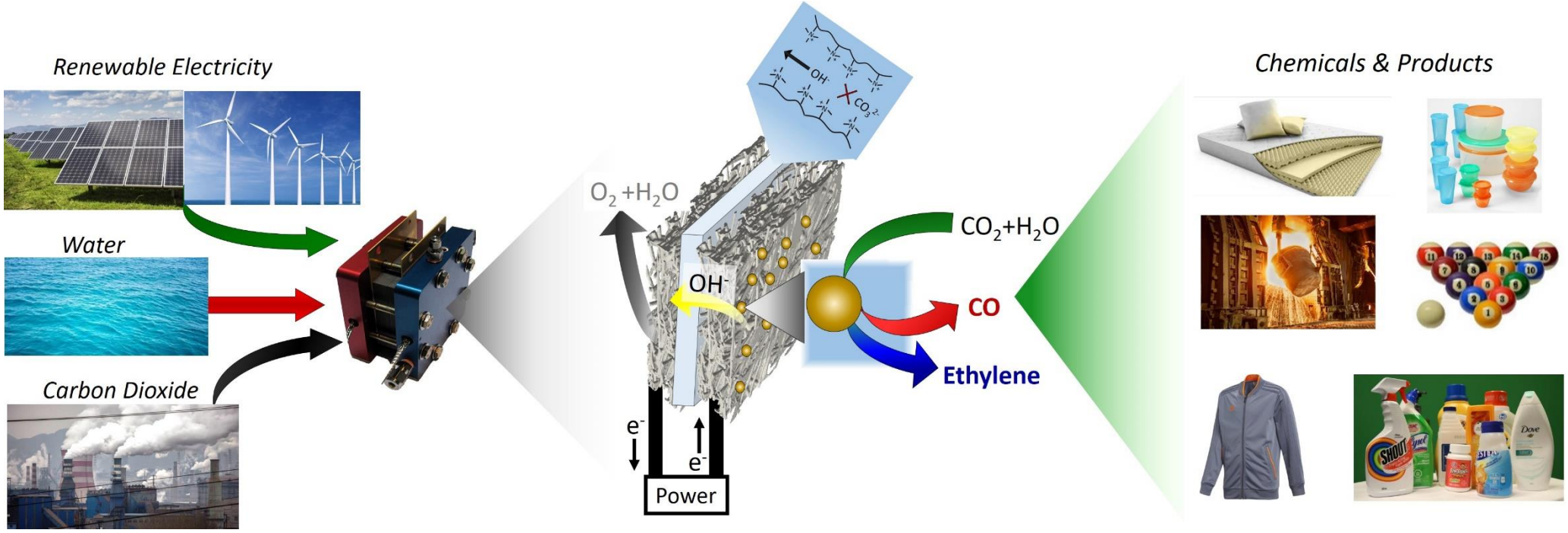
Analyzing the Complete Carbon Balance in High Current Density Electrochemical CO_2 Reduction Reactors

Brian Seger

2019 NanoGe Fall Meeting (SolCat19)
Nov 6, 2019



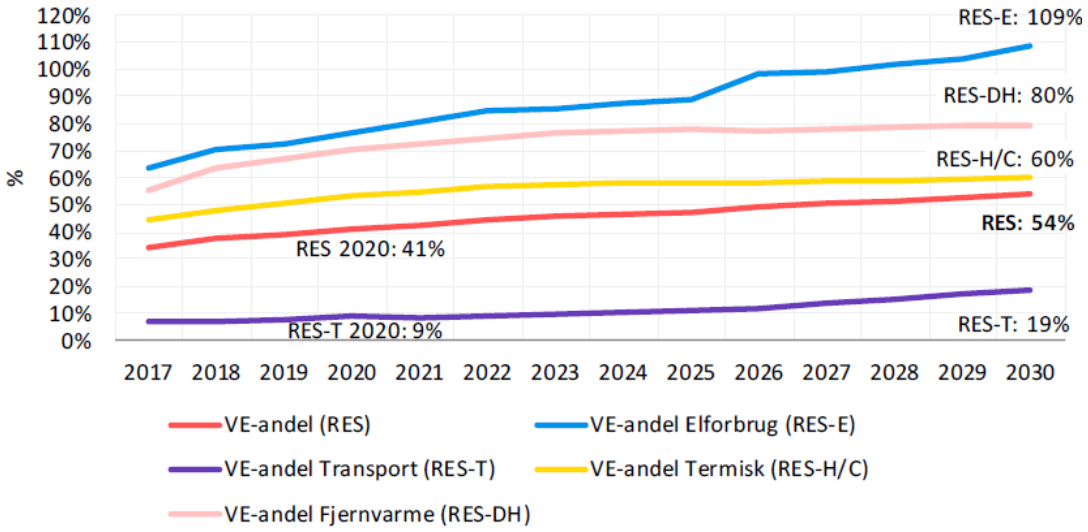
Chemicals Before Fuels

- Chemicals need functionality, and purity.
- Fuels just need to burn

Material	# of e⁻	Value		World Prod. (megaton)
		($/ton)	($/MC)	
Hydrogen	2	1000	**0.010**	60
CO	2	750-2200	**0.110**	75
Formic Acid	2	650	**0.150**	0.8
Formaldehyde	4	530	**0.041**	10
Methanol	6	496	**0.027**	160
Methane	8	150	**0.003**	4000
Ethanol	12	600	**0.024**	110
Ethylene	12	1050	**0.025**	180

H_2- https://www.hydrogen.energy.gov/ CO- https://www.openpr.com/ COOH- A. A. N. Afshar, Chemical Profile: Formic Acid. *TranTech Consultants, Inc.*, (2014). CHOOH - https://www.icis.com CH_3OH Methanex.com CH_4- EIA (www.eia.gov), Acetic Acid- Prnewswire.com/ , Ethylene Glycol- https://www.intratec.us/ , Ullmann's Encyc. of Ind. Chem. Acetone- Platts , Ullmann's Encyc. of Ind. Chem, Ethanol- Nasdaq, http://www.ethanolrfa.org Ethylene- Platts

- Denmark will reach 100% renewables by 2028



75 Mton/yr $\xrightarrow{\text{@ 3V}}$ 4.3×10^{11} kWh/yr

This is 100 times Denmark's electricity consumption

Industrial relevant approaches to eCO_2 reduction

Part 2

Advantages:

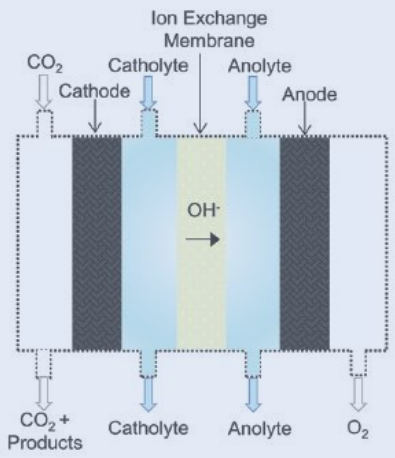
Part 1

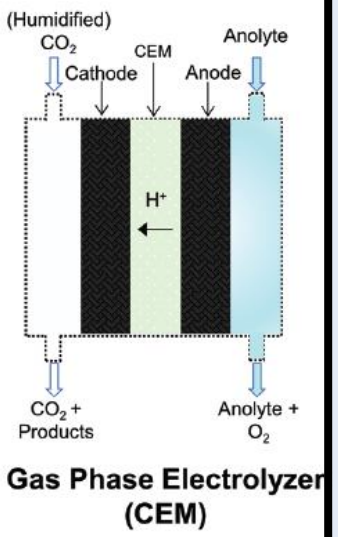
Liquid Product Extraction

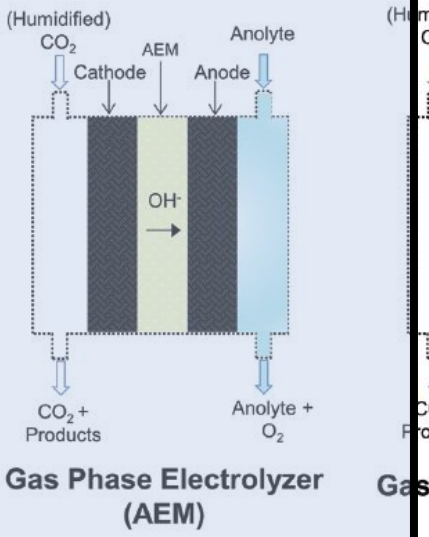
Low ohmic loss, stable

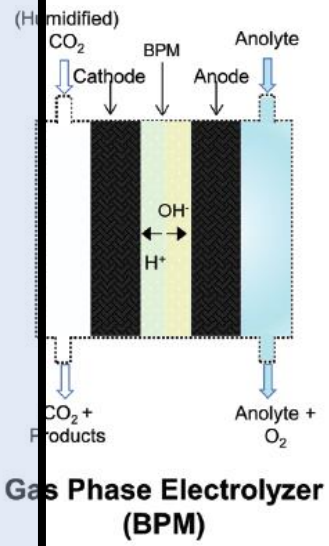
Helps selectivity

Cheaper anode









High ohmic losses

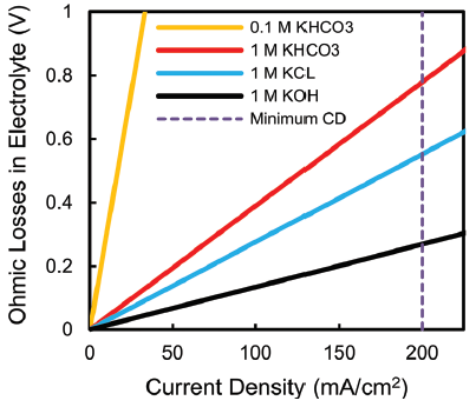
Non-H^+ crossing over membrane

CO_2 crossover

Mechanical stability issues

Disadvantages:

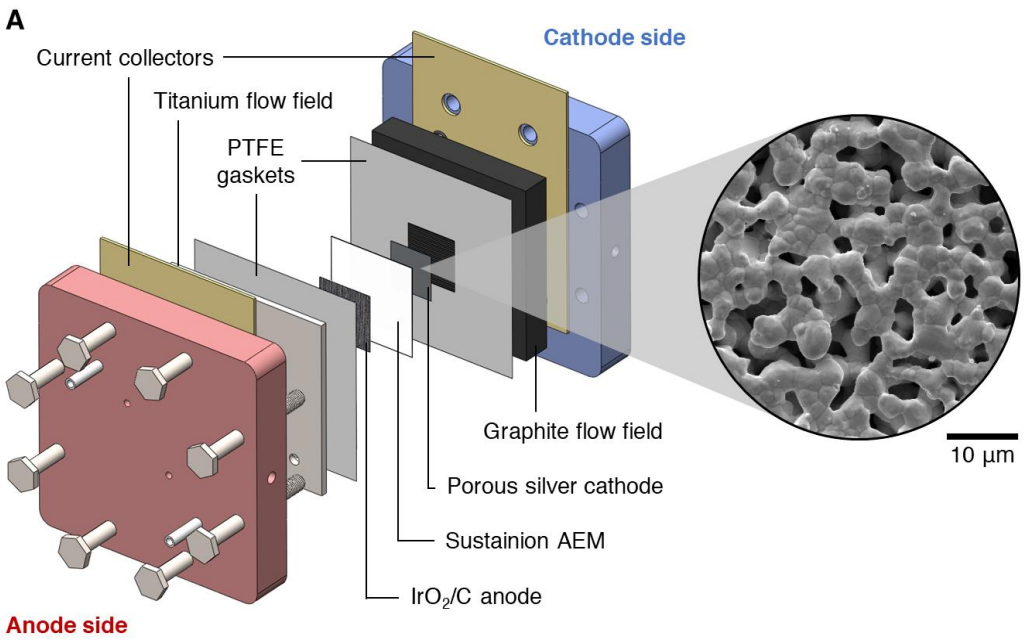
Kibria, et. al, Adv. Mat. , 1807166, (2019)

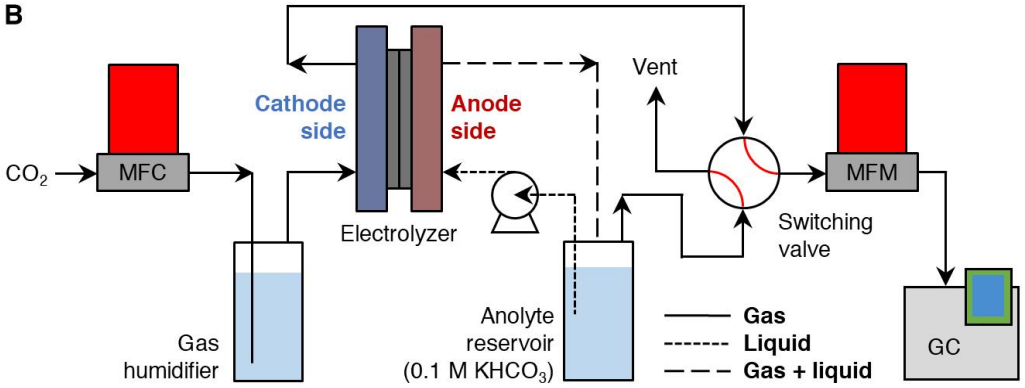


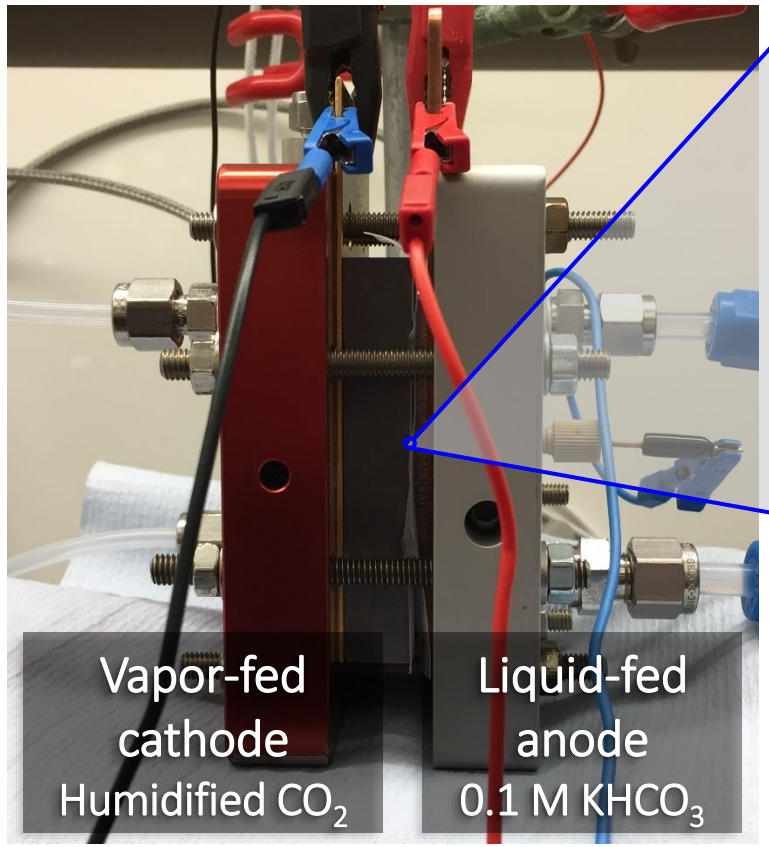
3 mm anolyte & catholye

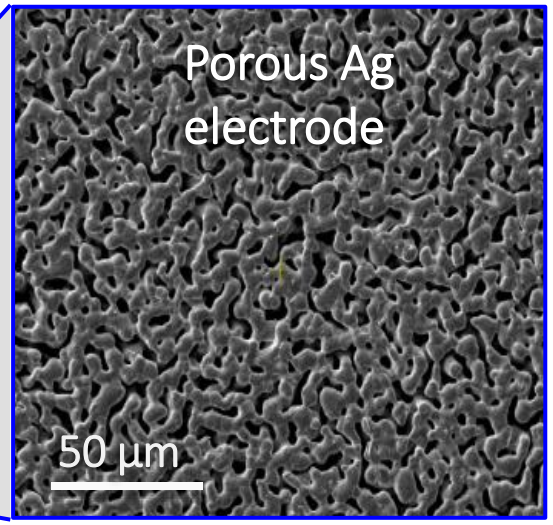
Burdyny and Smith, E&ES, 12, 1442—1453, (2019)

Electrochemical set-up









Cathode: silver membranes of 50 µm thickness

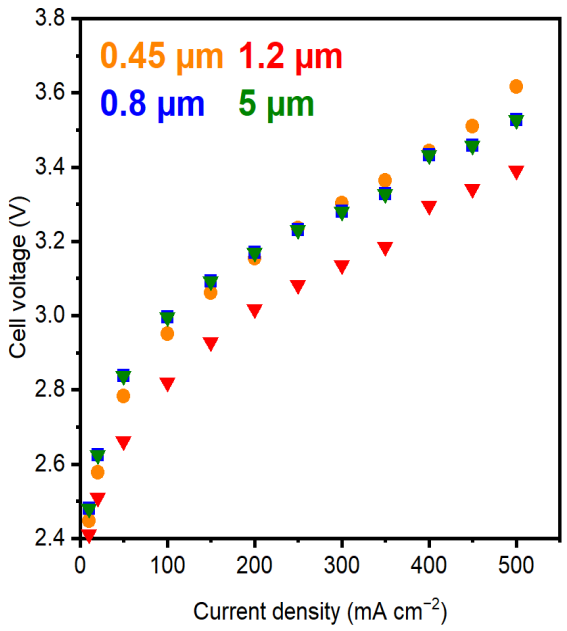
Anode: IrO_2 on carbon paper

Membrane: Sustainion 37-50 AEM

Temperature: 30 C

Characterization & performance data

- SEM shows uniform pores of varying size.
- We did not see any significant performance difference between membranes.



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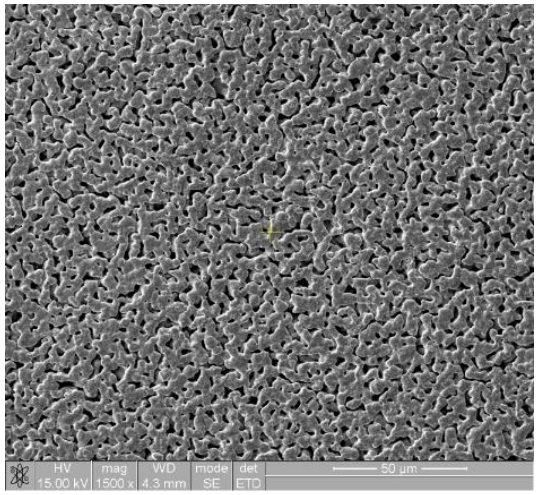
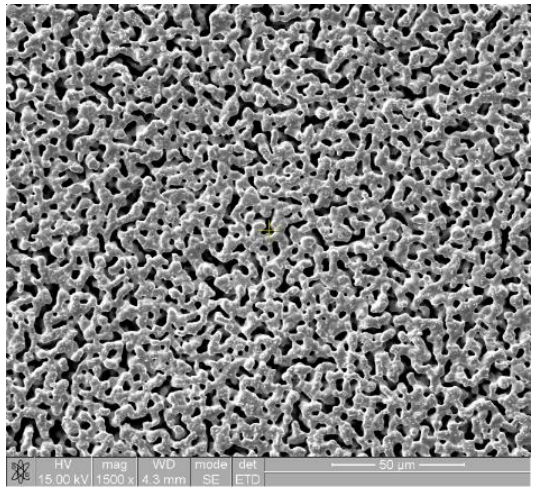
Faradaic Efficiency

Partial Current Density

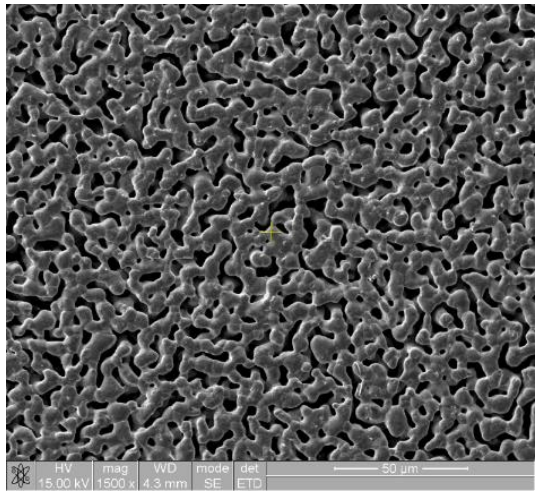
Larrazabal, G., et al., *ChemSusChem, 2019*



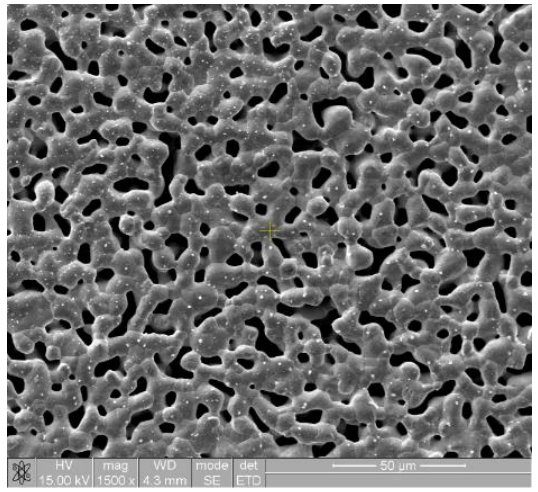
0.45 µm



0.8 µm



1.2 µm



5 µm

Reactors

What goes in is not what comes out

What goes in does not come out

- CO_2 that goes into the reactor can do multiple things.

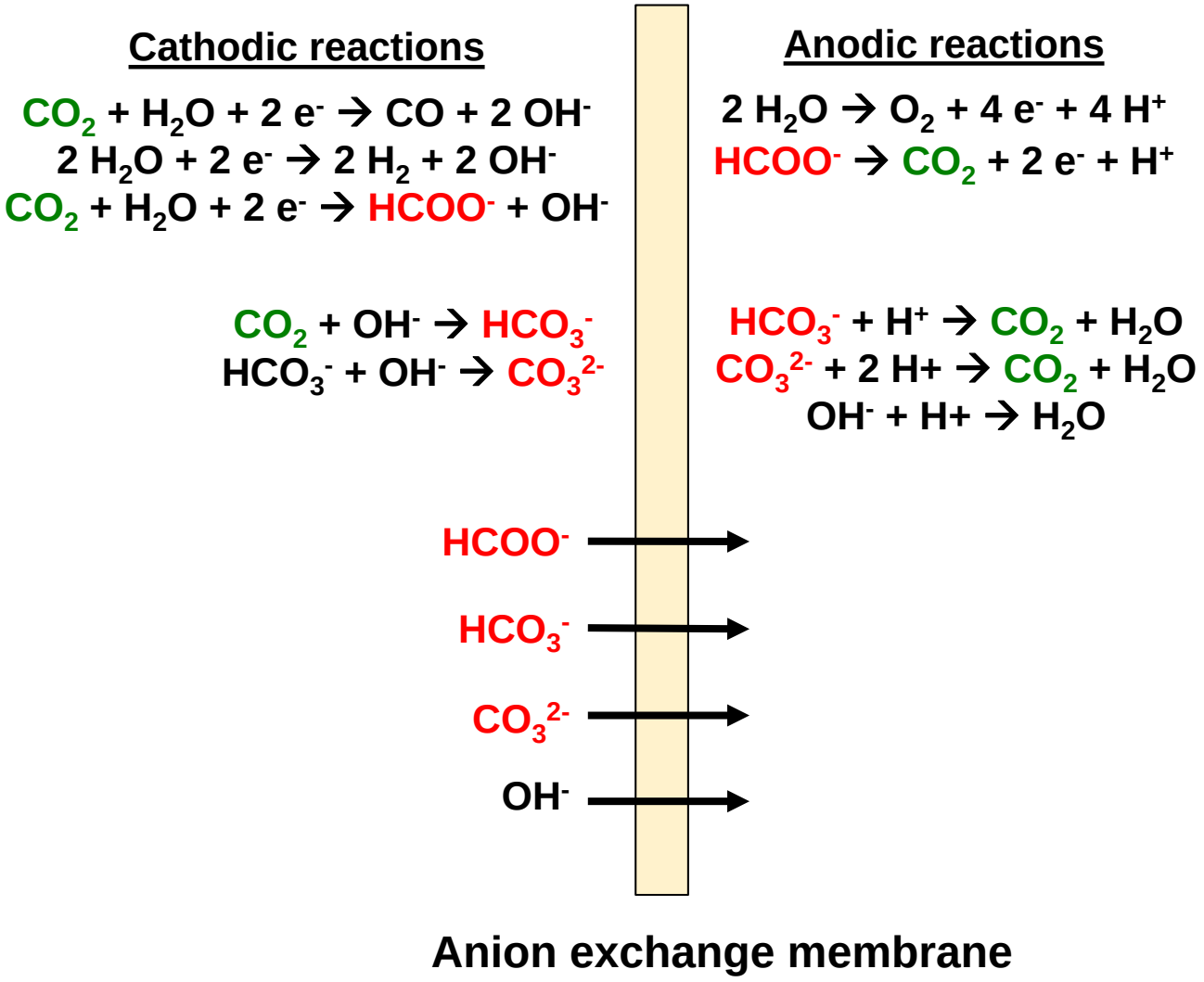
1) React to form
   - Liquid products, thus will not be in the gas flow
   - C2 products, which will ½ the gas flow rate

2) Equilibrate into the electrolyte

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

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

3) Get transferred across the membrane



Issues with outlet flow rate

- It is very hard to measure outlet flow rate

Inaccurate

(? Δ in conductivity)

Inaccurate

(? Δ in viscoscity)

Accurate

(Positive Displacement)

MESA Labs- Defender 530

Humidity locks up device

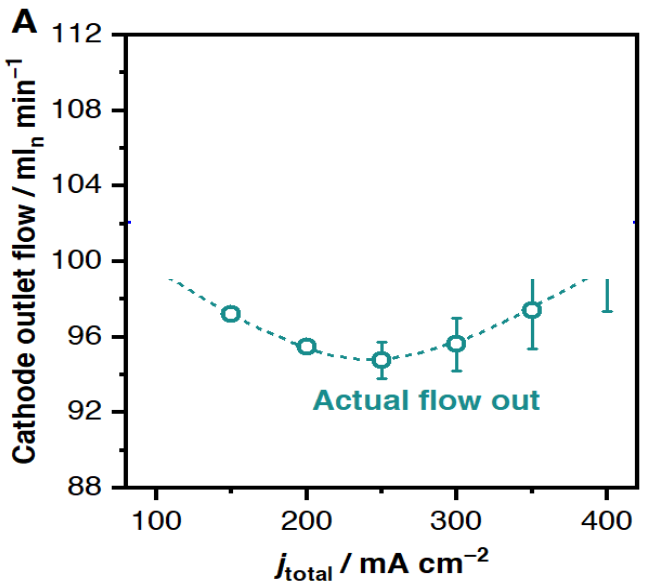
Old School

(Accurate, manual)

Accurate

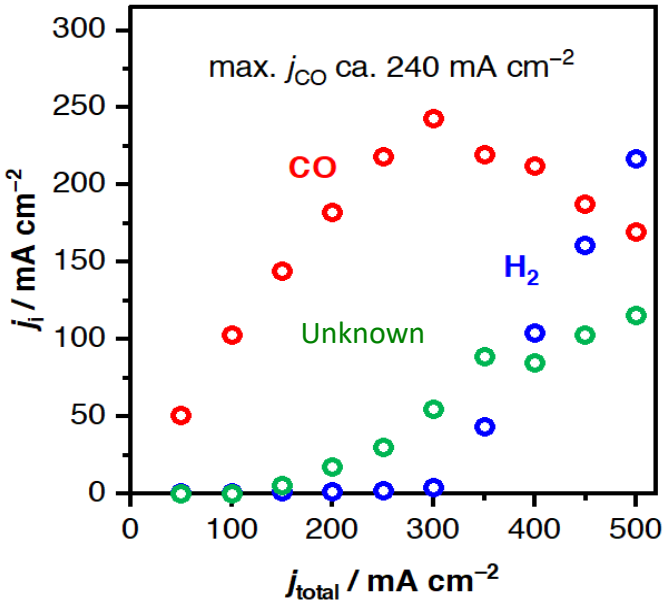
(Buoyancy)

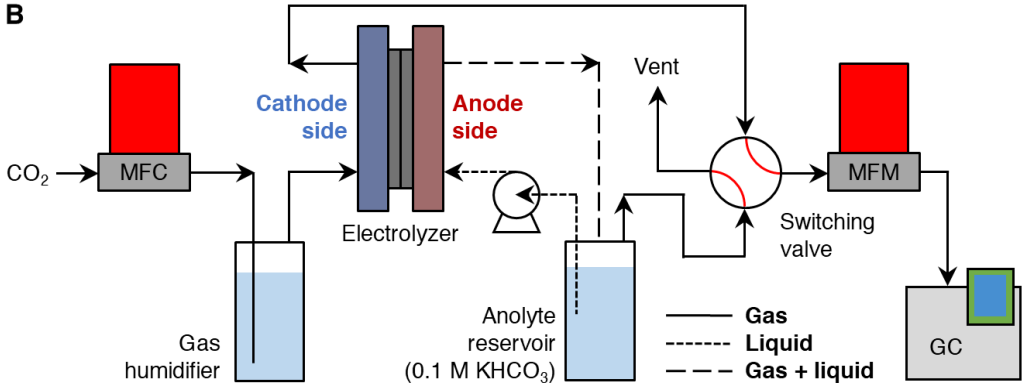
Bioprocess Control uFlow

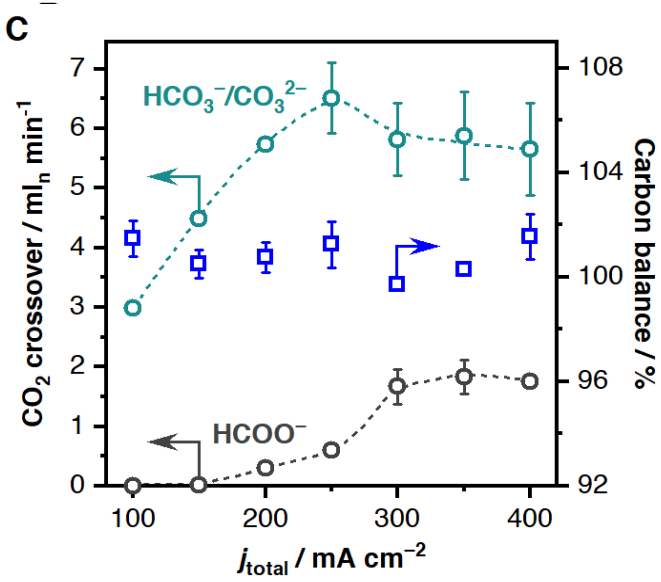


Cathodic reactions	Δ in outlet flow/2e-
$CO_2 + H_2O + 2\,e^- \rightarrow CO + 2\,OH^-$	0 mol
$2\,H_2O + 2\,e^- \rightarrow 2\,H_2 + 2\,OH^-$	1 mol
$CO_2 + H_2O + 2\,e^- \rightarrow HCOO^- + OH^-$	-1 mol

- We clearly have lots of CO_2 transferring over to the anode.

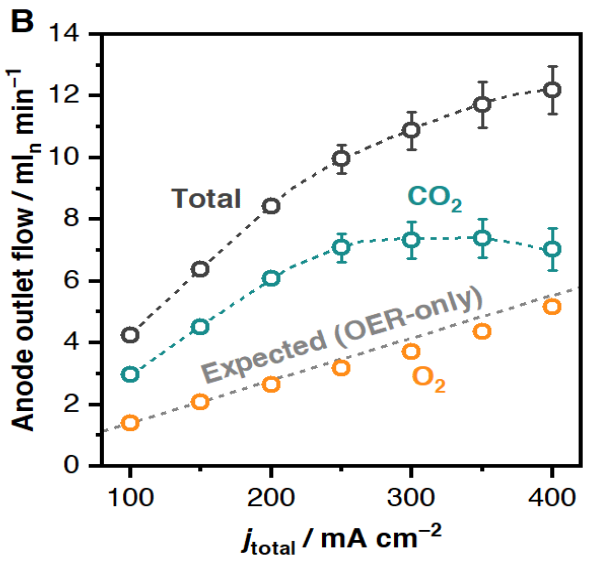


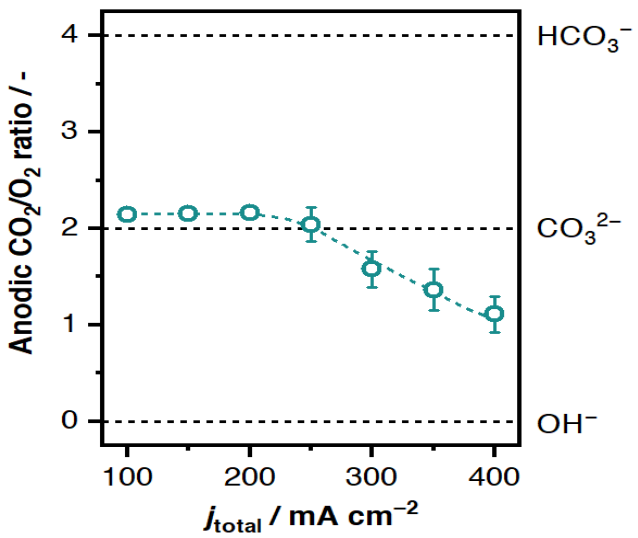


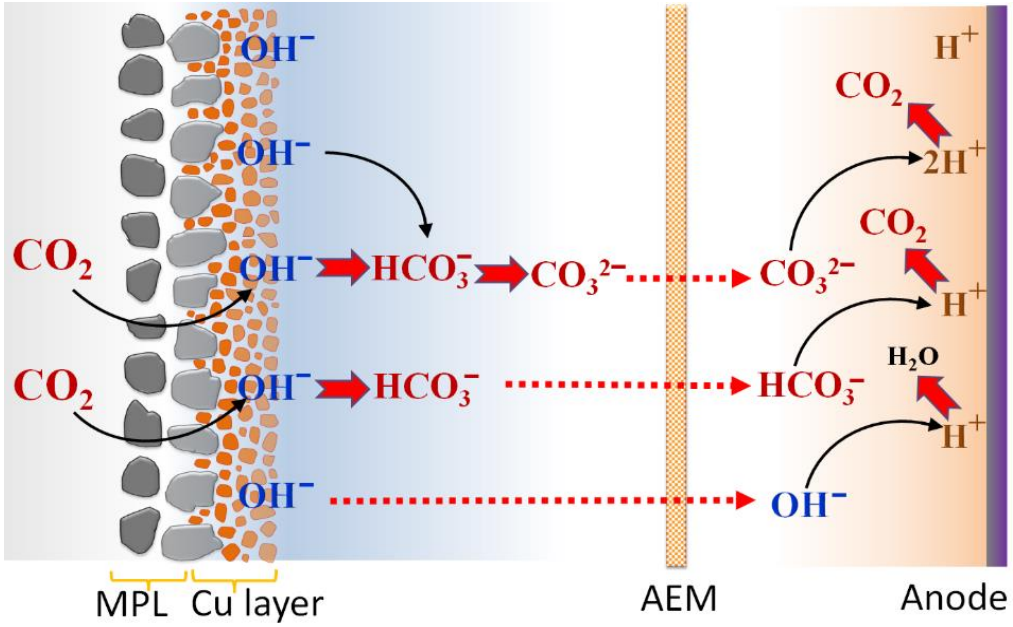


Larrazabal, G., et al., *ChemSusChem, 2019*

- A further analysis of anode gas flow gives insights into membrane crossover.
- This can give us details relating to:
  - Local pH
  - Membrane conductivity







Anode reactions: **CO_2/O_2 ratio**

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

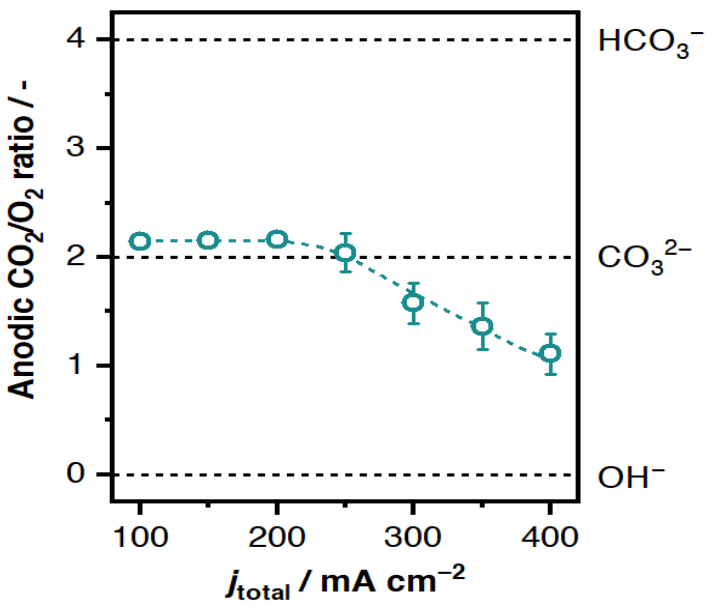
$$2CO_3^{2-} \rightarrow 2CO_2 + O_2 + 4e^- \longrightarrow 2$$

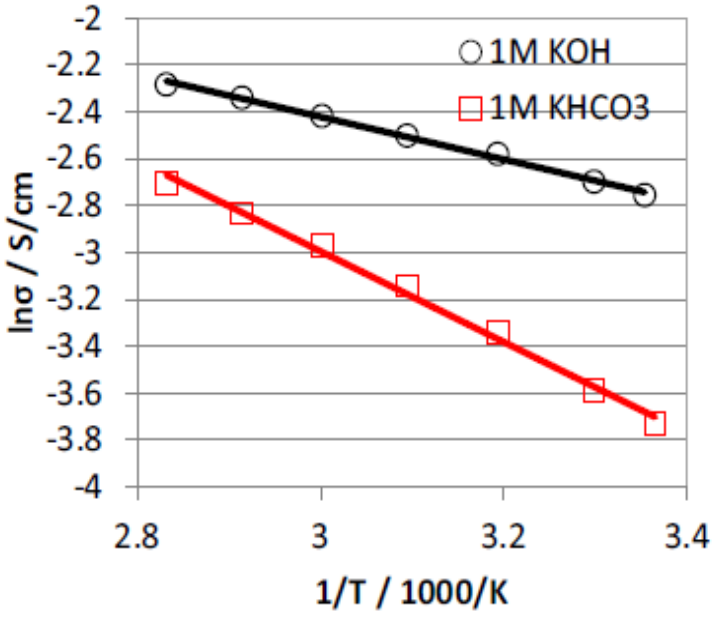
$$4OH^- \rightarrow 2H_2O + O_2 + 4e^- \longrightarrow 0$$

$$OH^- + COOH^- \rightarrow H_2O + CO_2 + 2e^- \longrightarrow 0$$

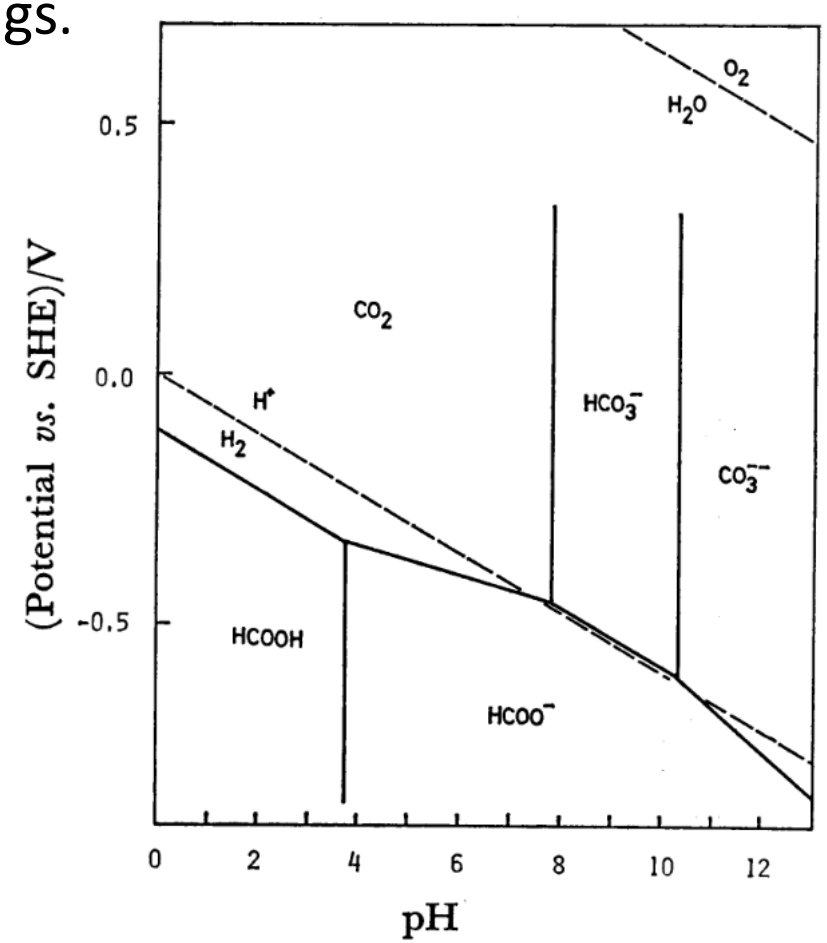
Analyzing our CO_2 crossover

- Carbonate transfer allows us to learn 2 very important things.
  1. Carbonate is going through, hurting conductivity
  2. Locally we are highly basic





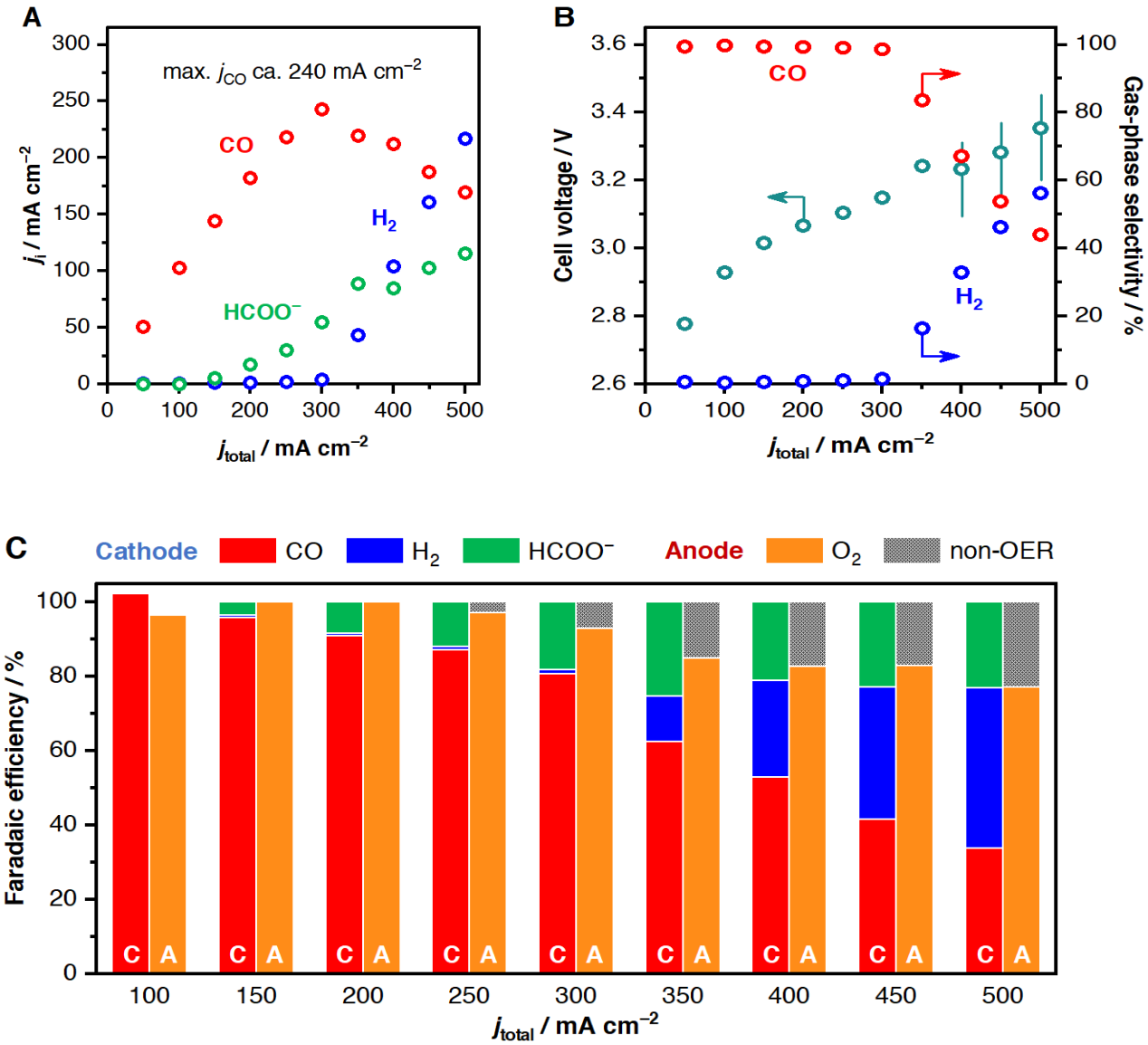
Liu, Z.;J. Electr. Soc.,165(15) J3371-J3377 (2018)



Hori and Suzuki, Bull. Chem. Soc. Jpn., 55, 660 (1982)

Total system analysis

- We have measures formate via NMR from condensed cathode droplets and at the anode
- Our cell voltage is compareable to other Ag based devices.
- Anolyte measurements show a loss in O_2 faradaic efficiencies at high currents.
- Non-OER consists of
  - Formate oxidation
  - Corrosion of carbon paper on anode.

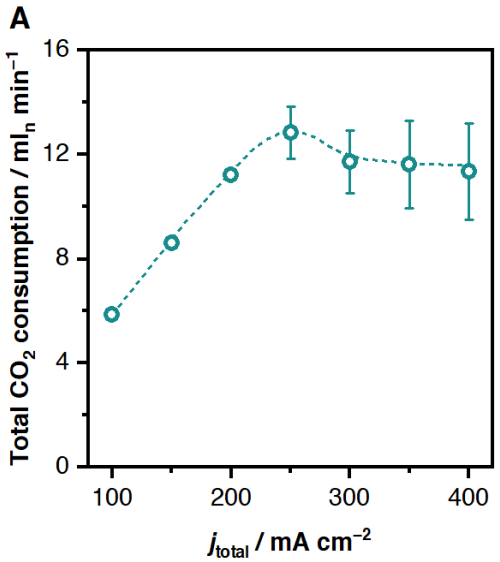


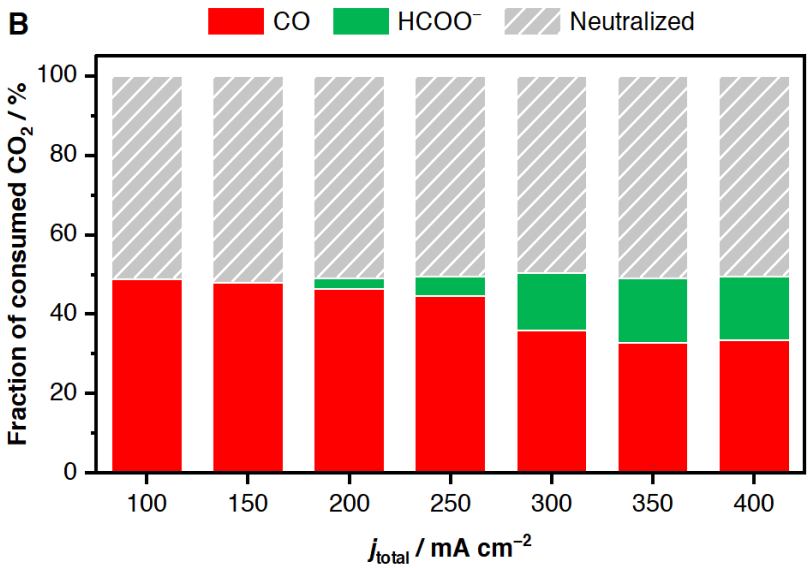
Larrazabal, G., et al., *ChemSusChem, 2019*

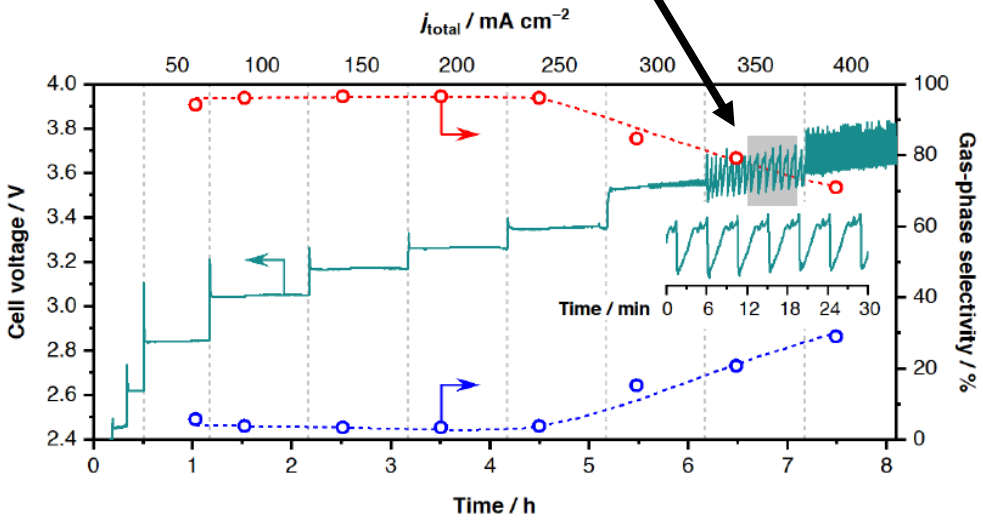
CO_2 conversion to CO

- Another important Figure of Merit is CO_2 conversion to CO.
- Our inlet CO_2 flow rate is 100 mL/min, thus our consumption is about 12%.
- Our CO_2 conversion to CO is between 30-40%.

Mass transfer issues prevent higher current densities

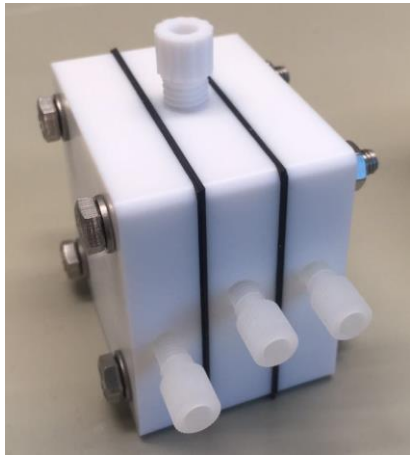


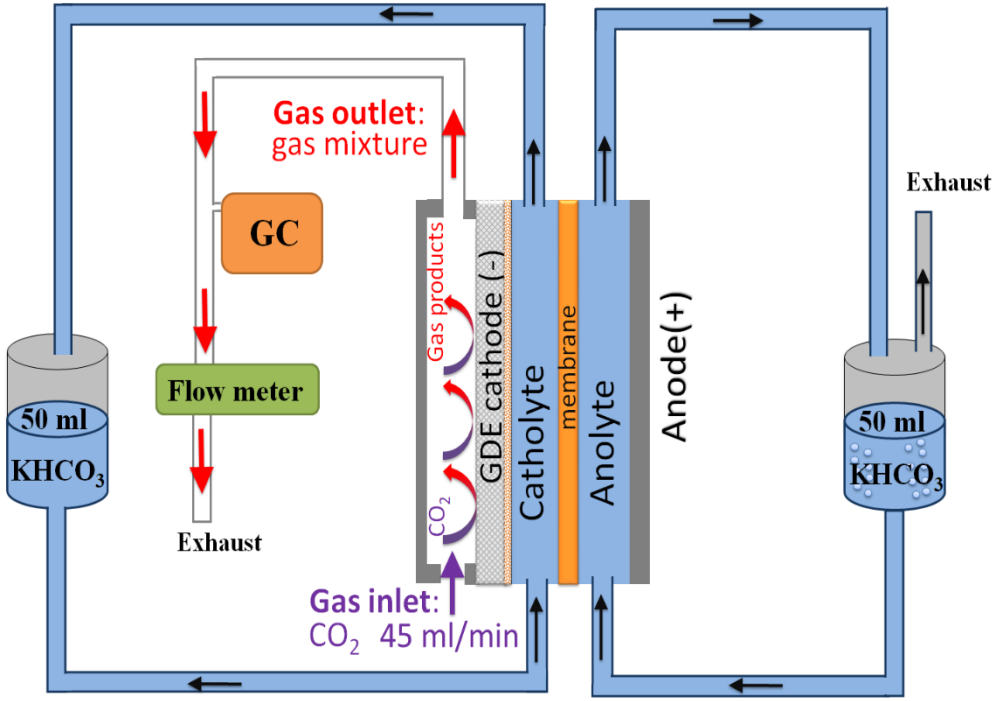




Analyzing copper for CO_2 reduction

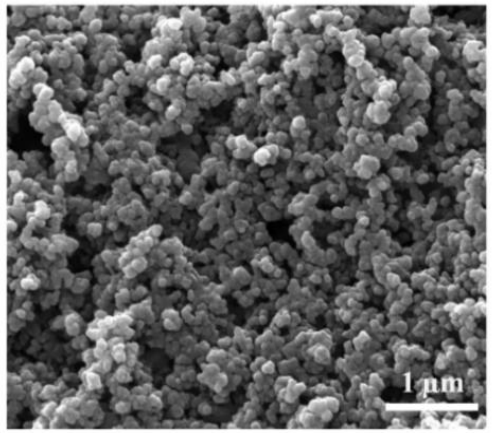
- With copper producing liquid products, we decided to go with a GDE approach.
- 70 nm sputtered Cu on a gas diffusion layer.





Electrode

SEM



Testing different electrolytes

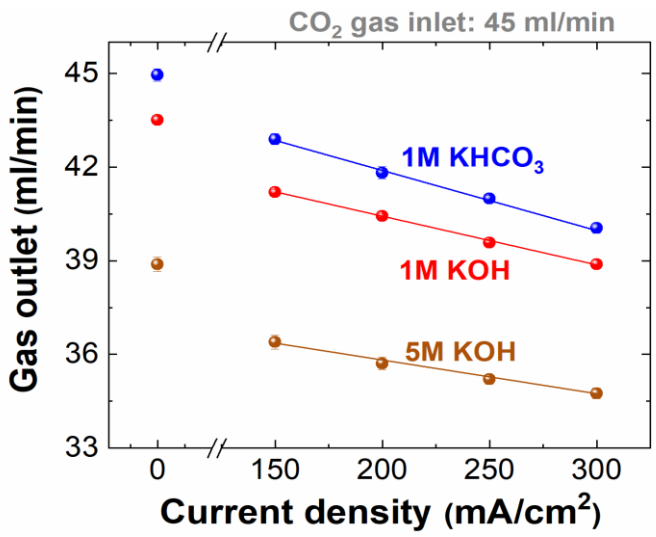
- We tested in both neutral and basic electrolytes.
- Basic electrolytes are effectively ‘ CO_2 scrubbers’

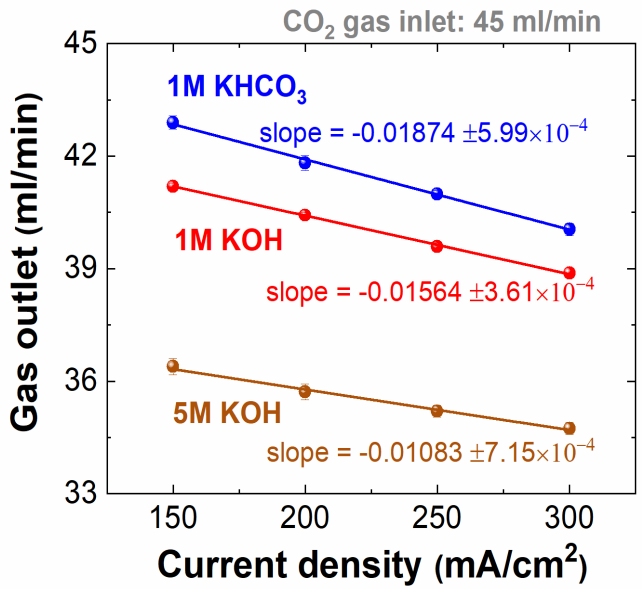
$$CO_2 + OH^- \rightarrow HCO_3^-$$ pKa (effective)=7.8

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

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

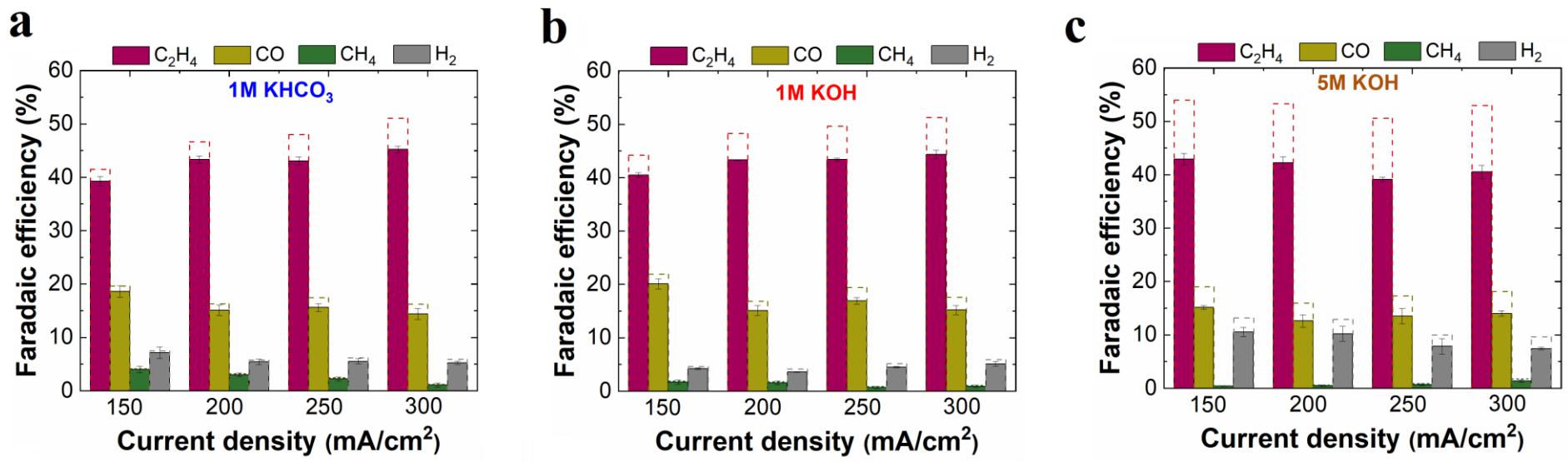




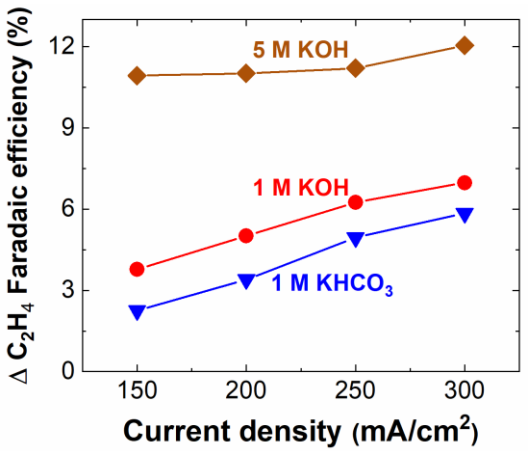
Ma, M., et al., *Submitted*

Comparison of selectivites in different electrolytes

- We could now test in varying alkalinities and test for selectivity.



Compared to uncorrected for outlet flow rate

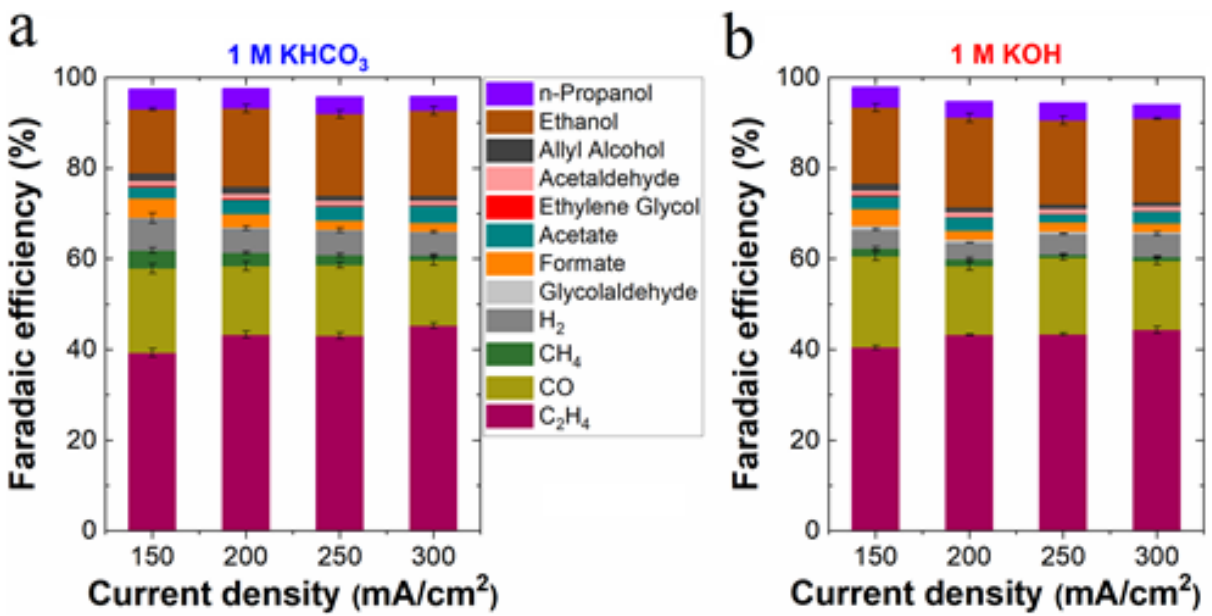


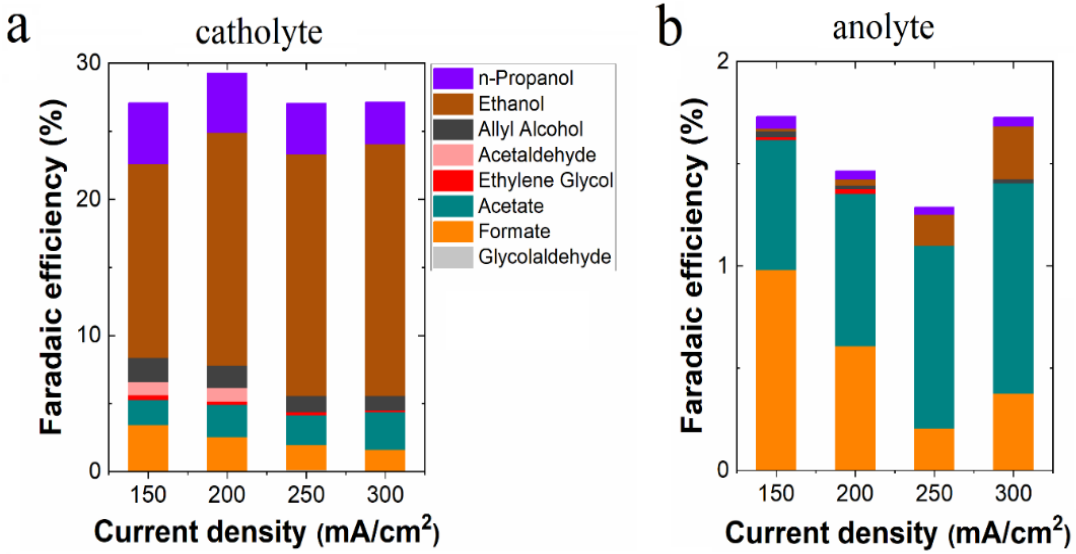
Ma, M., et al., *Submitted*

- Literature indicates that higher pH improves ethylene production.
- We show higher pH does not improve ethylene production.
- Methane is suppressed at higher pH though.

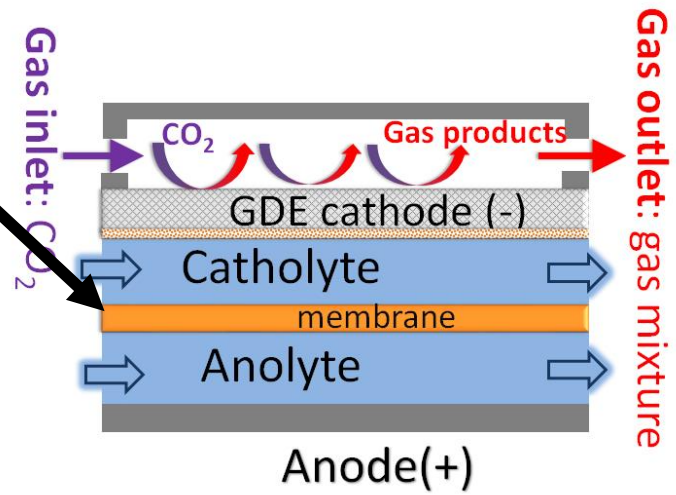
Liquid selectivites

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



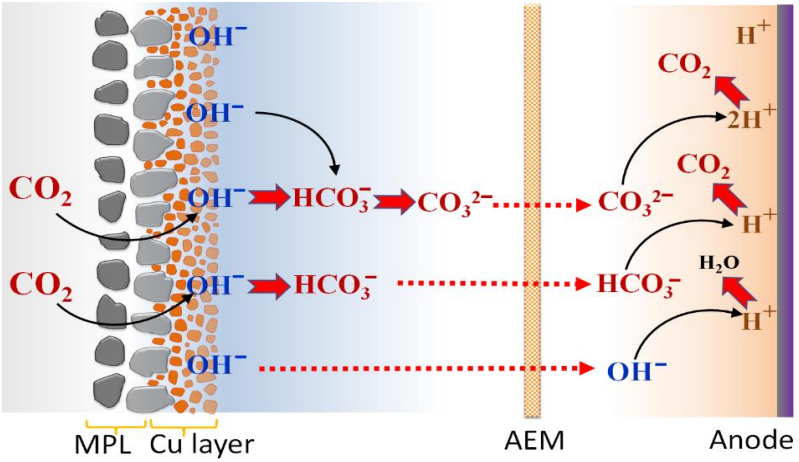


What is going on here

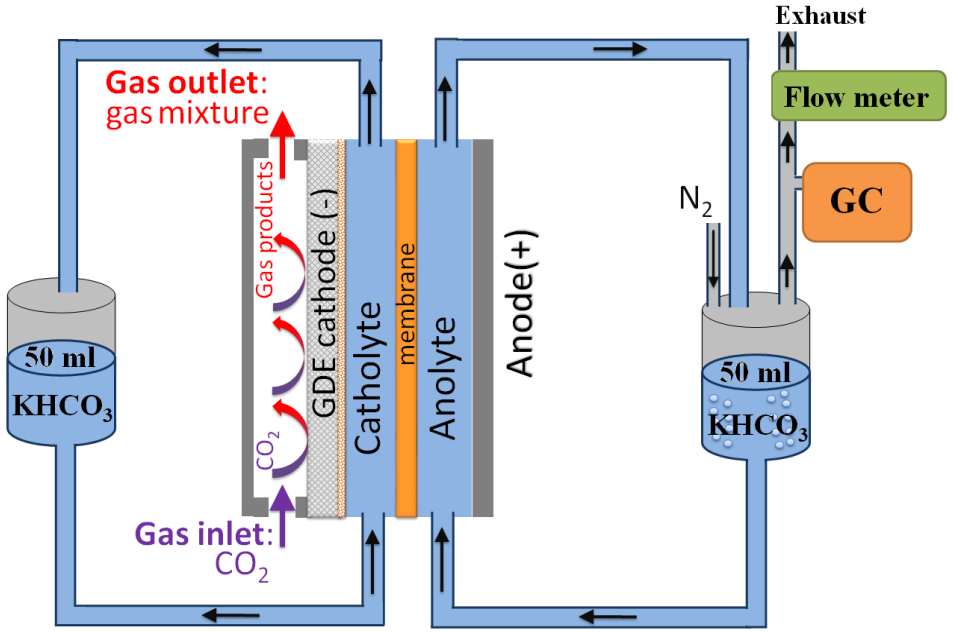


Ma, M., et al., *Submitted*

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^-



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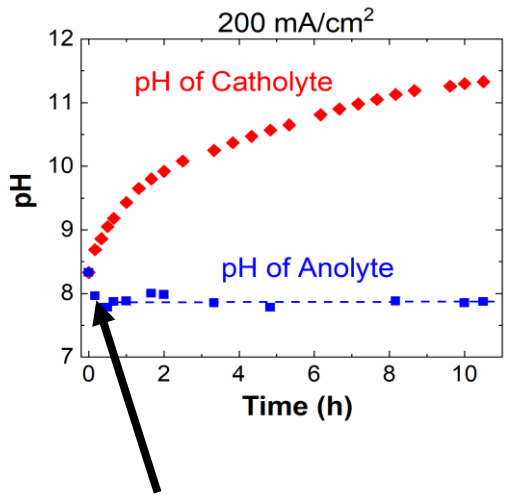
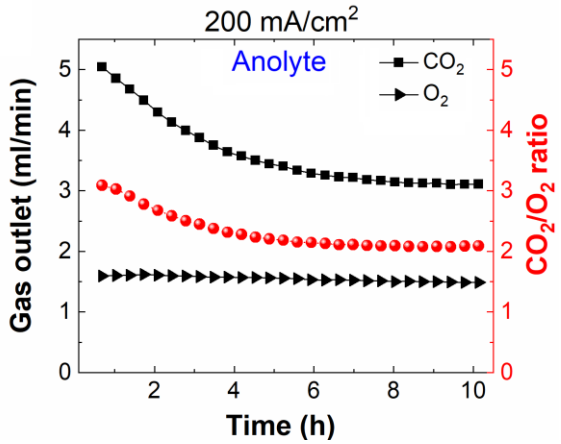
$$2CO_3^{2-} \rightarrow 2CO_2 + O_2 + 4e^- \longrightarrow 2$$

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

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

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

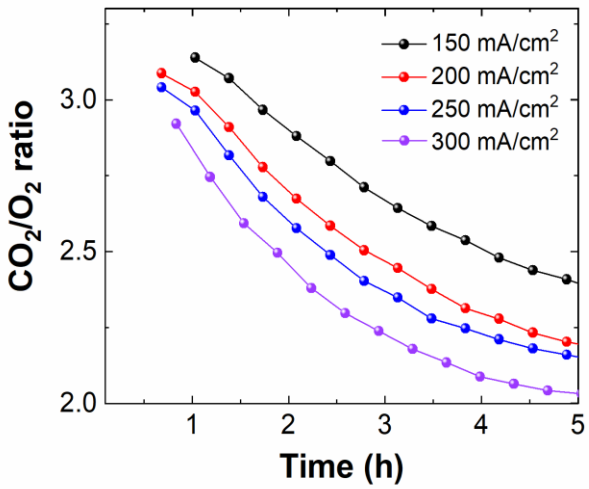


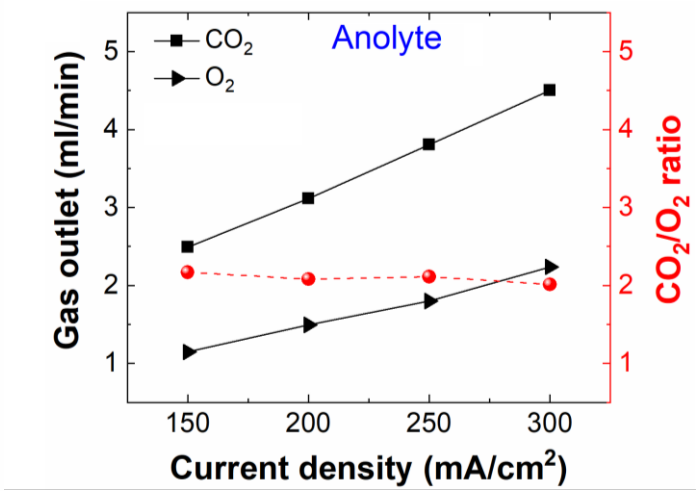


pKa of HCO_3/CO_2 = 7.8

- Varying the current densities accelerates pH modifications.

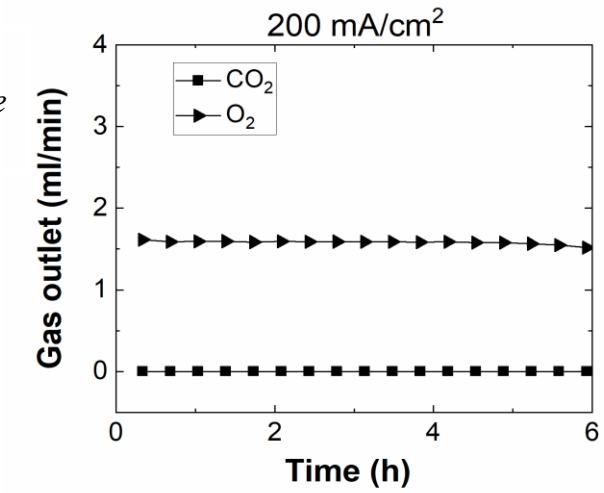
Initial solutions:
50 ml 1 M $KHCO_3$ catholyte
50 ml 1 M $KHCO_3$ anolyte



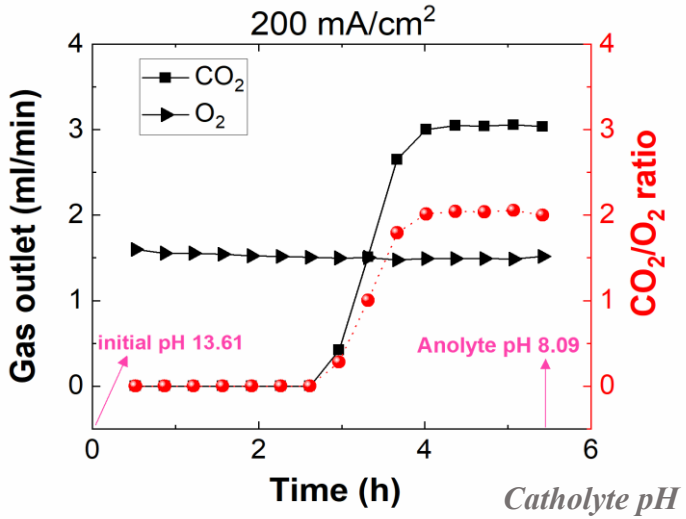


- With basic electrolytes there is no CO_2 emitting from anolyte.
- A smaller reservoir shows CO_2 just needs to satruate the solution.

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



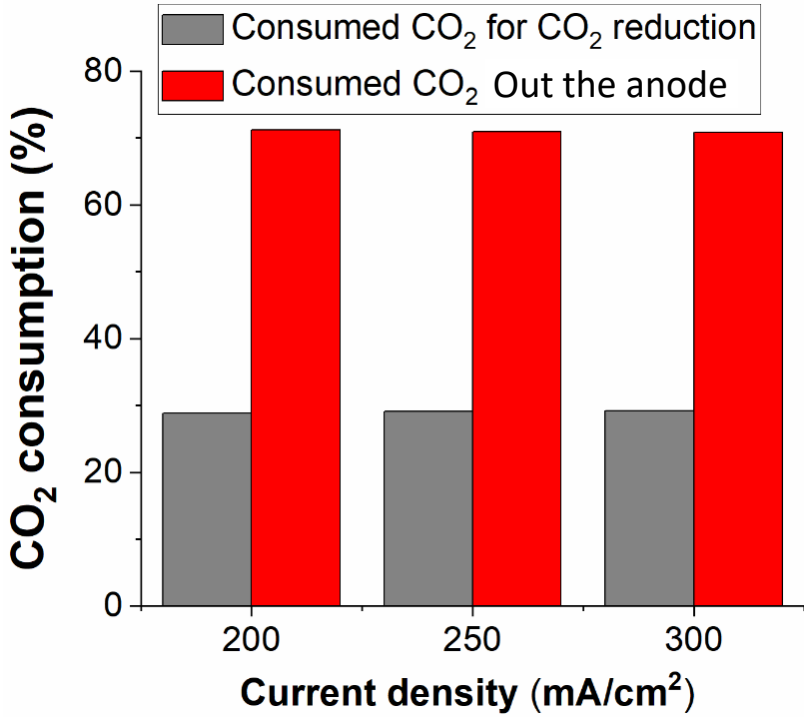
Initial solutions:
20 ml 1 M KOH catholyte
20 ml 1 M KOH anolyte



Catholyte pH reduced to 11.6

Carbon balance

- A full carbon balance helps validate our results.
- We have succeeded on this.
- 70% of our CO_2 is lost to the anode and only 30% is converted.
- The anode is a CO_2/O_2 mix, which is not good for recycling.



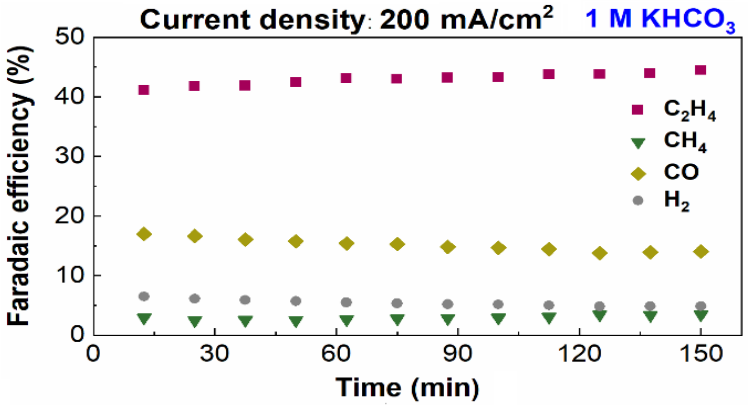
$$\emptyset_{inlet\ CO_2} = \emptyset_{unused\ CO_2} + \emptyset_{CO_2\ to\ gas} + \emptyset_{CO_2\ to\ liquid} + \emptyset_{out\ the\ anode}$$

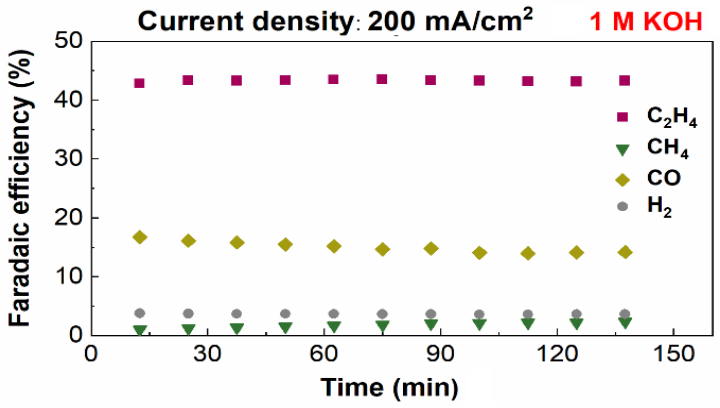
J (mA/cm²)	$\emptyset_{\text{unused } CO_2}$ (ml/min)	$\emptyset_{CO_2\ to\ gas}$ (ml/min)	$\emptyset_{CO_2\ to\ liquid}$ (ml/min)	$\emptyset_{Anode}$ (ml/min)	$\emptyset_{total\ CO_2}$ (ml/min)
200	40.806	0.922	0.3387	3.11156	**45.178**
250	39.735	1.169	0.3928	3.80596	**45.103**
300	38.616	1.379	0.4779	4.50385	**44.977**

Using 1 M $KHCO_3$ as initial electrolyte
Inlet CO_2 flow: 45 ml/min

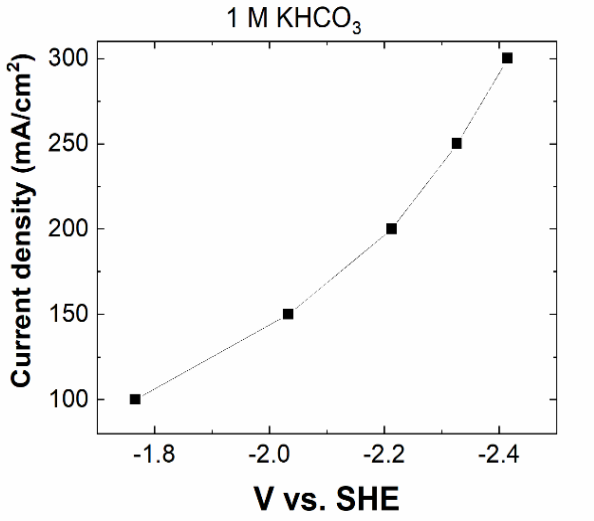
Stability

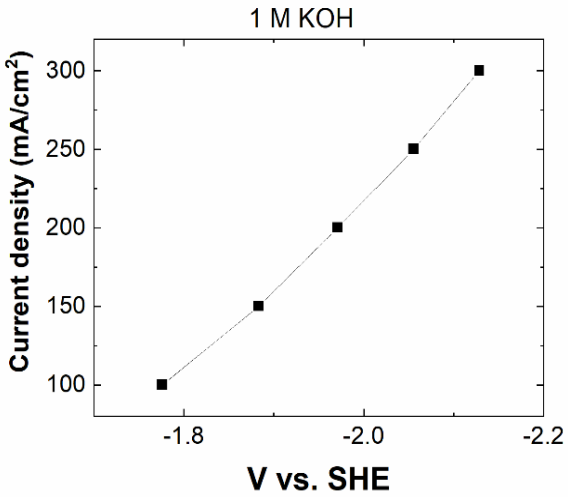
- The reactor's performance is relatively stable over a 2 hour time frame.





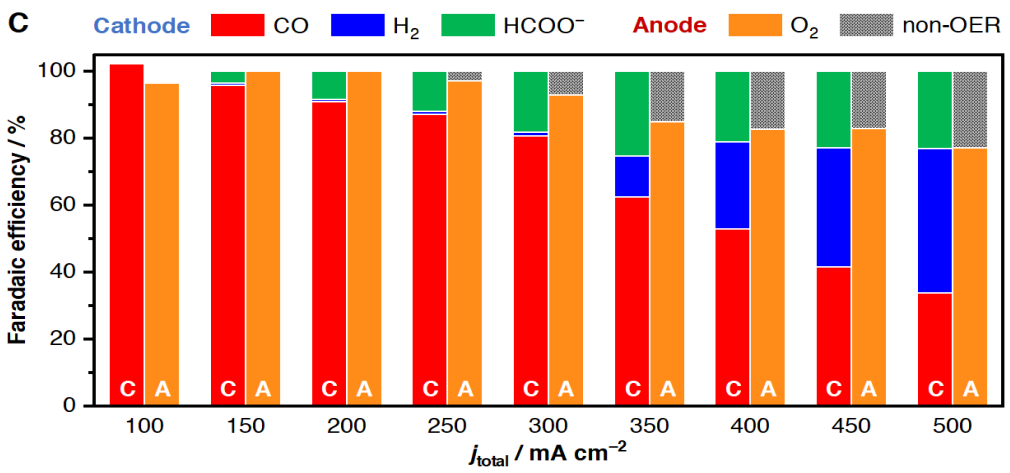
- We measured potential vs. current, but we can not plot this versus RHE.



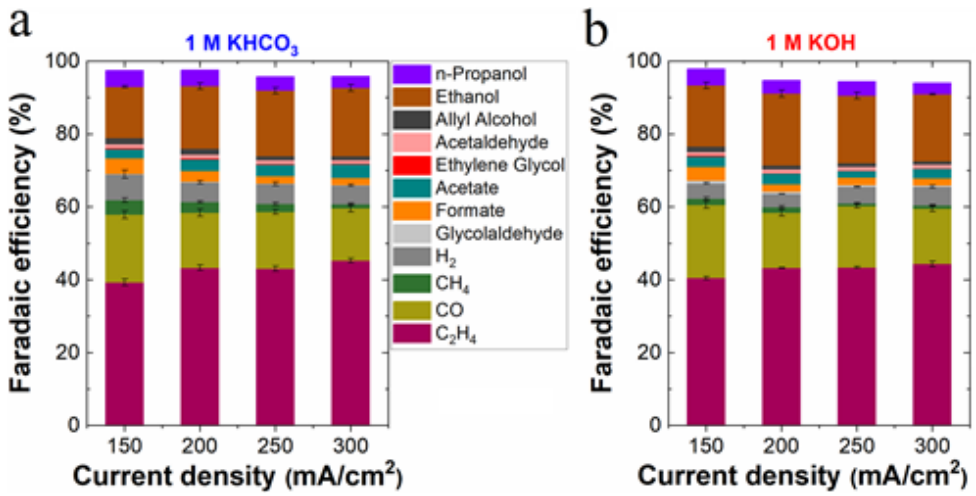


Conclusions and Future Directions

- Both near 100% faradaic efficiency and a carbon balance are neccessary to ensure proper analysis of high-current density reactors.
- Formate is a signficant product for Ag at high current densities.
- Using a basic electrolyte complicates the analysis, and is less beneficial than previously thought.



Larrazabal, G., et al., *ChemSusChem, 2019*



Ma, M., et al., *Submitted*

Acknowledgements

- I would like to acknowledge both the funding agencies and the DTU high current density CO_2 reduction group.

The VILLUM Center for the Science of Sustainable Fuels and Chemicals

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RESEARCH, TECHNOLOGY & GROWTH

SIEMENS

CO_2 to CO

Gaston Larrazabal

Patrick Strøm-Hansen

Kevin Zeiter

Jens Peter Heli

CO_2 to Ethylene

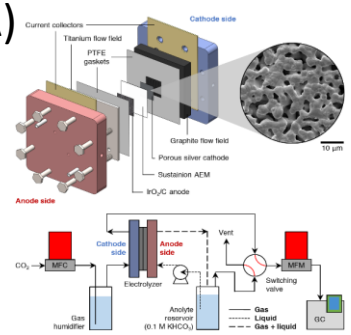
Ming Ma

Sebastian Dalsgaard

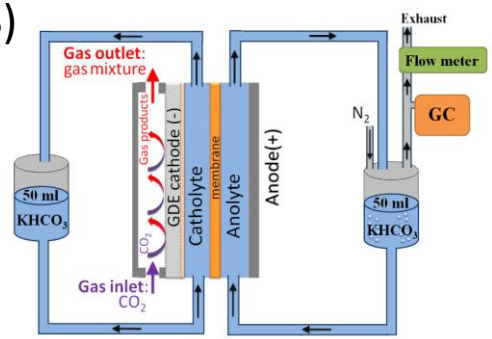
Ib Chorkendorff

Kasper Therkildsen

A)

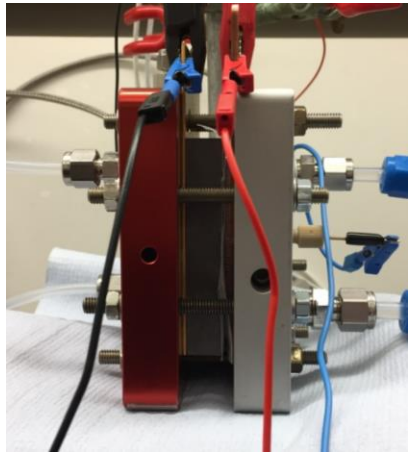

Current collectors
Titanium flow field
PTFE gaskets
Cathode side
Graphite flow field
Porous silver cathode
Sustainion AEM
IrO_2/C anode
Anode side
10 µm
CO_2
MFC
Cathode side
Anode side
Electrolyzer
Vent
Switching valve
MFM
Gas humidifier
Anolyte reservoir (0.1 M $KHCO_3$)
Gas
Liquid
Gas + liquid
GC

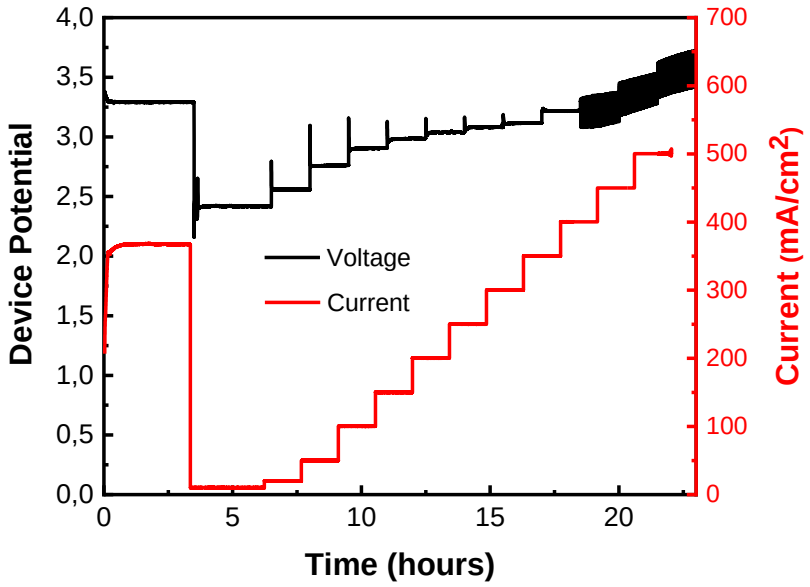
B)

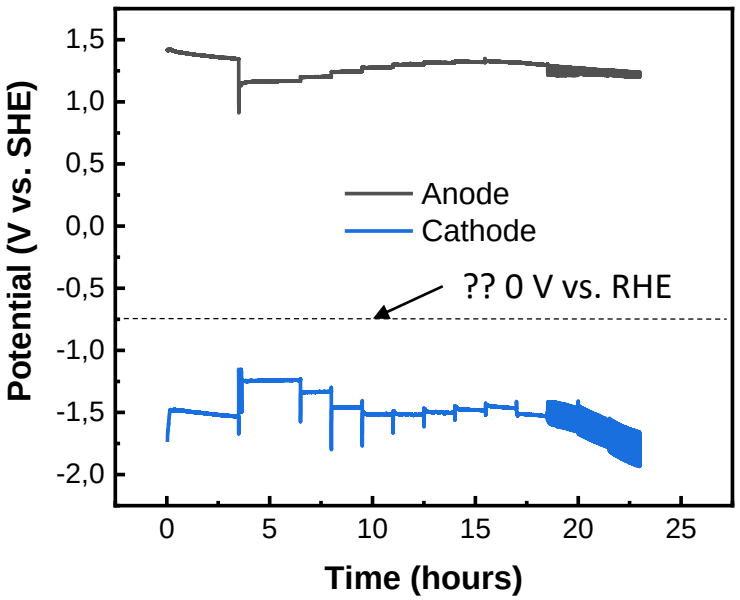

Exhaust
Flow meter
GC
N_2
Gas outlet: gas mixture
Gas products
CO_2
GDE cathode (-)
Catholyte
membrane
Anolyte
Anode(+)
50 ml $KHCO_3$
50 ml $KHCO_3$
Gas inlet: CO_2

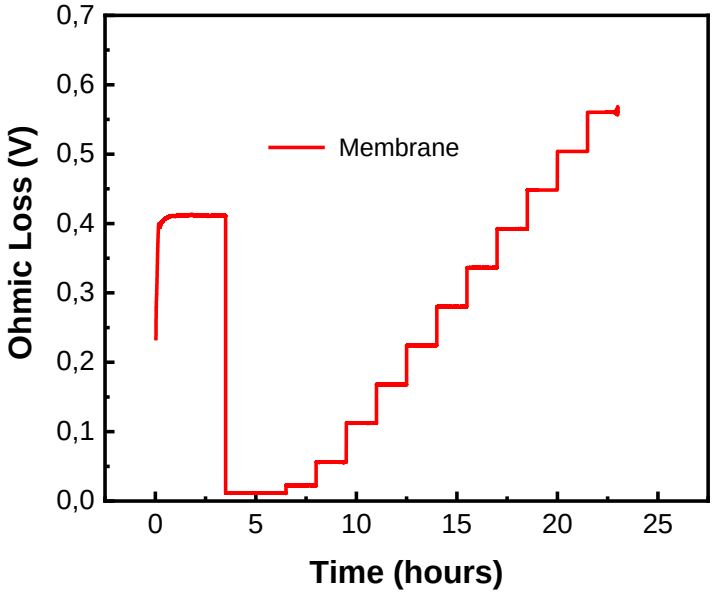
Including a Reference Electrode

- We put a reference electrode in through the anolyte.
- Impedance allowed us to determine membrane losses.
- Our cathodic potential is where we should expect formate production.

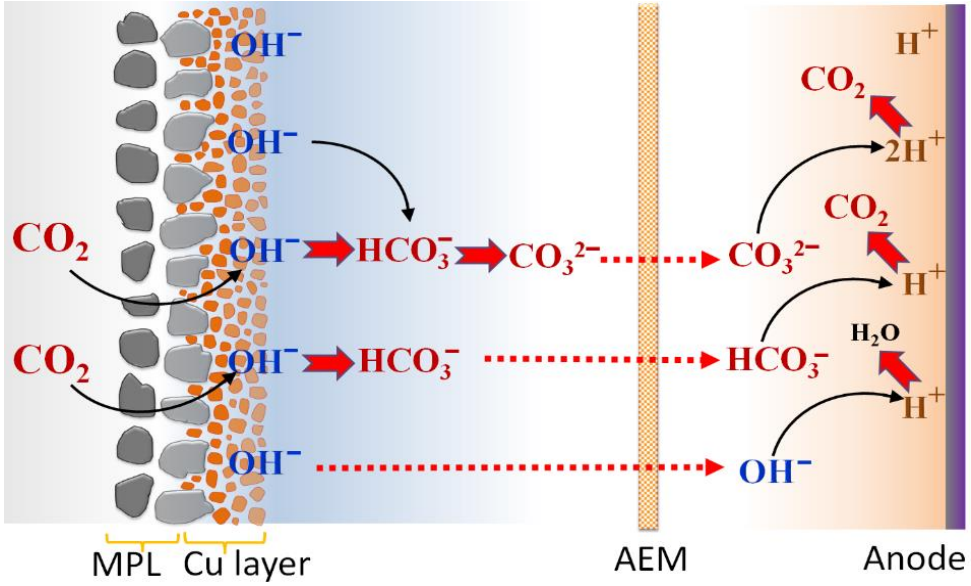








Larrazabal, G., et al., *ChemSusChem, 2019*



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^-

- A further analysis of anode gas flow gives insights into membrane crossover.
- This can give us details relating to:
  - Local pH
  - Membrane conductivity

Anode reactions: **CO_2/O_2 ratio**

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

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

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

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