

Ag Membranes for Electrochemical CO₂ to CO Conversion in an MEA Type Set-up

2019 Spring ECS Meeting
May 29, 2018

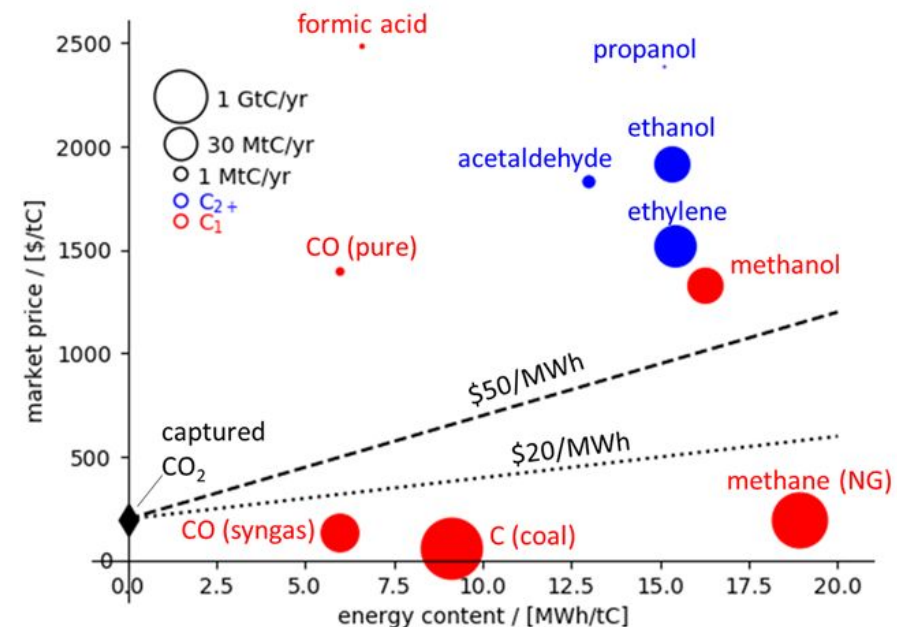
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1. *SurfCat Section, Physics Department Technical University of Denmark*
2. *Siemens, SCION, Kongens Lyngby, Denmark*

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
Carbon Monoxide	2	743	0.110	3.8 (150)
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
Acetic Acid	8	460	0.036	12
Ethylene Glycol	10	1000	0.065	7
Acetone	16	700	0.064	6
Ethanol	12	600	0.024	110
Ethylene	12	1050	0.025	180



Nitopi, S. et al, Chem. Review, 2019, DOI: [10.1021/acs.chemrev.8b00705](https://doi.org/10.1021/acs.chemrev.8b00705)

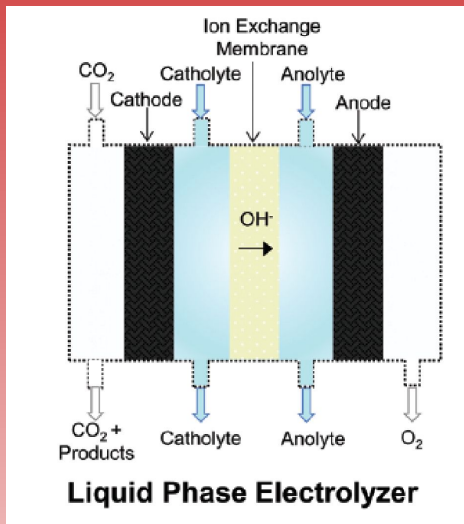
H₂- <https://www.hydrogen.energy.gov/> CO- <https://www.openpr.com/> COOH- A. A. N. Afshar, Chemical Profile: Formic Acid. *TranTech Consultants, Inc.*, (2014).
 CHOOH - <https://www.icis.com> CH₃OH [Methanex.com](https://www.methanex.com) CH₄- EIA (www.eia.gov), Acetic Acid- [Prnewswire.com/](https://www.prnewswire.com/), Ethylene Glycol- <https://www.intratec.us/>,
 Ullmann's Encyc. of Ind. Chem. Acetone- [Platts](https://www.platts.com), Ullmann's Encyc. of Ind. Chem, Ethanol- [Nasdaq](https://www.nasdaq.com), <http://www.ethanolrfa.org> Ethylene- [Platts](https://www.platts.com)

Industrial Relevant Approaches to eCO₂ Reduction

Advantages:

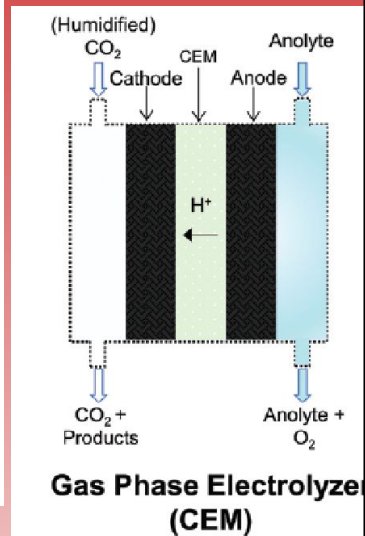
This talk

Liquid Product Extraction



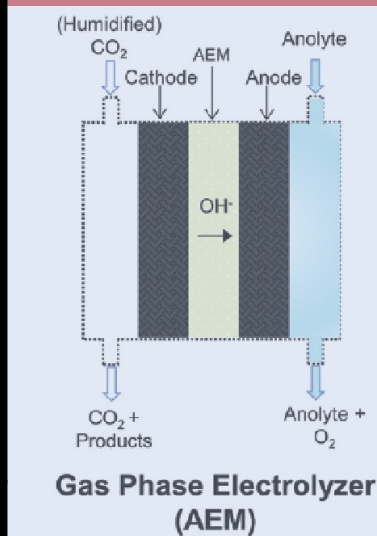
High ohmic losses

Low ohmic loss, stable



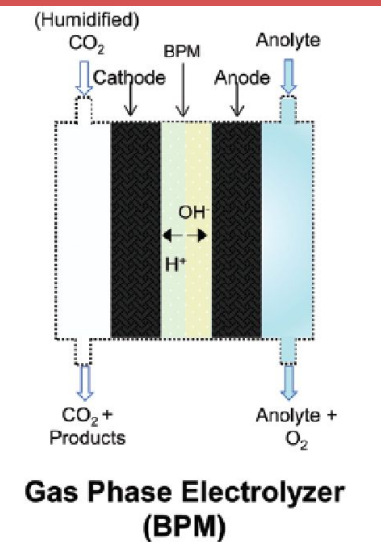
Bad selectivity

Helps selectivity

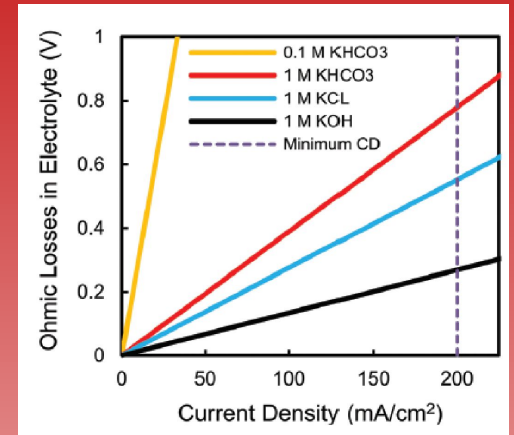


CO₂ Crossover

Cheaper anode



Inefficiency losses at interface

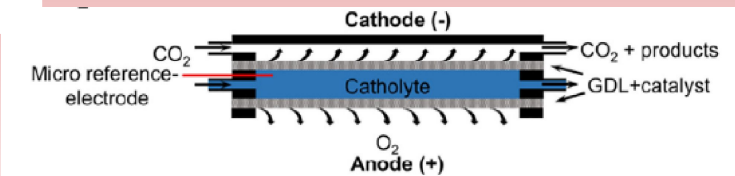


3 mm anolyte & catholyte

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

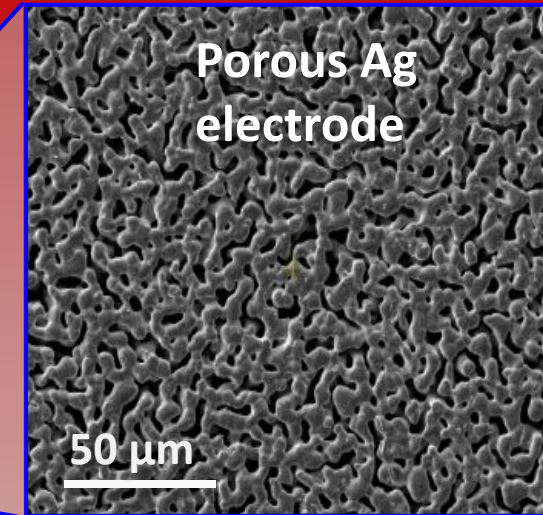
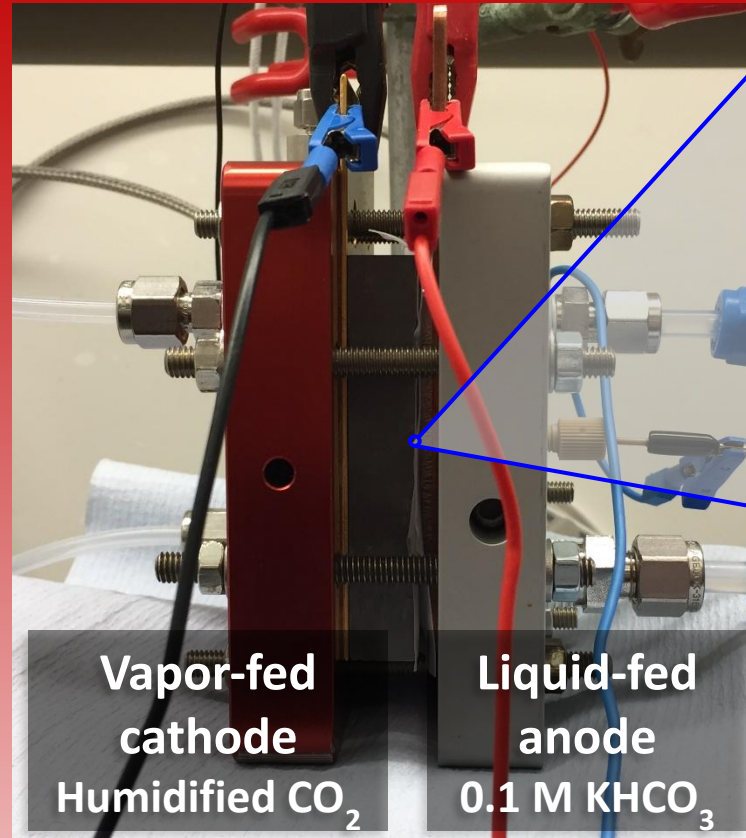
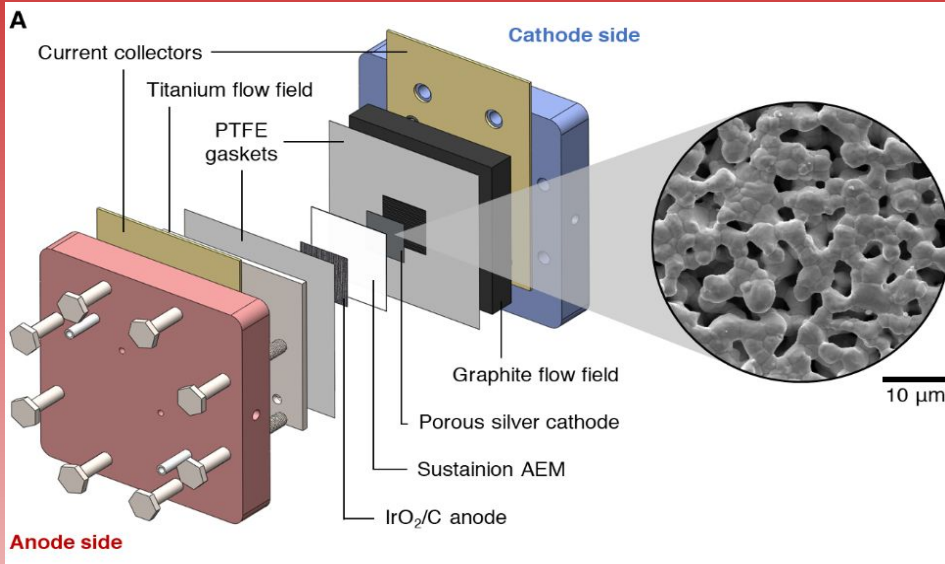
Disadvantages:

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

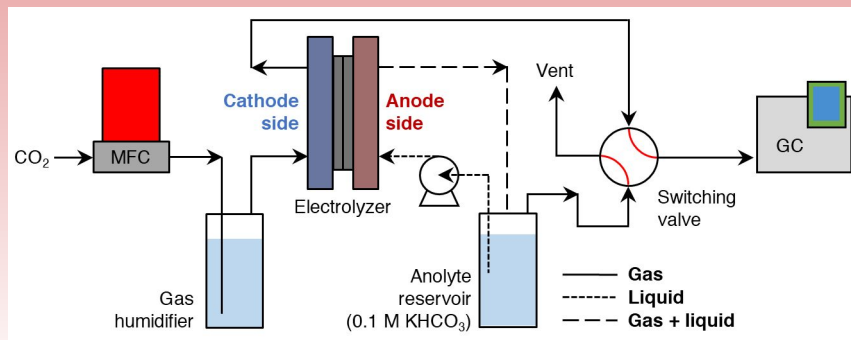


Endrodi, B. et al., Prog. Ener. & Combust. Science, 2017

Electrochemical Set-up



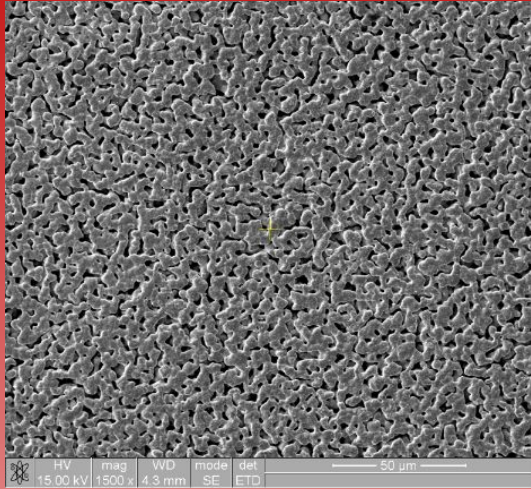
Cathode: silver membranes of 50 μm thickness



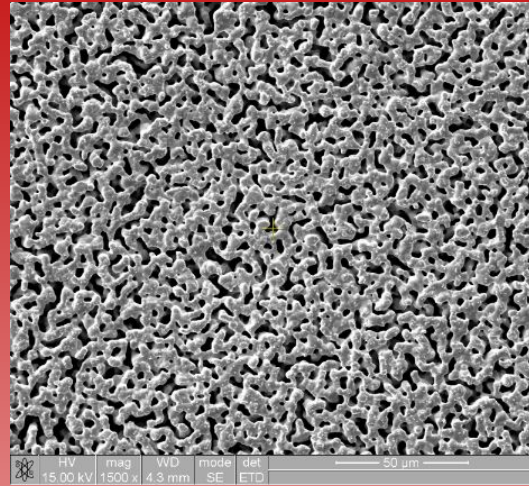
Anode: IrO₂ on carbon paper
Membrane: Sustainion 37-50 AEM
Temperature: 30 C



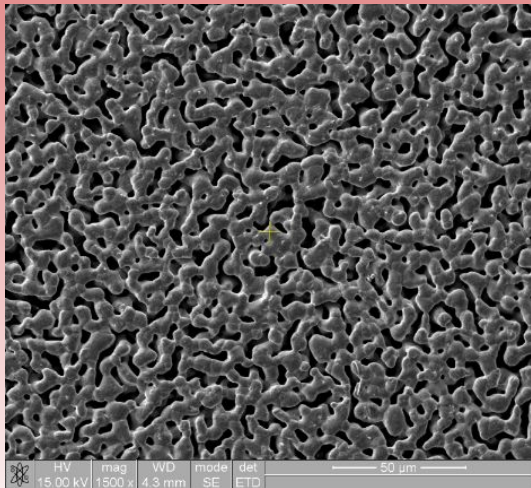
Testing Different Membrane Pore Sizes



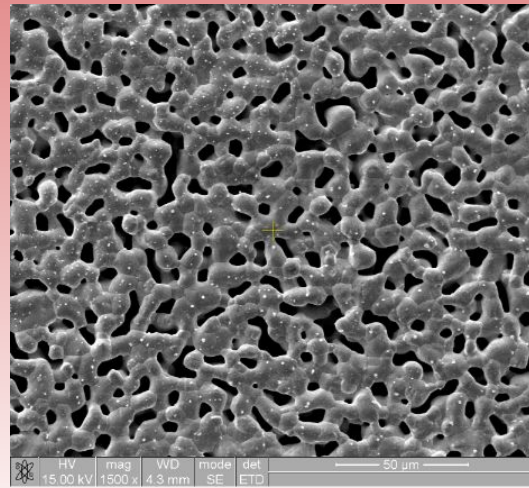
0.45 μm



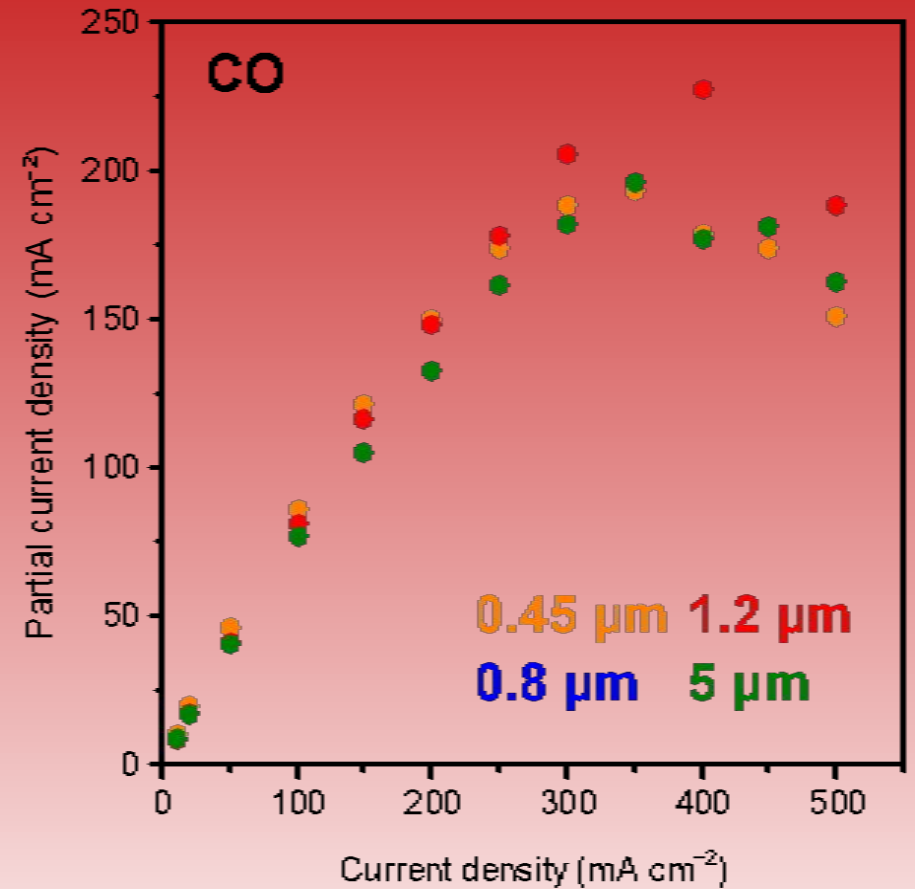
0.8 μm



1.2 μm



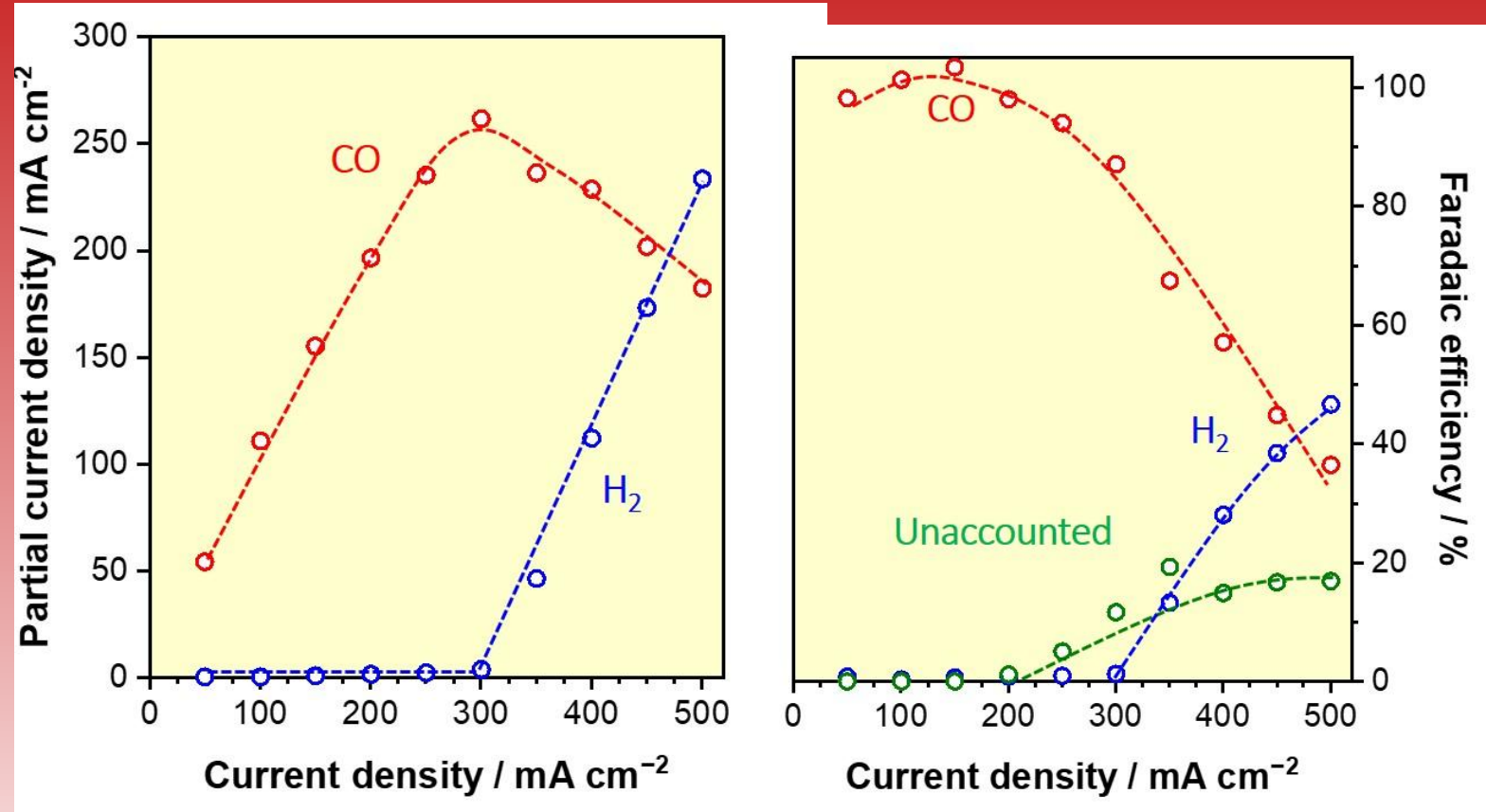
5 μm



Larrazabal, G., et al., *In Preparation*

Hydrogen Suppression

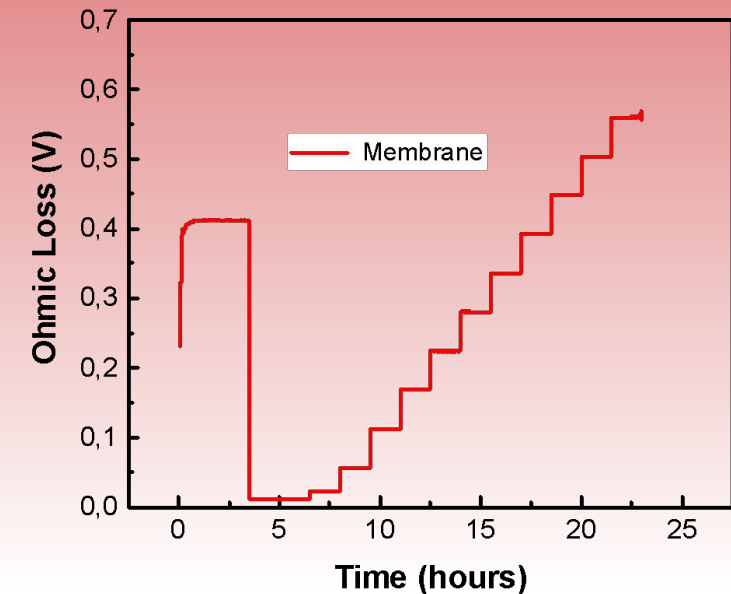
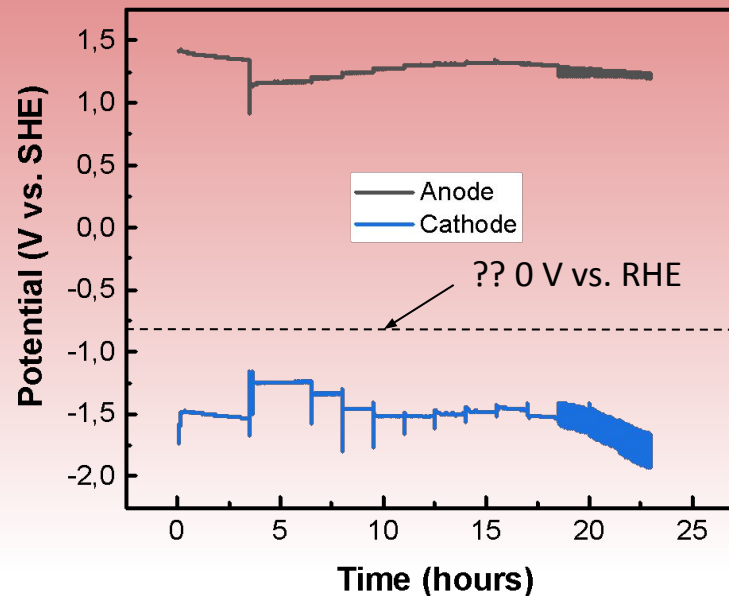
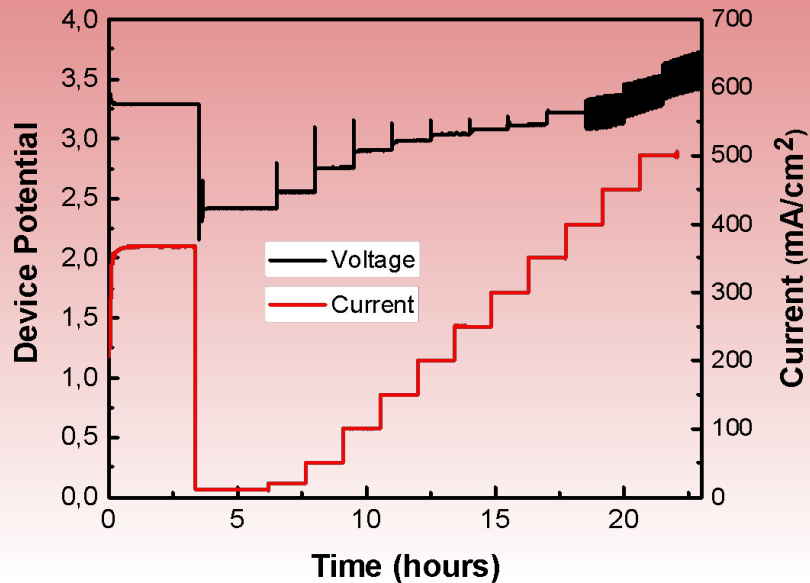
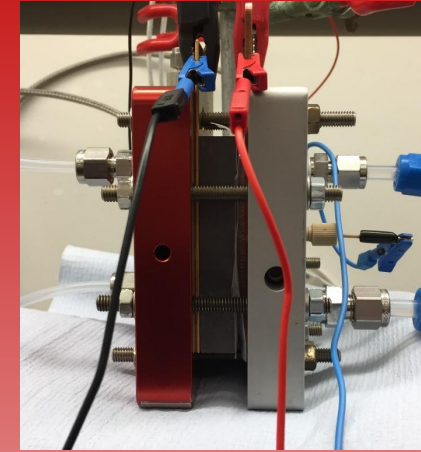
- We have suppressed hydrogen up to 300 mA/cm².
- Increasing temperature and operating drier has allowed us to move a little higher.
- Our unaccounted for was most probably a liquid product.



Larrazabal, G., et al., *In Preparation*

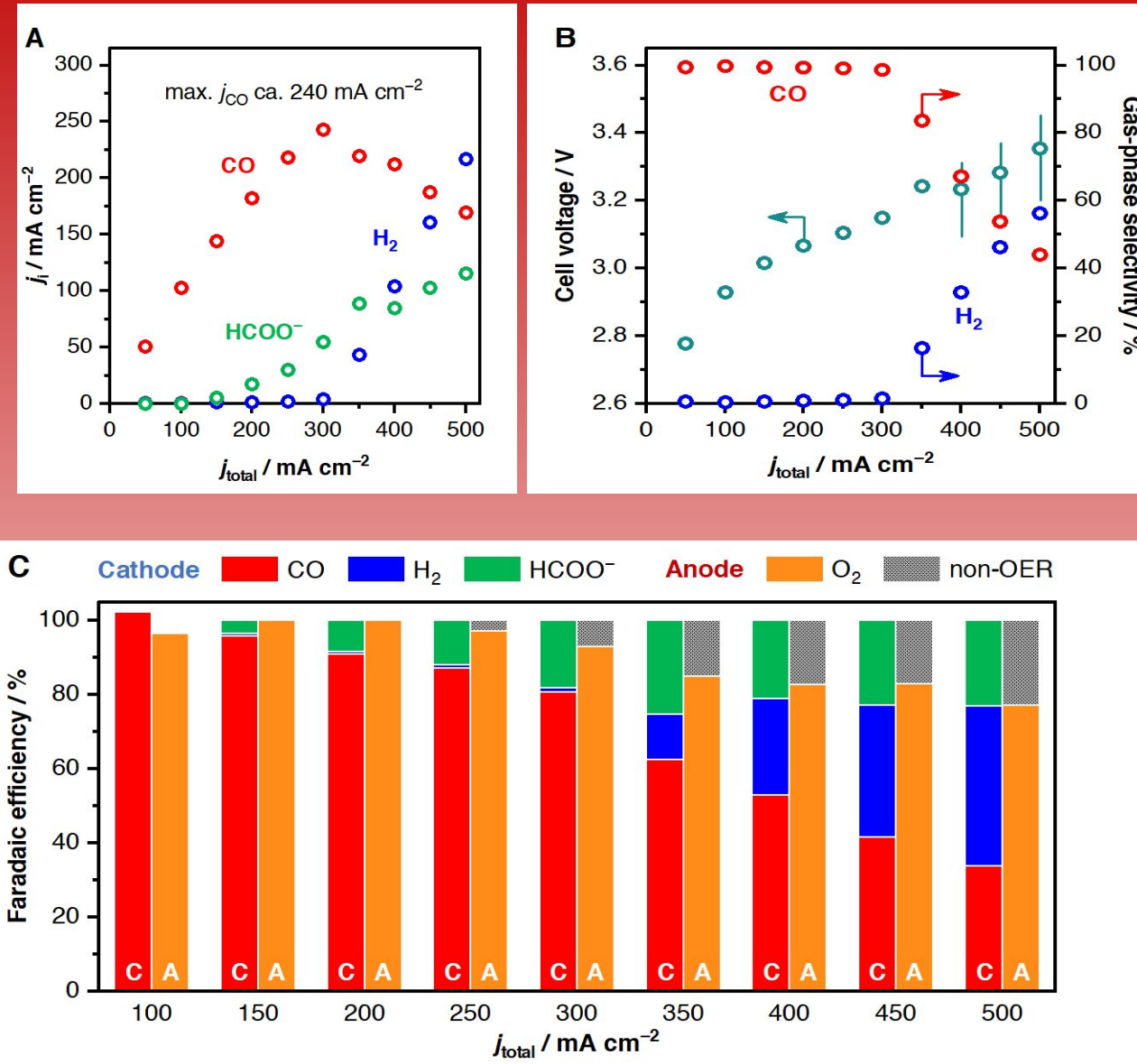
Including a Reference Electrode

- 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.



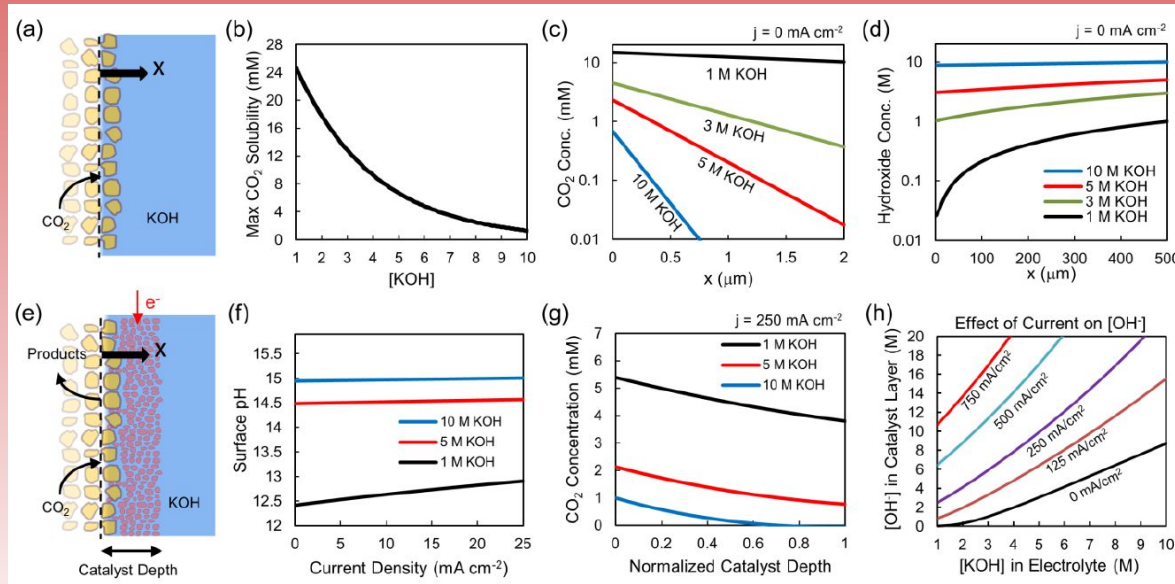
Faradaic Efficiency Analysis

- We have measures formate via NMR from condensed cathode droplets.
- Our cell voltage is comparable to other Ag based devices.
- Anolyte measurements show a loss in O_2 faradaic efficiencies at high currents.
- We attribute this to carbon corrosion at the anode.



Understanding our carbon balance

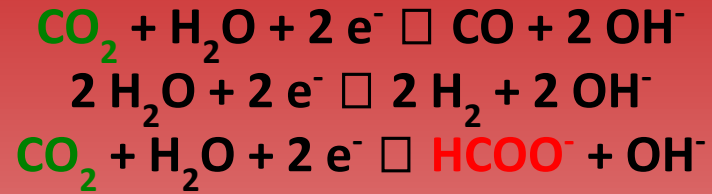
- Our 3 faradaic reactions produce OH⁻ ions.
- CO₂ naturally forms a carbonate ion.
- There is a competition for membrane crossover.



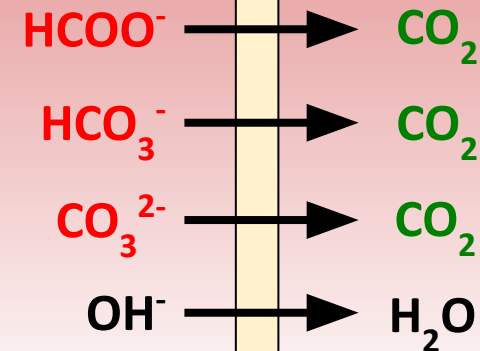
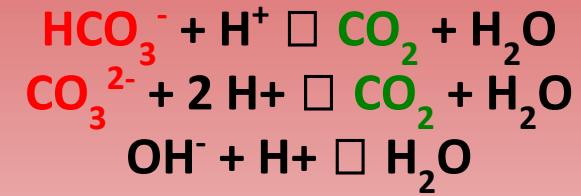
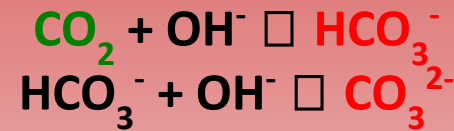
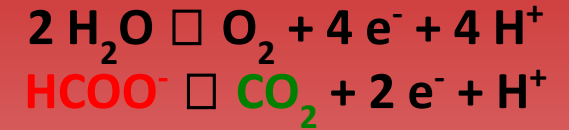
Dinh, C.T.; Science, 360, 783 (2018)

Anion exchange membrane (AEM)

Cathodic reactions

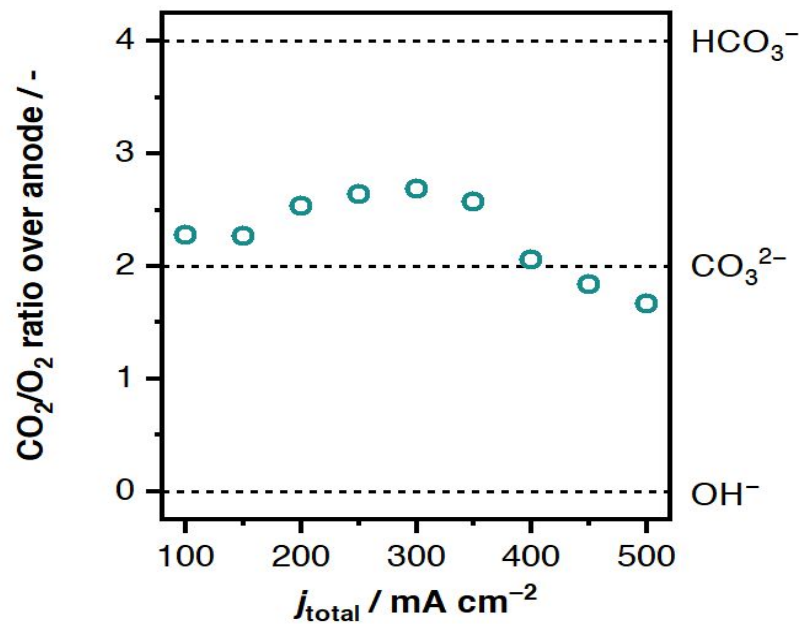


Anodic reactions

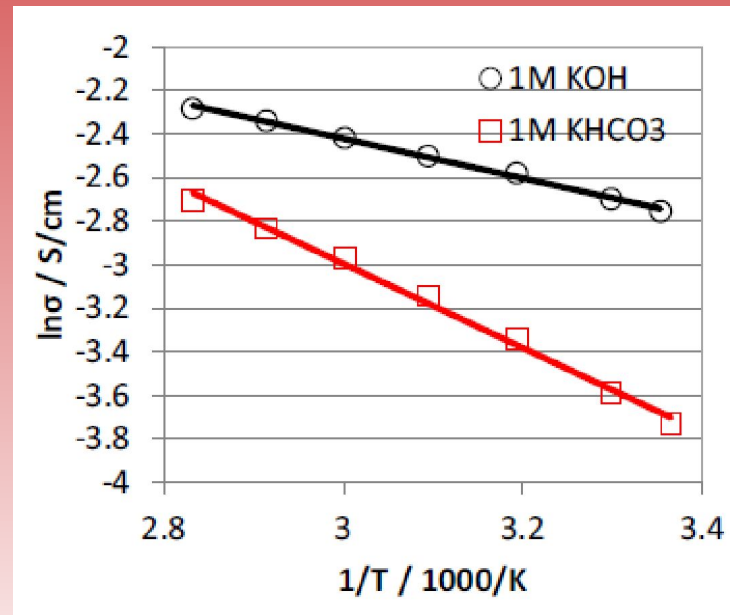


Analyzing our CO₂ crossover

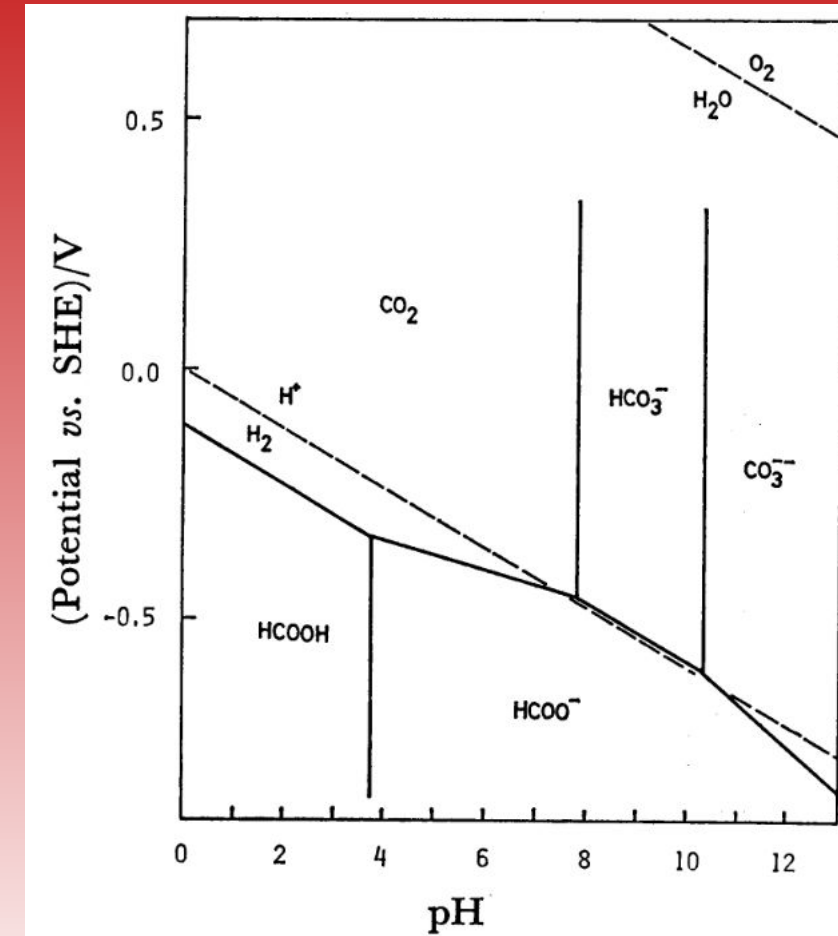
- From the anode we could measure CO₂ as a function of O₂ evolution (and current)
- This verifies:
 - Carbonate is going through, hurting conductivity
 - Locally we are highly basic



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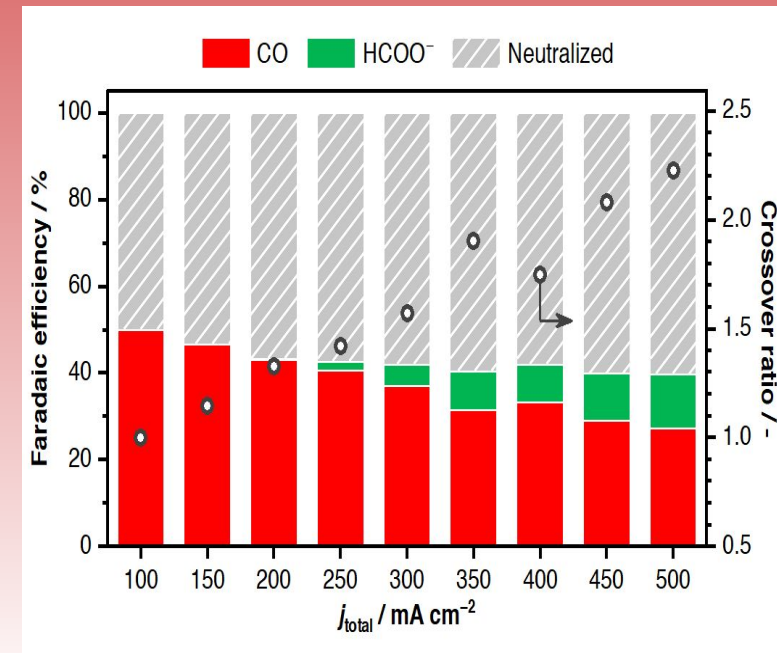
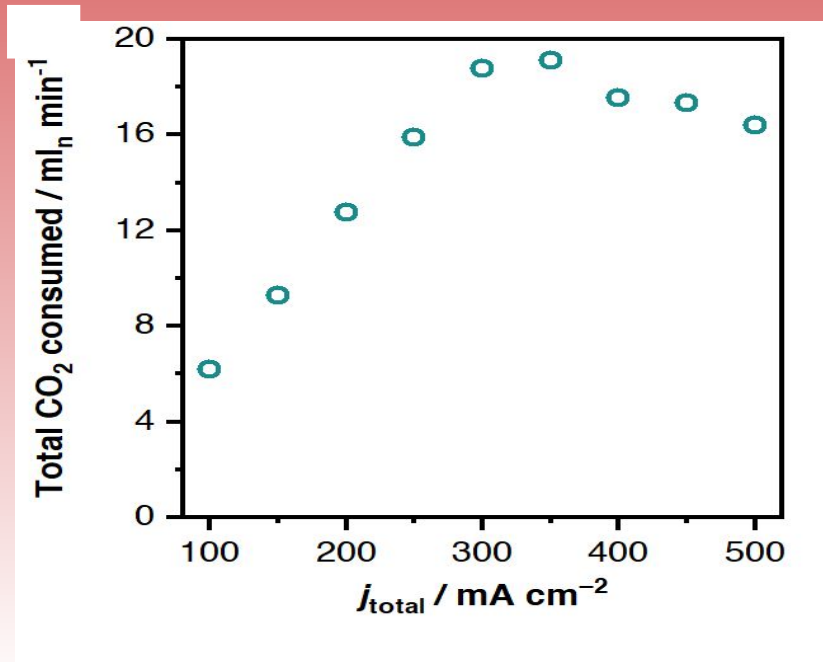
Liu, Z.; J. Electr. Soc., 165(15) J3371-J3377 (2018)



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

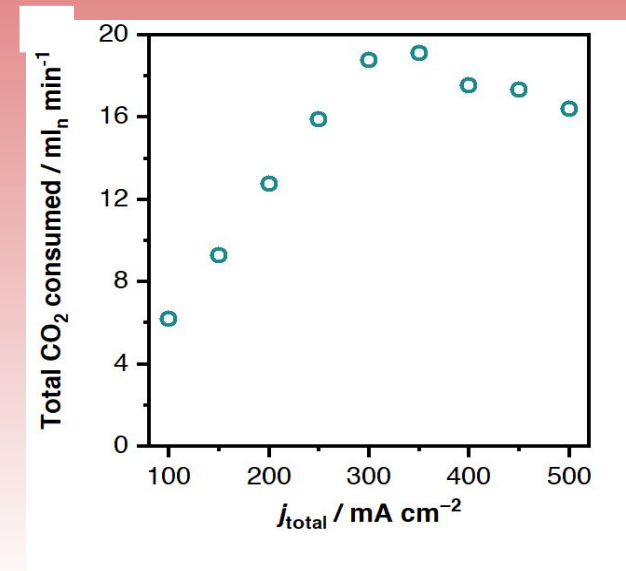
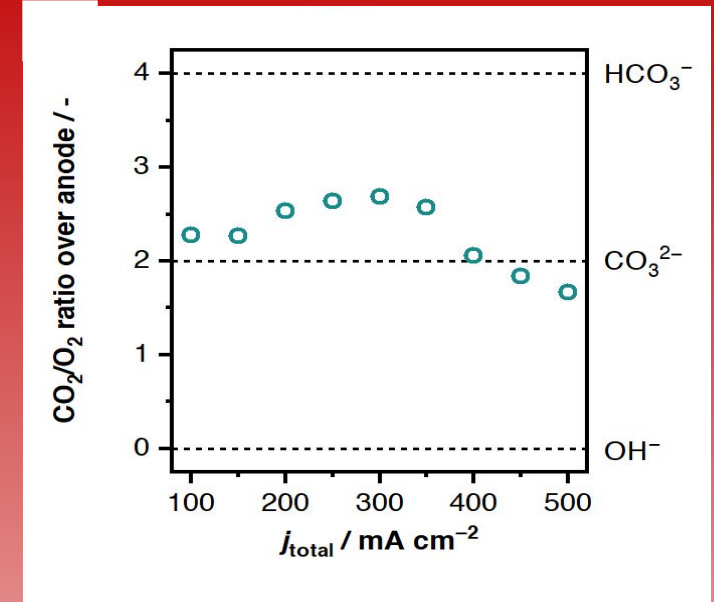
Mass Transfer Limits of CO₂

- Our total CO₂ usage is limiting performance.
- Once we are CO₂ limited, excess voltage, just switches from CO to formate production.
- It appears this 300 mA/cm² limit is occurring in other works as well



Conclusions and Future Directions

- Silver membranes work adequately, and thus are a nice benchmark.
- CO_2 crossover are severe in AEM's
 - *Future- Try different AEM's*
- AEM's appear to have a mass transport limit near 300 mA/cm^2 .
 - *Future- Try ionomers to increase triple phase boundary regime.*
 - *Future- Vary microstructure, change humidity, etc.*



Acknowledgements

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SIEMENS



Gaston
Larrazabal



Patrick
Strom-Hansen



Kevin
Zeiter



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