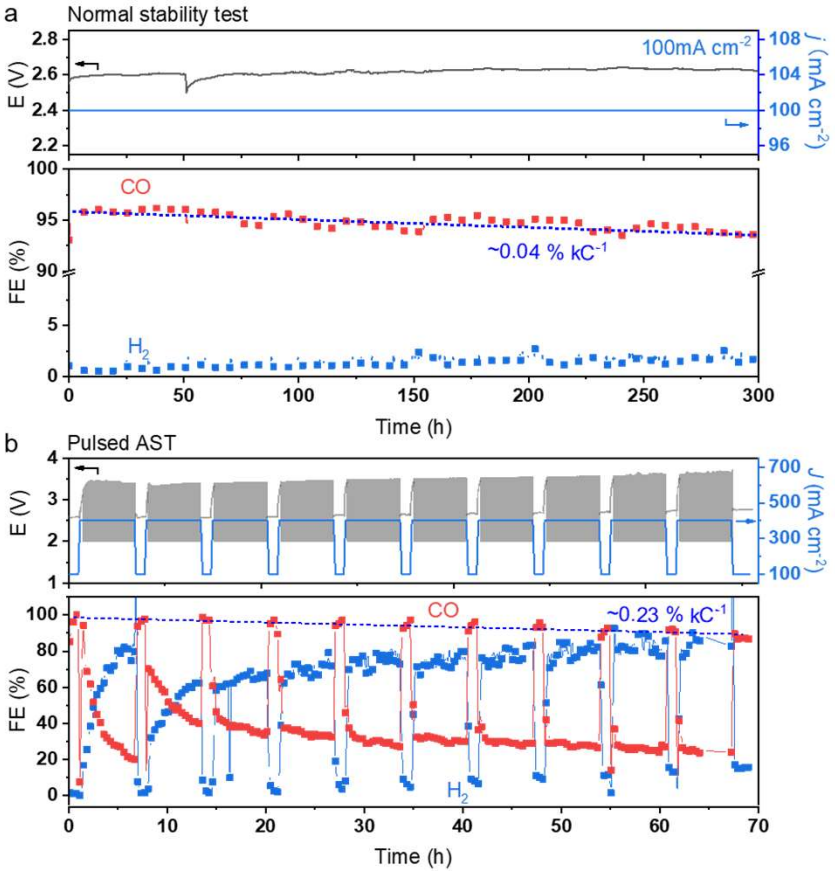


Stress test- Continous vs. Pulsed

- Au or Ag catalysts were used.
- Normal stability test- 100 mA/cm^2
- Stress tests at 400 mA/cm^2 done
  - 60s on,
  - 20s off (-2V)
- Focus on catalyst stability, not salt management.

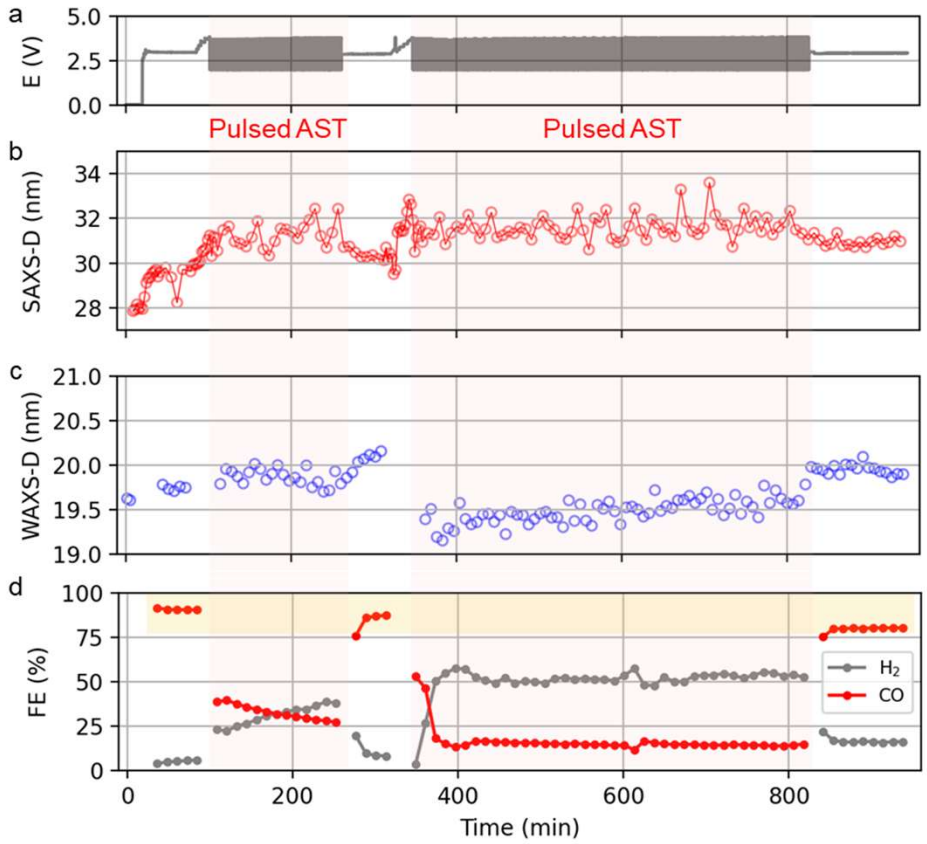


Durability Tests



SAXS & WAXS

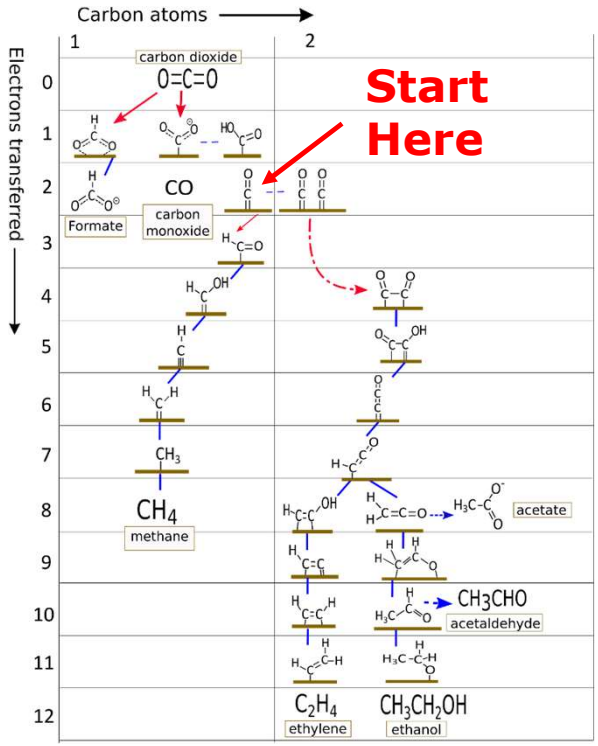
twelve



CO electrolysis

- What if we do CO electrolysis?

Fundamental



Scale-up

Cathodic reactions

$CO + H_2O + 2\ e^- \rightarrow C_2H_4 + 2\ OH^-$

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

Anodic reactions

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

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

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

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

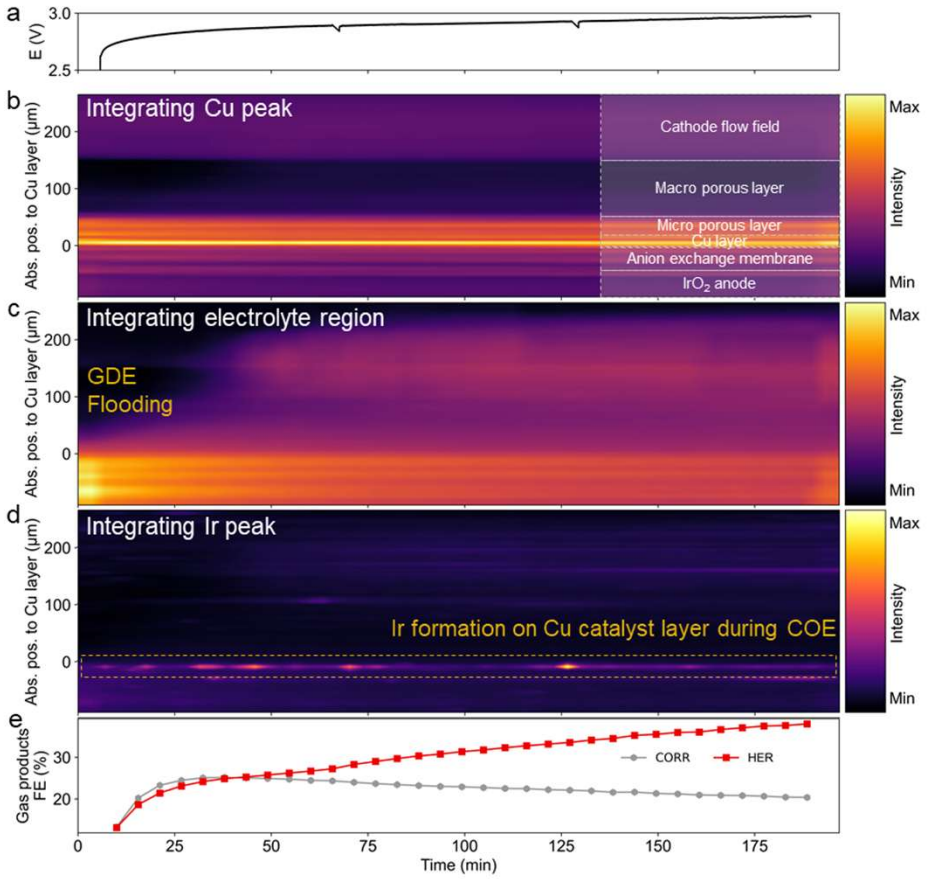
$CO_3^{2-} + 2\ H^+ \rightarrow CO_2 + H_2O$

Anion exchange membrane

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

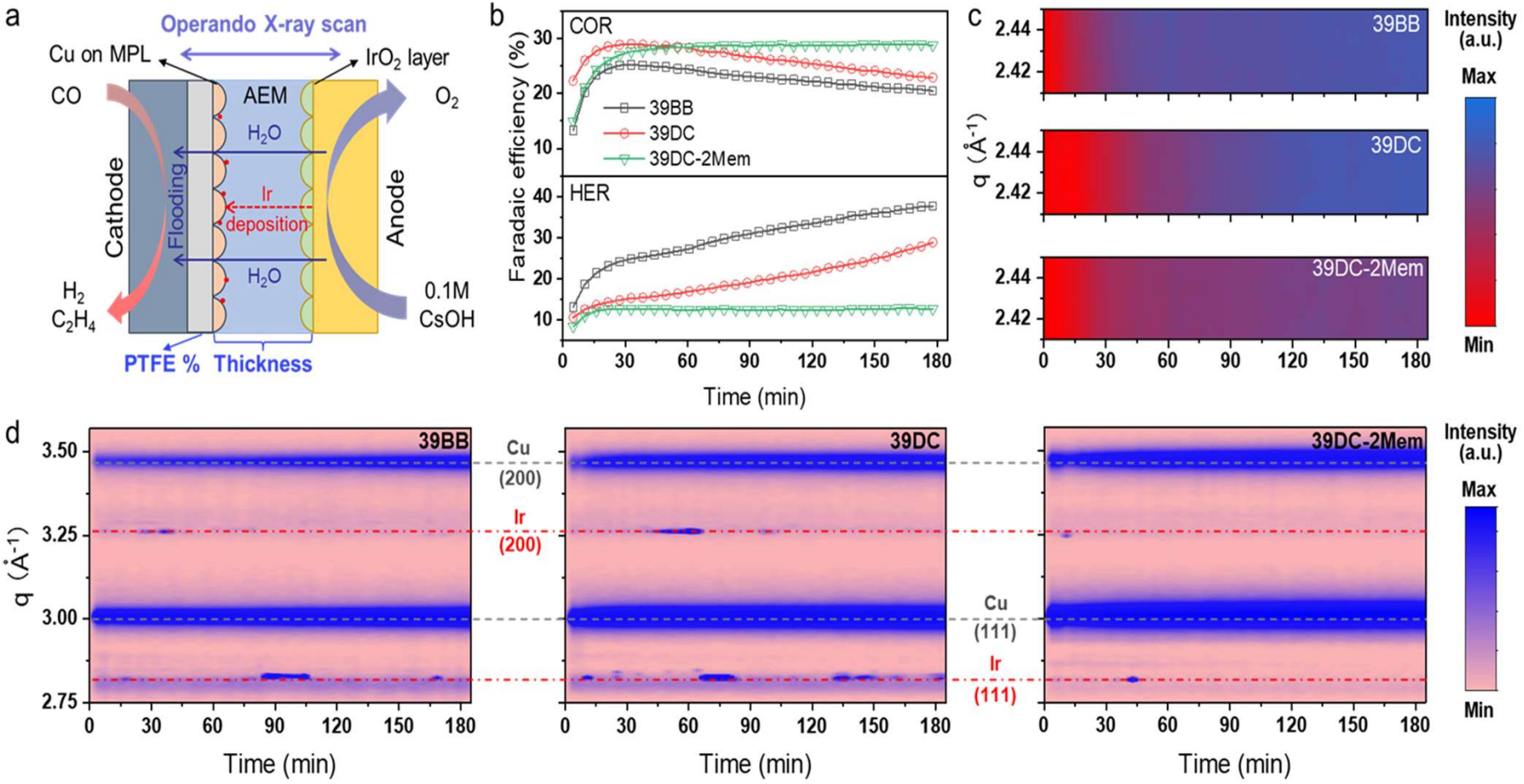
Issues with CO electrolysis

- 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)
- To prevent Ir crossover we can
  - Have a better membrane
  - Do not use Iridum

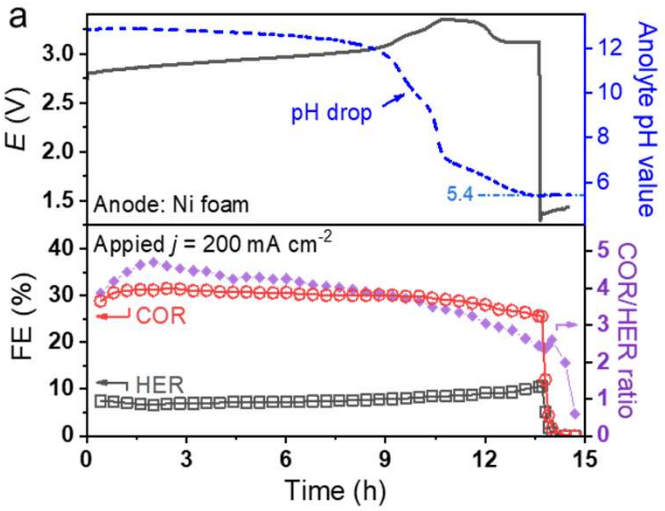


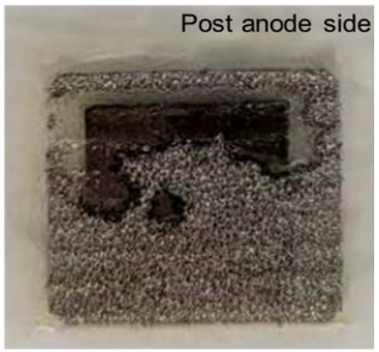
Xu. et al., Nature Catalysis, 2023

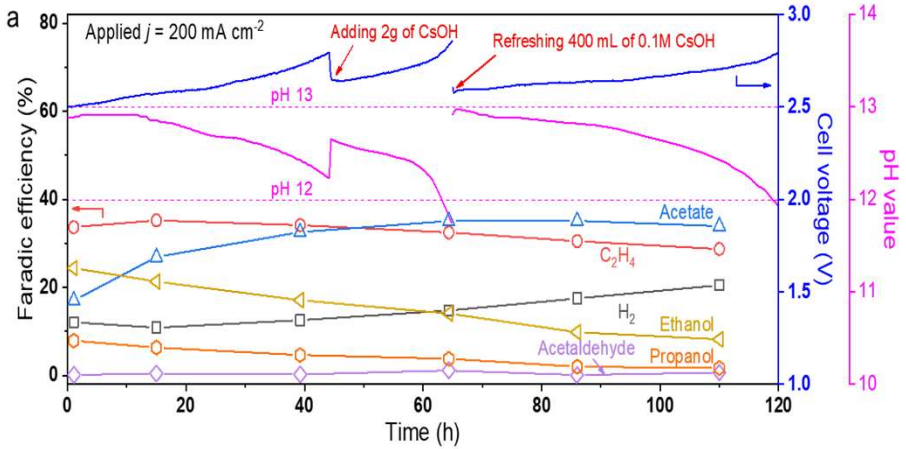
Different gas diffusion layers & double membrane

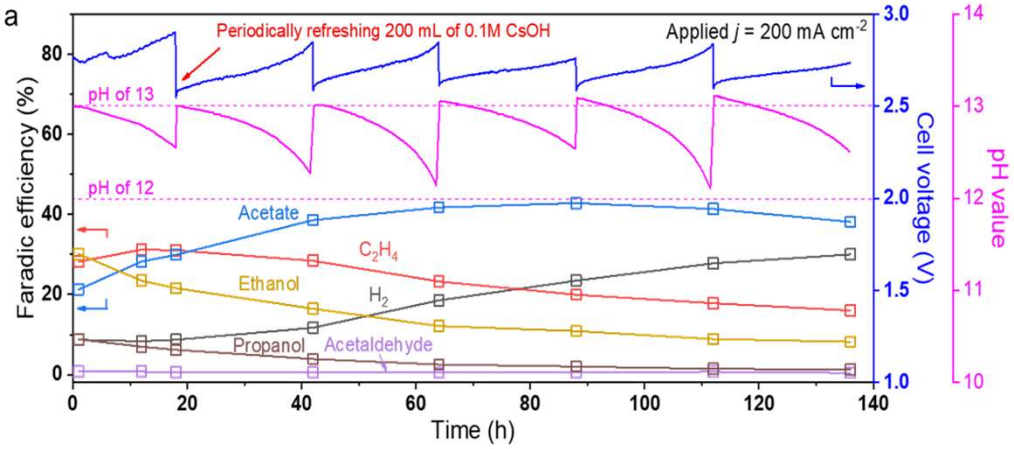


Varying alkalinity for CO electrolysis





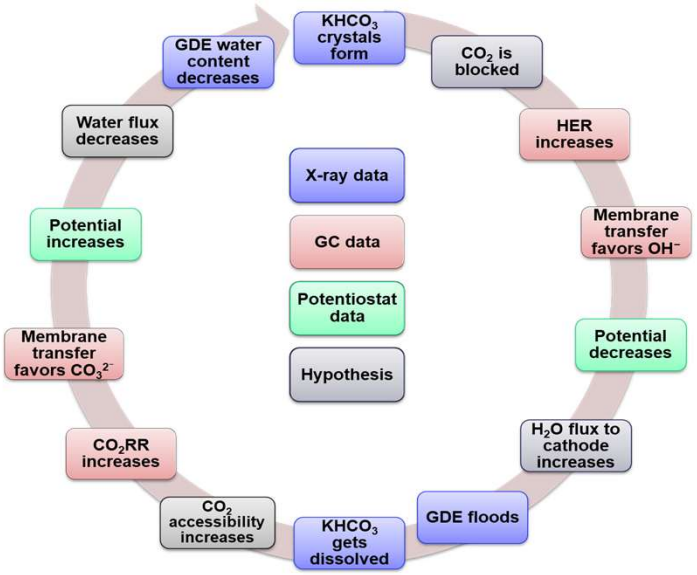




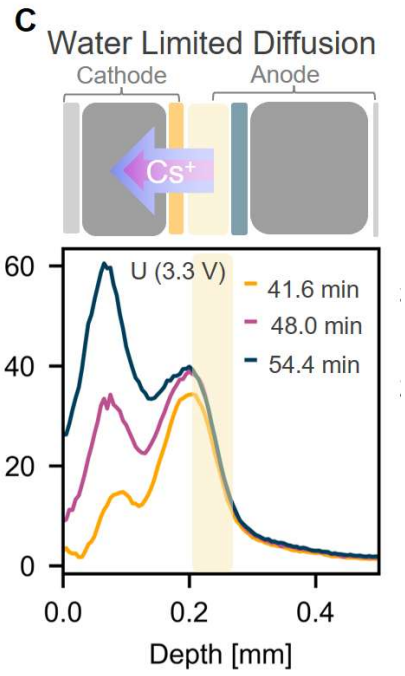
Xu. et al., Nature Catalysis, 2023

Conclusions

- Salt penetration through AEM's is a huge issue
- Cesium's high solubility makes it the optimal cation to use commerically.
- Fluorscence allows us to watch salt build-up in real time



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



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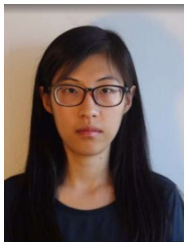
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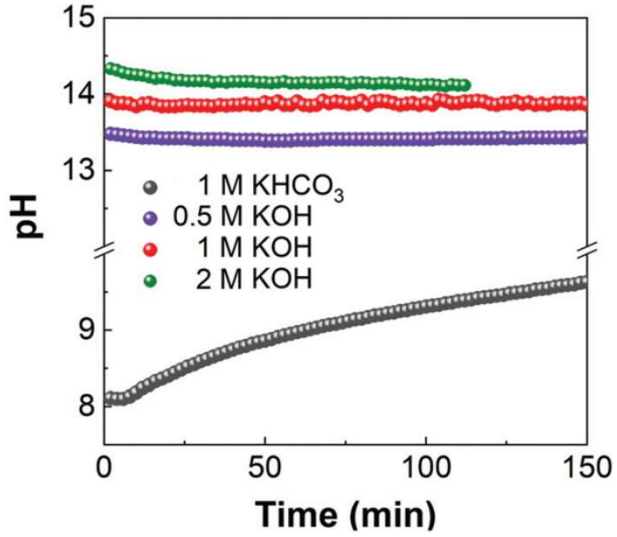
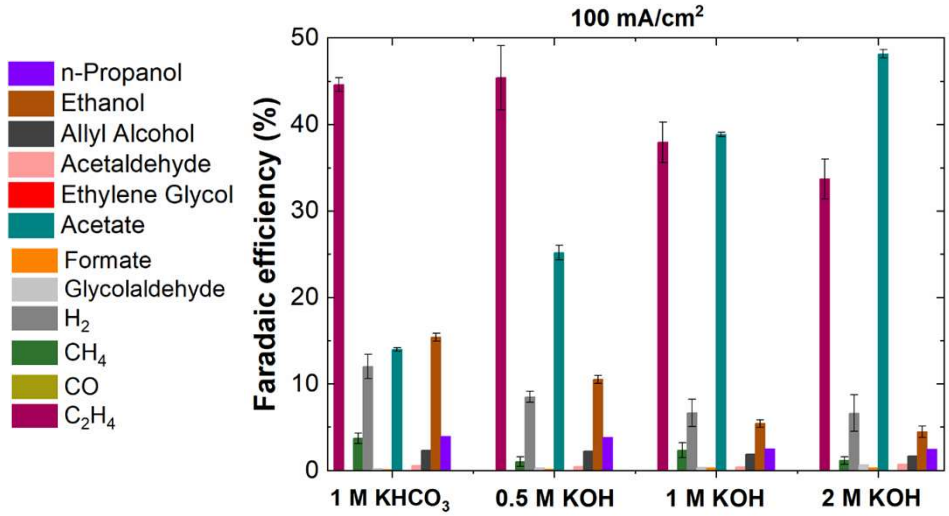
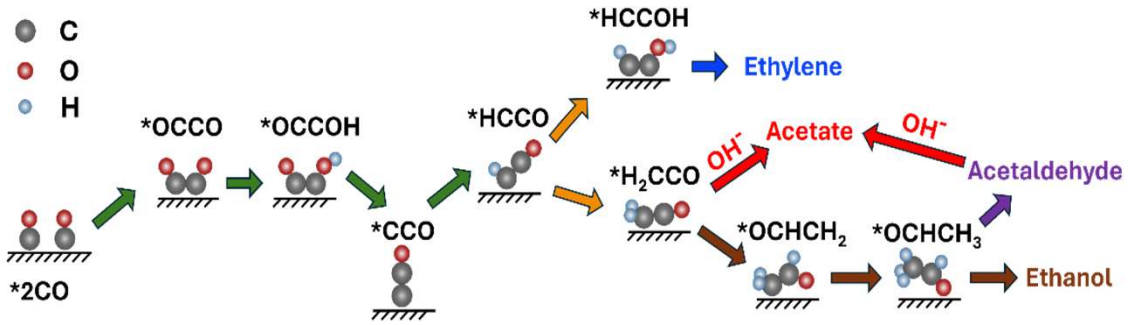
Maria Pinto

Modifications related to CO electrolysis

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







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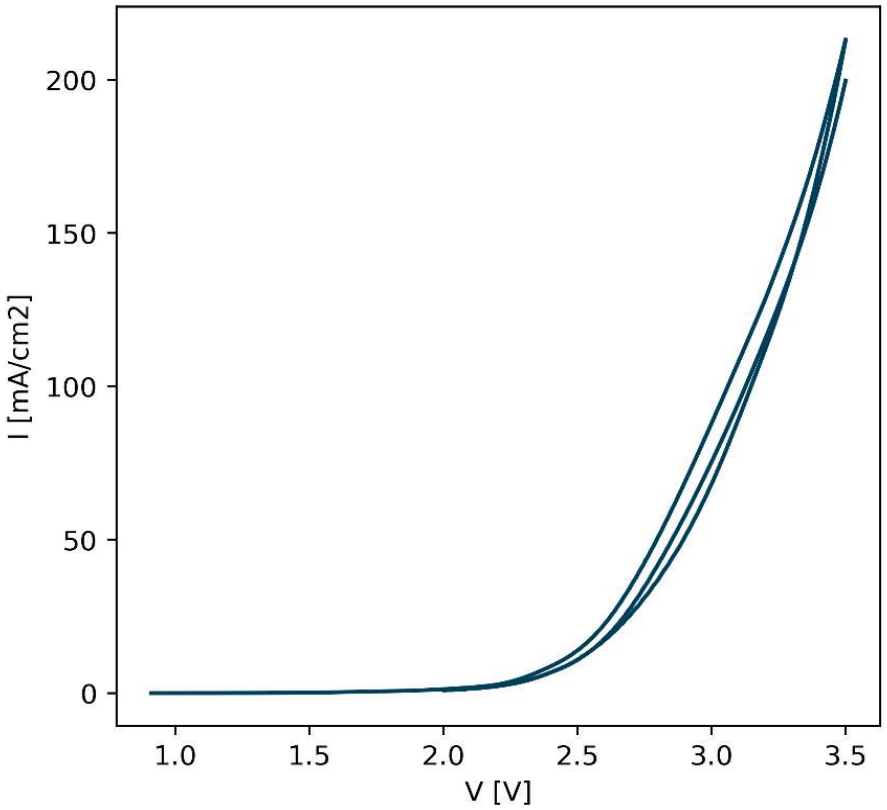
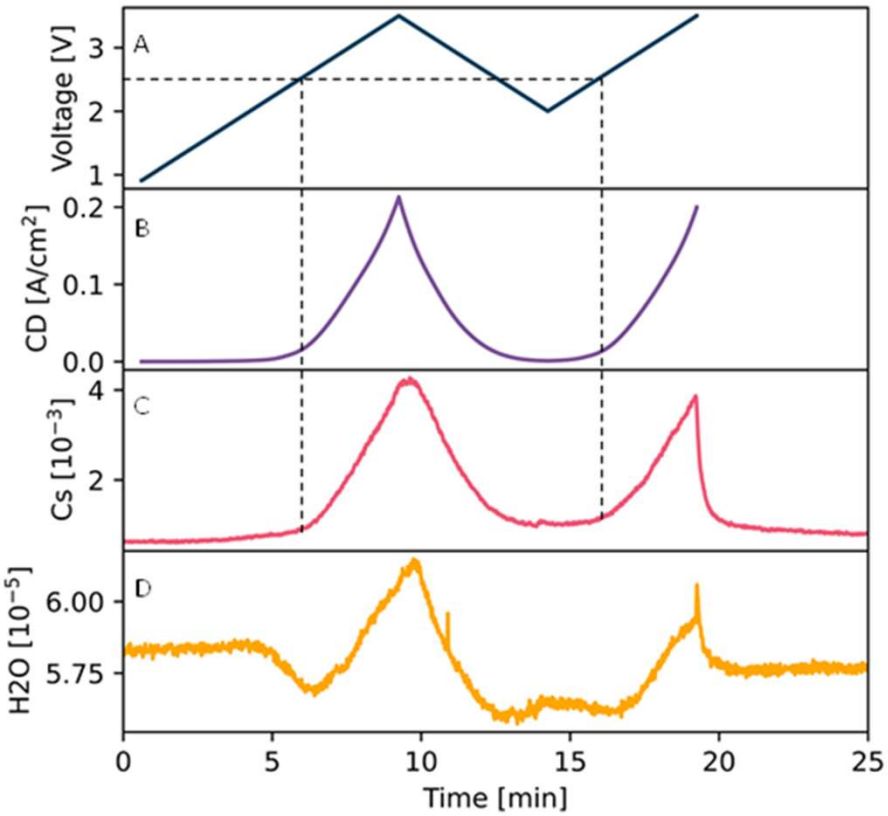
Analyzing a CV with Cs^+ cations





Analyzing Cs^+ and pulsing effects