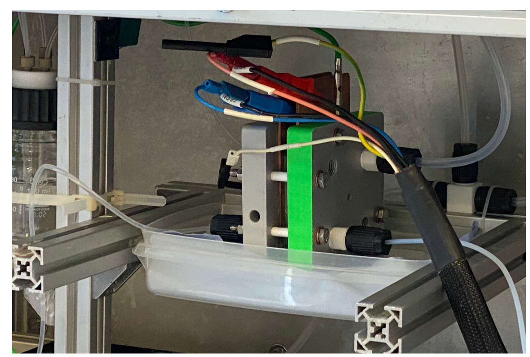
Non-H_2 Electrosynthesis (i.e. the fun stuff)

CO_2 electrolysis

Device by Siemens Energy



Chloro-alkali process (Cl_2+ NaOH)

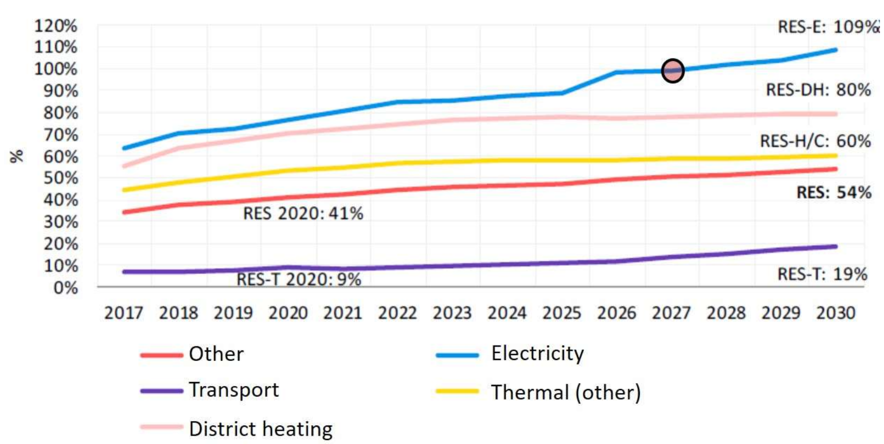
Chlorine electrolysis by Thyssen Krupp

Learning Objectives

- Chlorine electrolysis
- Fundamentals of CO_2 electrolysis
- Scale up of CO_2 electrolysis
- ? Electrowinning

Too much electricity- A very real issue in Denmark

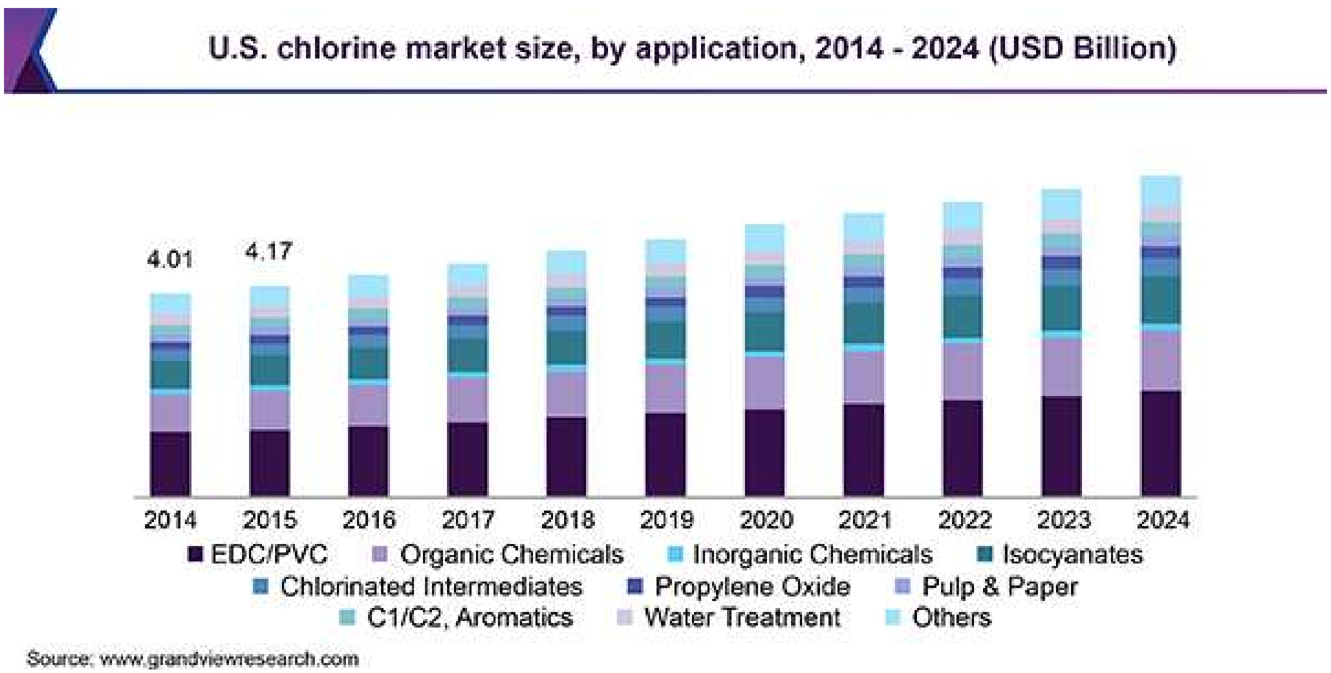
- Denmark will reach 100% renewables by 2027
- We are already in the process of building greater than 100% electricity
- 2 Energy Islands ~~will~~ *may* be built by ~~2030~~- *2035* Near Borholm & west of Jutland



Chlorine Production

Chlorine production

- Globally we produce about 70M ton of chlorine gas.

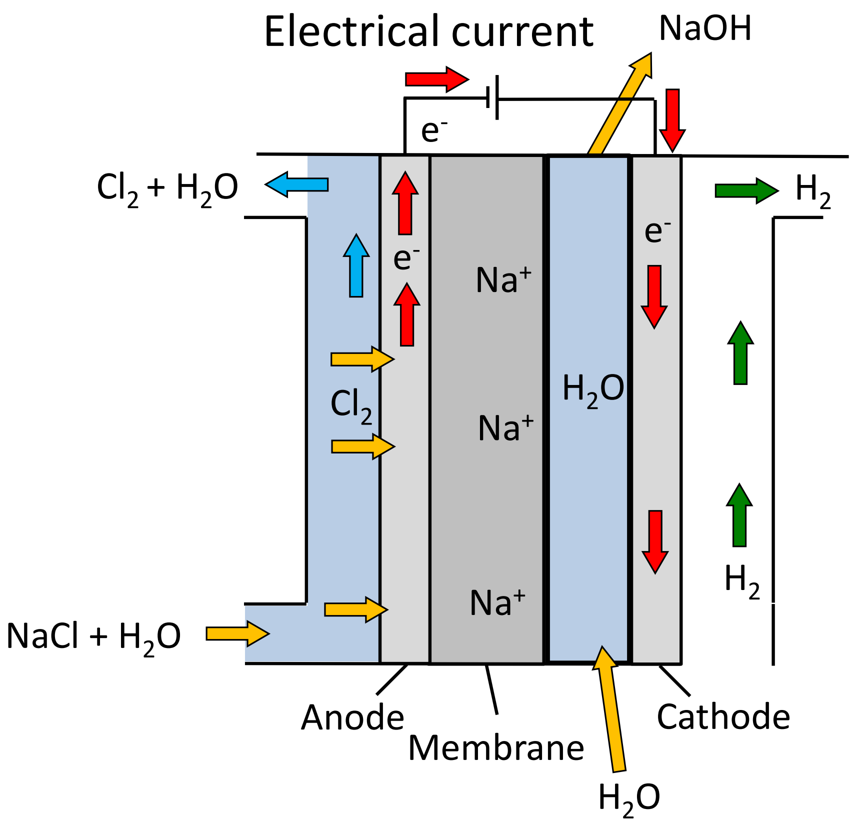


PVC piping

Cleaning agents
(e.g. bleach)

The Chloro-alkali process

- Chlorine has always been produced via electrolysis.



Compared to water electrolysis

- Chlorine is produced at the anode instead of oxygen.
- Na^+ diffuses through the membrane rather than H^+
- NaOH is produced at the cathode. (Thus 75Mton per year of NaOH is produced this way)
- This also works with KCl instead of NaCl as a starting material

The Chloro-alkali process

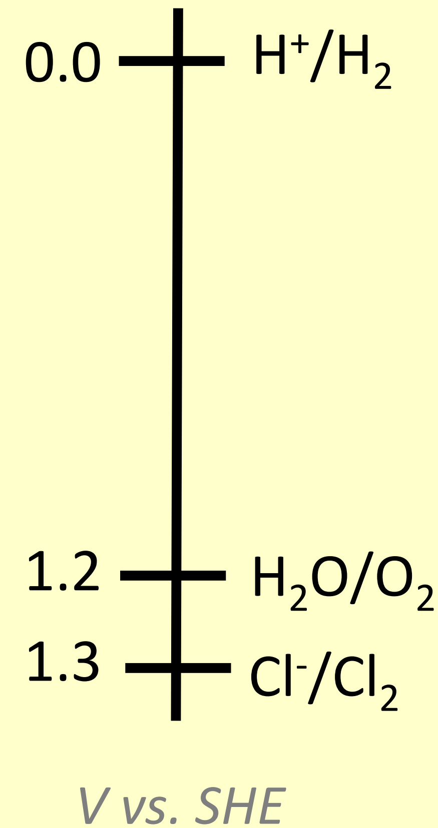
- Try to draw out the half reactions yourself for the Chloro-alkali process

Chlorine evolution thermodynamics

- Chlorine evolution is thermodynamically harder than O_2 evolution.
- Chlorine evolution does not involve a proton. What does that mean?

$$E_{Cl_2/NaOH/H_2} = E_{Cl_2/H_2} + \overbrace{\frac{RT}{2.303zF}}^{\text{59 mV @ 25C}} \Delta pH_{anode/cathode}$$

- Hopefully catalysis can save us



Chlorine Catalysis

- The optimal catalyst in RuO_2 or IrO_2, which is the same as for O_2 evolution.

2 electron transfer

Chlorine evolution $2Cl^- \rightarrow 2e^- + Cl_2$

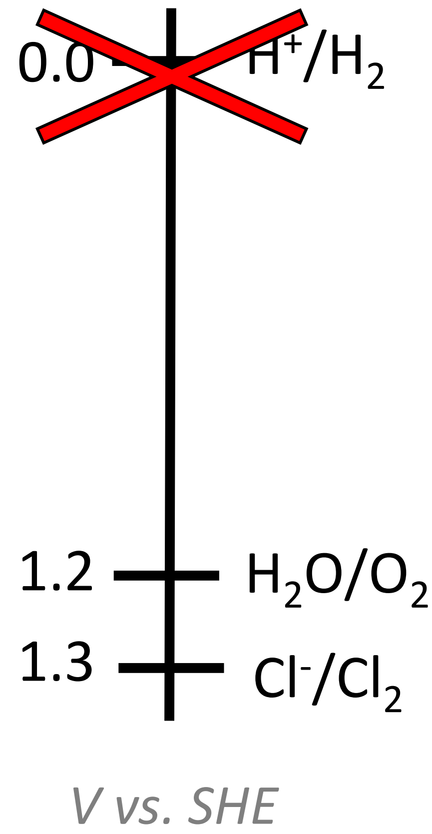
4 electron transfer

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

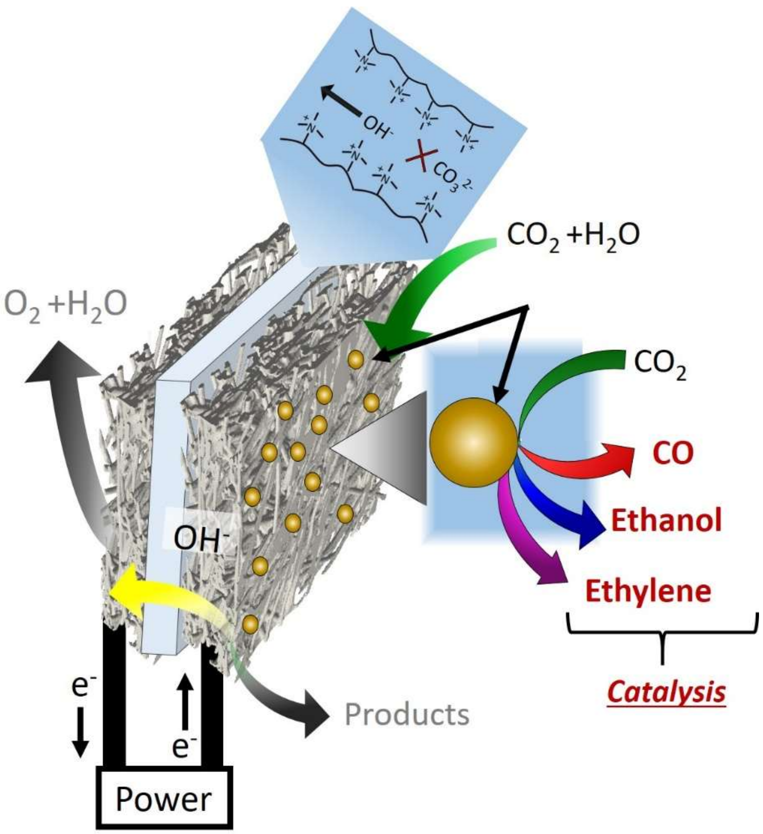
- Cl_2 evolution has no scaling relationship, thus the catalysis loss is quite minimal
- Selectivity is primarily Cl_2 (98- 99.6%).
- Membrane crossover of NaOH and Cl_2 leads to slight product losses

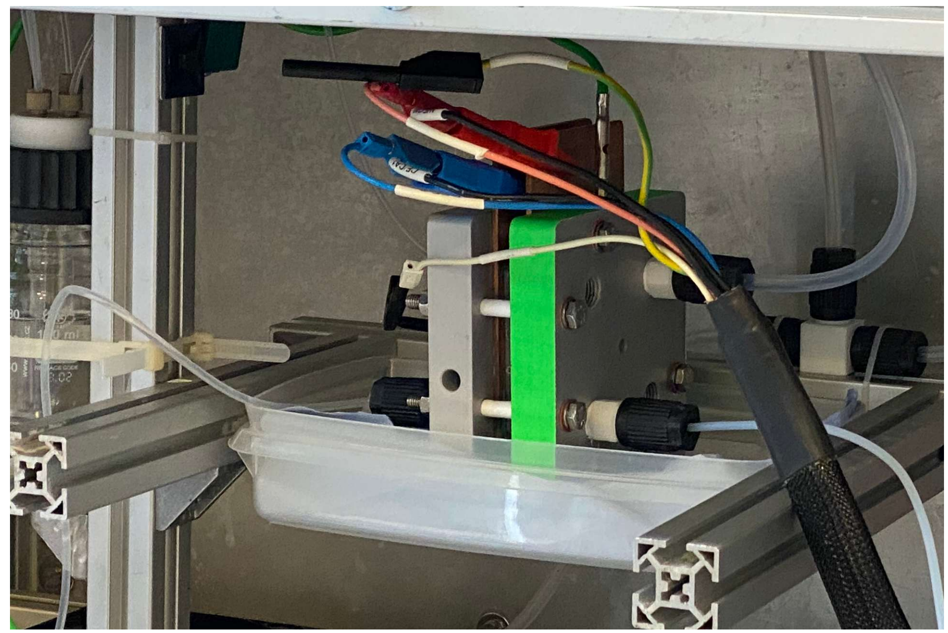
Oxygen Depolarized Cathodes (ODC)

- Recently the industry leaders (De Nora and Covestro) realized H_2 was of little value
- The decided to replace this with oxygen reduction at the cathode.
- They lose H_2, but save 1.2V (theoretically)
- The new electrodes are called Oxygen Depolarized Cathodes (ODC)



CO_2 Electrolysis & Other Electrosynthesis





What are we trying to do?

- We want to take CO_2 into some types of hydrocarbons:

Electricity →

$$CO_2 \rightarrow CO + \frac{1}{2}O_2$$

CO can be combined with H_2 and catalytically reacted to produce hydrocarbons (gasoline, 30% of world's energy)

$$CO_2 + 2H_2O \rightarrow CH_4 + 2O_2$$

Natural gas is 95% methane. (30% of world's energy)

$$CO_2 + H_2O \rightarrow C_2H_5OH + \frac{1}{2}O_2$$

Ethanol can be used in internal combustion engine and as a solvent

$$CO_2 + H_2O \rightarrow C_2H_4 + \frac{1}{2}O_2$$

Ethylene is the precursor to polyethylene, the world's most popular plastic (2% of world's energy)

$$CO_2 + H_2O \rightarrow 10\ other\ products$$

- Byproduct reaction:

$$H_2O \rightarrow H_2 + O_2$$

Overall: $H_2O + CO_2 \rightarrow C_xO_yH_z + O_2$

Cathode- CO_2 reduction

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

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

$$CO_2 + 8e^- + 6H_2O \rightarrow CH_4 + 8OH^-$$

$$2CO_2 + 9H_2O + 12e^- \rightarrow C_2H_5OH + 12OH^-$$

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

And many more

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

Anode-Water splitting

$$H_2O \rightarrow \frac{1}{2}O_2 + 2H^+ + 2e^-$$

CO_2 Reduction

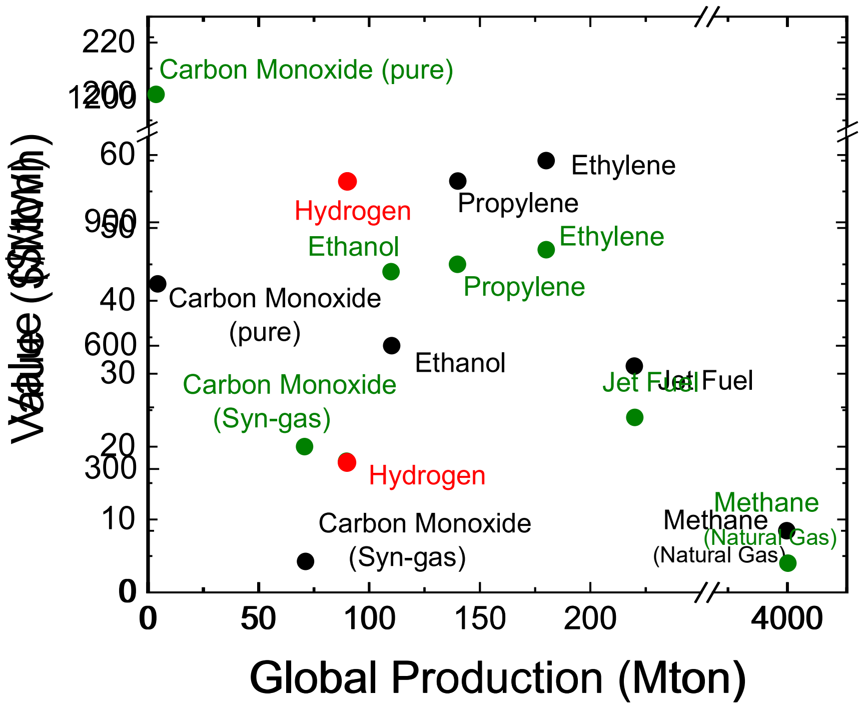
- The reduction potentials of most of the realistic CO_2 reduction catalysts are very close to the H^+/H_2 potential.
- Thus all of these reactions need ~1.2 V (or more if including losses)

Reaction	E^0 vs. RHE
$2H^+ + 2e^- \rightarrow H_2$	0.00 V
$CO_2 + H^+ + 2e^- \rightarrow HCOO^-$	- 0.11 V
$CO_2 + 2H^+ + 2e^- \rightarrow CO + 2H_2O$	- 0.11 V
$CO_2 + 6H^+ + 6e^- \rightarrow CH_3OH + H_2O$	+ 0.16 V
$CO_2 + 8H^+ + 8e^- \rightarrow CH_4 + 2H_2O$	+ 0.07 V
$2CO_2 + 12H^+ + 12e^- \rightarrow C_2H_5OH + 3H_2O$	+ 0.08 V
$3CO_2 + 12H^+ + 12e^- \rightarrow C_2H_4 + 4H_2O$	+ 0.09 V
$H_2O \rightarrow \frac{1}{2}O_2 + 2H^+ + 2e^-$	+ 1.23 V

All within 250 mV

What are we trying to do it

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



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

Electrocatalysis

What catalyst should we use

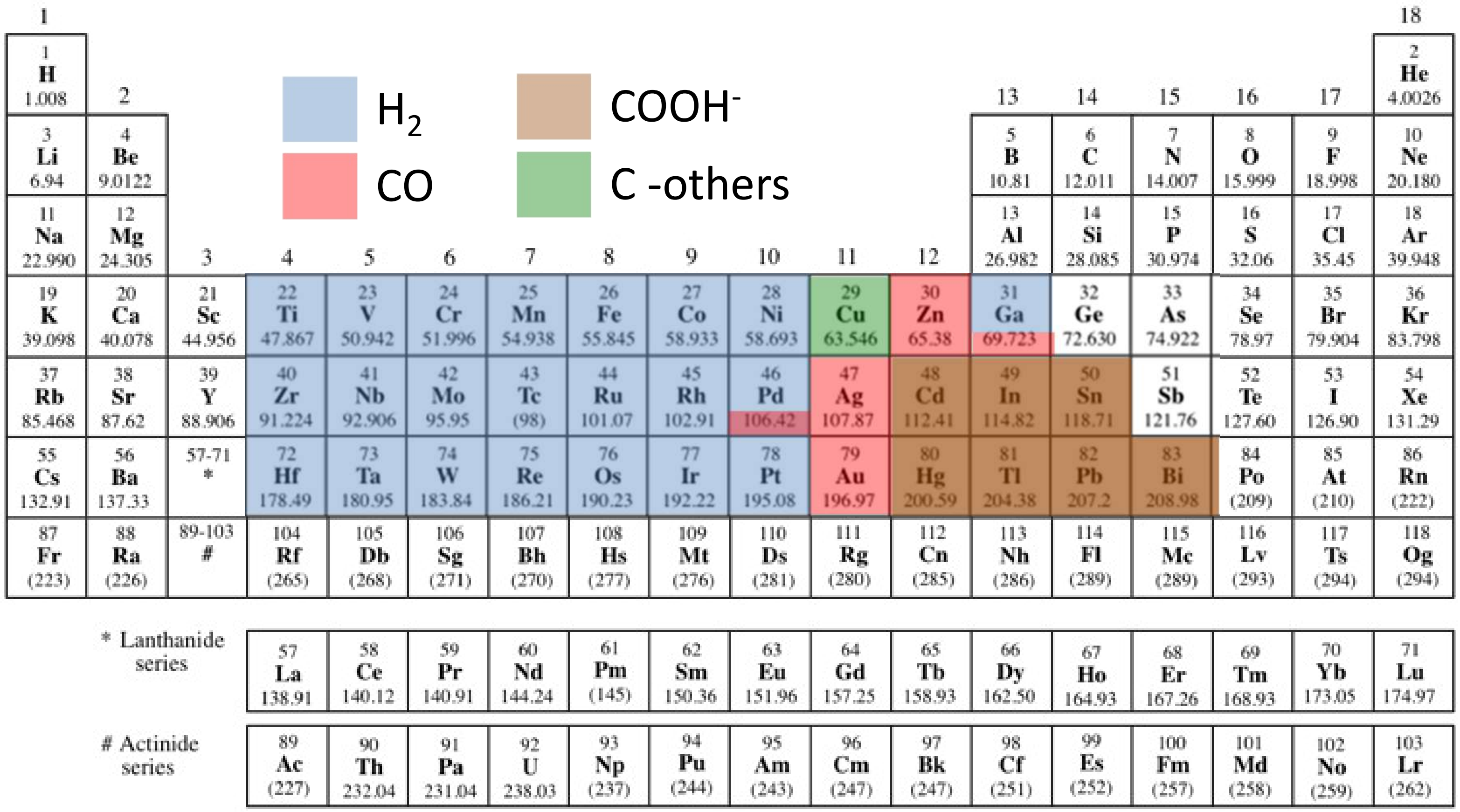
- We need a catalyst that is good at CO_2 reduction, but bad at H^+/H_2 evolution.
- Hori tested a lot of catalysts, and Cu was clearly the best.

Table 1. Various products from the electroreduction of CO_2

Electrode	Potential (V) vs. *nhe*	Current density (mA cm^{-2})	Faradaic efficiency/% CH_4	C_2H_4	EtOH	PrOH	CO	$HCOO^-$	H_2	Total
Cu	−1.44	5.0	33.3	25.5	5.7	3.0	1.3	9.4	20.5	103.5*
Au	−1.14	5.0	0.0	0.0	0.0	0.0	87.1	0.7	10.2	98.0
Ag	−1.37	5.0	0.0	0.0	0.0	0.0	81.5	0.8	12.4	94.6
Zn	−1.54	5.0	0.0	0.0	0.0	0.0	79.4	6.1	9.9	95.4
Pd	−1.20	5.0	2.9	0.0	0.0	0.0	28.3	2.8	26.2	60.2
Ga	−1.24	5.0	0.0	0.0	0.0	0.0	23.2	0.0	79.0	102.0
Pb	−1.63	5.0	0.0	0.0	0.0	0.0	0.0	97.4	5.0	102.4
Hg	−1.51	0.5	0.0	0.0	0.0	0.0	0.0	99.5	0.0	99.5
In	−1.55	5.0	0.0	0.0	0.0	0.0	2.1	94.9	3.3	100.3
Sn	−1.48	5.0	0.0	0.0	0.0	0.0	7.1	88.4	4.6	100.1
Cd	−1.63	5.0	1.3	0.0	0.0	0.0	13.9	78.4	9.4	103.0
Tl	−1.60	5.0	0.0	0.0	0.0	0.0	0.0	95.1	6.2	101.3
Ni	−1.48	5.0	1.8	0.1	0.0	0.0	0.0	1.4	88.9	92.4†
Fe	−0.91	5.0	0.0	0.0	0.0	0.0	0.0	0.0	94.8	94.8
Pt	−1.07	5.0	0.0	0.0	0.0	0.0	0.0	0.1	95.7	95.8
Ti	−1.60	5.0	0.0	0.0	0.0	0.0	tr.	0.0	99.7	99.7

Electrolyte: 0.1 M $KHCO_3$; temperature: 18.5 ± 0.5°C.
* The total value contains C_3H_5OH (1.4%), CH_3CHO (1.1%) and C_2H_5CHO (2.3%) in addition to the tabulated substances.
† The total value contains C_2H_6 (0.2%).

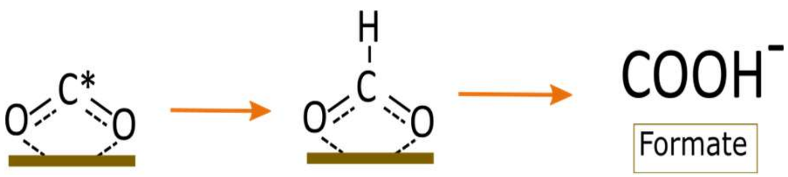
Hori, Y.; Wakebe, H.; Tsukamoto, T.; Koga, O., Electrochim. Acta., 1994


H2
CO
COOH-
C -others

Formate Production

48 Cd 112.41	49 In 114.82	50 Sn 118.71	
80 Hg 200.59	81 Tl 204.38	82 Pb 207.2	83 Bi 208.98

- P-block metals produce formate.
- The oxygens bind to the surface rather than the carbon.



- Formic acid is a useful product, formate is not.
- Many researchers are producing formate and then promoting the value of formic acid.

System	pKa
H_2O	14
CHOOH	3.7
HCO_3^-	6.1
CO_3^{2-}	10.3

Formate: Not a wanted product

- We never produce formate, but rather potassium formate (or sodium, lithium… formate)
- Where does the K^+ come from?
- KOH or $KHCO_3$ ($KHCO_3$ is produced via reacting CO_2 with KOH)

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

Name	**Value ($/ton)**	**Value ($/Mmole)**
Potassium hydroxide	1800	16
Potassium formate	1000	5

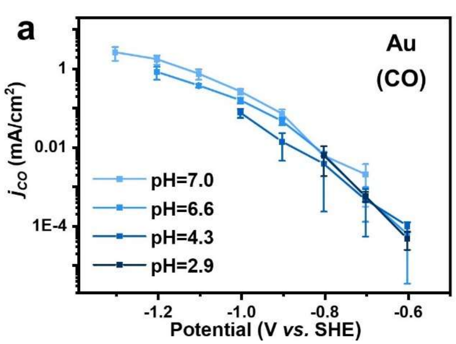
First step in CO_2 electrolysis to CO

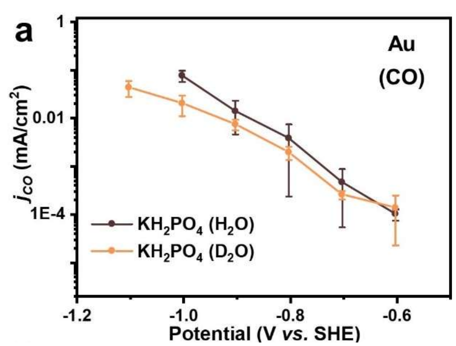
- The first step is a rate limiting adsorption of CO_2.

- How do we know this step is not a proton coupled electron transfer process.

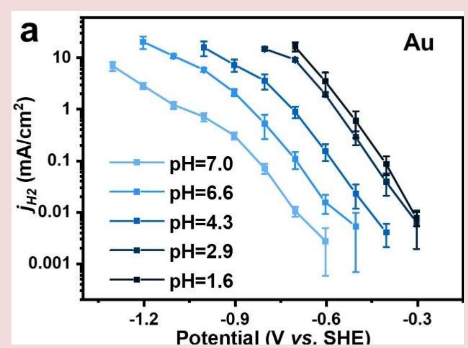
    1) It is not pH dependent

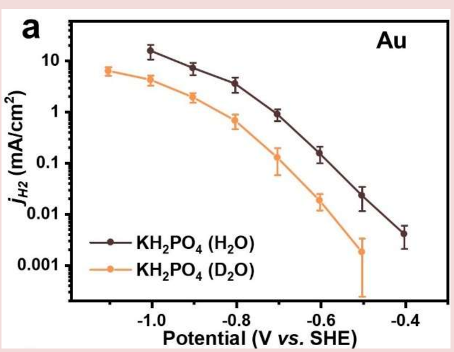
    2) It is not dependent on water (via D_2O experiments)





H_2 evolution

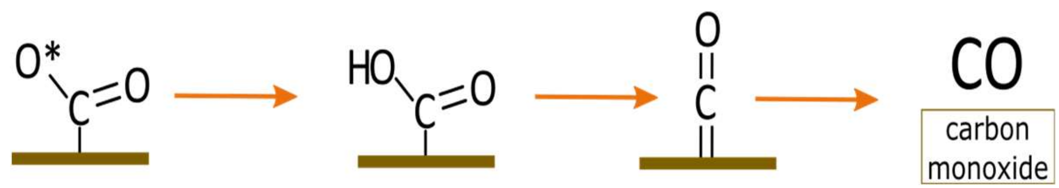




SHE= Standard Hydrogen Electrode= Standard Reference potential

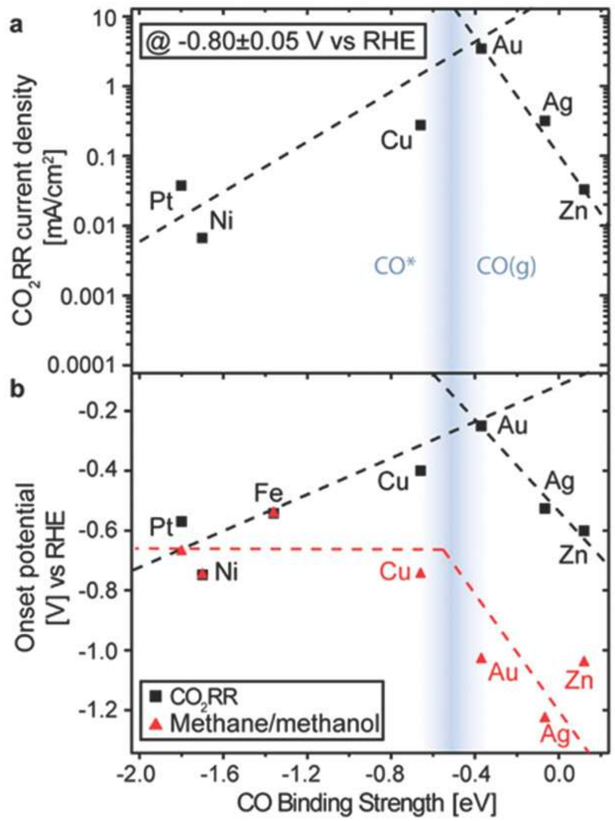
Further Reaction Progression

- The next steps are
  - Water protonates the oxygen
  - Electron adds to the intermediate
  - Another protonation of the oxygen
  - Desorption of water
- A surface-bound CO is left

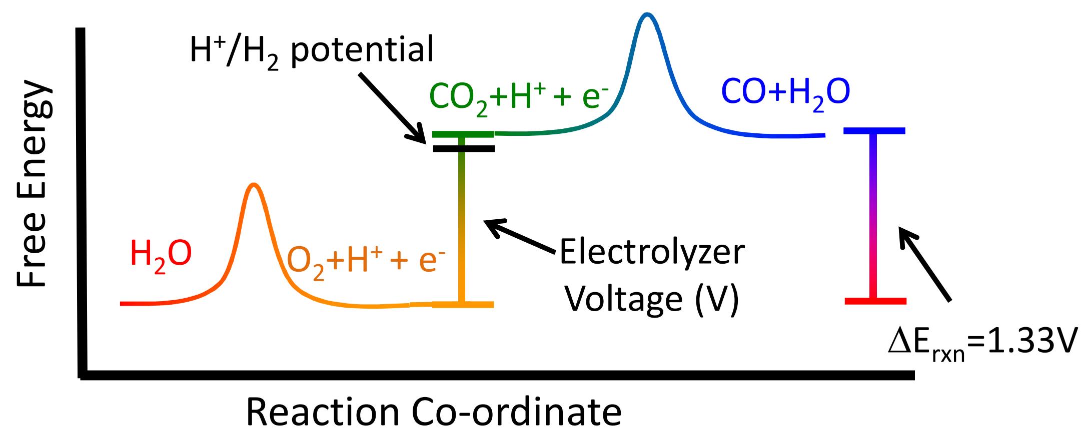


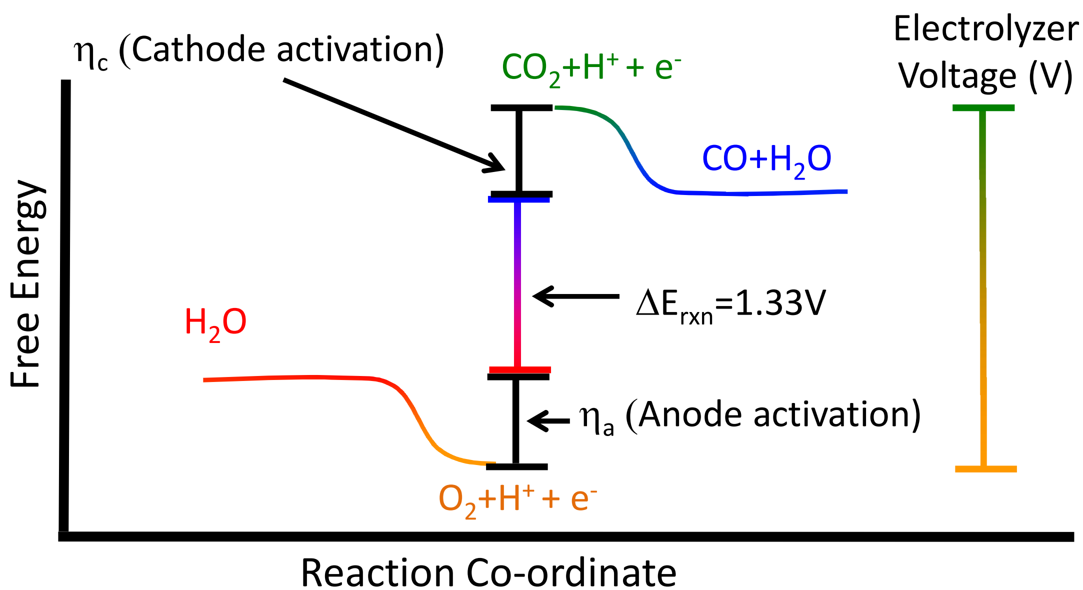
Catalyst-Intermediate binding strength

- The CO binding strength of Au, Ag, and Zn is weak, which is why they desorb



Kuhl et. al., 2014, JACS
https://doi.org/10.1021/ja505791r





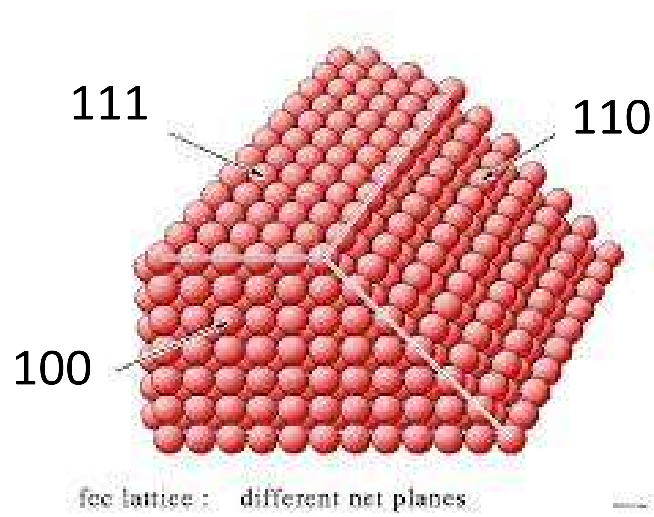
Tafel equation

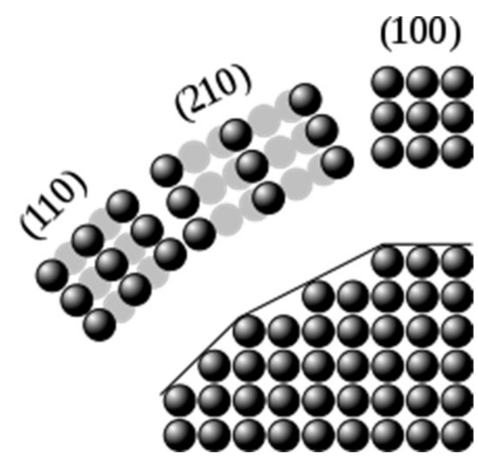
$$i = i_0 exp^{\left(F\alpha\frac{V-V_{Theory}}{RT}\right)}$$

$$\log i = \eta \frac{F\alpha}{2.3RT} + \log i_0$$

Analyzing crystal facets of a catalyst

- Au is like most pure metals and forms an FCC type crystal.
- We should expect different crystal facets to have different catalytic activities

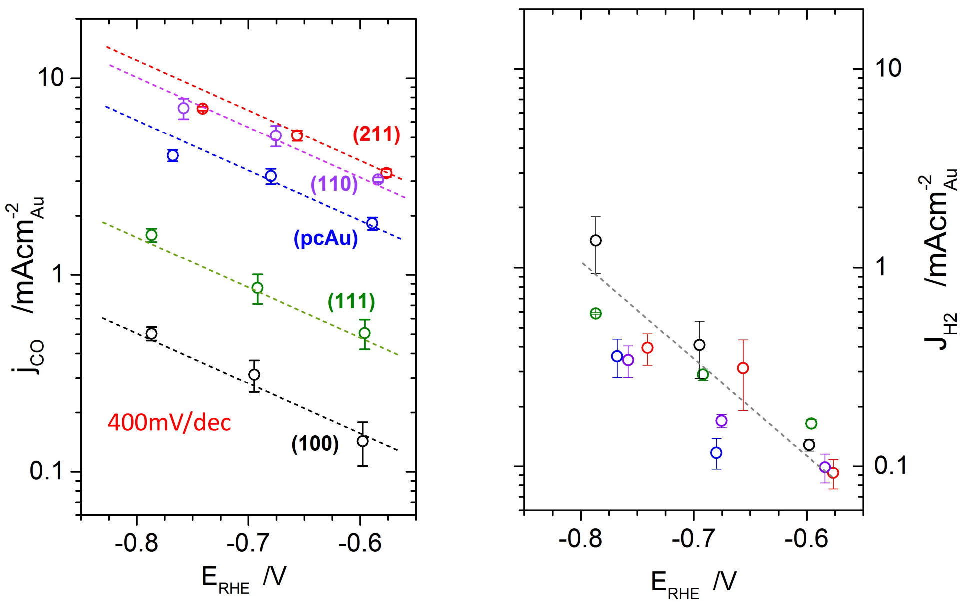




- You can buy single crystal Au that only contains 1 surface facet

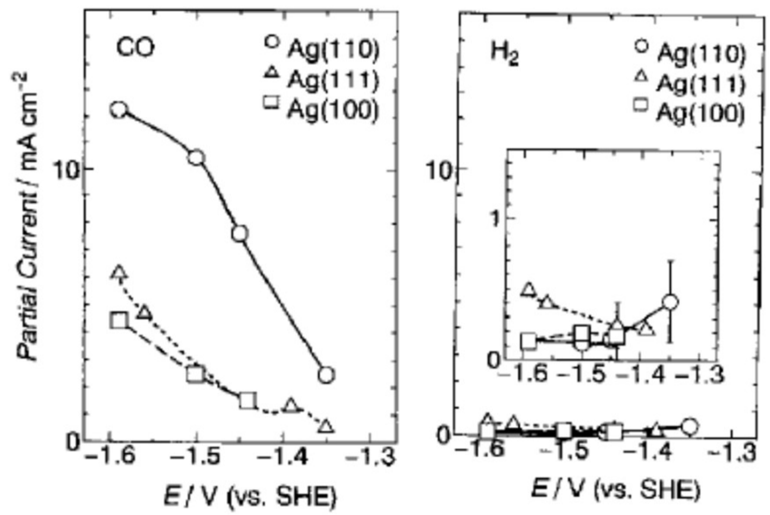
Single Crystal CO_2 to CO

- The crystal facets have a huge influence on CO_2 to CO catalysis.
- H_2 evolution is not that effected by crystal facet.
- Ag is not as good as Au, but suppresses H_2 better.

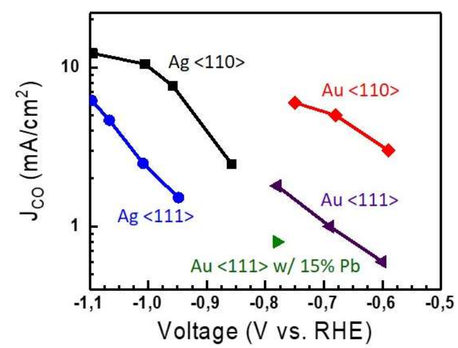


Mezzavilla, et. al. 2019, Ang. Chem. Int.

Previous tests on Ag

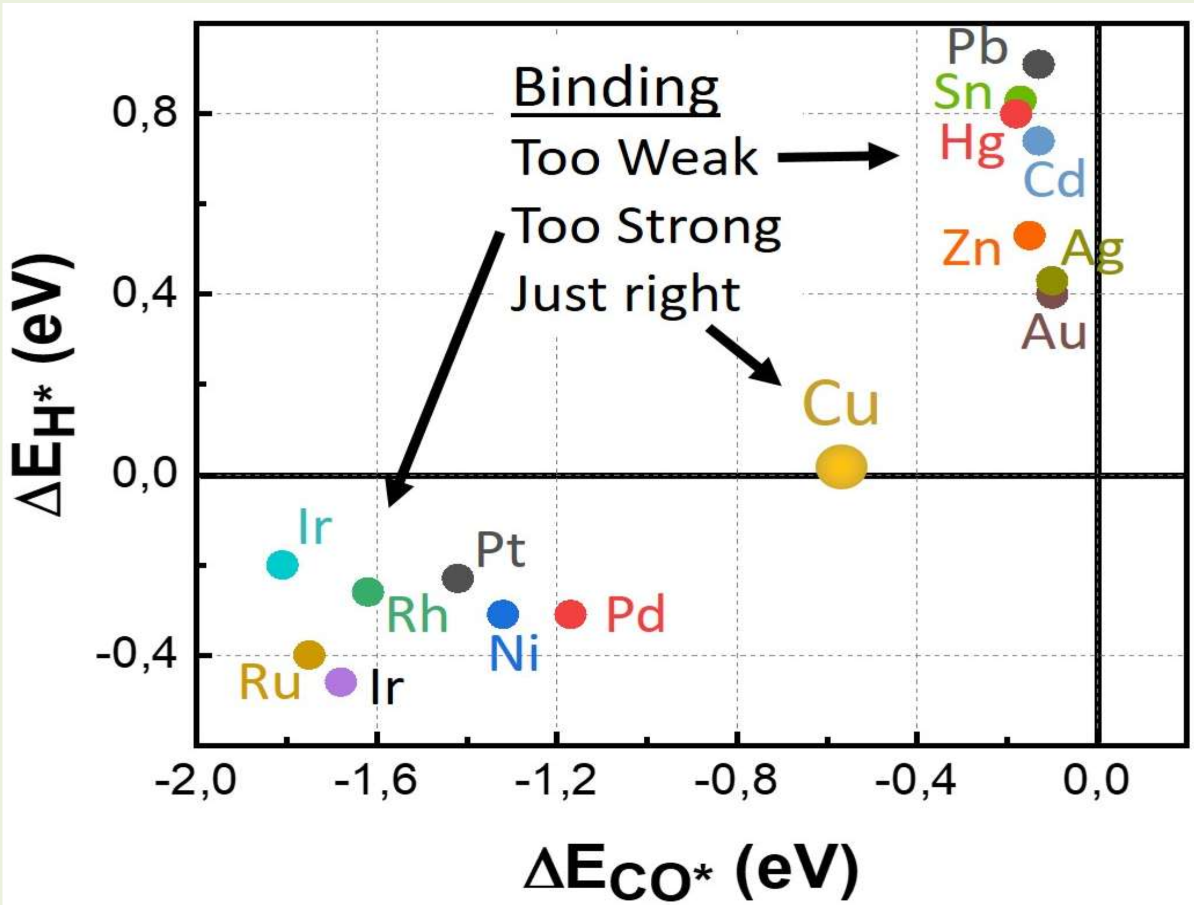


Ag single crystal data, Hoshi et. al, 1997



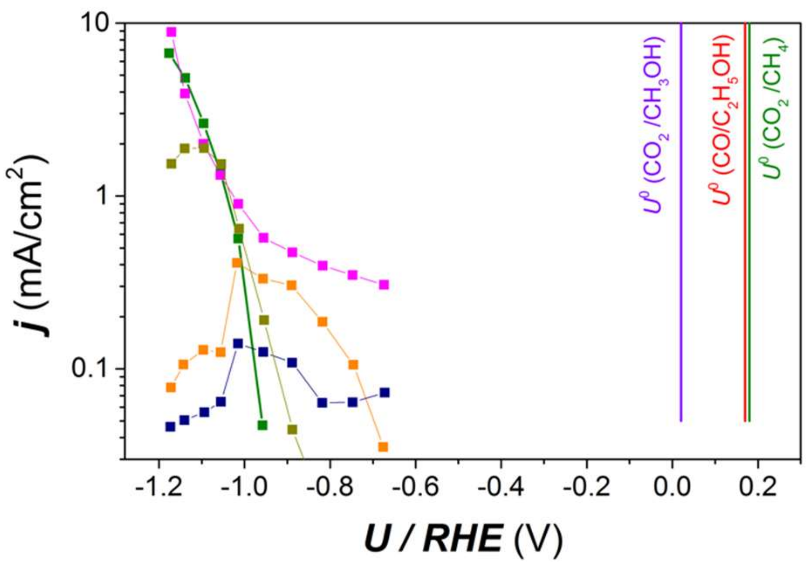
Enough with Au, lets move on to Cu

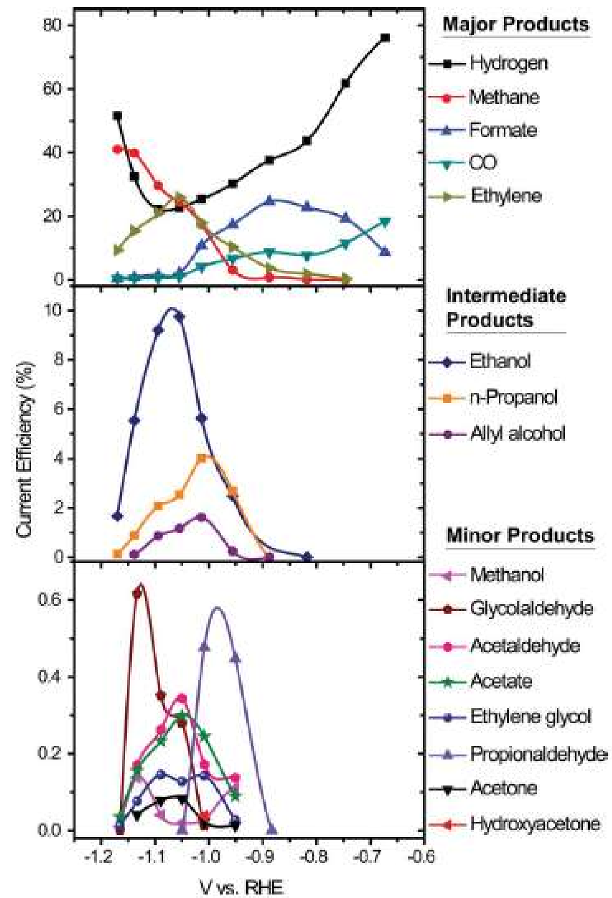
What makes copper special ?



Copper- Too many products

- Researchers have found at least 16 products for CO_2 reduction with copper.
- **Many products makes product separation difficult.**





Kuhl, Cave, Abram, Jaramillo *Energy Environ. Sci.* 2012

Strategy to producing a single product

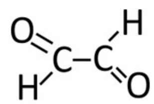
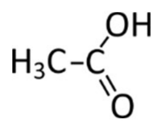
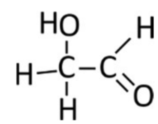
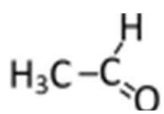
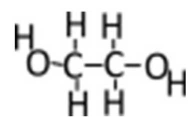
1. Understand what is going on

- We need to figure out the pathway/mechanism of all these products

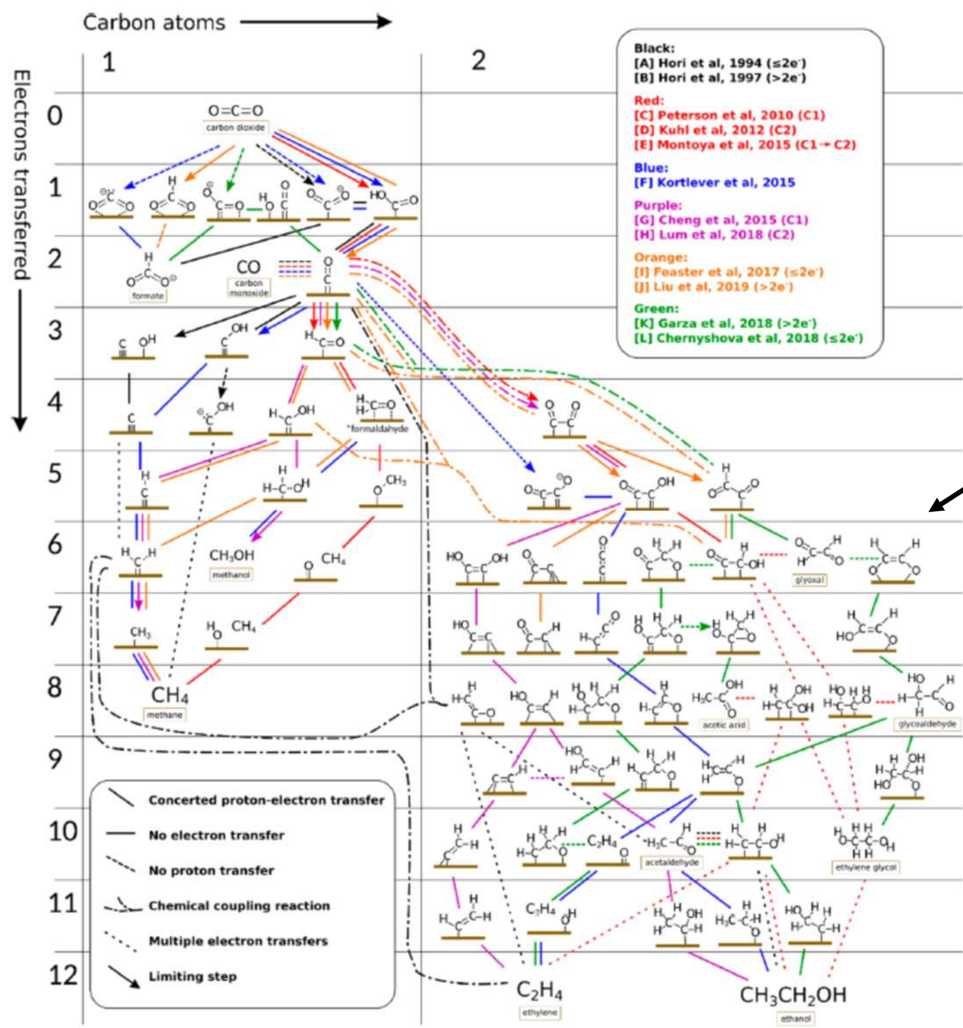
2. Use understanding to solve the problem

- We figure out what is the key parameter that controls selectivity, then we modify this.

Breaking down our products beyond CO

CO			
$2e^-$ more	 Glyoxal		
$4e^-$ more	 Acetate	 Glycoaldehyde	
$6e^-$ more	 Acetaldehyde	 Ethylene glycol	CH_4 Methane
$8e^-$ more	CH_3CH_2OH Ethanol	C_2H_4 Ethylene	

As of 2018, we had no clue what was going on



Søren Scott's DTU Masters thesis, 2017

Also put in Nitopi et al.,Chem Rev. 2018
Doi:10.1021/acs.chemrev.8b00705

Vary pH to give insights in mechanism

- Can we change pH to get insights into the mechanism?

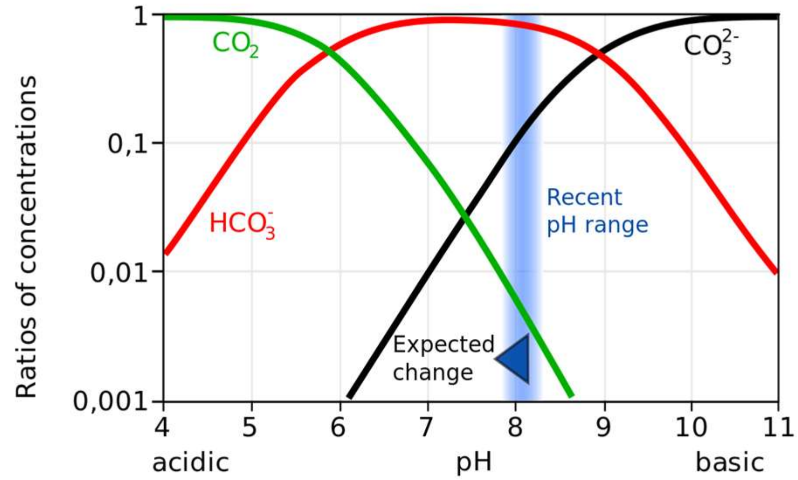
- *From the 1st lecture*

pKa = 6.5 pKa = 10.6

$$CO_2 + H_2O \rightarrow H_2\,CO_3 \rightarrow H^+ + HCO_3^- \rightarrow 2H^+ + CO_3^{2-}$$

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

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

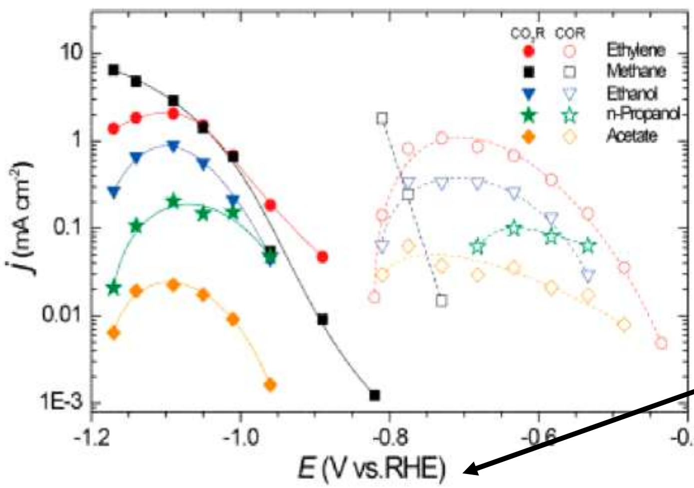


- The CO_2 acts as a buffer preventing us from going to alkaline solutions

pH dependence of CO_2 electrolysis

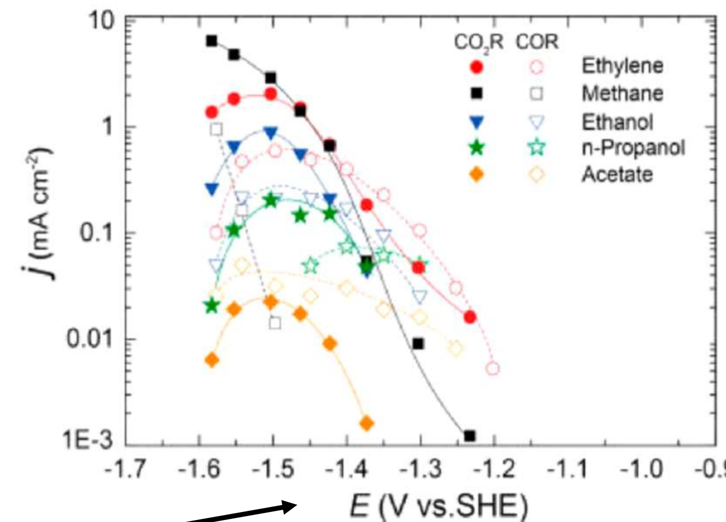
- Since CO_2 buffers alkaline, CO electrolysis allows us to investigate high pH effects
- Once we plot activity on an absolute scale everything lines up
- Methane does its own thing.

CO_2 reduction = pH 8,   CO reduction = pH 14



pH dependent reference

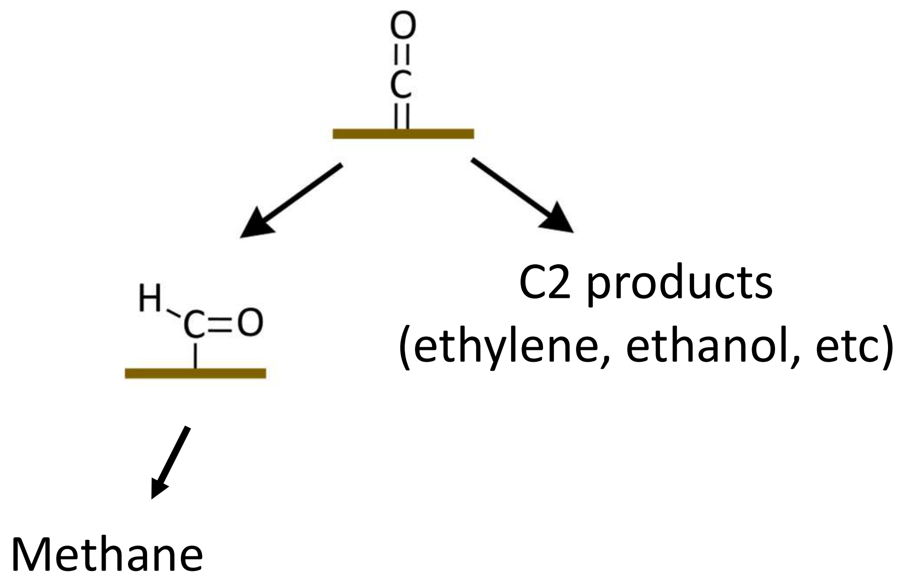
pH independent reference



Wang, L.; ACS Catal.2018, 8, 7445–7454.

Why is methane a rebel?

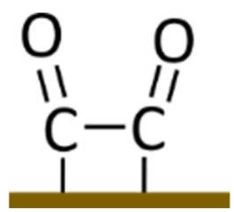
- Methane's mechanism differs from all the C_2 and C_3 products at a very early stage



- We are not exactly sure why methane is pH dependent. It needs lot of overpotential, and is low value so nobody cares about this.

A rate limiting step that does not involve a proton?

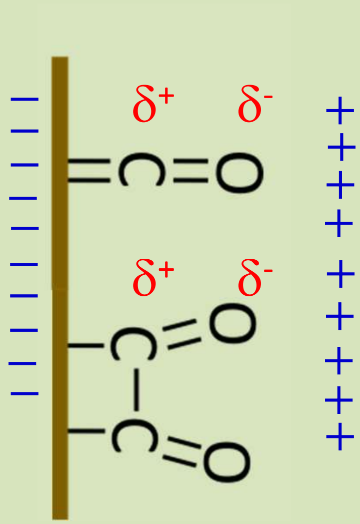
- If CO is already absorbed and the rate is not effected by H^+, what is the rate limiting step?
- The rate limiting step is a CO–CO 'coupling' reaction.

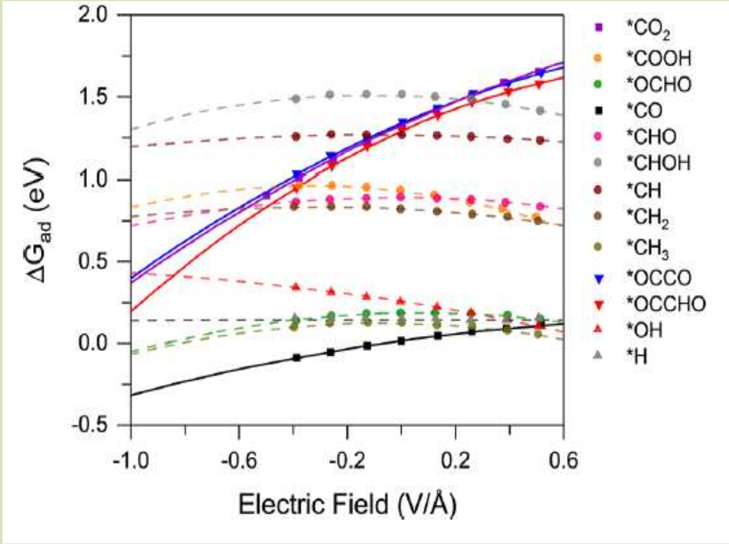


- This coupling is driven by an electrochemical potential, but does not really involve an electron transfer.– Strange
- It is the electric field that produces CO-CO coupling, not the actual potential.

Electric Field Effect

- CO and other intermediates have strong dipoles
- The electrode-electrolyte produces a double layer, which provides an electric field
- Could we modify the electric field to stabilize the dipoles?

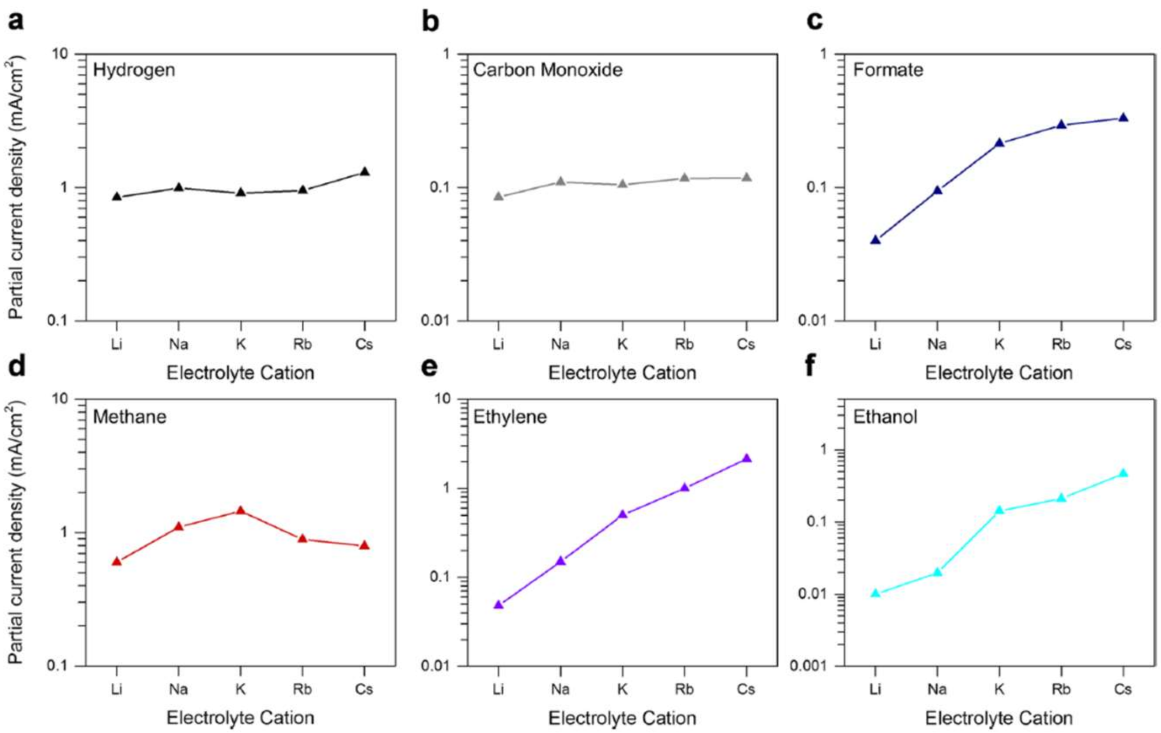




Resasco et. al, 2017, doi: 10.1021/jacs.7b06765

Varying cations in the electrolyte

- Varying cations modifies the double layer
- Smaller cations are more hydrated, thus produce a weaker electric field



Hydrated cation radius (Å)

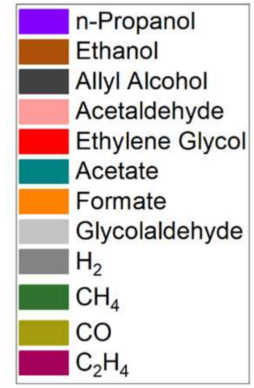
Cs	Rb	K	Na	Li
3.5	3.9	4.1	5.2	5.8

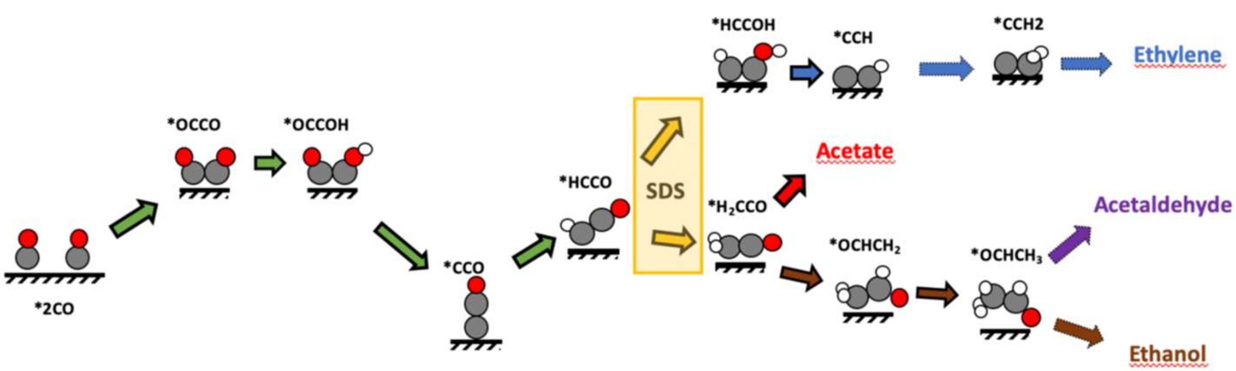
5000% increase switching from Li^+ to Cs^+

Resasco et. al, 2017, doi: 10.1021/jacs.7b06765

Varying alkalinity for CO electrolysis

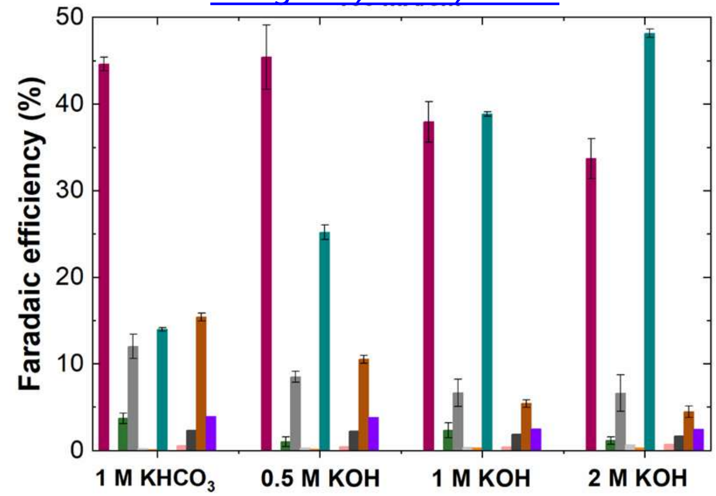
- As you go highly basic, acetate increases, ethanol decreases
- This tells us that acetate must be on the same path as ethanol.





Kastlunger, et al. ACS Catalysis 13 (7), 5062–5072, 2023

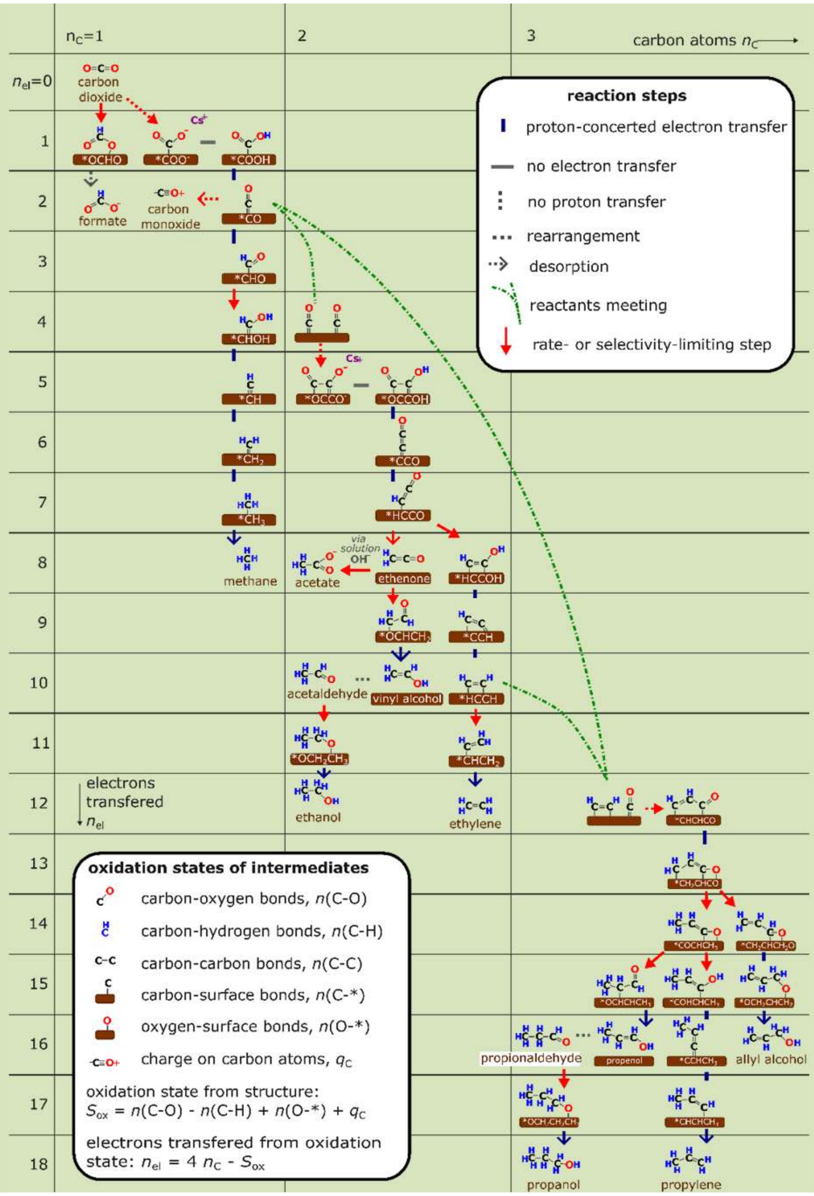
Ming Ma, 2022, E&ES



pH increase

Reaction Mechanisms-
Putting everything together

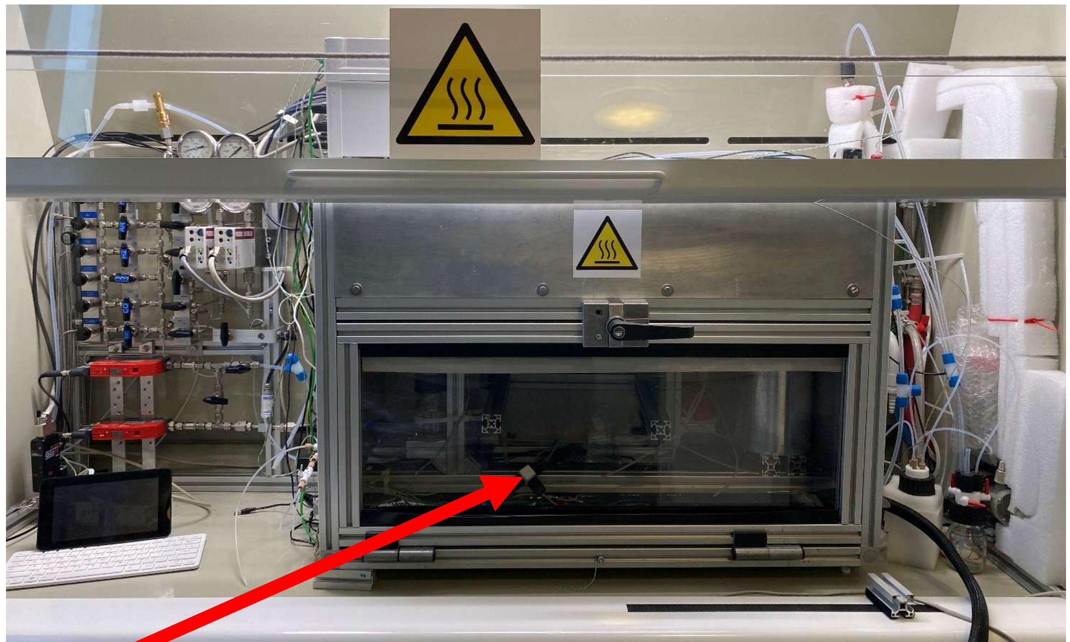
- **The rate limiting step for C2 products is CO-CO coupling reaction**
- The rate limiting step for methane is undetermined.
- C3 products (propanol, propanaldehyde, etc.) are not well studied, and thus the figure is mostly a guess on their mechanism

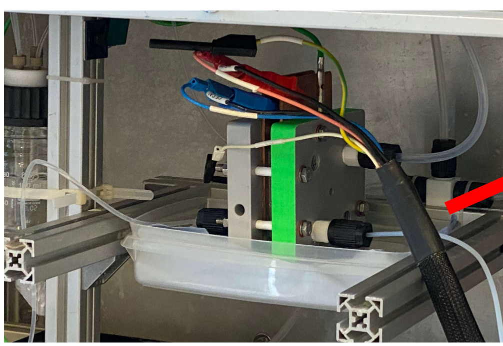


Seger et. al., (2025) ACS Energy Letters

Break

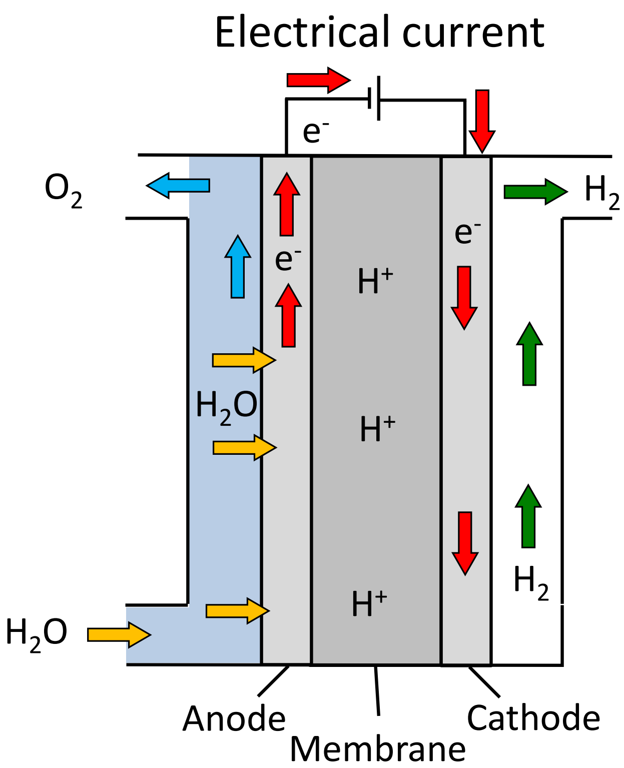
Scale up





Water electrolysis

- With water as a reactant, there is no problem with getting enough reactant to the catalyst.
- Both products are gases so they are easy to deal with.
- A membrane seperates our anode & cathode ensuring no product crossover.

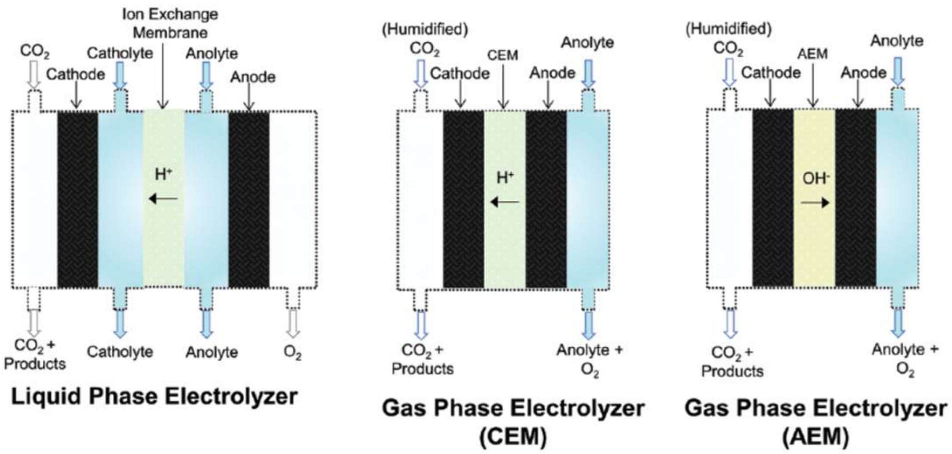


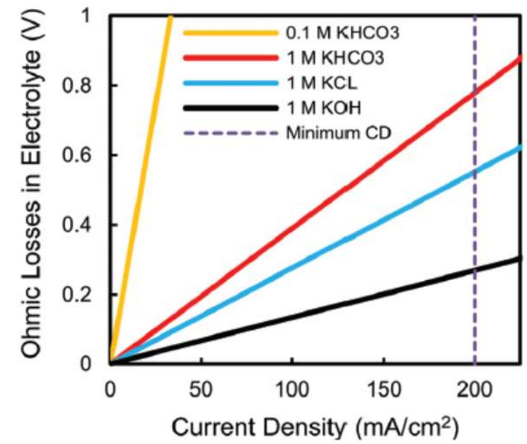
Industrial relevant approaches to CO_2 electrolysis

Advantages:

Liquid Product Extraction

Low ohmic loss





3 mm anolyte & catholye

High ohmic losses

Membrane issues

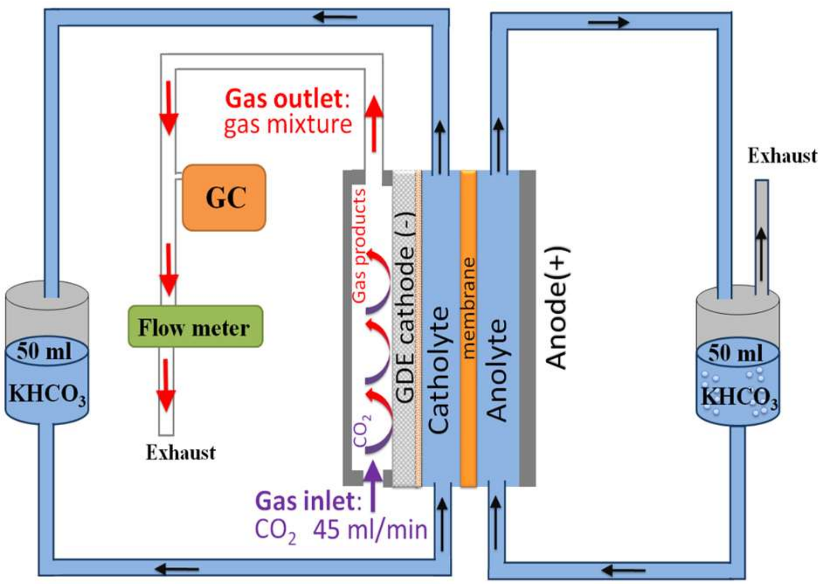
Burdyny and Smith,
E&ES, 12, 1442—1453, (2019)

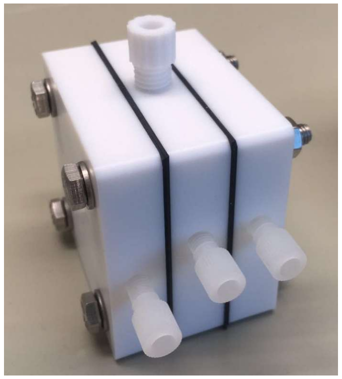
Disadvantages:

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

Analyzing copper for CO_2 reduction

- With copper producing liquid products, we decided to go with a flowing liquid on the cathode approach.
- The liquid catholyte allows us to vary pH





Reactors

What goes in is not what comes out

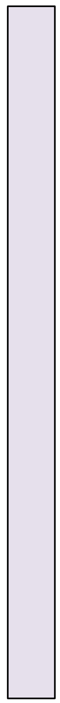
Cathodic reactions

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

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

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

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



Anion exchange membrane

CO_2 Equilbrium- *From 1st lecture*

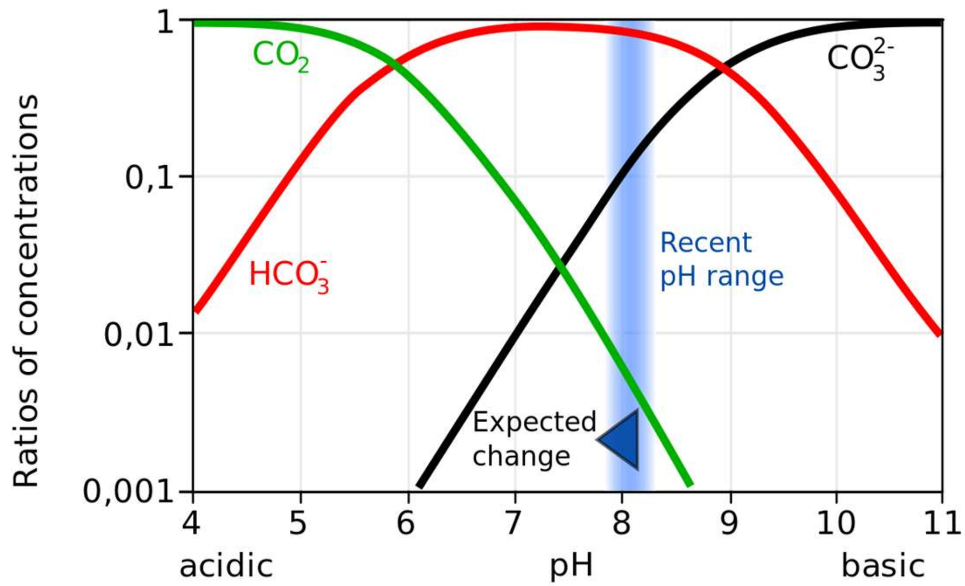
pKa = 6.5

pKa = 10.6

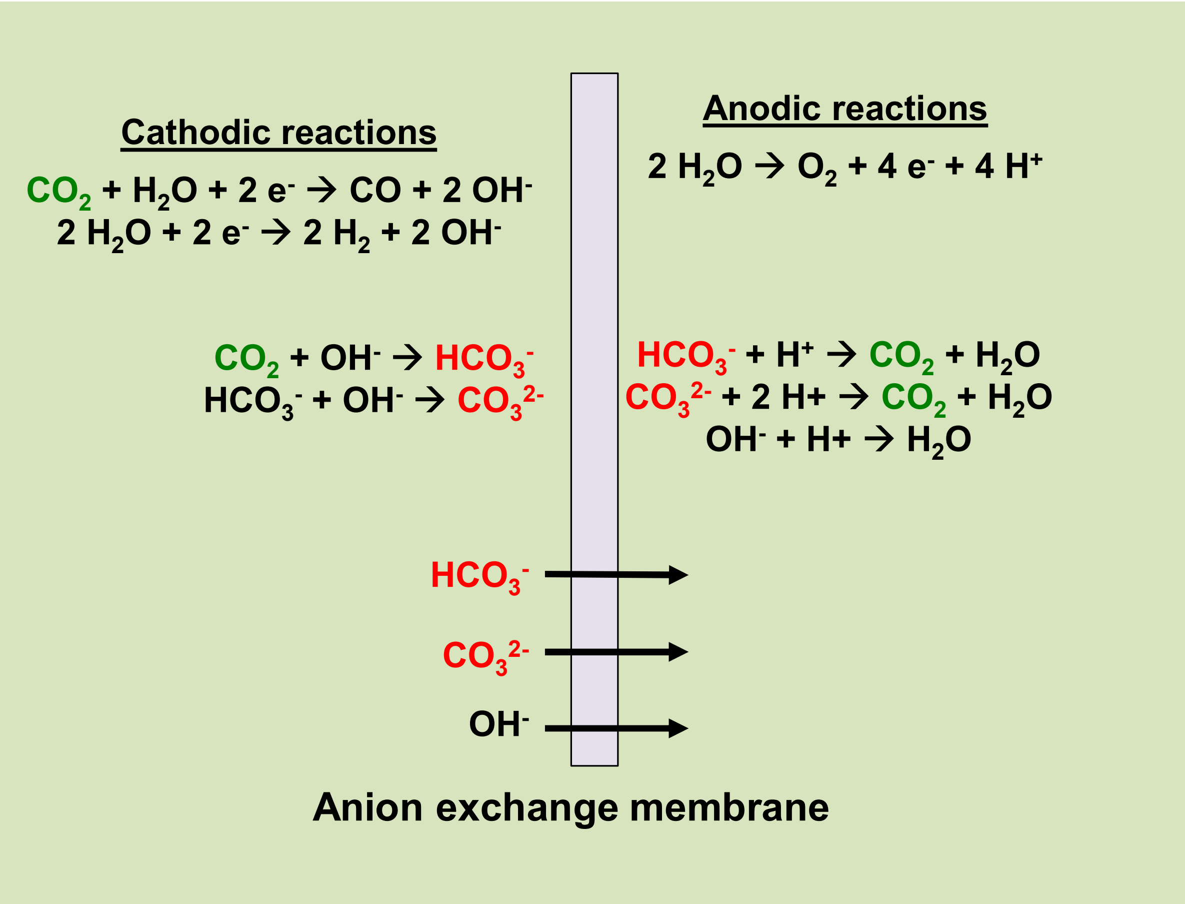
$$CO_2 + H_2O \rightarrow H_2\,CO_3 \rightarrow H^+ + HCO_3^- \rightarrow 2H^+ + CO_3^{2-}$$

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

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



$$pKa = Log_{10}\frac{[HA]}{[A^-][H^+]}$$



The Carbon/Charge Coefficient (CCC) is as followed

OH^- → CCC=0

CO_3^{2-} → CCC=1/2

HCO_3^- → CCC=1

Function of current

Function of carbon/charge ratio

$$Gas\ out = Gas\ in \pm Reaction - Crossover$$

Testing different electrolytes

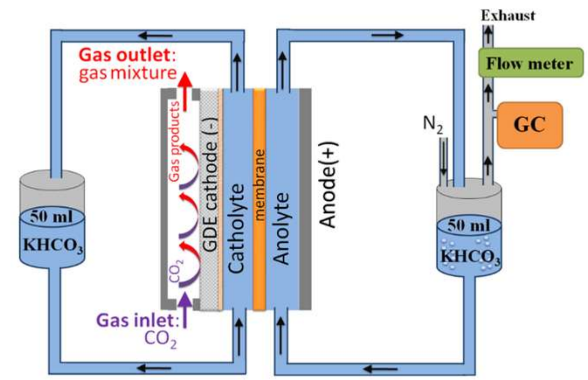
- We can also vary the electrolyte composition.
- Basic electrolytes are effectively ‘ CO_2 scrubbers’

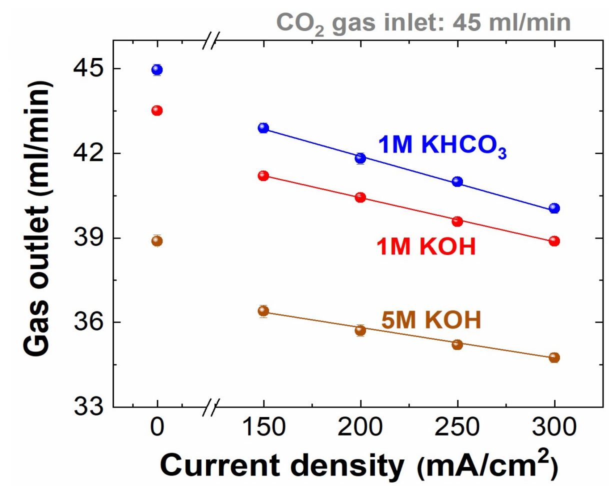
$$CO_2 + OH^- \rightarrow HCO_3{}^-$$

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

- Even at open-circuit, significant CO_2 is consumed.

$$Gas\ out = Gas\ in \pm Reaction - Crossover - Scrubbed$$



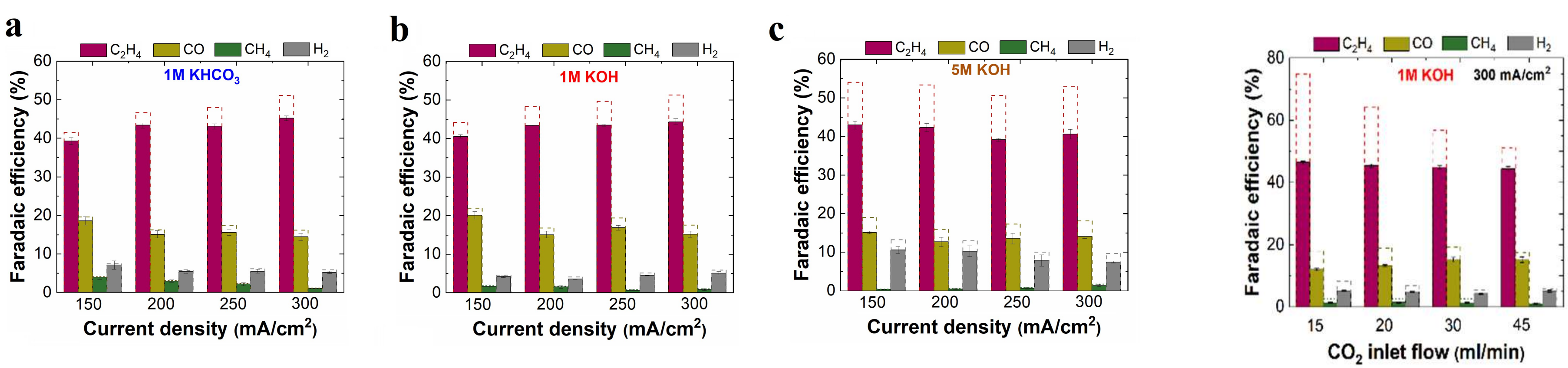


Ma, M., et al E&ES 2020

Comparison of selectivites in different electrolytes

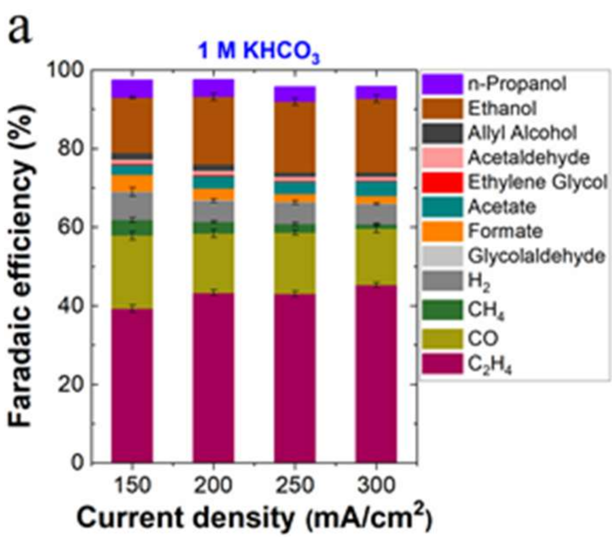
- The dotted lines are if we measured product concentrations, but did not account for lost CO_2 gas from OH^- equilibration.

- Thus it was very easy to cheat/lie on efficiency results. From 2018-2020 this was a huge issue, but now most researchers stopped doing this.



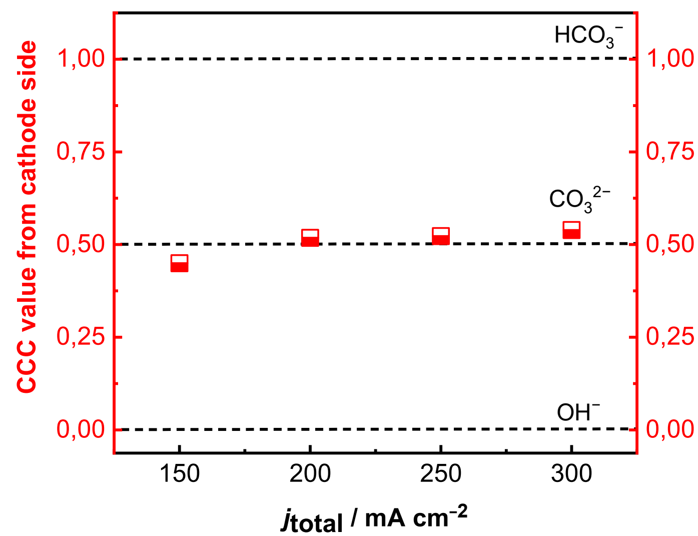
Liquid selectivites

- Calculating liquid products and getting 100% total selectivity of products verifies accurate results.
- We can also see our carbon crossover is pure carbonates.



Ma, M., et al E&ES 2020

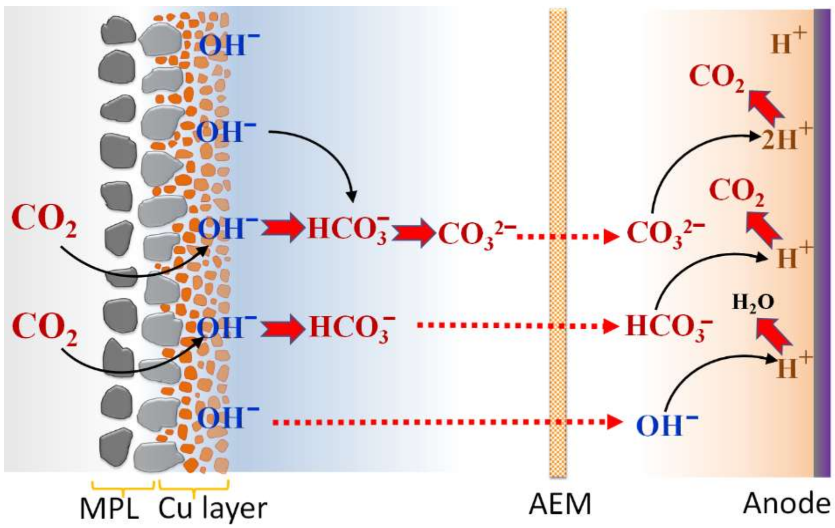
Tests in 1M $KHCO_3$

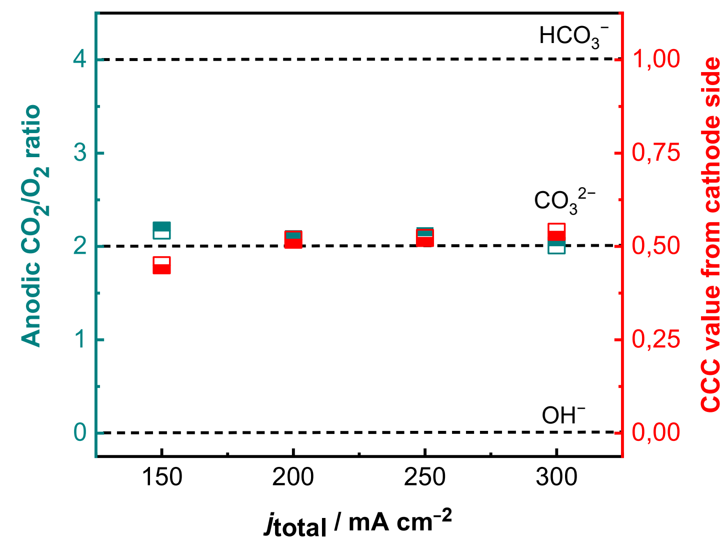


Larrazabal, G., et al., *Account. Mat. Res., 2021*

Analyzing the anode

- We can also analyze our anode gas to see what crosses the membrane





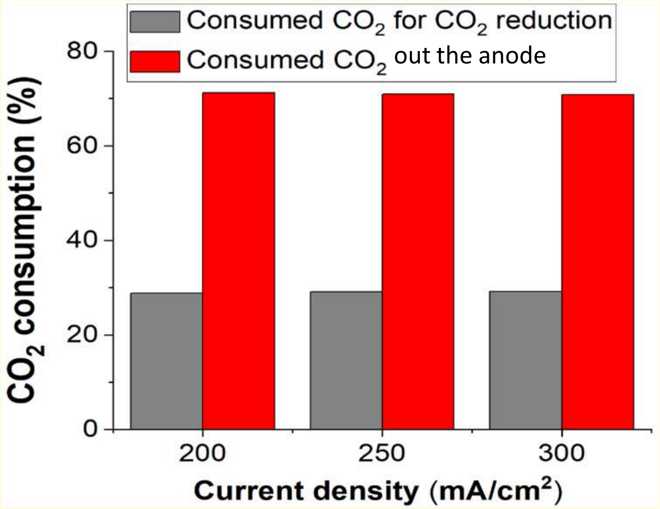
Larrazabal, G., et al., *Account. Mat. Res., 2021*

Anode reactions:

	CO_2/O_2 ratio	CCC
$4HCO_3^- \rightarrow 4\ CO_2 + O_2 + 2H_2O + 4e^-$	4	1
$2CO_3^{2-} \rightarrow 2CO_2 + O_2 + 4e^-$	2	1/2
$4OH^- \rightarrow 2H_2O + O_2 + 4e^-$	0	0

How bad is the CO_2 crossover

- We lose 70% of the CO_2 out the anode and only use 30% of it for products



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

- If we had pure carbonate cross over our membrane, and were making 100% ethylene, what percentage of CO_2 would we lose?

Who is doing this?

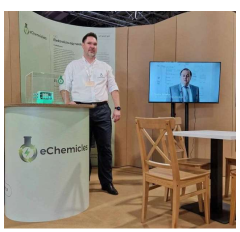
- Twelve is a company based off previous Stanford PhD students

  - Focuses on CO_2 to CO
  - Received ~800 Million $ in funding over last 2 years

- CERT is a company based off U. of Toronto PhD students.

  - Focuses on CO_2 to ethylene
  - Started in about 2018

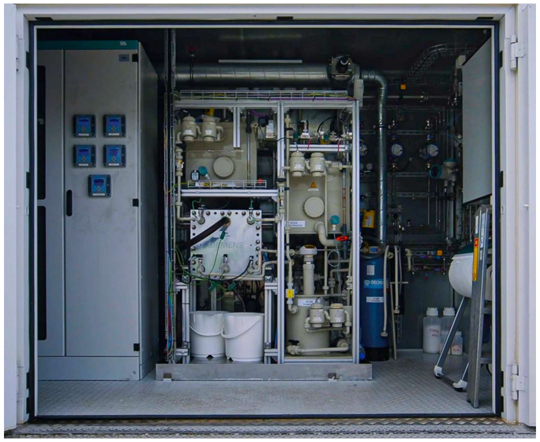
- eChemicles is a company derived from U. of Szegad in Hungary



  - Focuses on CO_2 to CO
  - Started in about 2020

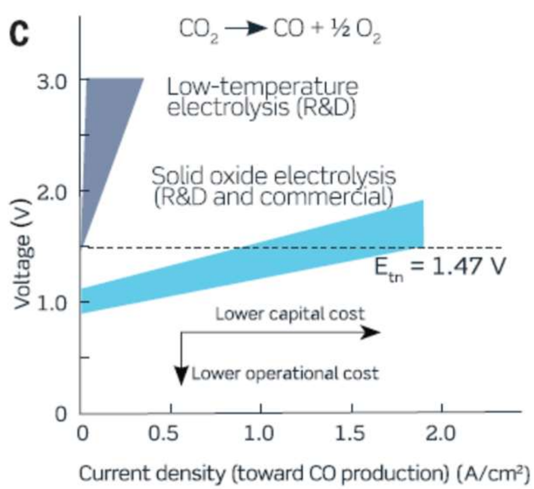
Who is doing this?

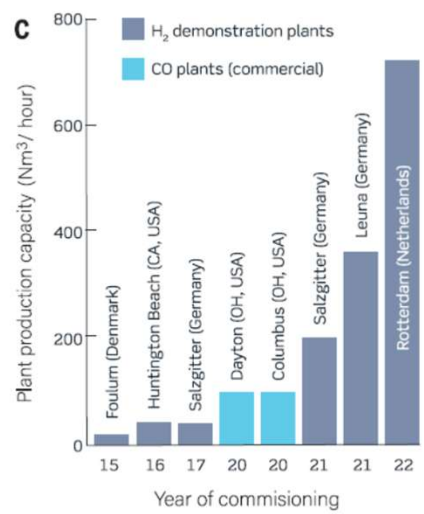
- Dioxide Materials is a company based off a retired professor Richard Masel
  - Membranes and parts for research groups is their specialty
  - Completely unorganized company, but somehow has great membranes
- Siemens is also doing this on a large scale. Most of the work is being done with Maximillian Fleischer being the lead scientist.
  - Focuses on CO_2 to CO and Ethylene
  - Already have a protoype operating

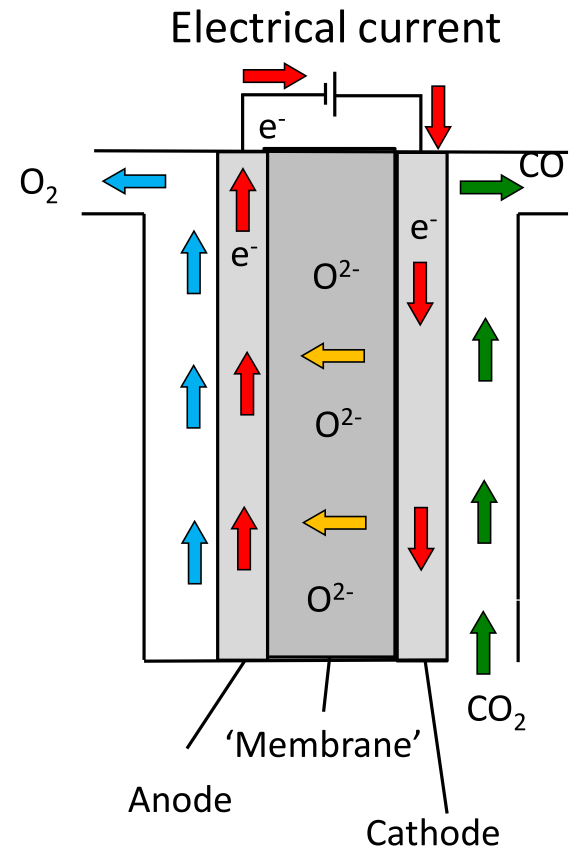


Solid Oxide CO_2 electrolysis

- They use basically the same reactor as H_2O to H_2 electrolysis
- Same advantages and disadvantages of H_2 production- low voltage, but durability issues







Hauch, A., et al. Science 2020 Doi: 10.1126/science.aba6118

Who is doing this?

- Haldor Topsoe, who are located 1km from DTU
  - Originally focused on solid oxide fuel cells
  - Is currently on hold as they push the solid oxide business for H_2.

- Sunfire is a German start-up (from 2010) that employs 250 people
  - Focus on H_2, CO, and syngas production
  - Highly developed, maybe a little behind Topsoe in commercialization
  - Parterning with a lot of other companies

What is the limiting factors?

- The conductivity of the solid oxide ‘membrane’ is a function of temperature
- Membranes are made out of yittrium stabilized zirconium
- Formation of coke can be an issue.
- The high temperatures prevent any carbon based product other than CO
- Capital costs. They are expensive.

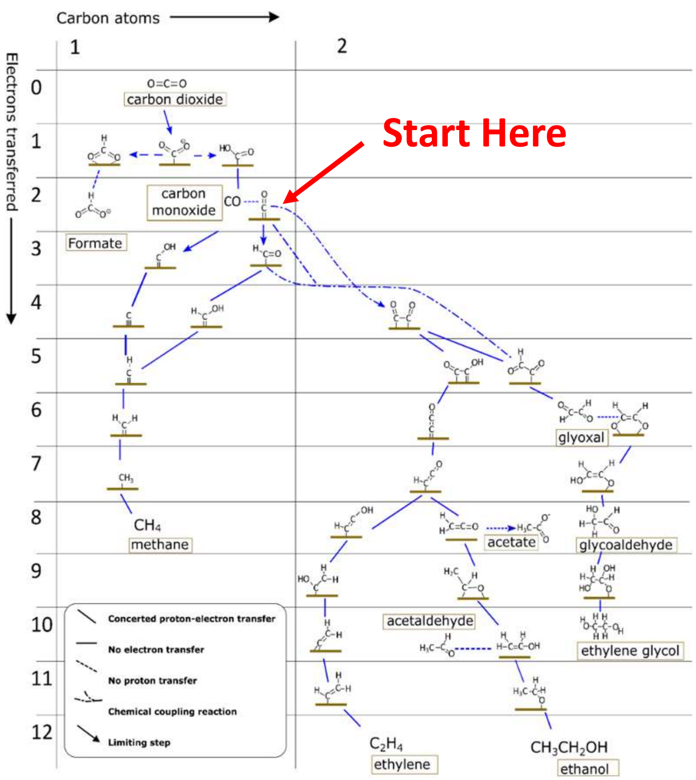
Coking Reaction

$$CO_2 \rightarrow C + O_2$$

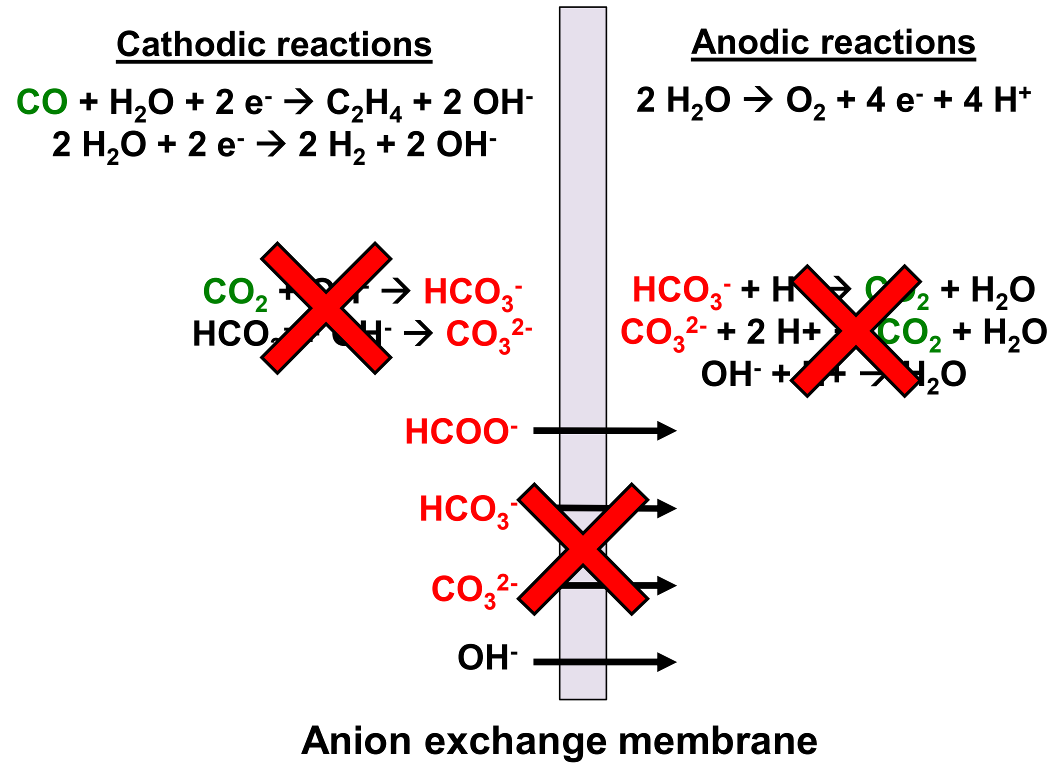
Low temperature CO electrolysis

- What if we do CO electrolysis with our low temperature approach?

Fundamental

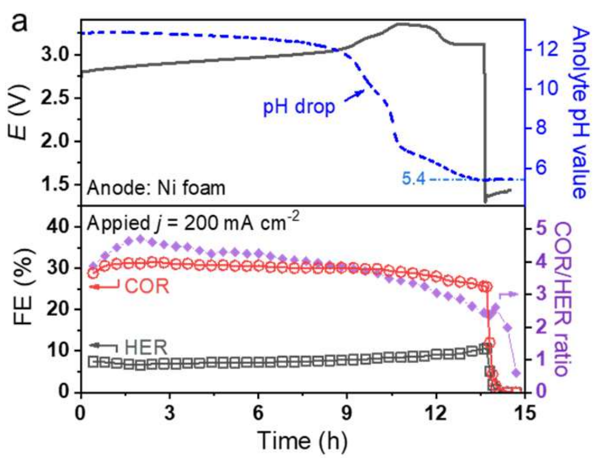


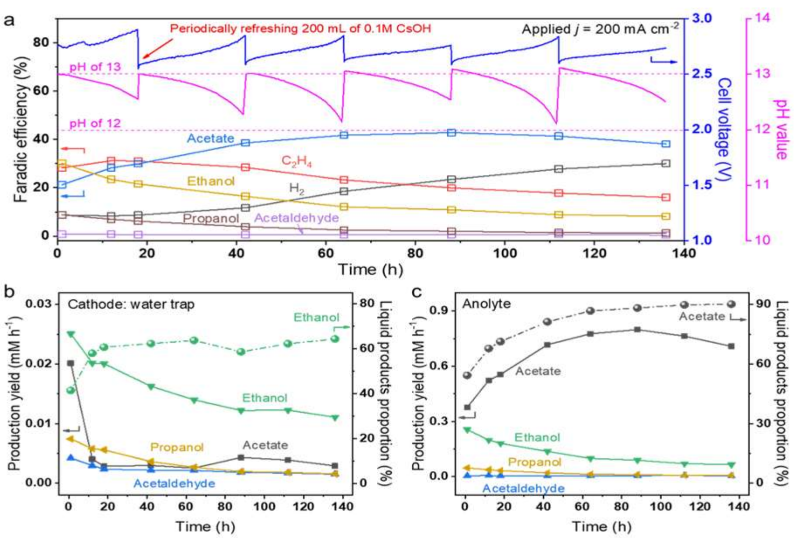
Scale-up



Low temperature CO electrolysis

- Salts are more soluble in alkaline, which helps in durability
- Acetate build-up on the anode, slowly pH shift the electrolyte so it is acetic acid.
- Catalysts need to be stable in a changing pH, which our original catalyst (nickel) was not.
- Removing the acetate allowed us to go for over 100 hours





Xu, et al. Nat. Cat., 2023, Doi: [10.1038/s41929-023-01034-y](https://doi.org/10.1038/s41929-023-01034-y)

Options

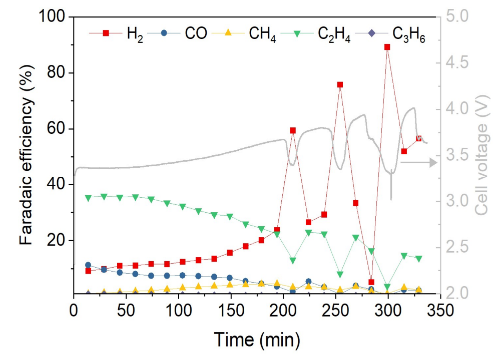
1) How to involve x-rays into CO2 electrolysis research

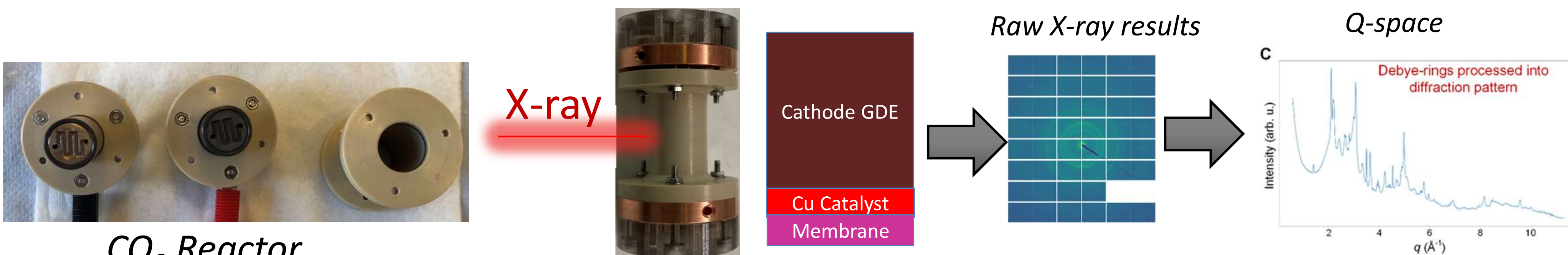
2) Electrowinning (i.e. using electricity to mine/extract metals)

Where is research in this field

- Water build-up on the cathode over time prevents CO_2 to get to the catalyst and favors hydrogen evolution.

- We are using synchrotron analysis to understand this



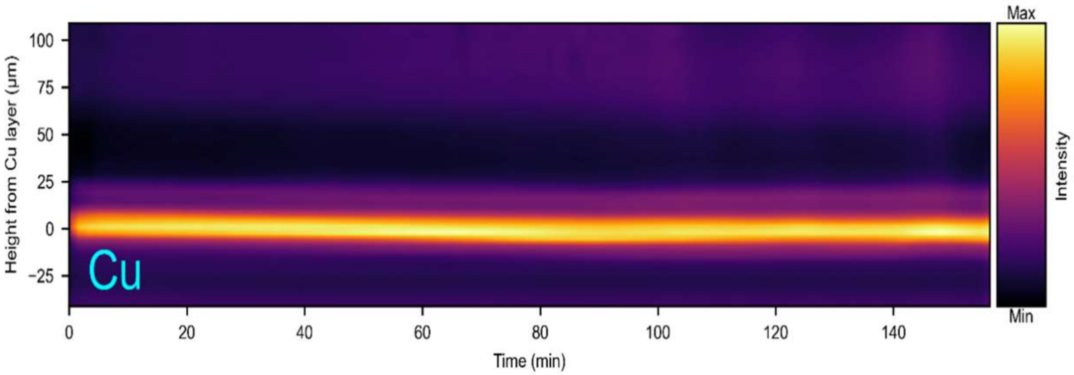


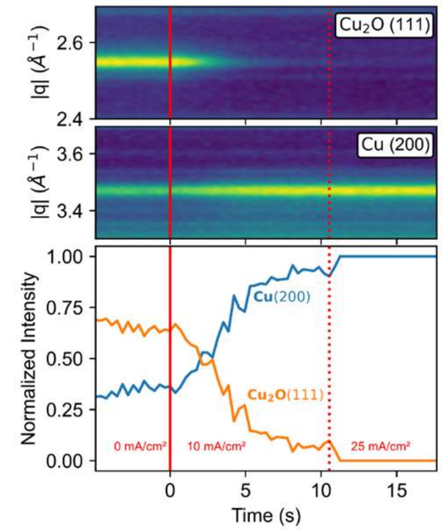
CO_2 Reactor

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

Things we can do – Catalyst peaks

- We can see copper's location within our device

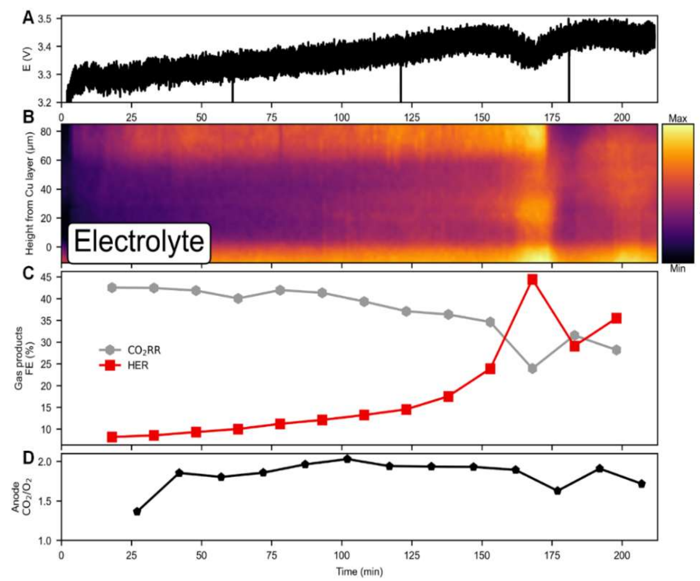




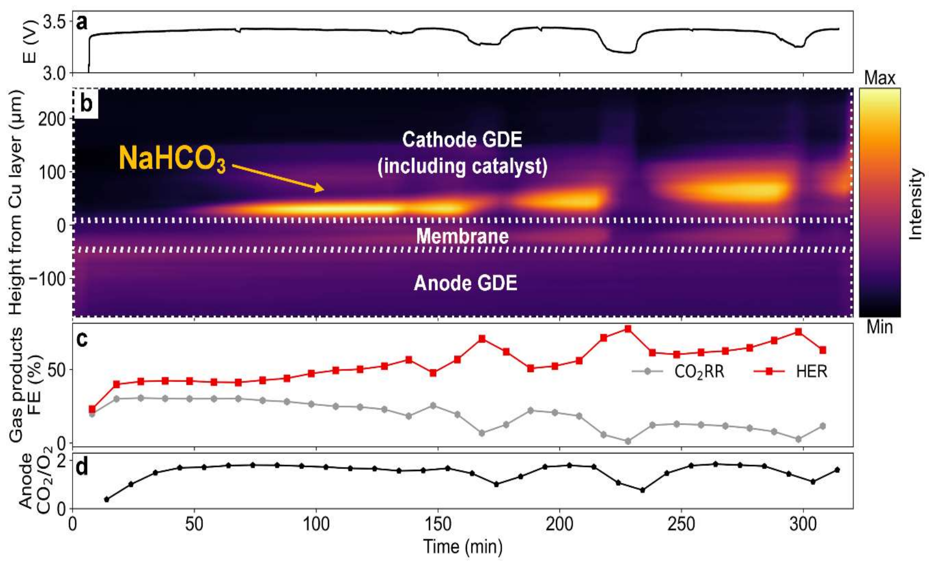
- We can see copper reduce from an oxide to a metal over time

Things we can do – Water and Salts

- We can see water by monitoring changes in background peak



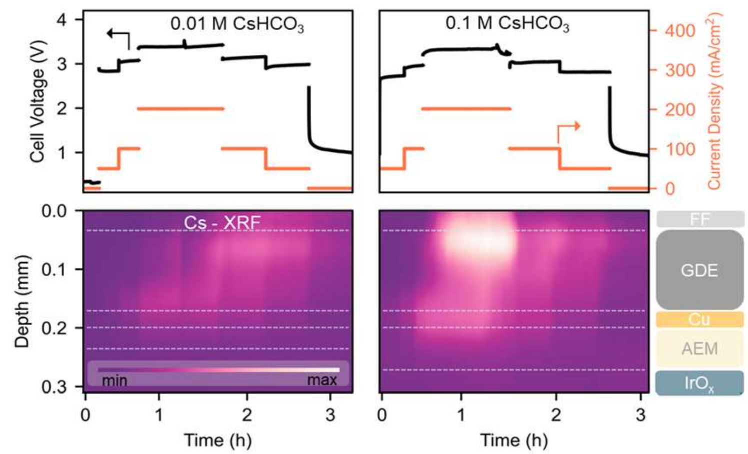
- We can see salt depositing in our reactors

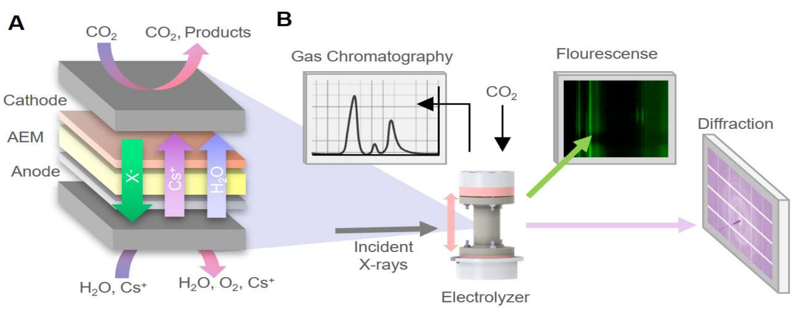


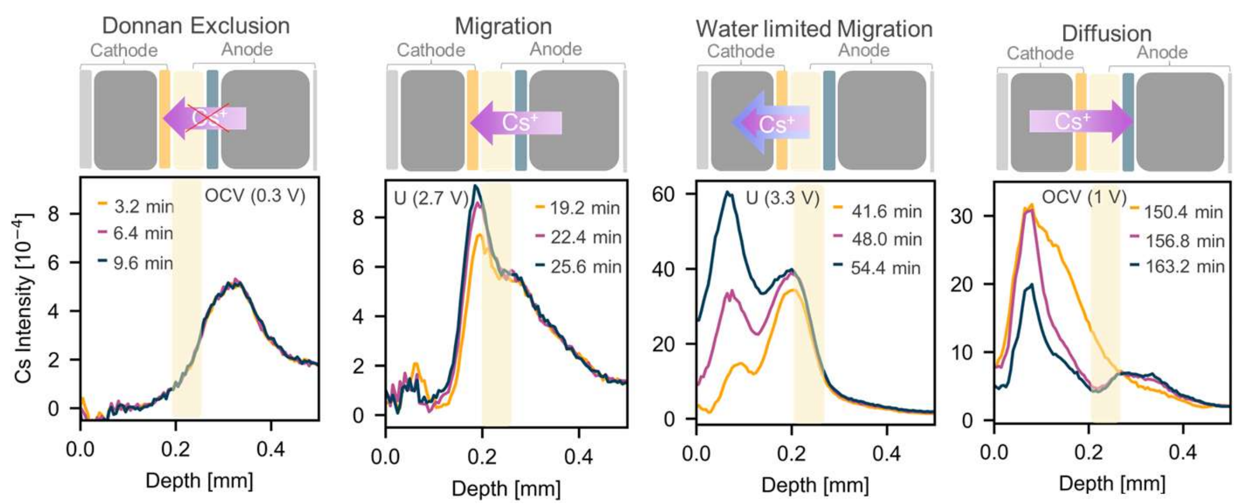
Things we can do- Salt movement

- X-ray fluorescence allows us to watch ions move in the electrolyte.

- Only diffusion and an electric field will move cations, but we still can’t figure out what is going on.







Electrowinning- Basics

- Electrowinning is metal mining/production via electrochemical reducing the oxidized state of a metal.

- Ores of metal are typically mined as oxides

Simplified copper example:

Copper Ore

(Actually we normally take the CuO and mix it with acid to give Cu^{2+})

Overall $2CuO \rightarrow Cu + O_2$

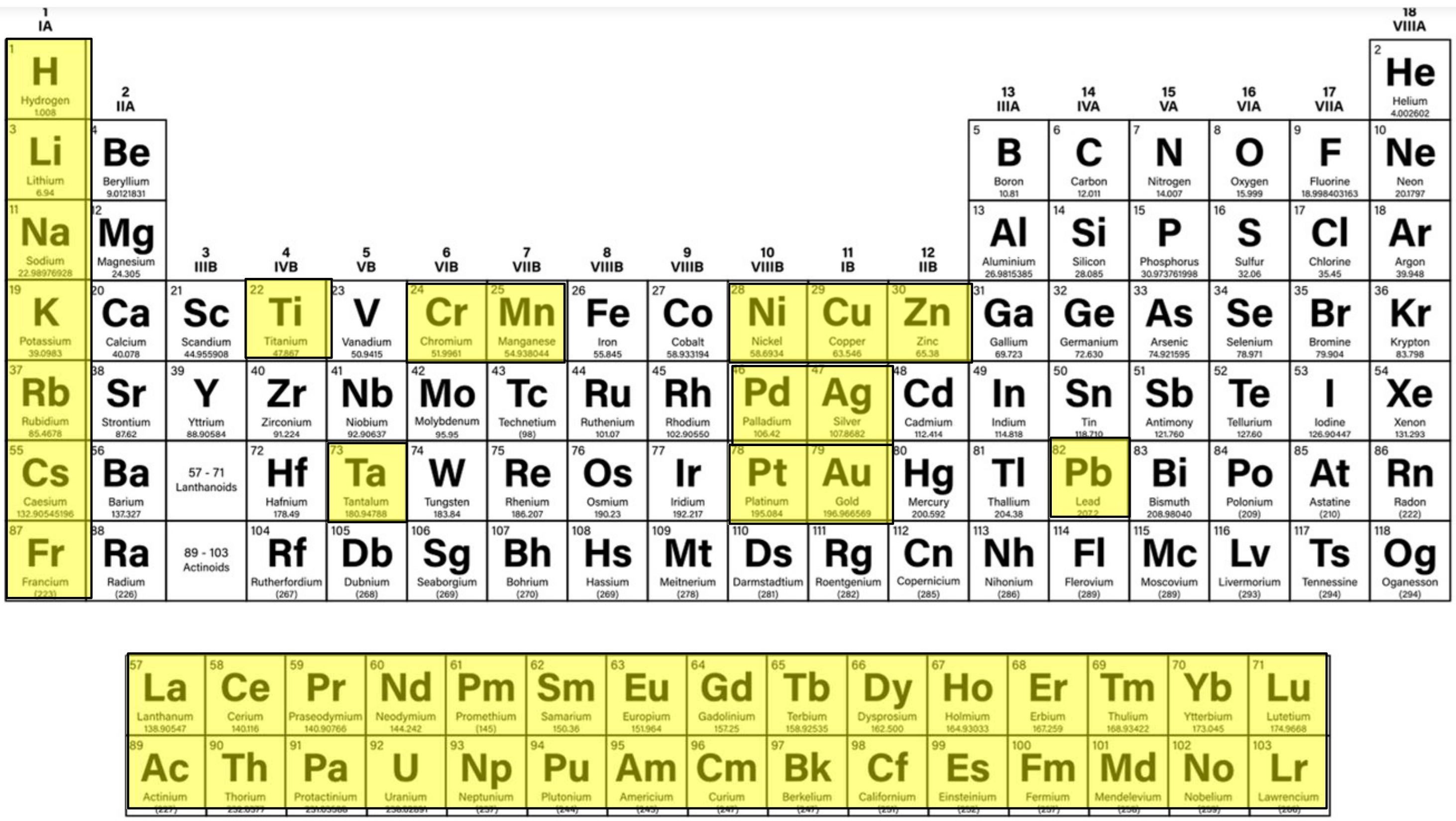
Cathode $2CuO + 2H_2O + 4e^- \rightarrow 2Cu + 4OH^-$

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

- The exact process is a function of the metal

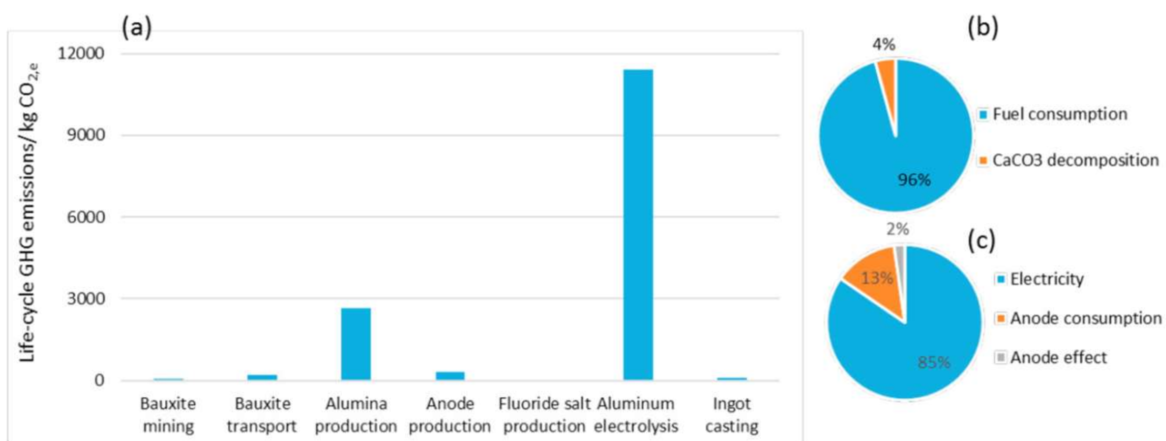
Electrowinning- Basics

- Many metals have as least some electrowinning in their processing.



Aluminum Production

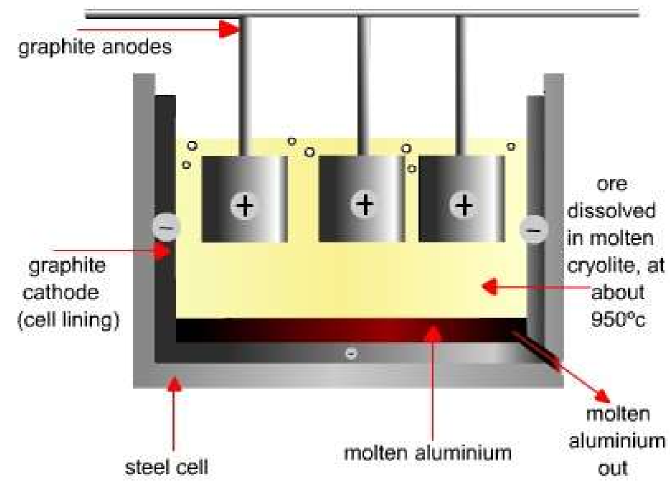
- Aluminum consumes 0.6%-3% of world's energy use.
- Aluminum is only produced through an electrolysis process
- China & US has the same energy intensity.
- Who discoverd aluminum?



[Chinese energy use and CO_2 emissions]

Hall-Heroult Process

- Mined Al_2O_3 is very stable, thus removing the oxygen is hard
- Al_2O_3 melts at 2000 °C, but adding Na_3AlF_6 (called cryolite) drops this to 900-1000 °C
- When Al_2O_3 melts it ionizes to Al^{3+} and O^{2-}
- Oxidizing graphite to CO_2 is the anodic reaction



Overall	$Al_2O_3 + C \rightarrow CO_2$
Cathode	$\mathrm{Al}^{3+} + 3e^- \leftrightarrow Al$
Anode	$O^{2-} + C \rightarrow CO_2$

Hall-Heroult Process- Anode Reaction

- The high temperatures means finding a stable anode is very hard
- Graphite is conductive and very stable, thus it can work both as the electrode and the reaction.
- CO_2 is inert, a gas, and won't oxidize Al (unlike O_2 production).
- Researchers are working on O_2 anodes, but the C/CO_2 redox potential is ~0V vs. RHE whereas H_2O/O_2 means an extra 1.2V is needed for the reaction.

Villum P2X

- The Villum Foundation has grants for ‘pre-startup’ companies
- They are only for Power-to-X technologies, who have a prototype.
- The funding is 4.7M DKK over 2-3 years
- If they get re-funded, they will have money for 40 projects in the next 2-3 years
- Vpx.dtu.dk

Power-to-X Success

- Air Co is a company run by a Yale PhD scientist and a former Shmirnoff marketing exec.
- Air Company's started with CO_2 to Vodka.
  - Then they went to perfumes
  - After Covid, they made hand sanitizers
- Now they are into Sustainable Aviation Fuels (SAF), and are one of the leaders in that.
- The scientist co-founder got kicked out of the company and is sueing the company under a whistleblower act.

Learning Objectives

- Chlorine electrolysis
- Fundamentals of CO_2 electrolysis
- Scale up of CO_2 electrolysis

Exercises

- For CO_2 electrolysis to CO, we always have competing H_2 evolution. If we have a catalysts that for CO evolution has an exchange current density (j_o) of 10^$^{-4}$ A/cm^2 and a Tafel slope of 100 mV and for H_2 evolution has j_o of 10^$^{-6}$ A/cm^2 and a Tafel slope of 120 mV. At what potential will we be producing equal amounts of H_2 and CO.

- What is the thermodynamic potential of a chlorine electrolyzer if our NaOH outlet is pH 12? What about if the pH is 14?

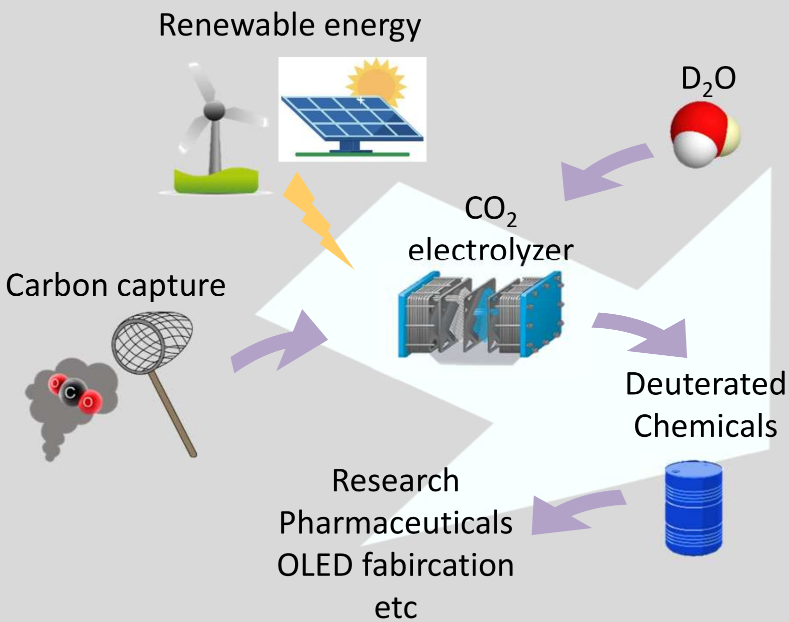
- Sometimes in CO_2 reduction we produce a bit of proponal. How many electron transfer process is the reduction of CO_2 to propanol? What about CO_2 to propene?

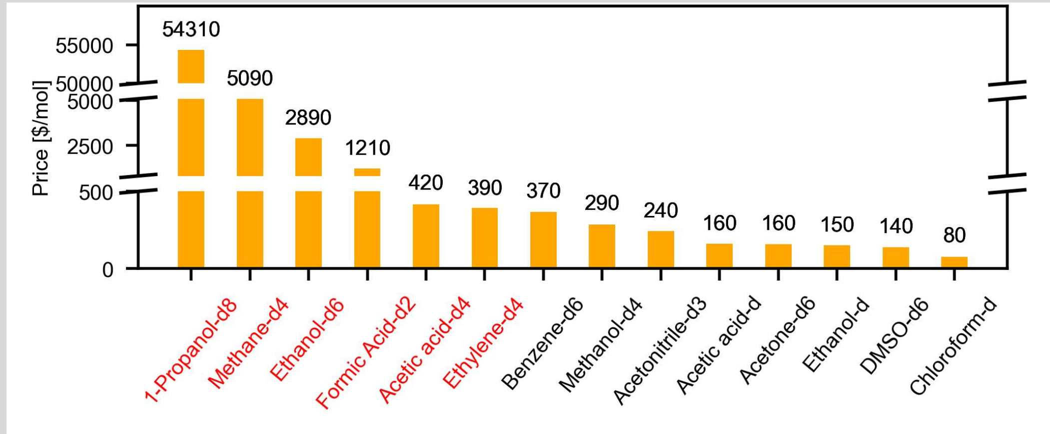
Exercises

- A typical aluminum electrolysis operates at about 4.2V.
  - If instead of oxidizing carbon at the anode, we oxidize oxygen, how much extra energy will we need to add. Put this in terms of percentage extra energy needed. (Assume at the high temperatures these devices operate at, catalytic losses are negligible).
  - Also determine how much CO_2/ton of aluminum switching from carbon to O_2 we can save.
  - Finally we are going to say that electricity costs 0.04 $/kWh. What price would the carbon tax need to be for a supplier to switch from CO_2 at the anode to O_2 at the anode. (Assume the only cost difference between CO_2 and O_2 evolution is the electricity costs)

High-value chemicals from CO_2

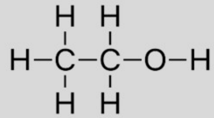
CO_2 electrolysis & deuteration



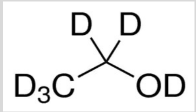


<u>For reference</u>
(high purity)

1L Ethanol
$20



1 L d6-Ethanol
$42,200

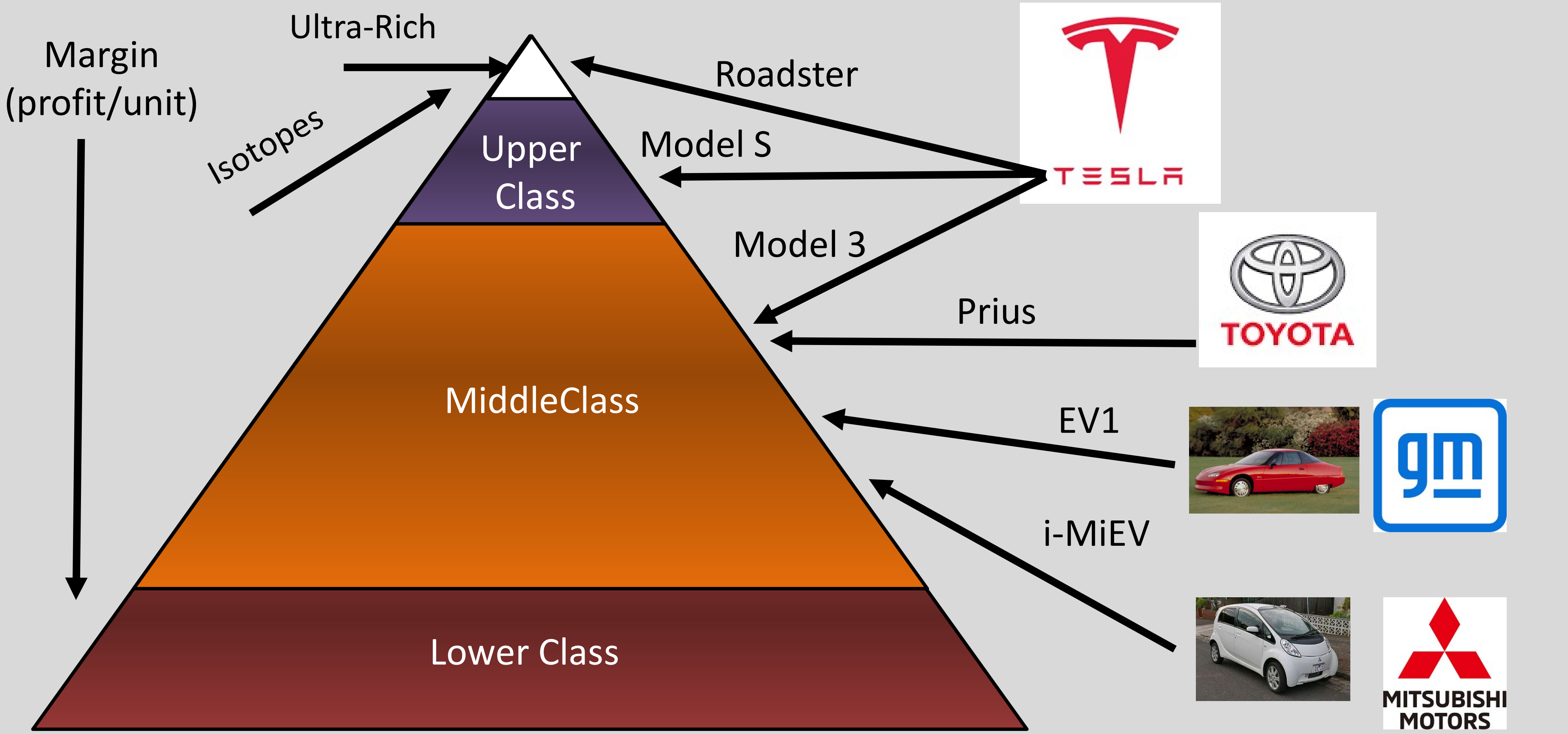


Potential Market – Pharmaceuticals
2 FDA approved deuterated drugs since 2017

Higer C-D bond:
- Slower methabolism
- Lower dosis
- Fewer side effects

<u>Bjørt Joensen</u>
Boljo@dtu.dk

Electric Cars



Carbon Based Products