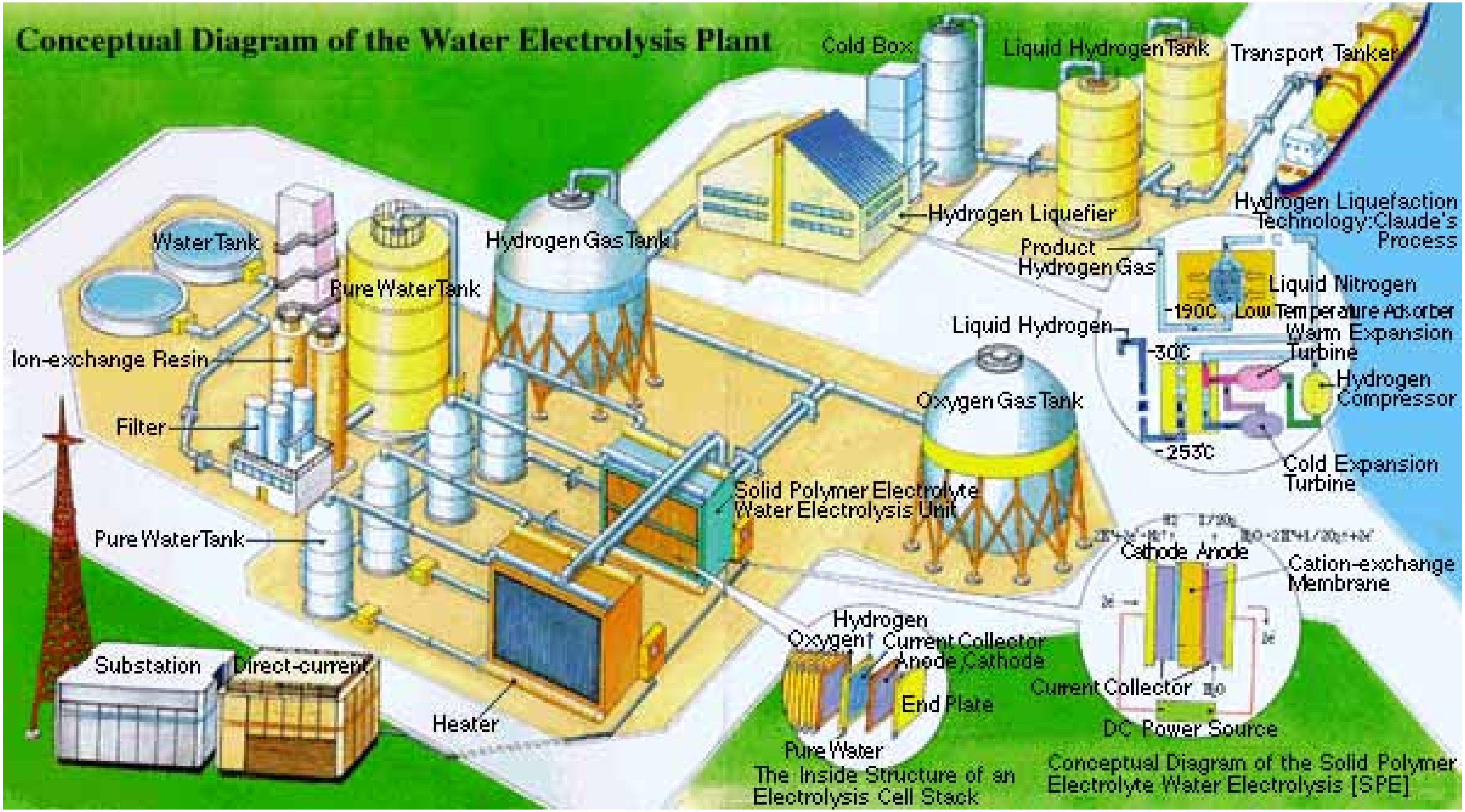
Electricity to fuels

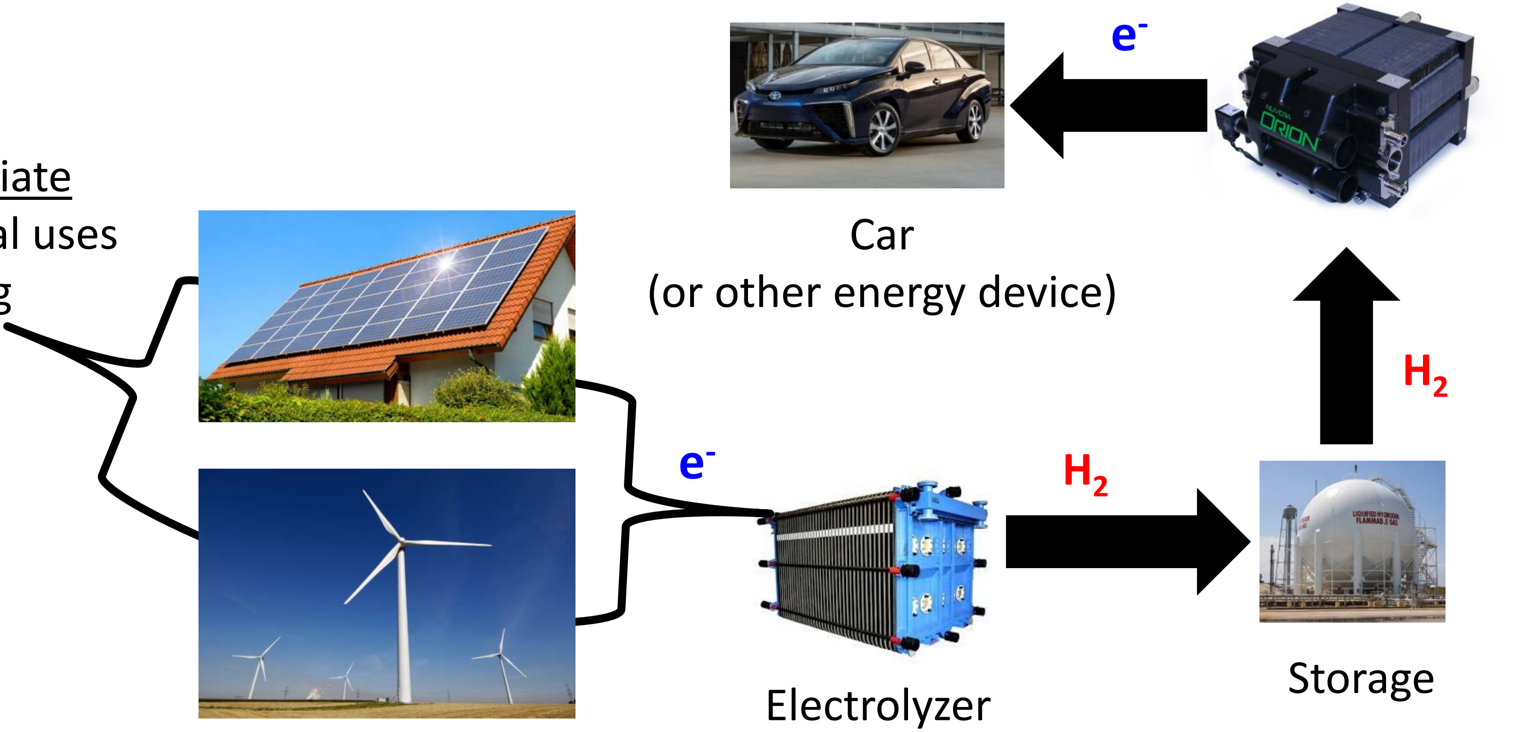


Learning Objectives

- From this lecture you should be able to understand:
  - The fundamental physics behind electrolyzers.
  - How to improve the efficiency/costs of electrolyzers.
  - The fundamental scientific principles behind CO_2 reduction.

The H_2 economy

- The issue with the hydrogen economy is how do we produce hydrogen? – Currently we use fossil fuels.
- Electrochemistry can provide the solution.



Fuel Cell

$H_2 + O_2 \rightarrow H_2O$

e^-

Car

(or other energy device)

<u>Immediate</u>

Electical uses

Heating

H_2

e^-

H_2

Electrolyzer

$H_2O \rightarrow H_2 + O_2$

Storage

Electrolyzers

- Electrolyzers only produce about 3-5% of the total hydrogen.
- All the H_2 the electrolyzers produce in 1 year corresponds to 0.35 EJ. This is enough energy storage to support the world for 8 hours.
- Their basic fundamentals are like a fuel cell in reverse.
- Unlike fuel cells, you can keep adding voltage to get more H_2 and O_2.
  - Fuel cells run from 0.2-1.5 A/cm^2, electrolyzers run at 4-10 A/cm^2.
- There are 3 major types of electrolyzers.
  - Alkaline electrolyzers (done in a basic environment).
  - Proton Exchange Membrane (PEM) electrolyzers (done in an acidic environment).
  - Solid Oxide fuel electrolyzers- can also work with organic/fossil fuels

Alkaline (basic) electrolyzers

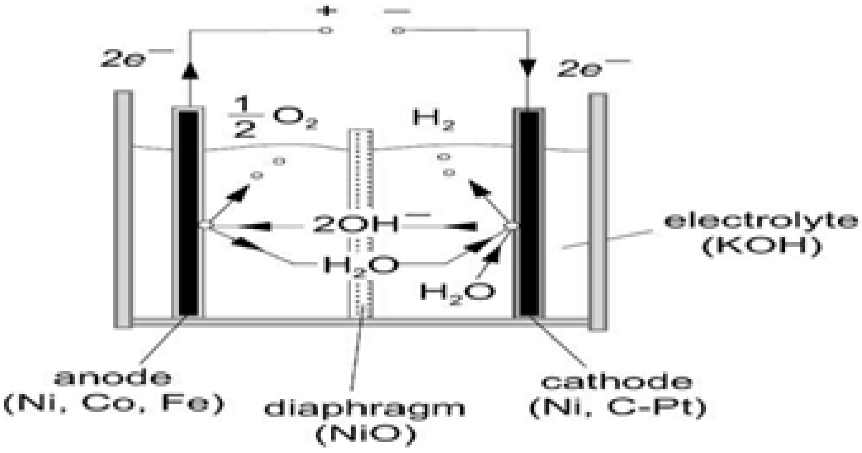
- Alkaline electrolyzers currently have the dominant market share.
- They are similar to an alkaline fuel cell, except done in reverse.

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

Cathode: $2OH^- \rightarrow \frac{1}{2}O_2 + 2H_2O + 2e^-$

Overall: $H_2O \rightarrow H_2 + \frac{1}{2}O_2$ $\quad 1.23\ V$

- They typically use a diaphragm rather than a membrane to keep the gases from mixing.
- Very recently (last 5 years) anionic membranes have been commercialized.

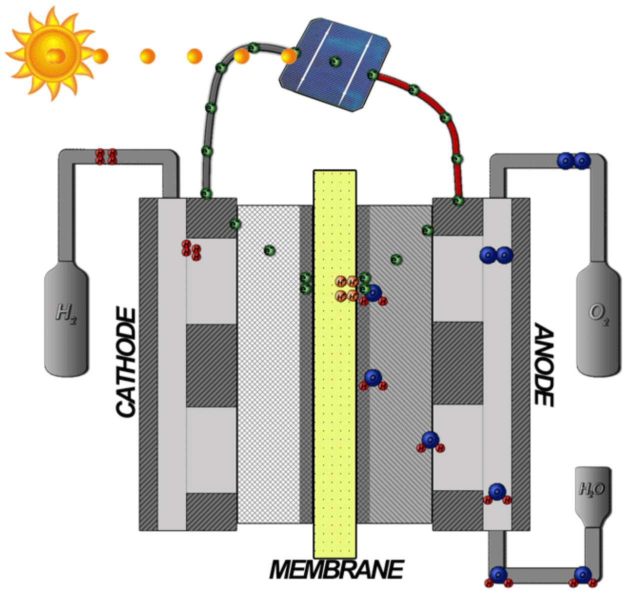


Alkaline (basic) electrolyzers

- The great thing about alkaline electrolyzers are they use no noble metals.
- Their major disadvantage is inefficient ionic conductivities / gas crossover.
- The alkaline electrolyte can easily cause corrosion as well.
- Electrolyzer cells are stacked just like fuel cells.
- Each device to the right produces roughly 33 kg/s of H_2.

PEM electrolyzers

- The new approach to electrolyzers is to basically run a proton exchange membrane fuel cell in reverse.
- The key advantage is that the efficiencies can be higher especially at high current densities.
- This is due to ionic conductivity advantages of a PEM
- The major issue with these is the best catalysts are noble metals.



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

Cathode: $2H^+ + 2e^- \rightarrow H_2$

Overall: $H_2 + \frac{1}{2}O_2 \rightarrow H_2O$

Competing Technologies

🟩 Advantages 🟥 Disadvantages

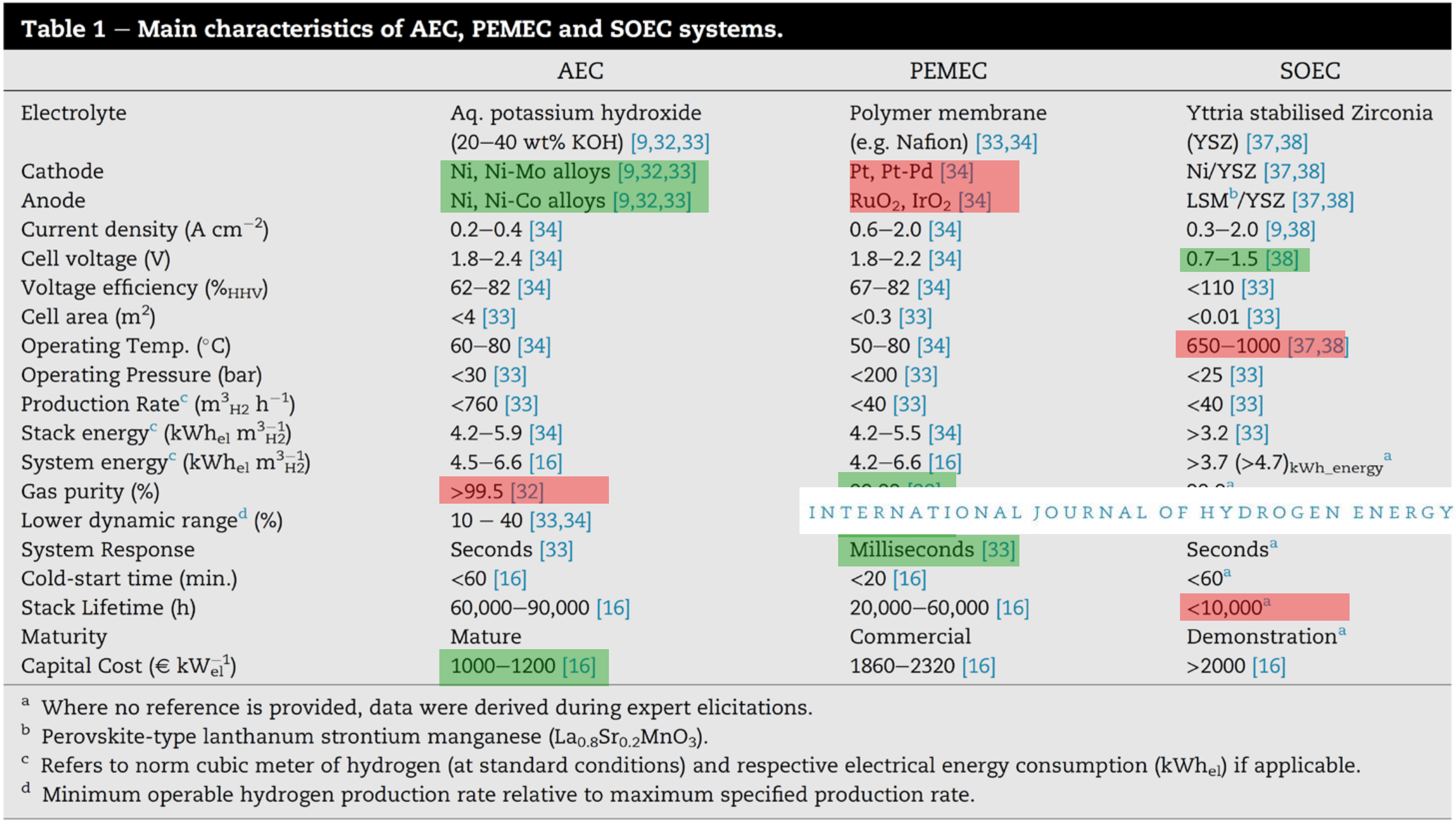


Table 1 — Main characteristics of AEC, PEMEC and SOEC systems.

	AEC	PEMEC	SOEC
Electrolyte	Aq. potassium hydroxide (20–40 wt% KOH) [9,32,33]	Polymer membrane (e.g. Nafion) [33,34]	Yttria stabilised Zirconia (YSZ) [37,38]
Cathode	🟩 Ni, Ni-Mo alloys [9,32,33]	🟥 Pt, Pt-Pd [34]	Ni/YSZ [37,38]
Anode	🟩 Ni, Ni-Co alloys [9,32,33]	🟥 RuO_2, IrO_2 [34]	LSM[b]/YSZ [37,38]
Current density ($A\ cm^{-2}$)	0.2–0.4 [34]	0.6–2.0 [34]	0.3–2.0 [9,38]
Cell voltage (V)	1.8–2.4 [34]	1.8–2.2 [34]	🟩 0.7–1.5 [38]
Voltage efficiency ($\%_{HHV}$)	62–82 [34]	67–82 [34]	<110 [33]
Cell area (m^2)	<4 [33]	<0.3 [33]	<0.01 [33]
Operating Temp. (°C)	60–80 [34]	50–80 [34]	🟥 650–1000 [37,38]
Operating Pressure (bar)	<30 [33]	<200 [33]	<25 [33]
Production Rate[c] ($m^3_{H2}\ h^{-1}$)	<760 [33]	<40 [33]	<40 [33]
Stack energy[c] ($kWh_{el}\ m^{-1}_{H2}$)	4.2–5.9 [34]	4.2–5.5 [34]	>3.2 [33]
System energy[c] ($kWh_{el}\ m^{-1}_{H2}$)	4.5–6.6 [16]	4.2–6.6 [16]	>3.7 (>4.7)$_{kWh\_energy}$[a]
Gas purity (%)	🟥 >99.5 [32]	🟩 [illegible]	[illegible]
Lower dynamic range[d] (%)	10 – 40 [33,34]	[illegible]	[illegible]
System Response	Seconds [33]	🟩 Milliseconds [33]	Seconds[a]
Cold-start time (min.)	<60 [16]	<20 [16]	<60[a]
Stack Lifetime (h)	60,000–90,000 [16]	20,000–60,000 [16]	🟥 <10,000[a]
Maturity	Mature	Commercial	Demonstration[a]
Capital Cost (€ kW^{-1}_{el})	🟩 1000–1200 [16]	1860–2320 [16]	>2000 [16]

INTERNATIONAL JOURNAL OF HYDROGEN ENERGY 4

[a] Where no reference is provided, data were derived during expert elicitations.

[b] Perovskite-type lanthanum strontium manganese ($La_{0.8}Sr_{0.2}MnO_3$).

[c] Refers to norm cubic meter of hydrogen (at standard conditions) and respective electrical energy consumption (kWh_{el}) if applicable.

[d] Minimum operable hydrogen production rate relative to maximum specified production rate.

Schmidt et al., 2017 Int, Jn. of Hyd. Energy, 42, 30470-30492

Why acidic or basic electrolyzers

- All electrolyzers (and fuel cell cells) need to minimize ionic conductivity losses.
- H^+ is the most conductive ion, and OH^- is the 2nd most conductive.
- If we try things at neutral pH, the ionic conductivity losses dominate.

$$V = i \times R_{Cond}$$

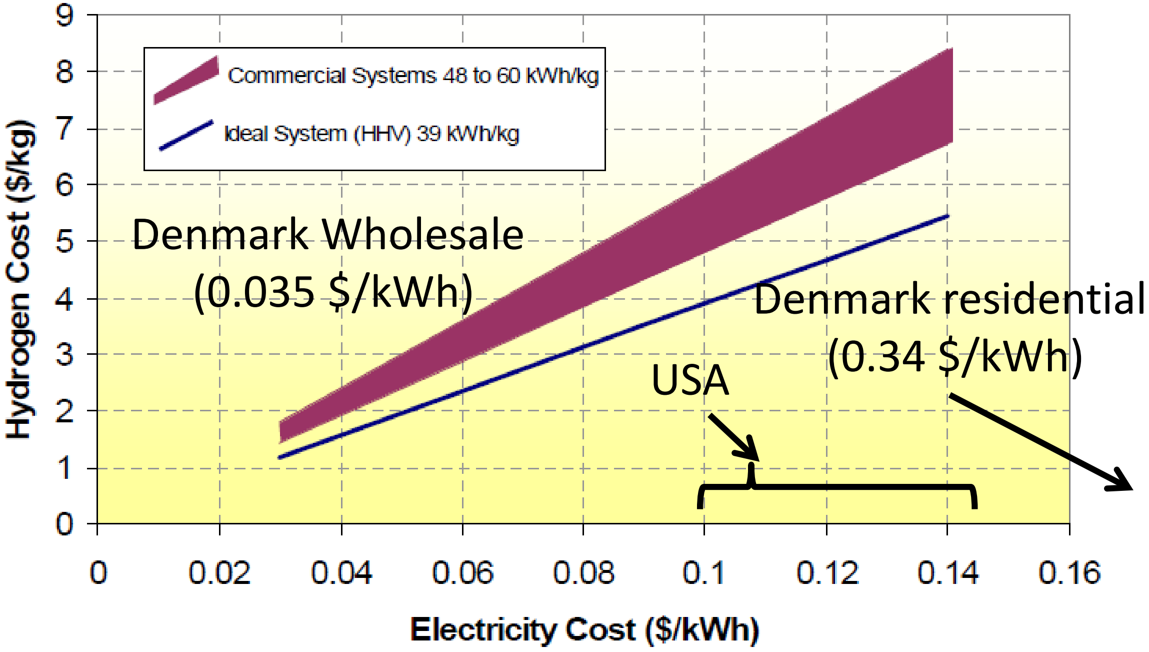
- Many researchers brag about electrolyzer catalysts that work at pH=7. *Who cares?*

Cations	λ_+^0 mS m^{2}mol^{-1}	Anions	λ_-^0 mS m^{2}mol^{-1}
H^+	34.96	OH^-	19.91
Li^+	3.869	Cl^-	7.634
Na^+	5.011	Br^-	7.84
Mg^{2+}	10.612	SO_4^{2-}	15.96
Ca^{2+}	11.900	NO_3^-	7.14

Ionic conductivities (from wikipedia)

Electrolyzers- economic limits

- The chart below related electricity cost to hydrogen cost.
- The blue line is the thermodynamic limit (1.23 V)
- This chart does not include any capital costs, maintenance, etc. It is a 'best-case scenario' chart.
- 1 kg H_2≈ 1 gallon gasoline ≈ 4 L gasoline.
- A large electrolyzer plant will get significantly cheaper electricity than the residential costs.



Denmark Wholesale (0.035 $/kWh)

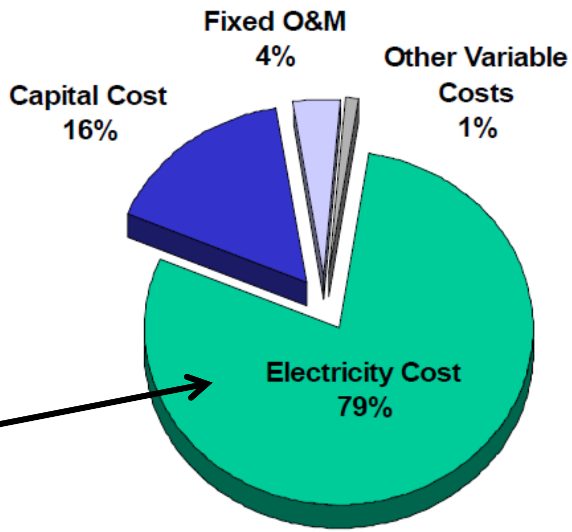
Denmark residential (0.34 $/kWh)

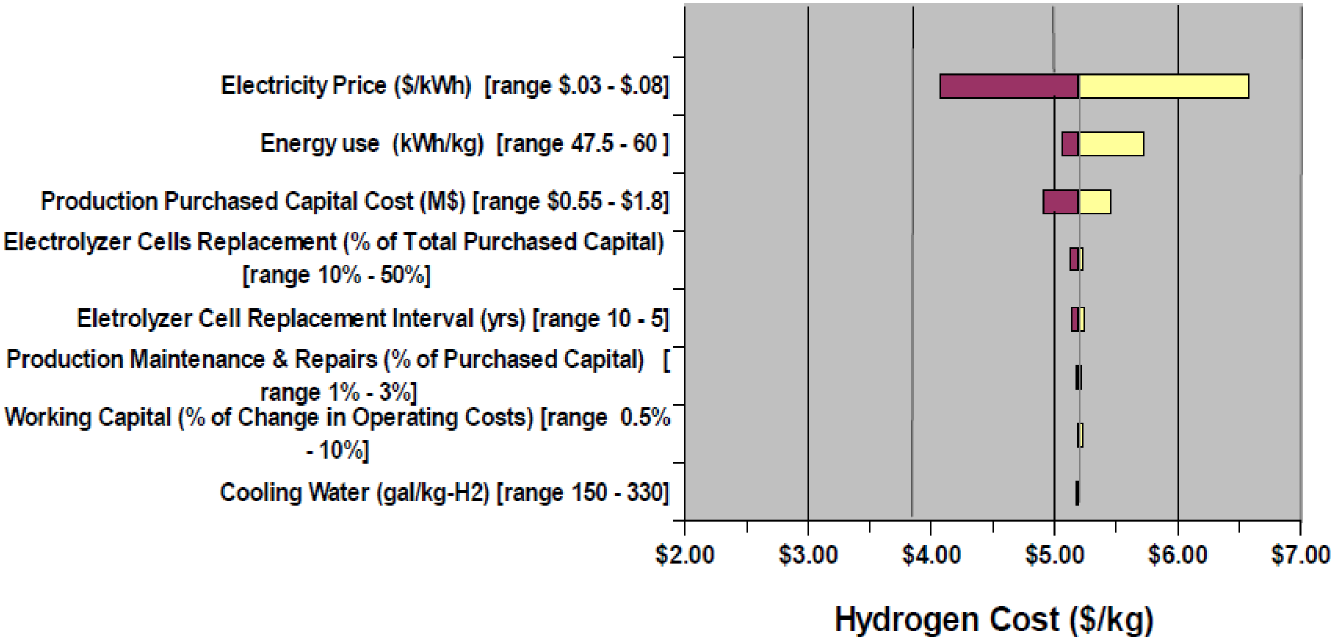
USA

NREL Electrolyzer report (NREL/BK-6A1-46676)

PEM electrolyzers- economic limits

- The DOE did a sensitivity analysis with regards to electrolyzer cost.
- There are certain areas we can ‘technology our way out of’.
- There are other areas we can’t (directly).

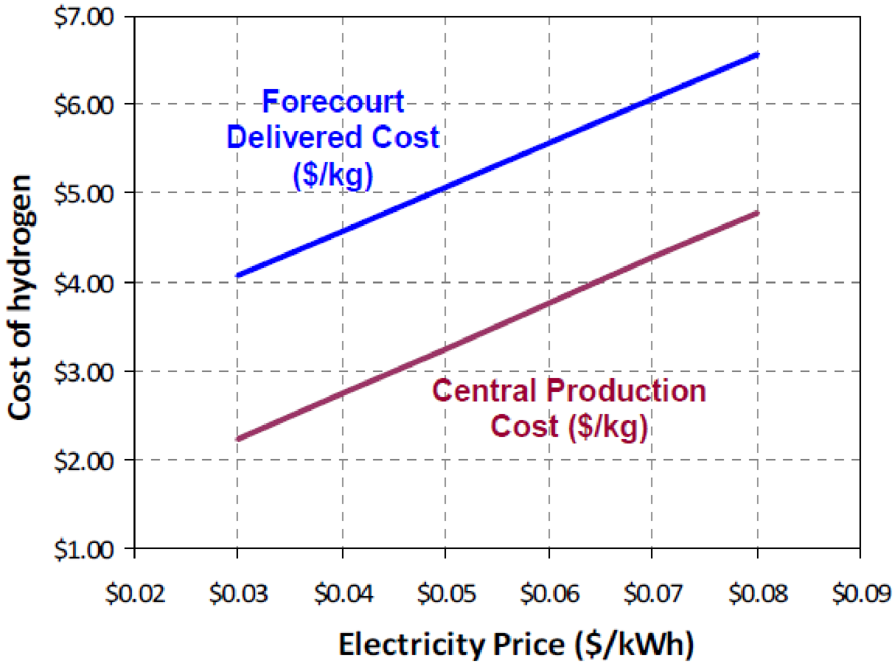




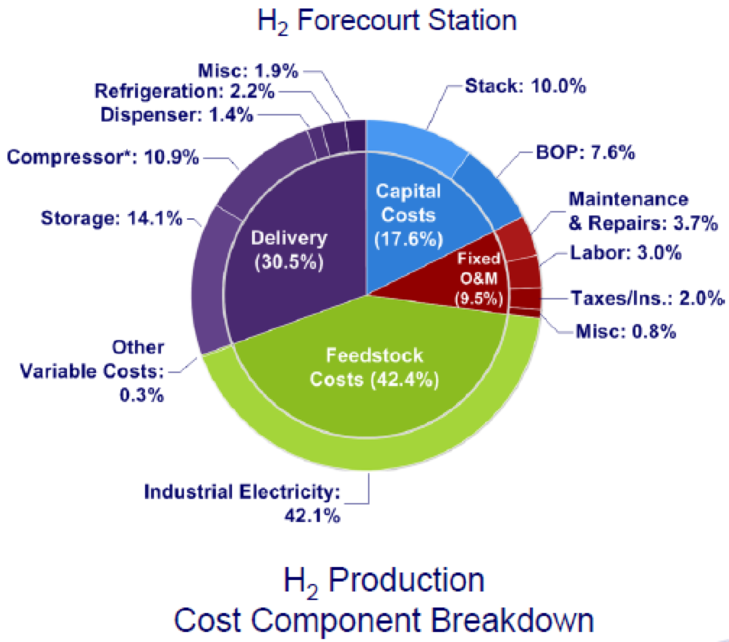
Both Figures from
NREL Electrolyzer report
(NREL/BK-6A1-46676)

PEM electrolyzers

- There are significant delivery costs (Forecourt costs) compared to the cost of H_2 leaving the plant.
- Note the x-axis- The price tends to get quite high as the electricity price increases.



NREL Electrolyzer report (NREL/BK-6A1-46676)



Giner: Presented at Hannover Messe 2014, April 7-11

Break

Electrolyzer Thermodynamics

- Electrolyzers are the opposites of fuel cells in many ways

	PEM Fuel cells	PEM Electrolyzers
Overall reaction:	$H_2 + \frac{1}{2}O_2 \rightarrow H_2O$	$H_2O \rightarrow H_2 + \frac{1}{2}O_2$
Anode:	$H_2 \rightarrow 2H^+ + 2e^-$	$H_2O \rightarrow 2e^- + 2H^+ + \frac{1}{2}O_2$
Cathode:	$2e^- + 2H^+ + \frac{1}{2}O_2 \rightarrow H_2O$	$2H^+ + 2e^- \rightarrow H_2$
Max Efficiency (η):	$\frac{\Delta G}{\Delta H}$	$\frac{\Delta H}{\Delta G}$
Operational Voltage:	$V_{op} < 1.23$ V	$V_{op} > 1.47$ V

Thermodynamic efficiency

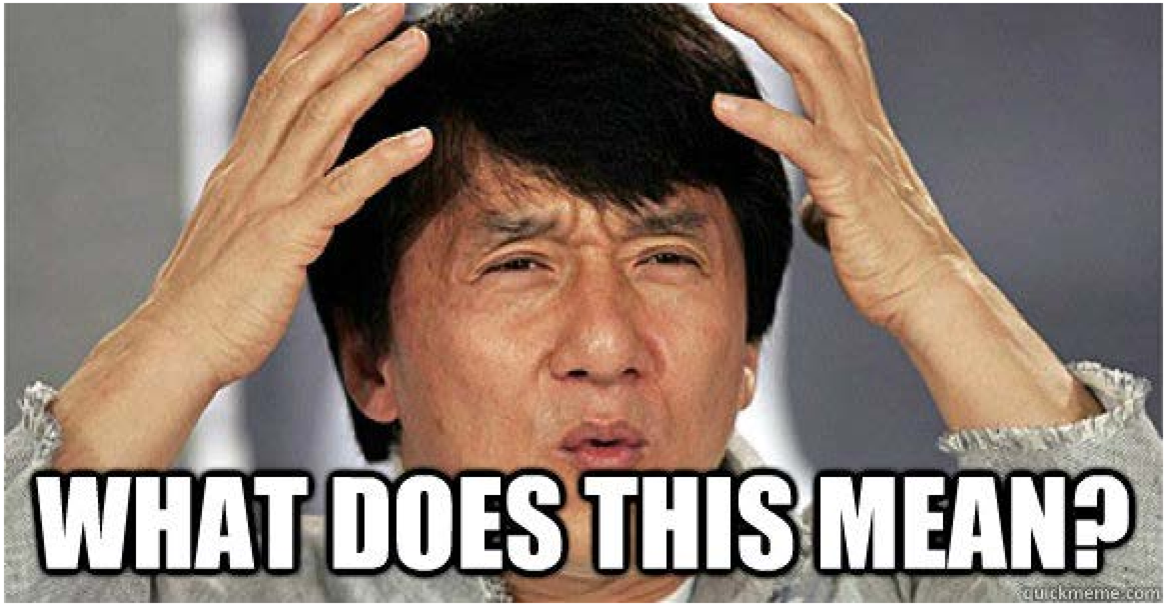
- Can we get over 100% thermodynamic efficiency in our electrolyzer?

$$\eta_{Fuel\ Cell} = \frac{\Delta G}{\Delta H} = \frac{1.23\ V}{1.47\ V} = 83\%$$

$$\eta_{Electrolyzer} = \frac{\Delta H}{\Delta G}$$

- G^f=-237 KJ/mol,
- H^f=-286 KJ/mol (HHV)

Yes!



- Can we get over 100% thermodynamic efficiency in our electrolyzer?
- You need to think of the entire system.

Thermodynamic efficiency

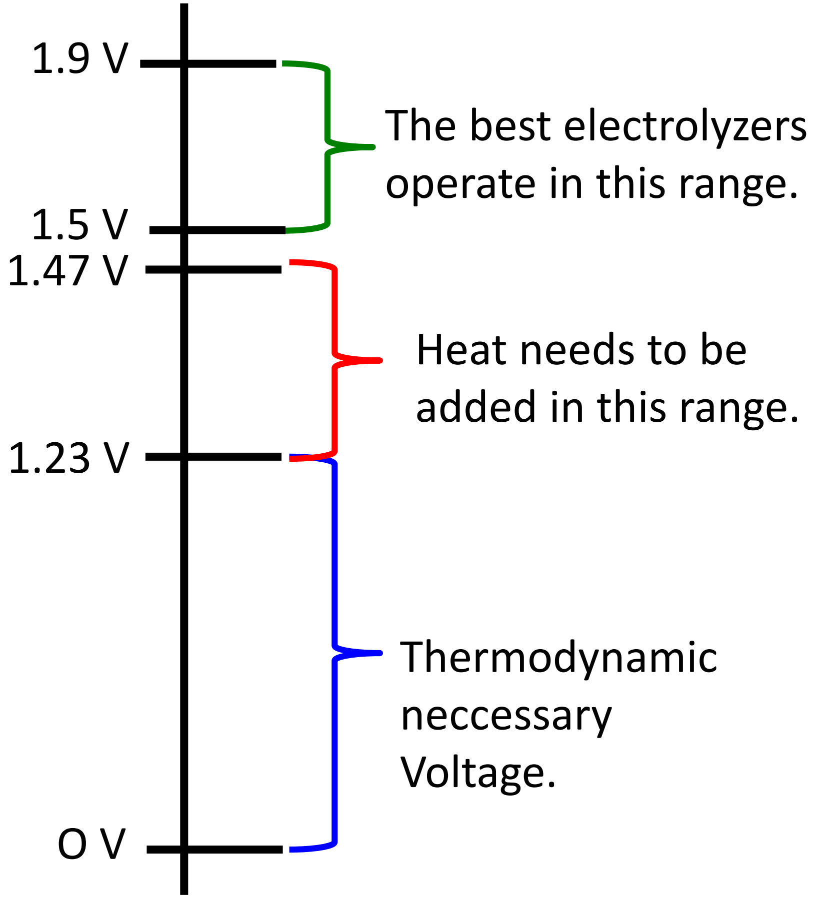
- The key is the entropy.
- If the electrolyzer is over 100% efficient, the entropic term will cool the reaction.

$$\eta_{Electrolyzer} = \frac{\Delta H}{\Delta G} = \frac{\Delta H}{\Delta H - T\Delta S} = \frac{1.48\ V}{1.23\ V} = 119\%$$

- In the case of >100% efficiency, heat would needed to be added to the cell to maintain the temperature.
- Thus the added heat would need to compensate from the entropic advantage the electrolyzer gets.
- However heat is a ‘cheap’ form of energy, so getting a little excess heat is easy from a practical standpoint.

Thermodynamic efficiency

- The 1.48 V is sometimes referred to as the thermo-neutral water splitting potential.
- Our efficiencies are almost to the point where we reach 100% efficiency.
- We normally add extra voltage to give higher current (Tafel equation).
- This means we need a smaller electrolyzer, thus cheaper capital costs.



Pressure effects on voltage

- Just like fuel cells, modifying the pressure, modifies the theoretical voltage.
- Using the Nernst Eqn and only modifying pressure, we have:

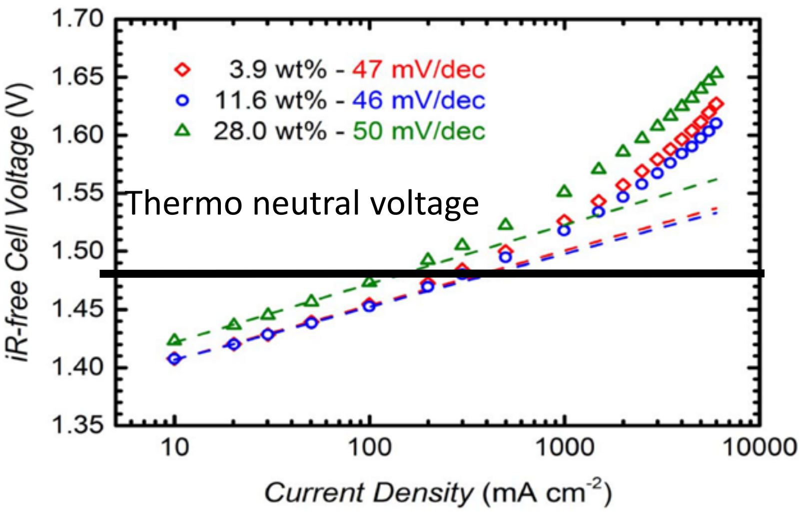
$$E = E^0 + \frac{RT}{F} Ln\left(\frac{\frac{P_{H_2O}}{P}}{\left(\frac{P_{O_2}}{P}\right)^{0.5}\frac{P_{H_2}}{P}}\right) = E^0 + \frac{RT}{2F} Ln\left(\frac{1}{P^{0.5}}\right)$$

This is effectively a concentration

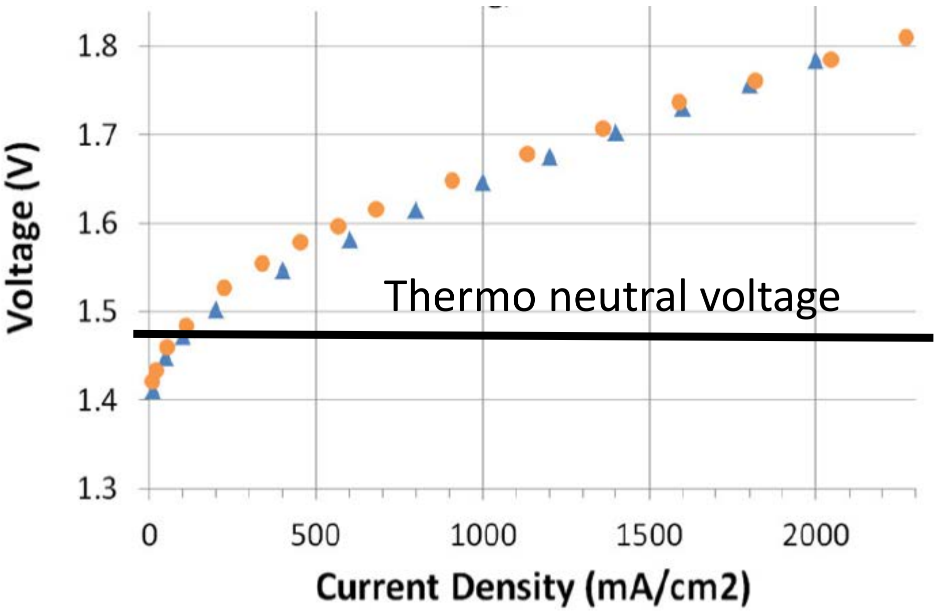
- An increase in pressure from 1 atm to 200 atm changes the voltage needed by 34 mV (@25 C)
- Since H_2 is typically stored at high pressures, operating electrolyzers at high pressures some benefits as long as the device can handle the pressure.

Efficiency

- Below are i-V curves of the best PEM electrolyzers.
- At low currents, it is possible to be below the thermoneutral voltage.
- Higher currents help out in minimizing capital costs.



[Bernt, et al., J.Elec. Soc., 163 (11) F3179-F3189 (2016)]()

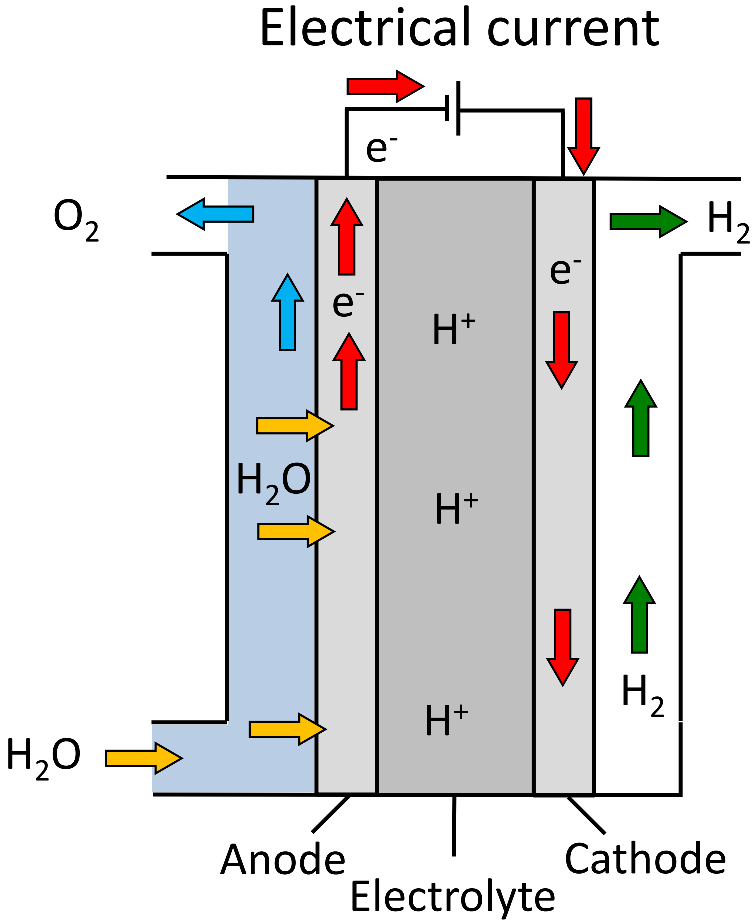


Theoretical limiting voltage

PEM Electrolyzer

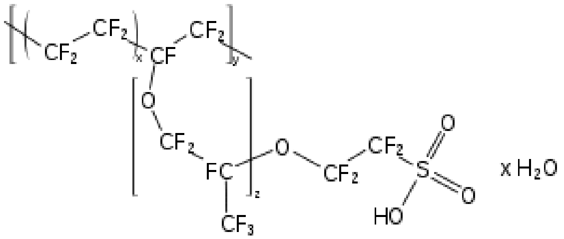
Places for potential energy loss

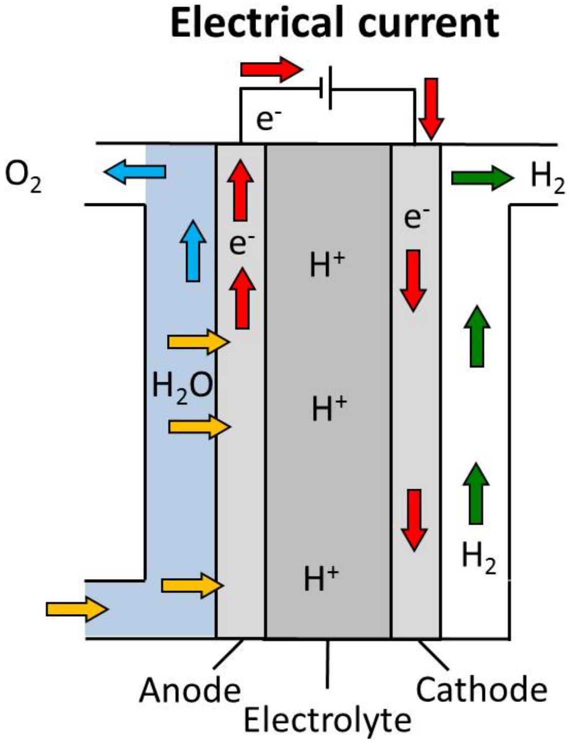
- Proton transfer
- Electron transfer
- Anode
- Cathode



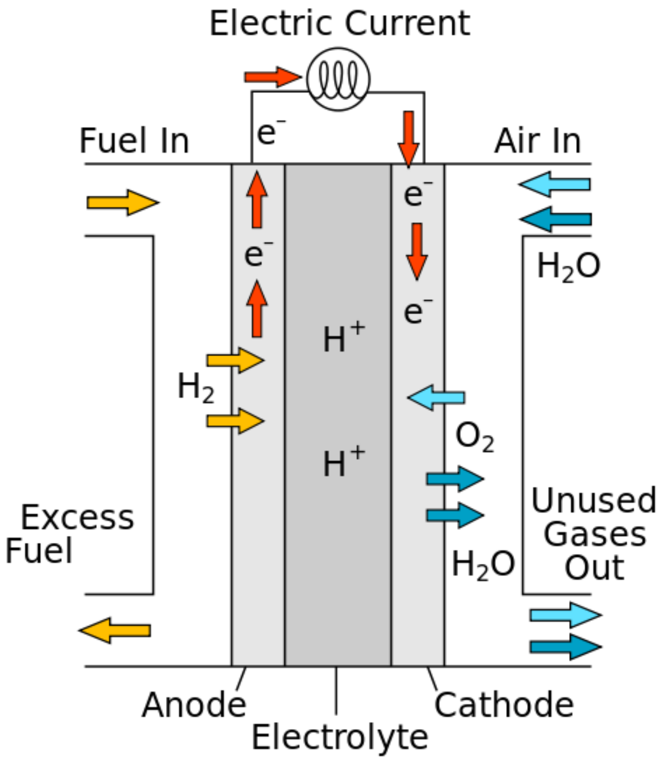
Proton transfer

- This is just like fuel cells, but in reverse.
- In this field Nafion is also the best proton exchange membrane.

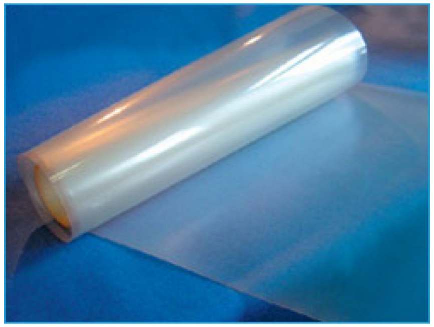




Electrolyzer



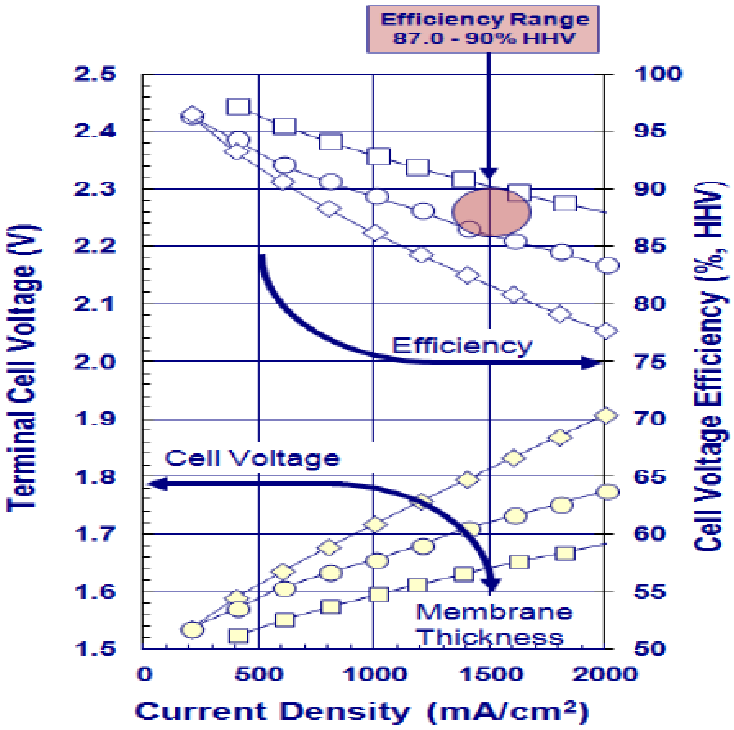
Fuel Cell



Nafion

Proton exchange membrane

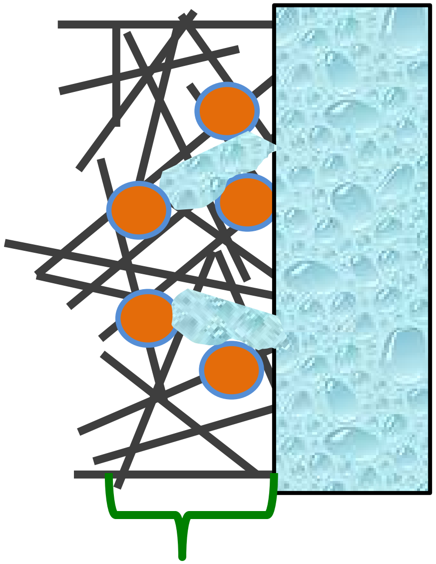
- In fuel cell we really needed to work in keeping the membrane fully hydrated (i.e. 100% relative humidity.)
- The electrolyzer is in water, so the membrane is always fully humidified.
- H_2 crossover through the membrane is dangerous because H_2 and O_2 can combust.
- This is solved by a thicker membrane.
- Thicker membrane = higher resistance.



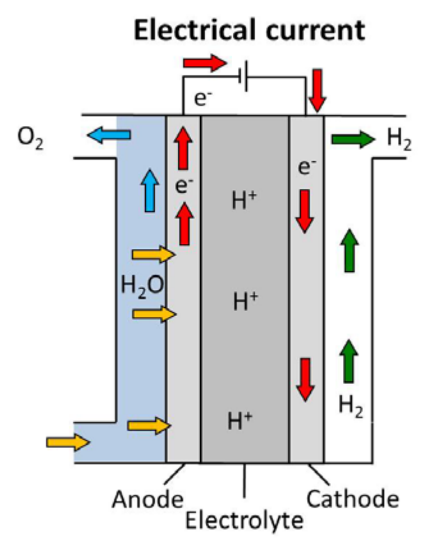
Giner: Hannover Messe, 2014

Triple phase boundary

- In the fuel cell maximizing the triple phase boundary was extremely important.
- In electrolyzers the electrolyte the aqueous solutions works as a quasi-proton transfer medium.
- However these devices run in pure water rather than an acidic environment to prevent corrosion.
- It is still important to spread out the catalysts for minimizing gas transport issues due to bubble formation.

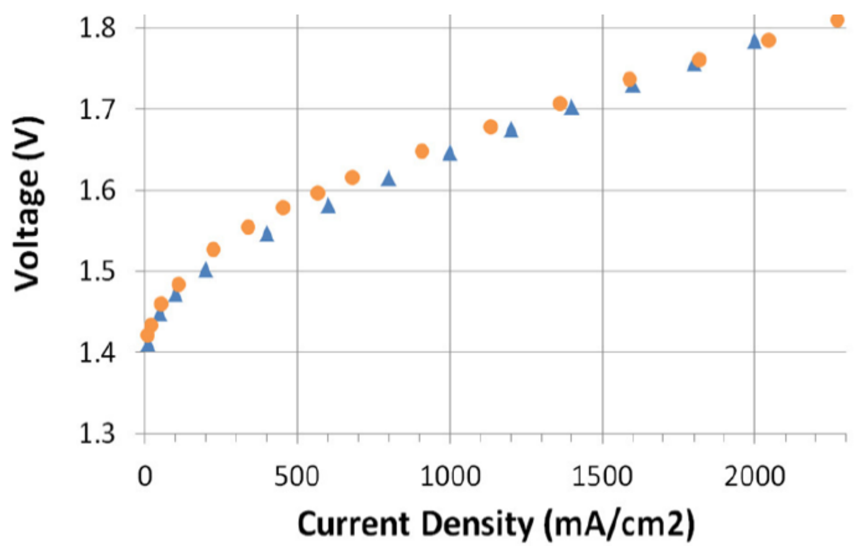


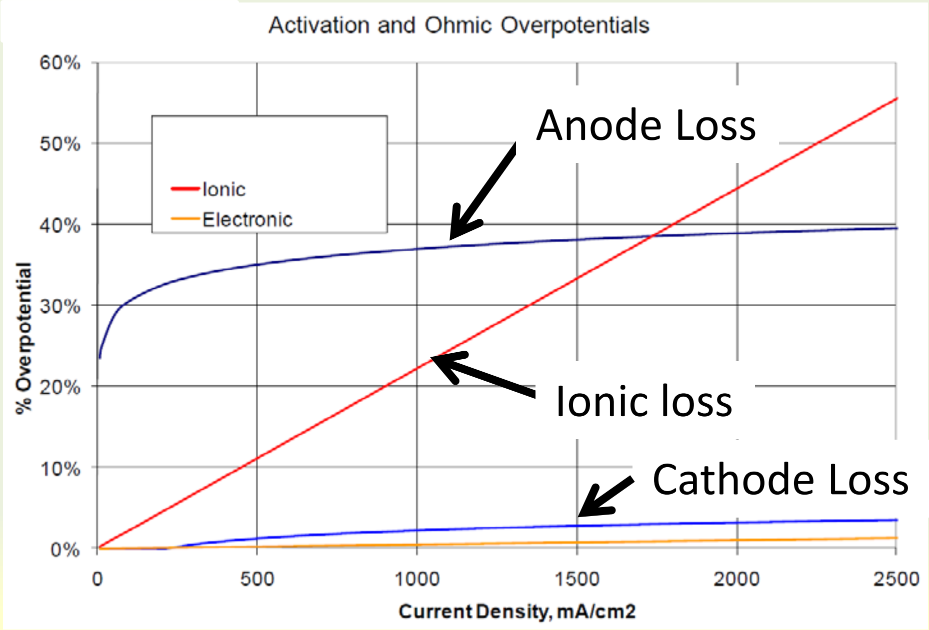
Efficiency



Places for potential energy loss

- Proton transfer
- Electron transfer
- Anode
- Cathode




Activation and Ohmic Overpotentials

Anode Loss

Ionic loss

Cathode Loss

Proton On-site data

- Discuss why the anode and ionic losses look the way they do.

Understanding electrolysis

If you have a standard 9V battery (with 500 mA x hr), how much hydrogen can you produce with:

A) 2 Pt wires (assume no ohmic resistance, no mass transfer loss and a constant 300 mV overpotential).

B) 2 Graphite pencils (assume no ohmic resistance, no mass transfer loss and a constant 1.5 V overpotential).

What is the conversion efficiency (i.e. H_2 stored energy/battery stored energy)

Understanding electrolysis

If the voltage of your electrons are at 9V, you will split water no matter what your overpotential (unless you are mass transfer limited).

500 mA x hr= 0.5 C/s x 3600 s = 1800 C

1800 C ÷ 96,485 C/mol e^- ÷ 2 mole e^- / mol H_2 = 0.009 mol H_2.

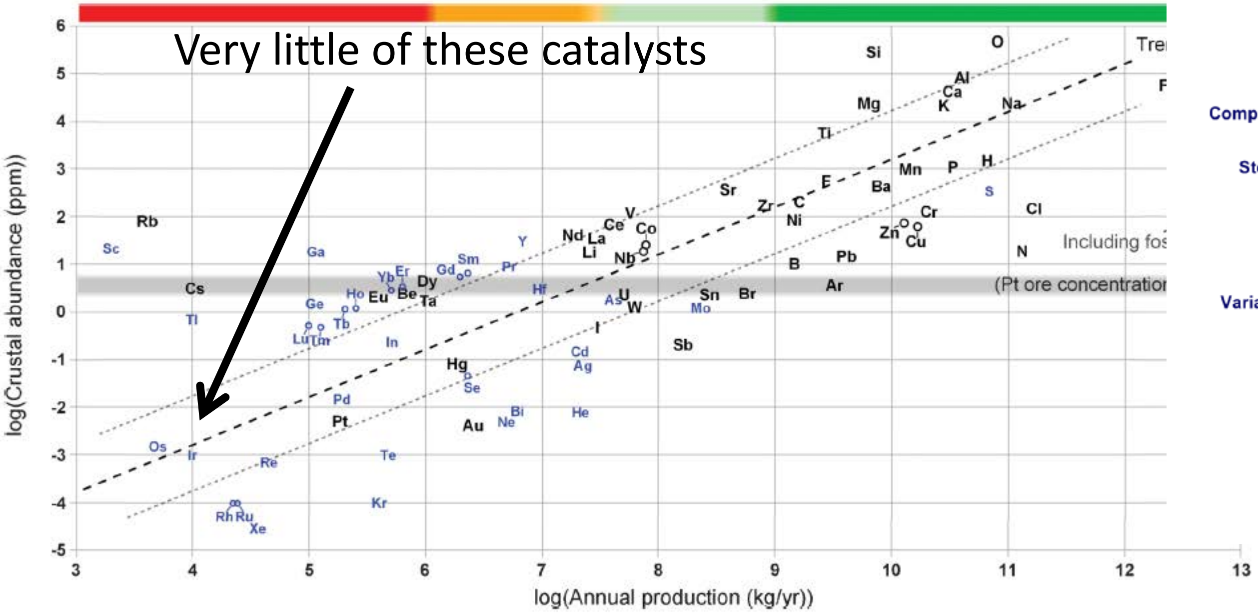
Energy from H_2 = 1.23 V x 1800C = 2.24 kJ
Energy from Battery= 9V x 1800 C = 16.2 kJ
= 14%

Point to make: Don’t use a higher voltage than you need to split water.

Scalable catalysts

- Currently electrolyzer’s small market share allow them to use large amount of noble metals. This is not scalable.
- Much of the issues are engineering issues.
- However the catalysis is still a fundamental science issue.

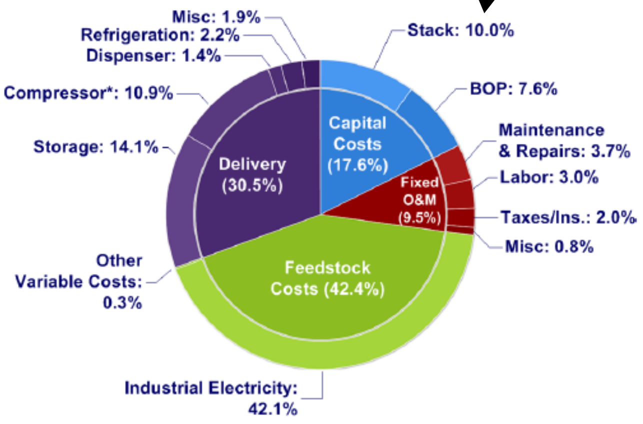
~10% of this is catalysis
(1% total)



Very little of these catalysts

Vesborg and Jaramillo, RSC Advances, 2013

H_2 Forecourt Station



H_2 Production
Cost Component Breakdown

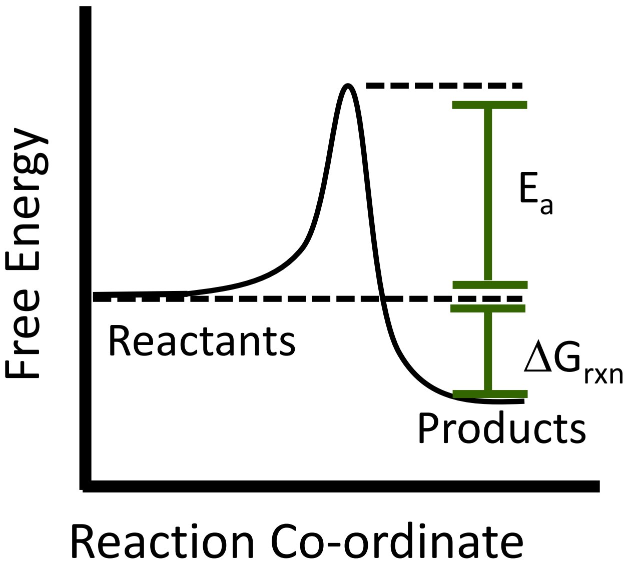
Giner: Presented at Hannover Messe 2014, April 7-11

Anode and cathode

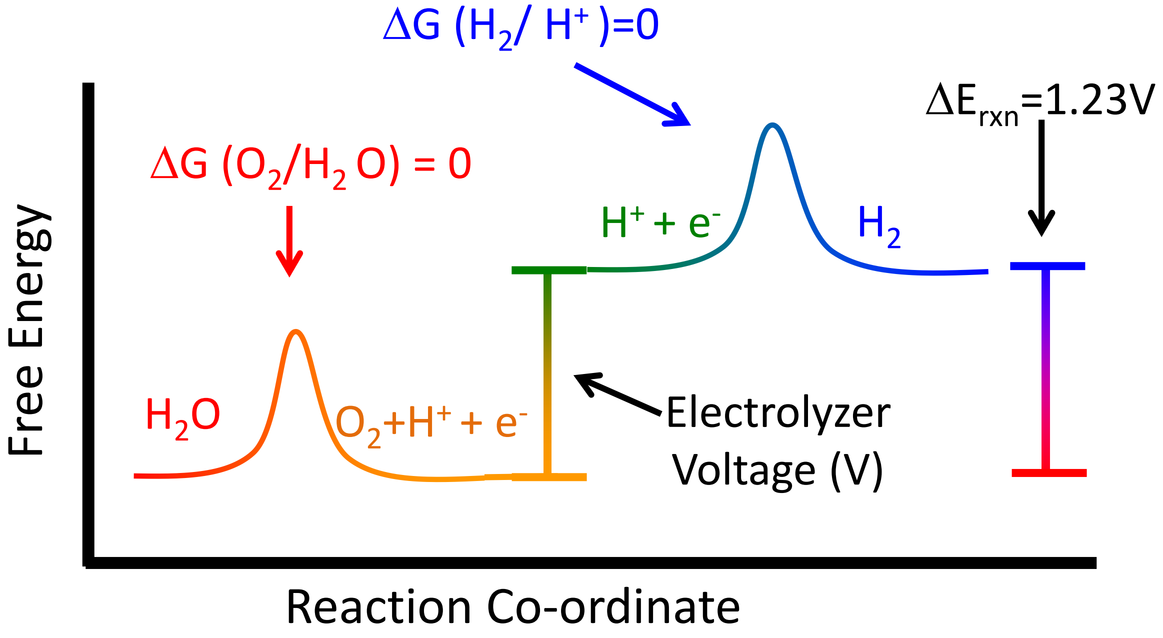
- We can use a similar approach as the fuel cells to understand the electrolyzer reactions.

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

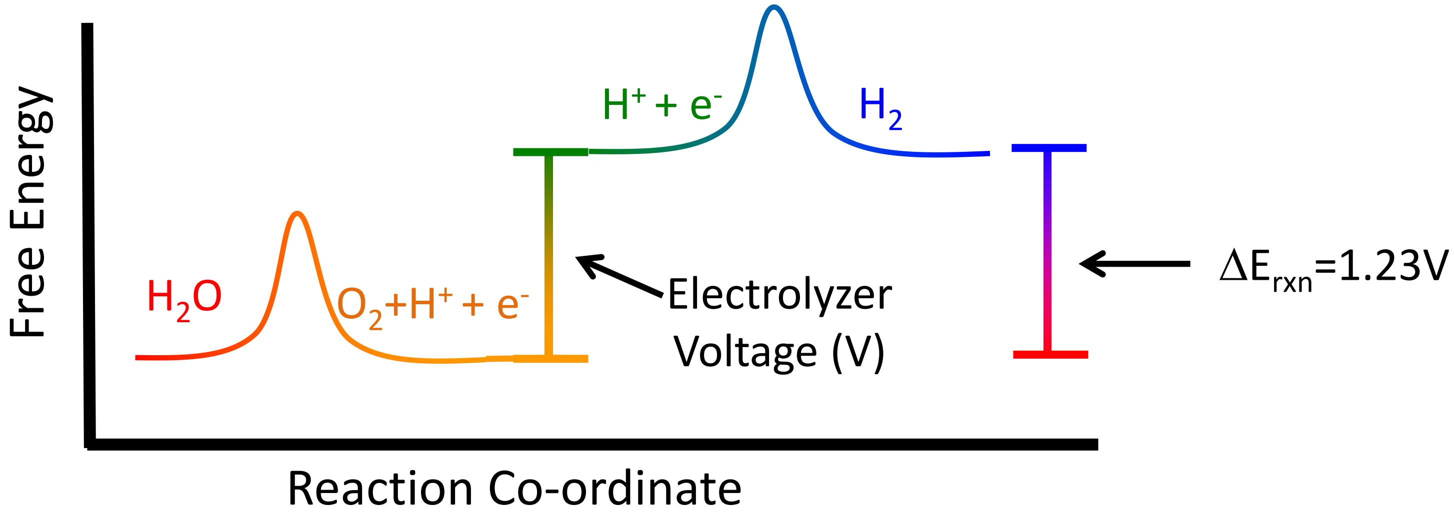
Cathode: $2H^+ + 2e^- \rightarrow H_2$

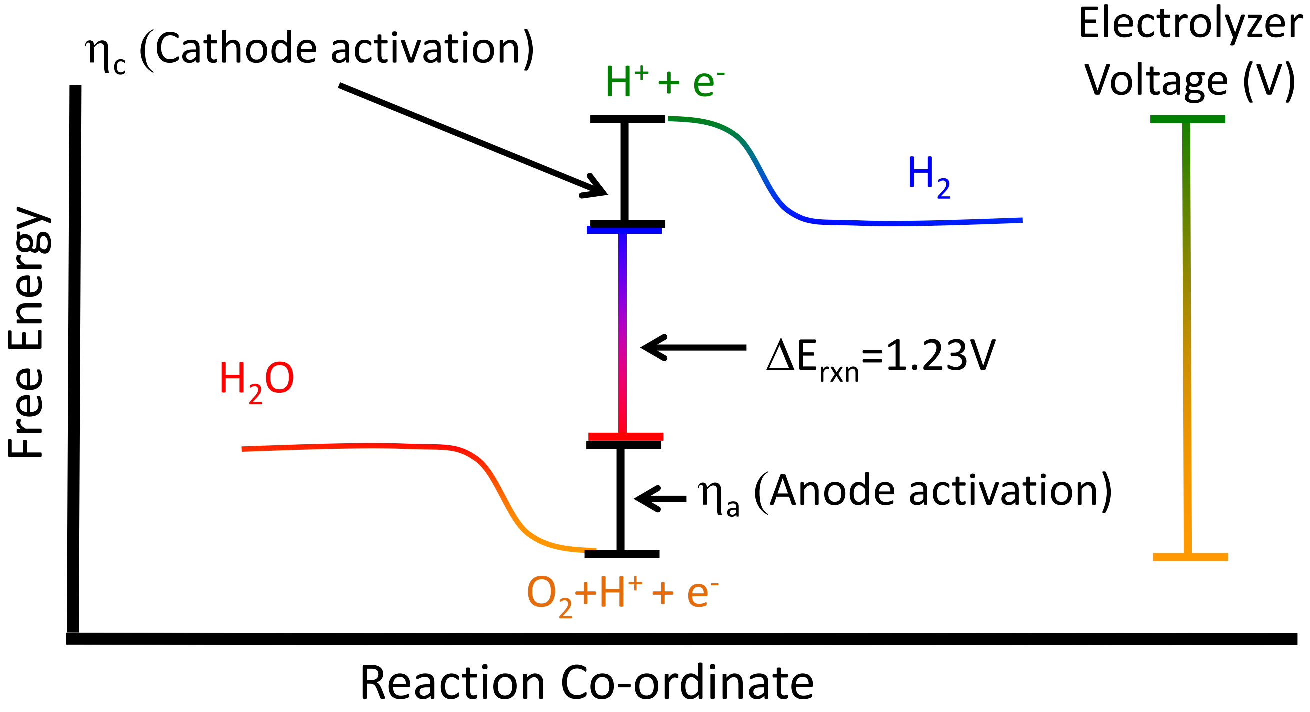


Heterogeneous Catalysis



Electrochemical Catalysis


Free Energy
$H^+ + e^-$
H_2
H_2O
$O_2 + H^+ + e^-$
Electrolyzer Voltage (V)
ΔE_{rxn}=1.23V
Reaction Co-ordinate

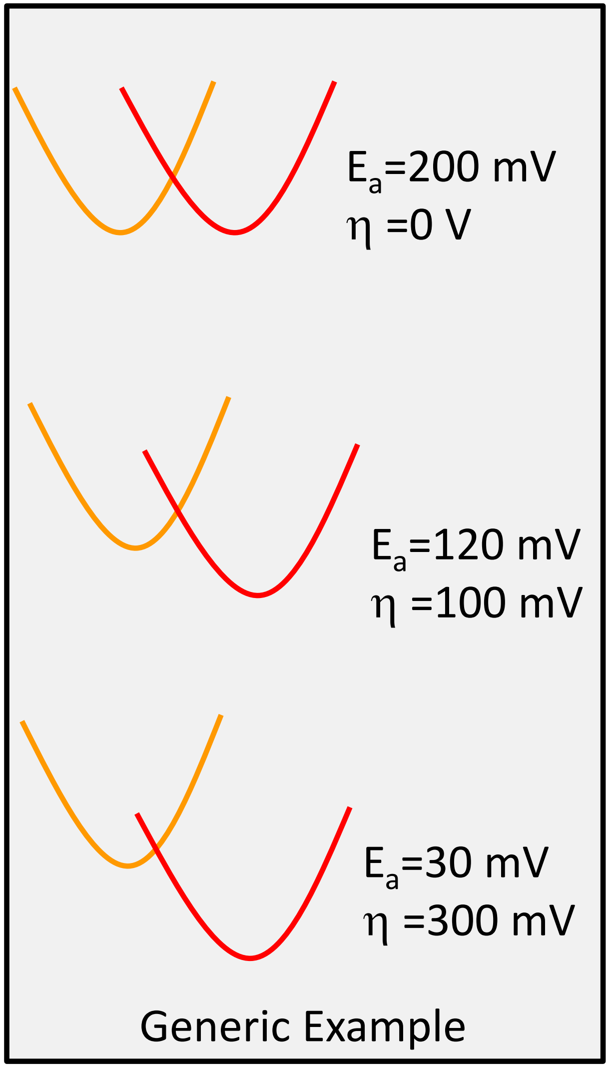

η_c (Cathode activation)
Electrolyzer Voltage (V)
$H^+ + e^-$
H_2
Free Energy
ΔE_{rxn}=1.23V
H_2O
η_a (Anode activation)
$O_2 + H^+ + e^-$
Reaction Co-ordinate

Quantifying losses

- As you increase the voltage drop (η) you decrease the Ea.
- Again, the Tafel equation is used

$$i = i_0 exp^{\frac{\eta}{A}} \quad \text{or} \quad \eta = ALn\left(\frac{i}{i_0}\right)$$

i is the current (mA/cm^2)
i_0 is the current exchange density (mA/cm^2)
η is the overpotential (i.e. voltage drop) (V)
A is the Tafel slope



Generic Example

Catalysis

- Both the anode and cathode follow the same electrochemistry principles as the fuel cell.

- The hydrogen reaction is the easiest to understand, so we will start there first.

Cathode: $2H^{+} + 2e^{-} \rightarrow H_2$

- Platinum is good, but expensive.

- Can we find an alternative that is just as good, but much cheaper.

- Why is platinum a good catalyst?

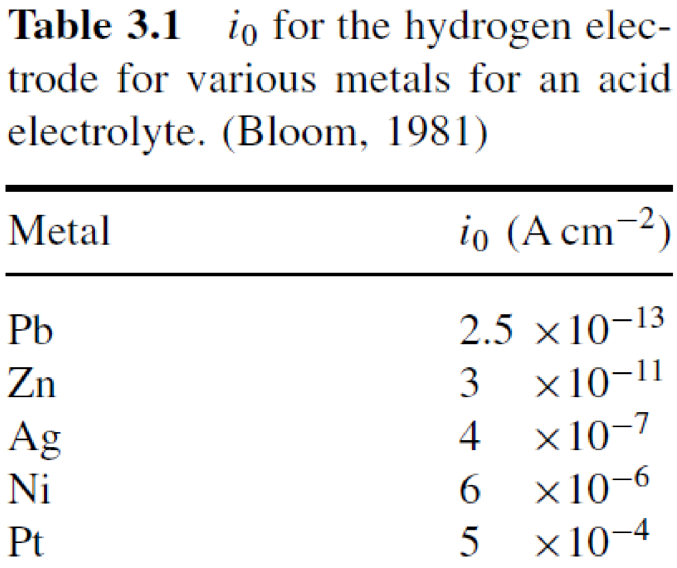
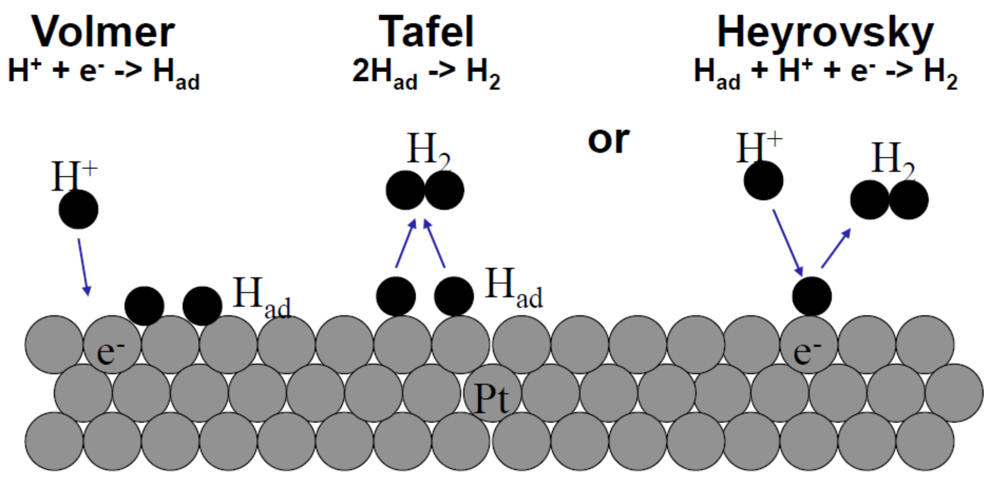


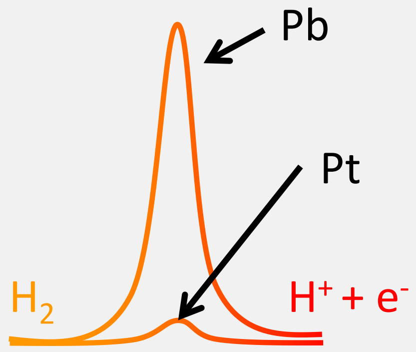
Table 3.1 i_0 for the hydrogen electrode for various metals for an acid electrolyte. (Bloom, 1981)

Metal	i_0 (A cm^{-2})
Pb	2.5×10^{-13}
Zn	3×10^{-11}
Ag	4×10^{-7}
Ni	6×10^{-6}
Pt	5×10^{-4}

Designing good catalysts

- Pt for H_2 evolution is almost the perfect catalyst, but why?
- First we need to understand the intermediates.
- Overall reaction: $H_2 \rightarrow 2H^+ + 2e^-$



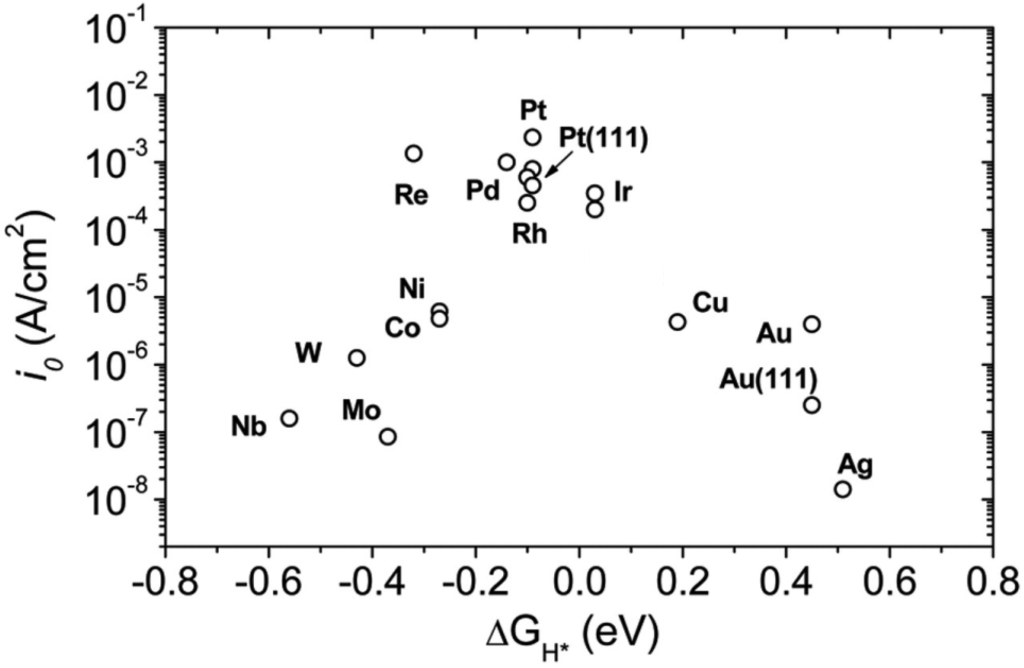


Qualitiative barrier of Pt and Pb

- Either the Tafel or the Herovsky mechanism occurs first (debated)
- The Volmer mechanism is the 2nd step to removing the protons

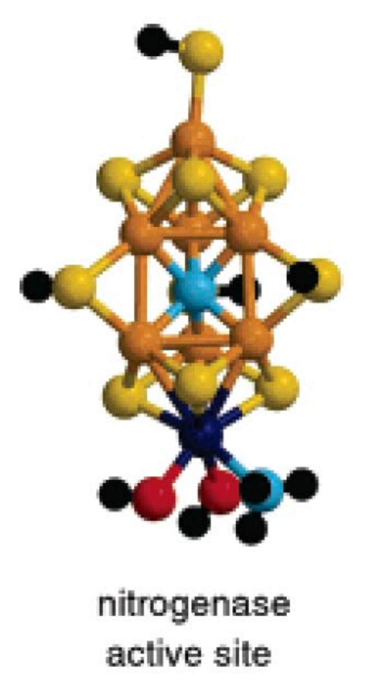
Volcano plot

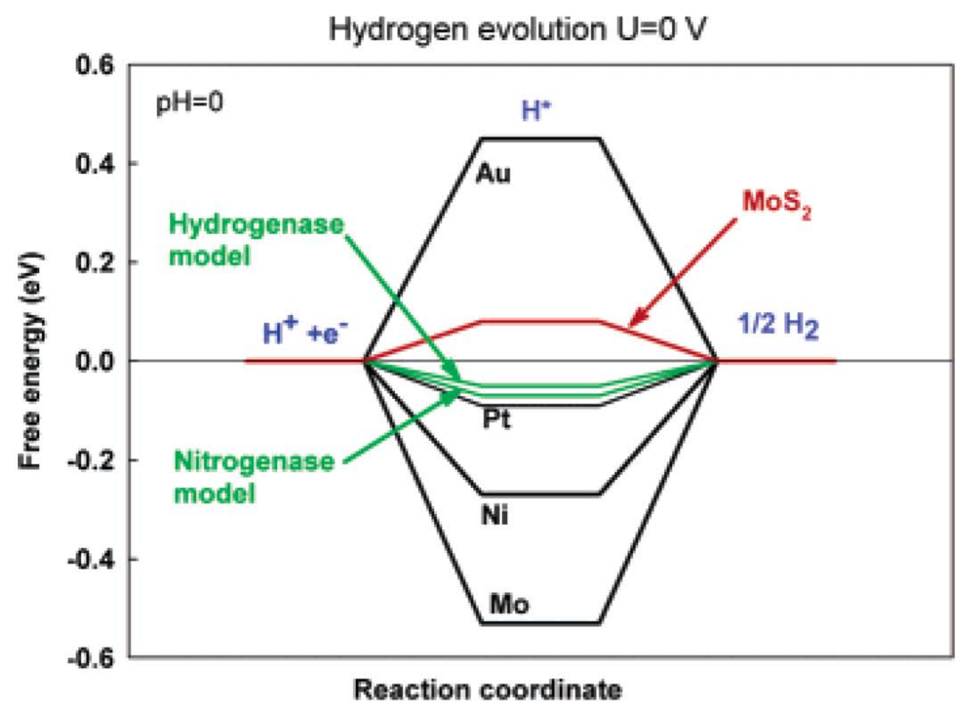
- With the hydrogen reaction there are two things that happen
  - The proton binds to the surface
  - It combines with another hydrogen
  - The hydrogen leaves the surface
- If the hydrogen binds too weakly, it won’t stick, but if it binds too strongly if will never leave.
- Thus there is an optimal binding energy.
- Plotting catalysts versus binding energy yields a ‘volcano’ plot.
- All noble metals are at the top.



How nature resolves this issue

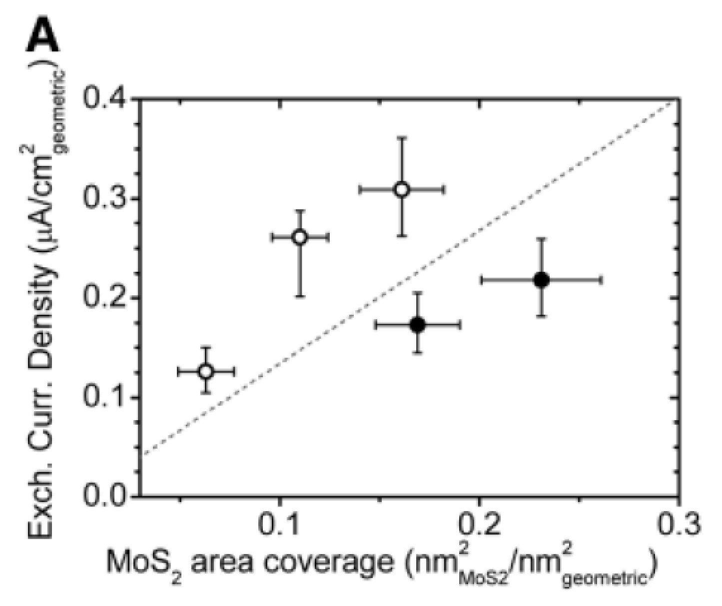
- The nitrogenase enzyme produces hydrogen and doesn't use noble metals.
- Ib Chorkendorff, Jens Nørskov, and Tom Jaramillo realized that MoS_2 was pretty similar.

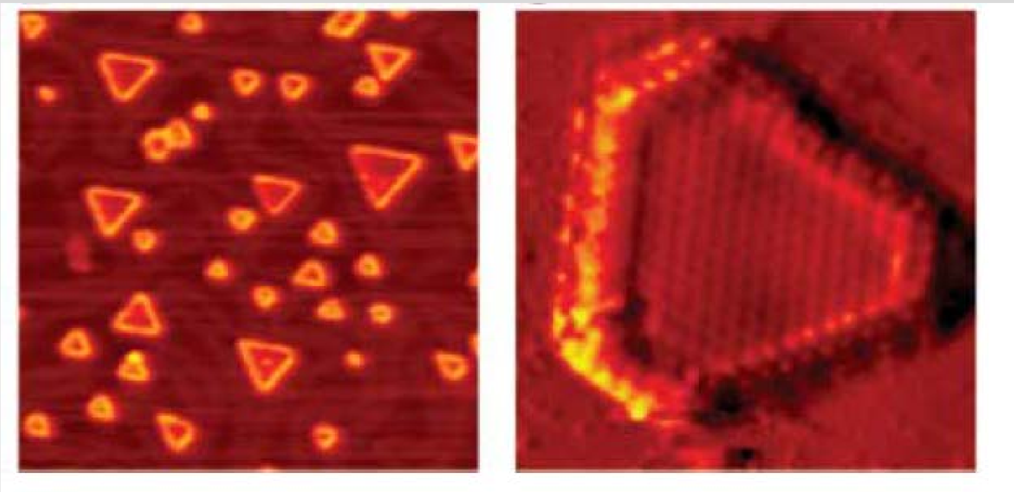




MoS_2

- The current exchange density was about the same as Ni (100x worse than Pt), but was stable in acid.
- Interestingly, it was only the edges that were active. The bulk was in-active.



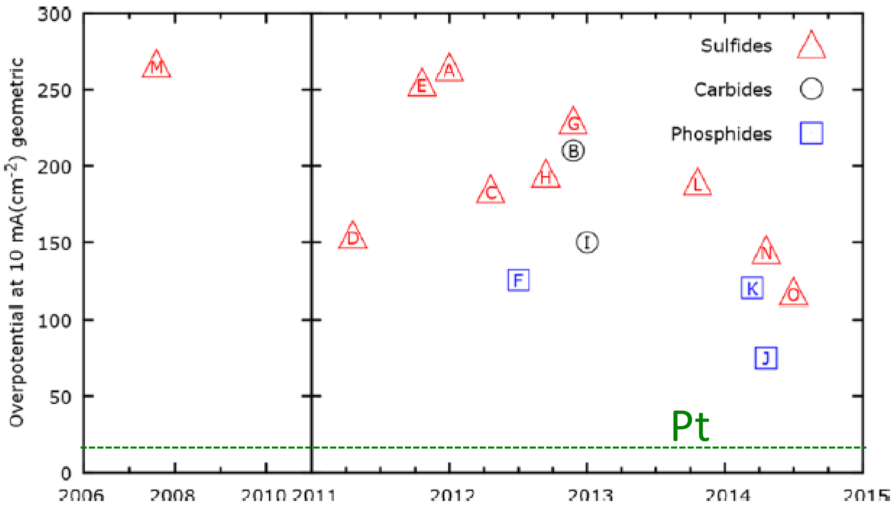


Microscopy images of MoS_2

Figures from Jaramillo, et al., Science, 2007

Progression over time

- The scientific community has slowly optimized this catalysis.
- Using a ‘follow nature’ approach phosphides such as MoS_2, CoP, NiP, and FeP all have been shown to be quite effective.
- Pt is so good though, we need such a small amount, it is actually scalable to the TW scale.



Vesborg, et al., JPC-L, 2015

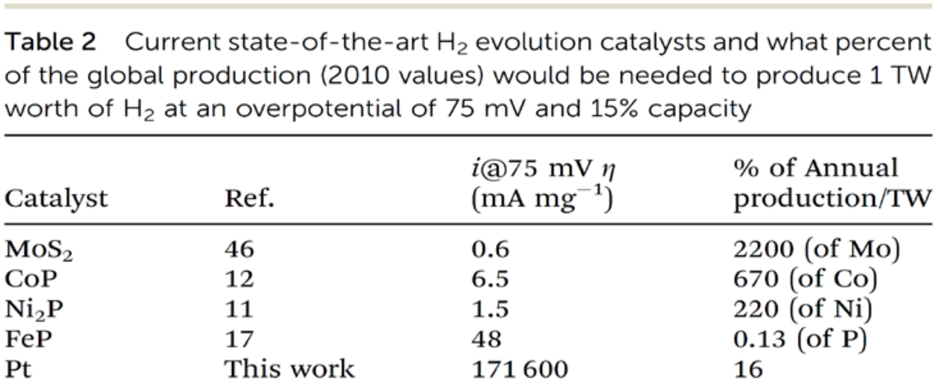


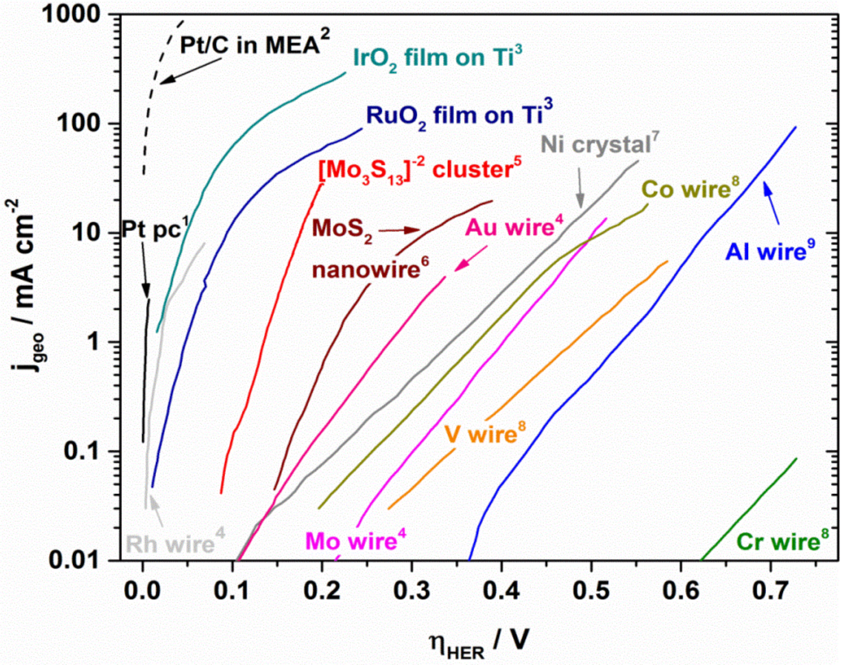
Table 2 Current state-of-the-art H_2 evolution catalysts and what percent of the global production (2010 values) would be needed to produce 1 TW worth of H_2 at an overpotential of 75 mV and 15% capacity

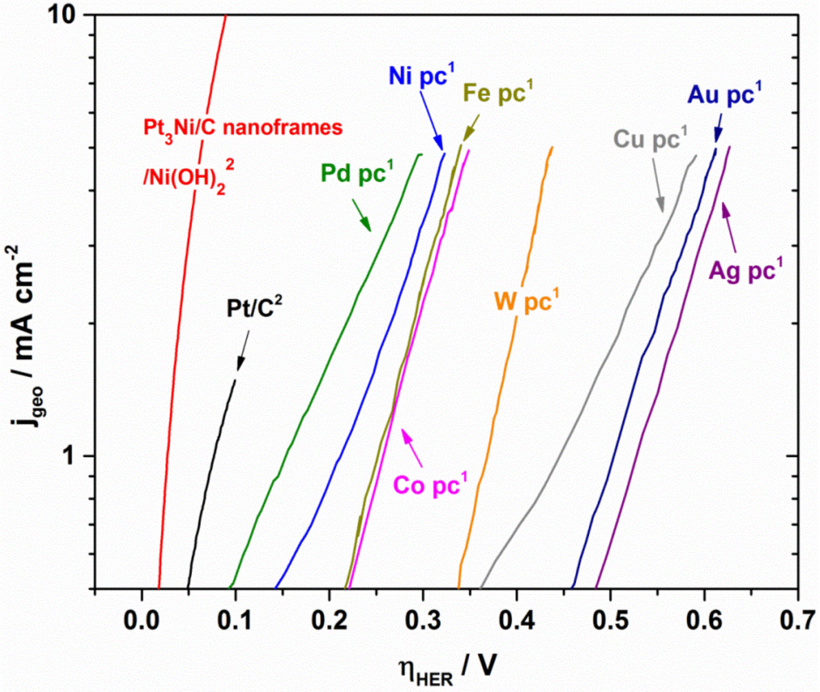
Catalyst	Ref.	i@75 mV η (mA mg^{-1})	% of Annual production/TW
MoS_2	46	0.6	2200 (of Mo)
CoP	12	6.5	670 (of Co)
Ni_2P	11	1.5	220 (of Ni)
FeP	17	48	0.13 (of P)
Pt	This work	171 600	16

Kemppainen, et al., E&ES, 2015

Hydrogen Evolution Catalysts Acid vs Base

- Acid is better, but basic conditions have many cheap alternatives.
- Ionic resistance is worse in basic solutions.

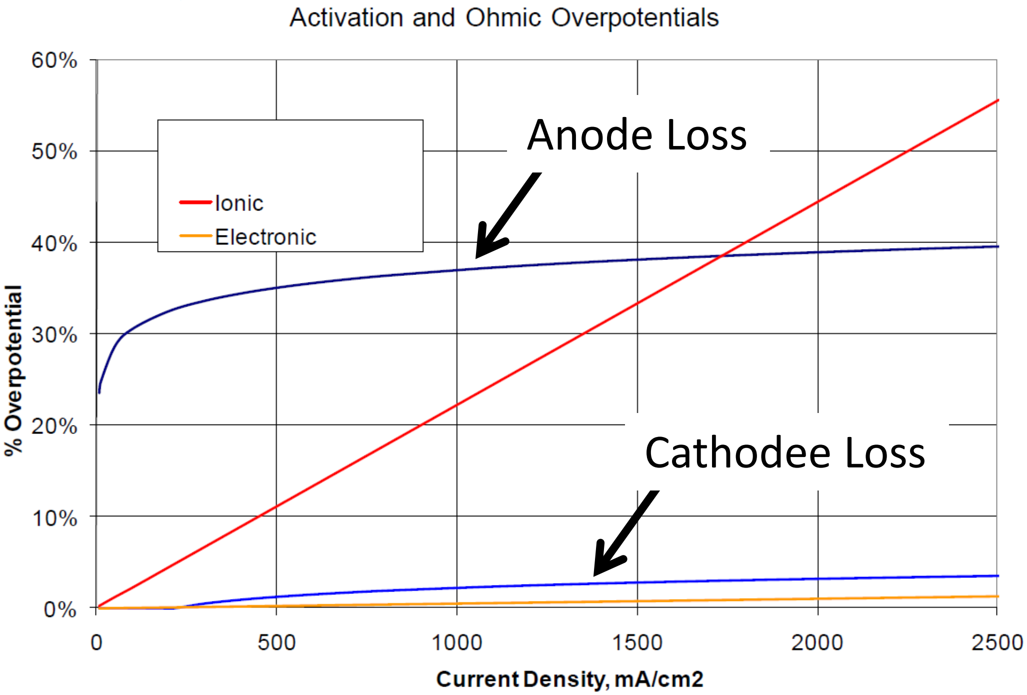




Oxygen evolution

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

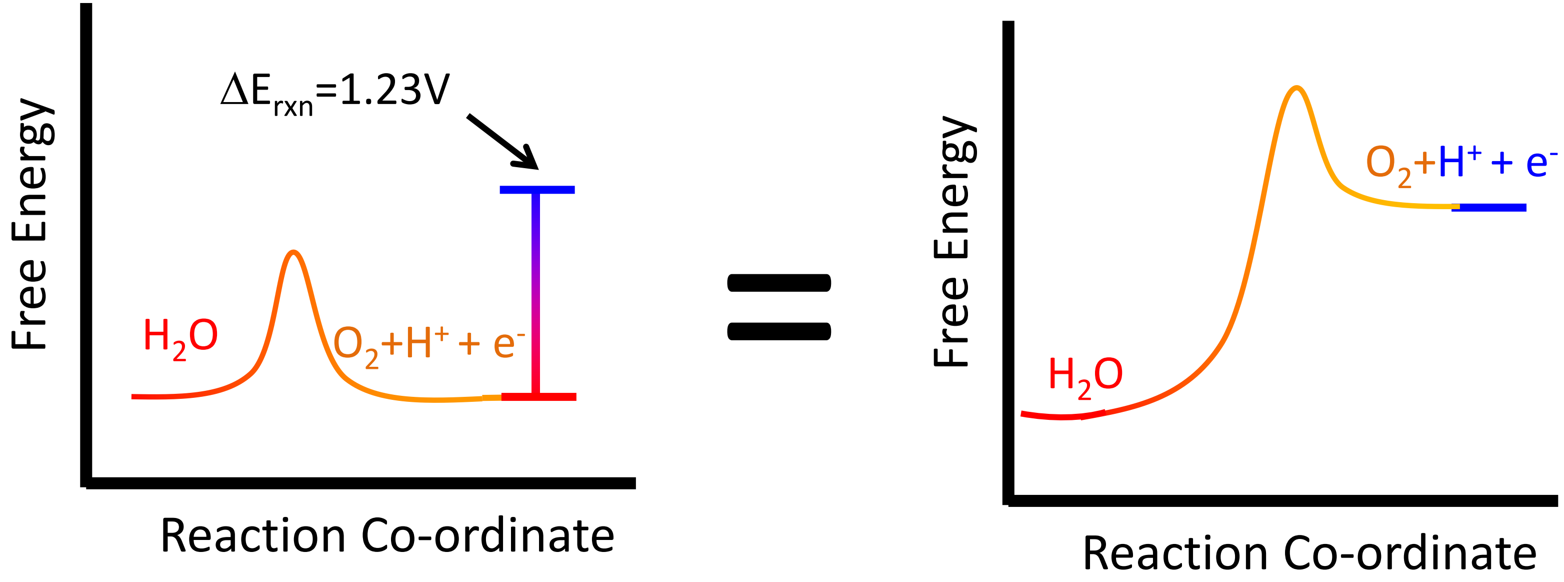
- The oxygen evolution reaction involves more electrons so it probably will be harder.
- Since this is the opposite of the fuel cell oxygen reduction reaction, it should be quite similar.
- If we take the same approach of looking at binding energies we should be able to minimize this loss.



Proton On-site data

Oxygen evolution mechanism

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



- We can equivalently state that when the H_2O oxidation progresses, the electrons need to move to a higher energy.
- This equivalent approach helps is explaining this mechanism.

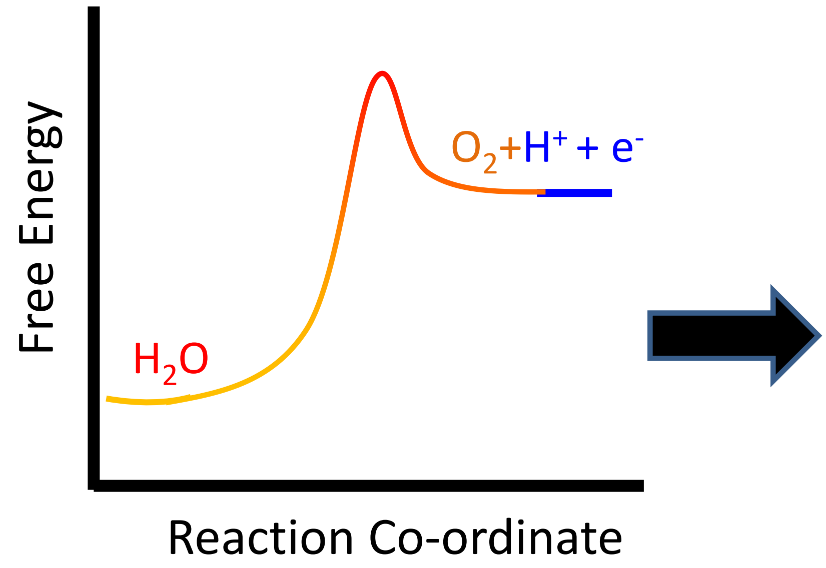
Oxygen evolution mechanism

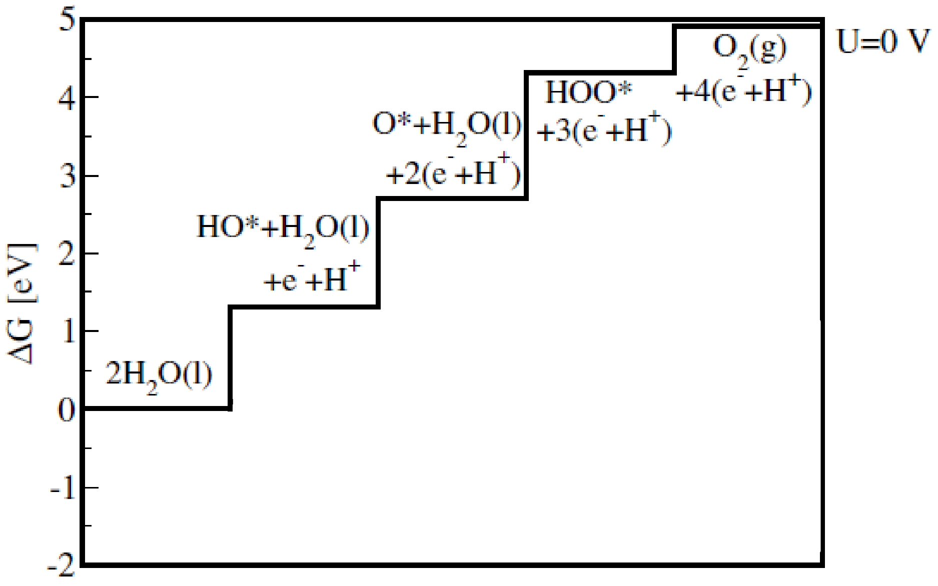
- The most commonly proposed mechanism is shown below:

$$\left.\begin{aligned} 2H_2O &\rightarrow H_2O + HO^* + H^+ + e^- \\ &\rightarrow H_2O + O^* + 2H^+ + 2e^- \\ &\rightarrow HOO^* + 3H^+ + 3e^- \\ &\rightarrow O_2 + 4H^+ + 4e^- \end{aligned}\right\}$$

Exact opposite of ORR for fuel cells

*- Catalyst site

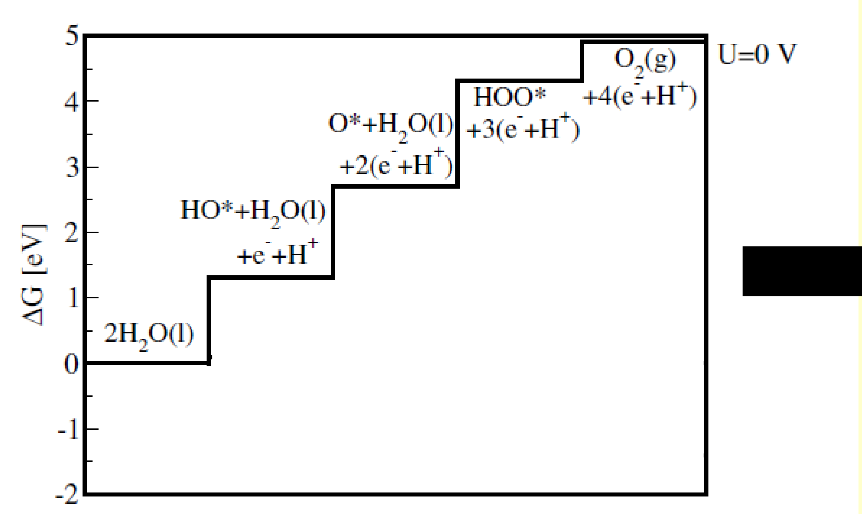




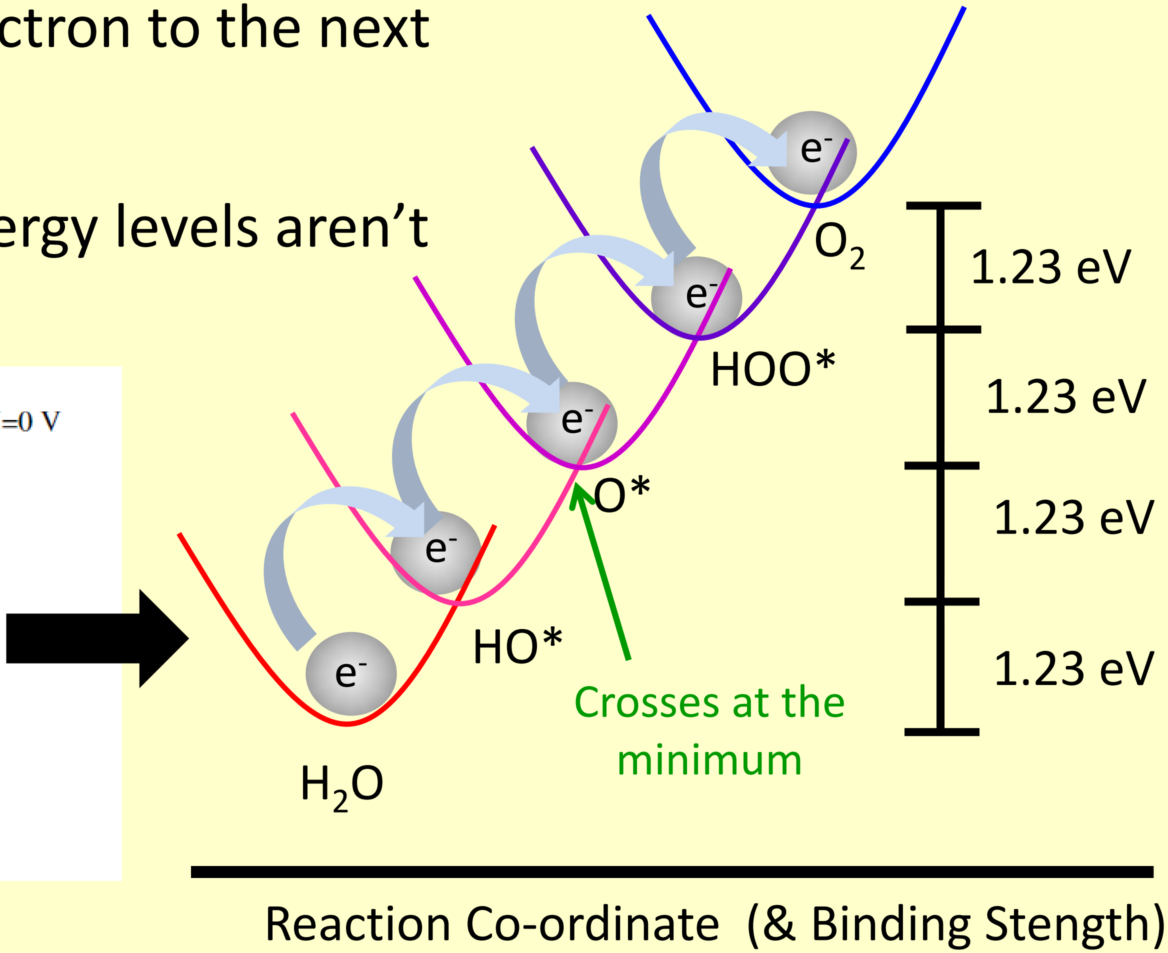
Rossmeisl, 2007, JEAC

Oxygen evolution mechanism

- Using the principles of transition state theory/Marcus theory, we can look at the individual steps.
- In theory each of the 4 steps should need 1.23 eV to move the electron to the next step.
- What happens if the energy levels aren't aligned properly.

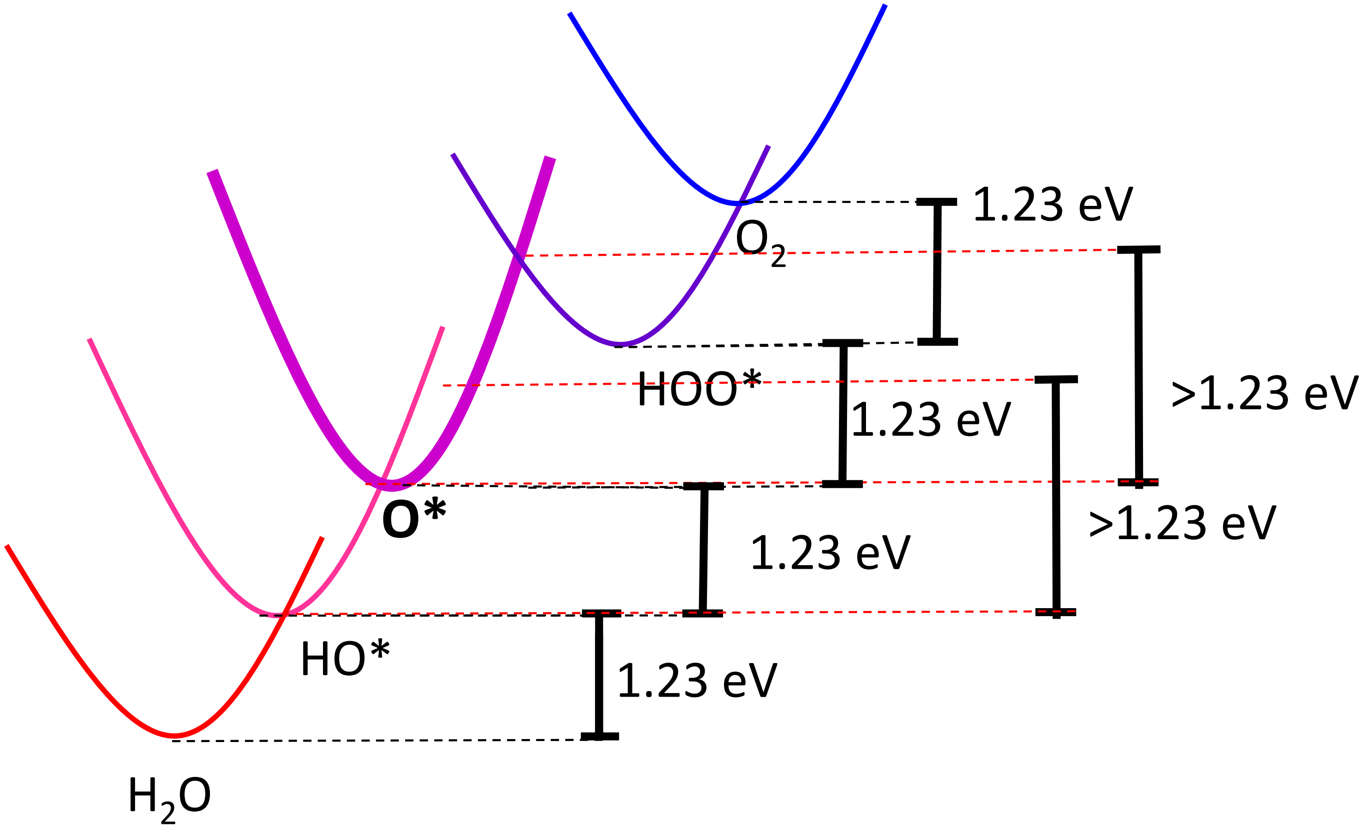


Rossmeisl, 2007, JEAC



Oxygen evolution mechanism

- What if one of the catalyst site is not perfectly aligned
- Your operating voltage is only as low as your slowest (i.e. highest voltage) intermediate

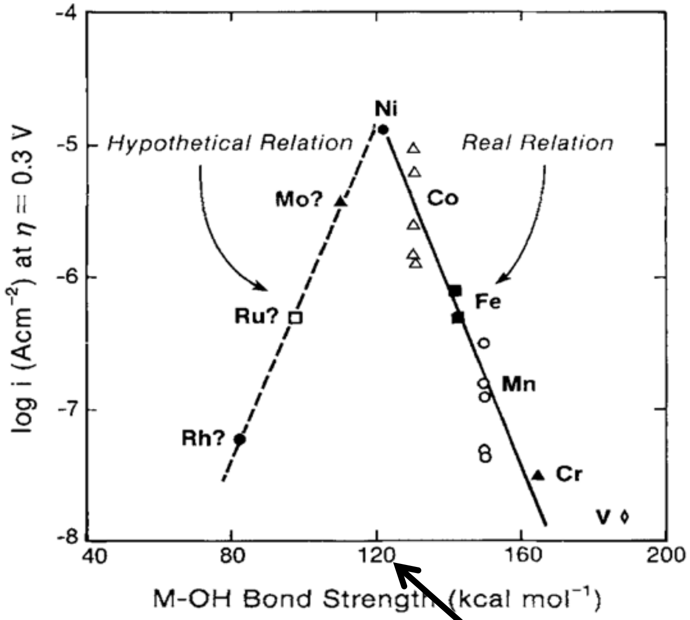


Oxygen evolution mechanism

- The rate limiting step is catalyst dependent.
- It is not directly the binding of the HO*, O*, or HOO*.

Mechanism

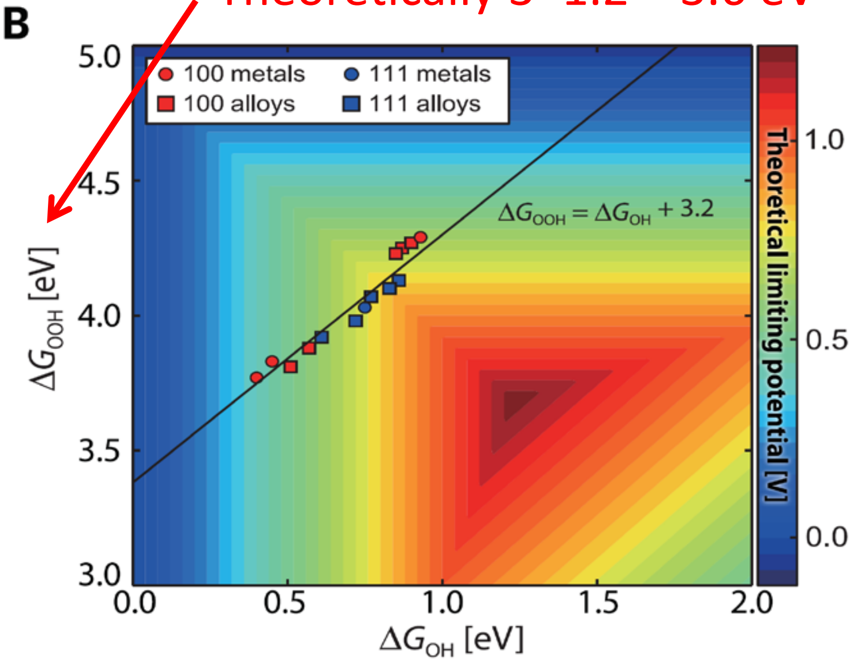
$$
\begin{aligned}
2H_2O &\rightarrow H_2O + HO^* + H^+ + e^- \\
&\rightarrow H_2O + O^* + 2H^+ + 2e^- \\
&\rightarrow HOO^* + 3H^+ + 3e^- \\
&\rightarrow O_2 + 4H^+ + 4e^-
\end{aligned}
$$



120 kcal/mol =1.23 eV

Bockris et al., JES, 1984

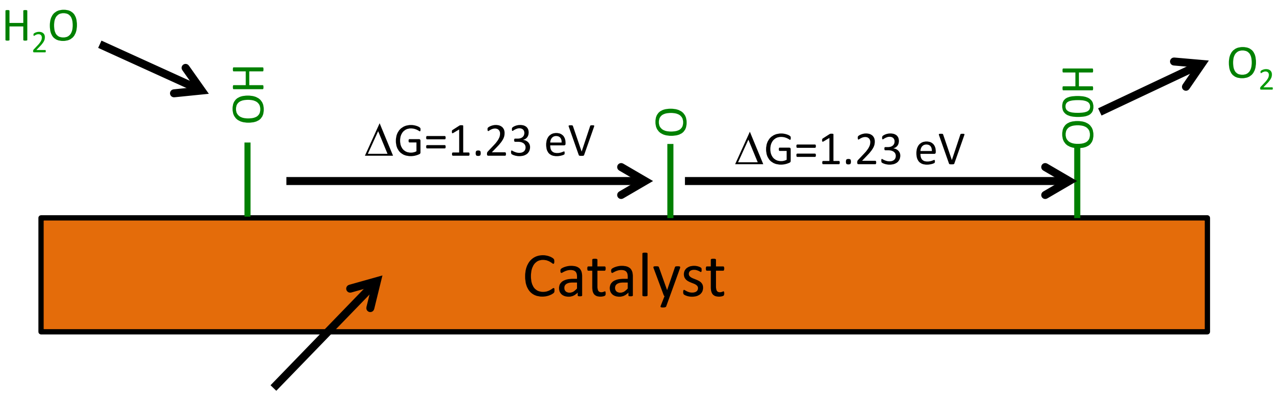
Theoretically 3*1.2 = 3.6 eV



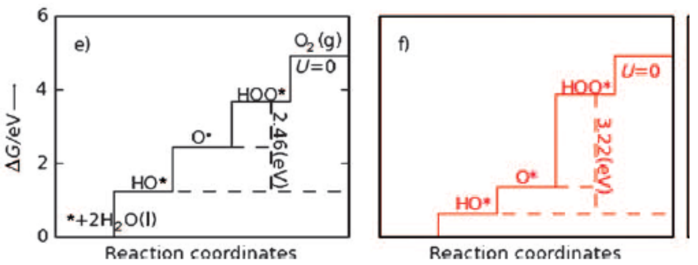
Seh et al., Science, 355, 146 2017

Oxygen evolution mechanism

- **Why can't our volcano plot reach 0 V overpotential?**



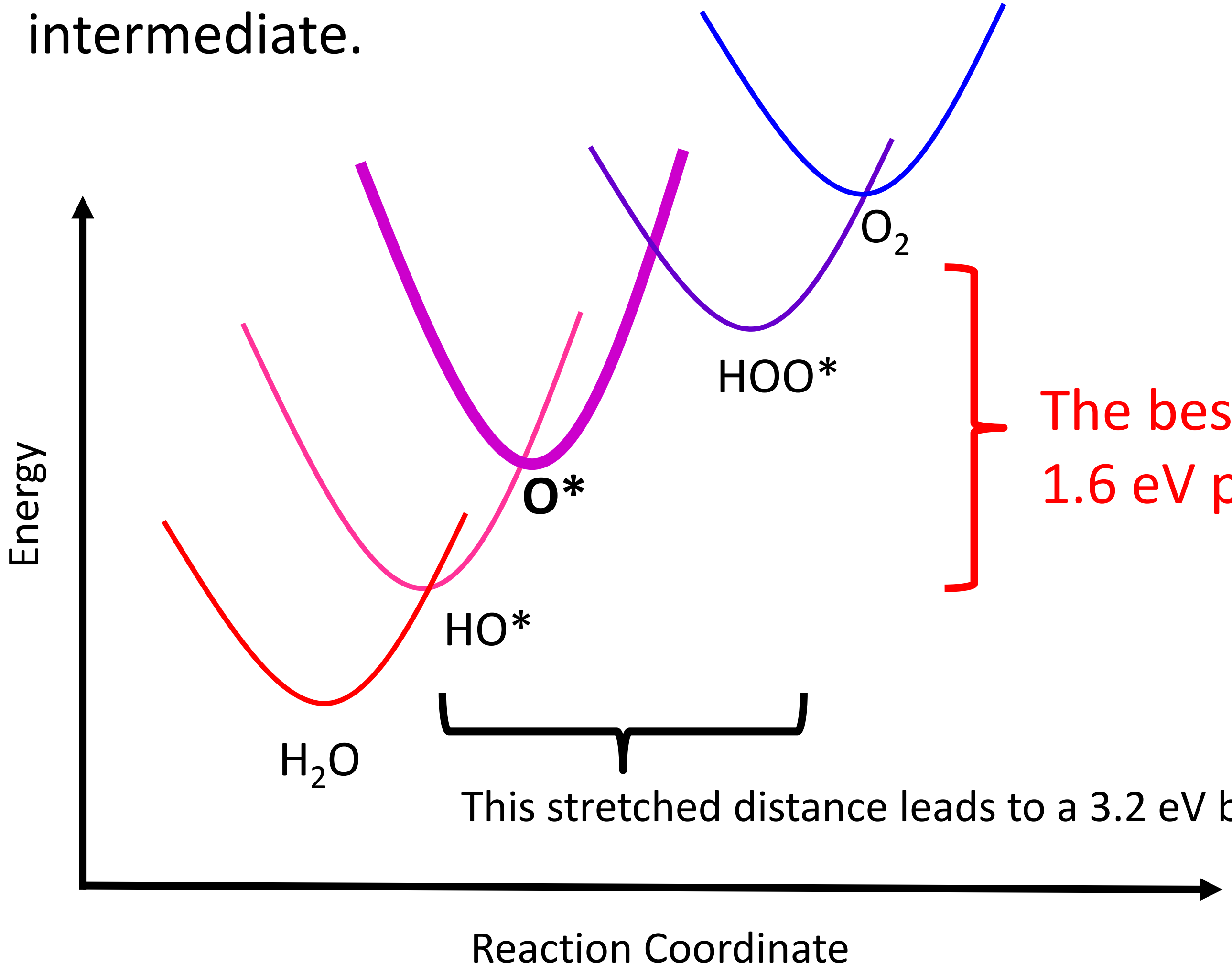
- All 3 intermediates have O bonded to the surface.
- We have 2 ΔG's we want to optimize, and only 1 parameter (bonding strength)
- The result is optimizing one DG, deoptimizes the other.
- **This is known as a scaling relationship.**



Man et al., ChemCat Chem, 2011

Oxygen evolution mechanism

- We can only vary the oxygen-catalyst site
- The scaling relationship does not allow us to optimize each reaction intermediate.



The best we can do is 1.6 eV per step

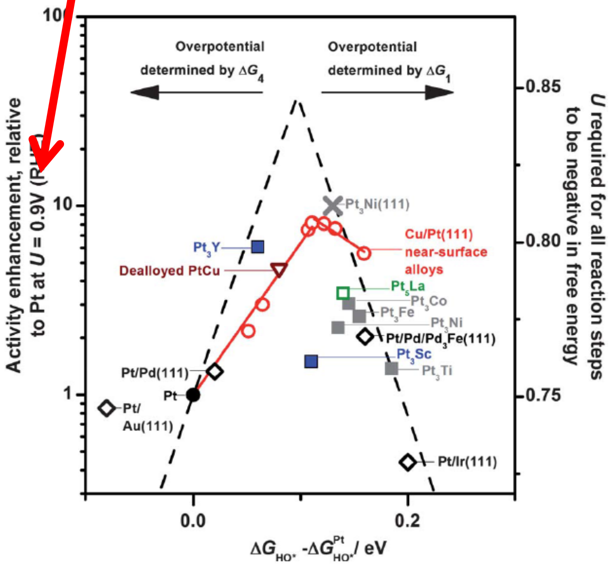
This stretched distance leads to a 3.2 eV barrier for these 2 steps

Oxygen evolution mechanism

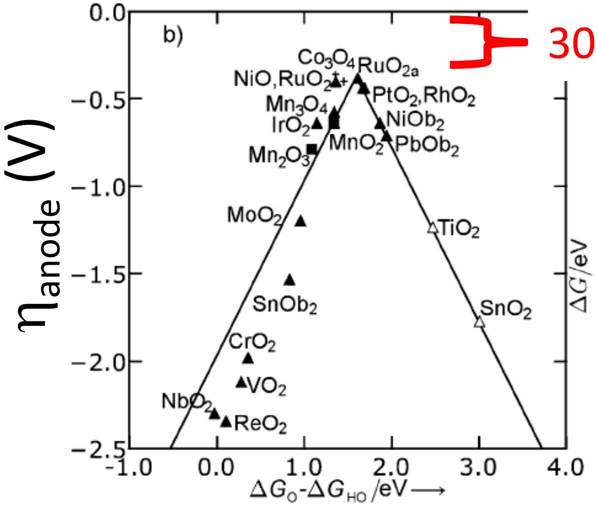
- The scaling relationship forces the 2 electron process of HO*→O*→ HOO* to have a minimum ΔG=~3.2 eV, (1,6 eV/electron.)
- Thus we are forced to have ~400 mV of loss due to this process. In reality high surface area lets us minimize this to ~300 mV.
- This scaling relationship applies to the fuel cell ORR reaction as well.

1.23V - 300 mV=

Fuel cell



Electrolyzer



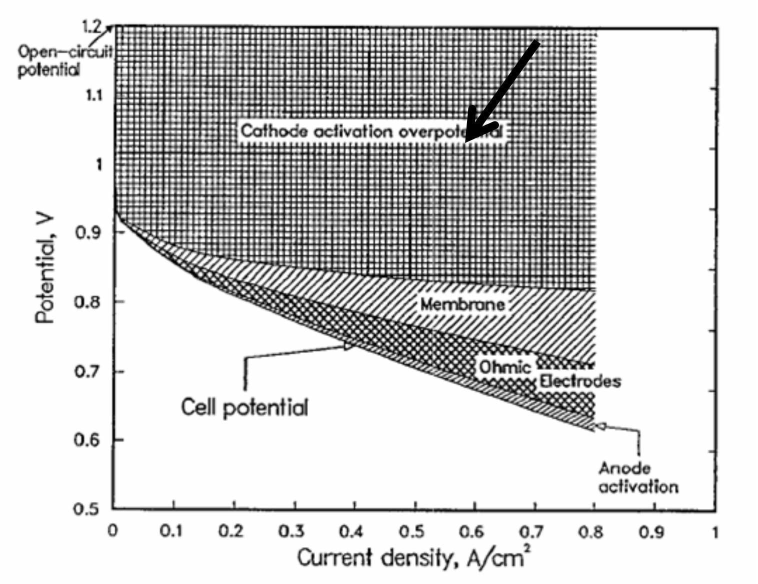
300 mV

Stephens et al., EES, 2012

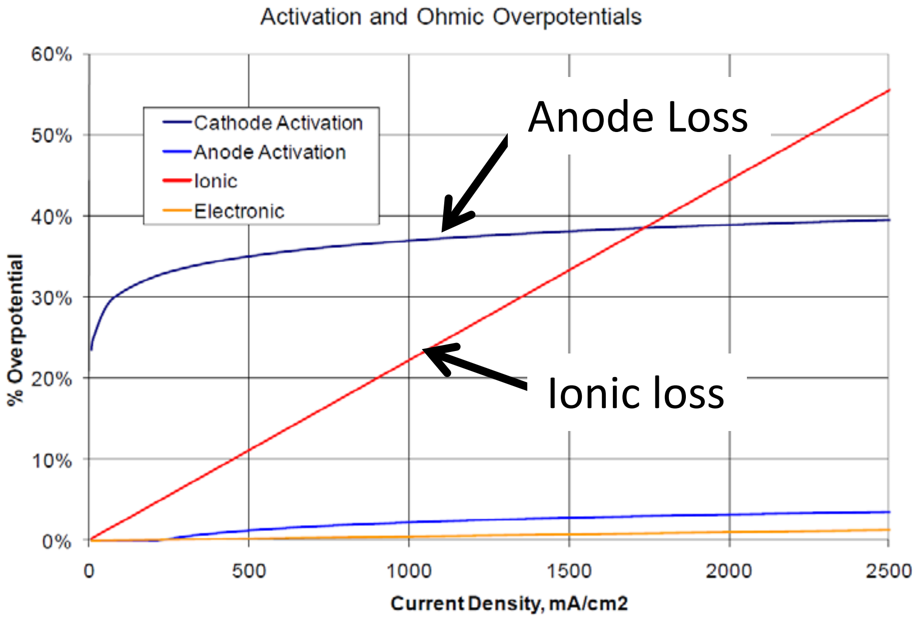
Garcia-Moto et al., ChemCatChem, 2011

Effect of scaling relationship

- The scaling relationship is the cause of the majority of losses in both fuel cells and electrolyzers.
- If it we didn't have the scaling relationship issue, the losses on the oxygen side could be realistically as low as the losses on the hydrogen side.



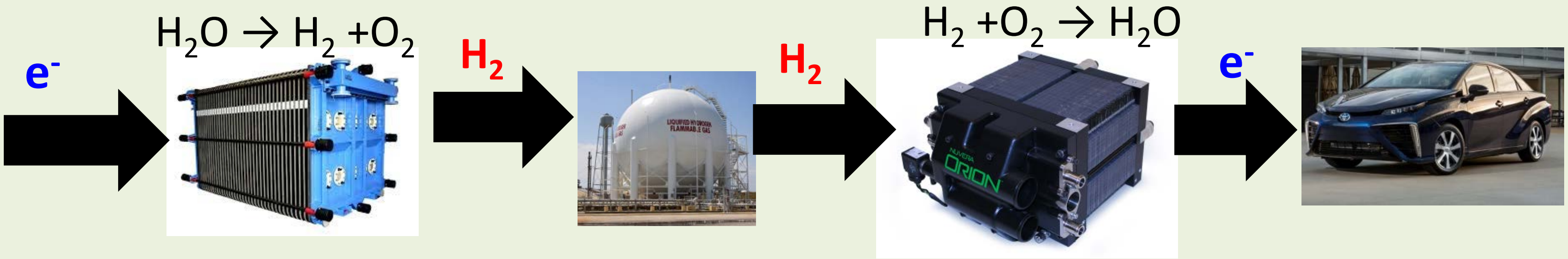
Bernardi and Verbrugge, JES, 1992



Proton On-site data

Efficiency Math

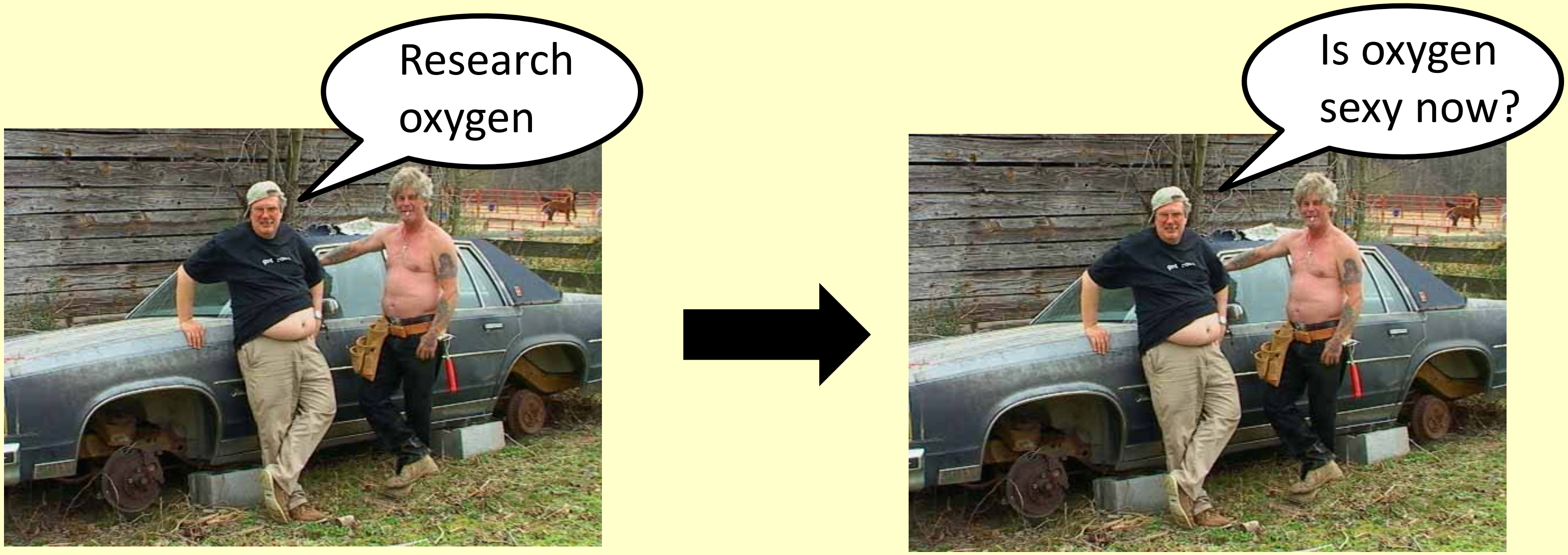
- How efficient is our Hydrogen economy?
- How bad is this scaling relationship issue hurting us.



Efficiency (using 1.23V as 100%)	Electrolyzer		Storage (Assumption)		Fuel Cell		Electric motor		Car (or other device)
Current Status	66%	X	~ 90%	X	57%	X	90%	=	34%
Without scaling issues	88%	X	~ 90%	X	81%	X	90%	=	58%
Gasoline / normal engine	Oil → gasoline 88%	X	~ 100%	X	Diesel engine 40%			=	44%
Battery	Charging 92%	X	~ 100%	X	Discharging 92%	x	90%	=	76%

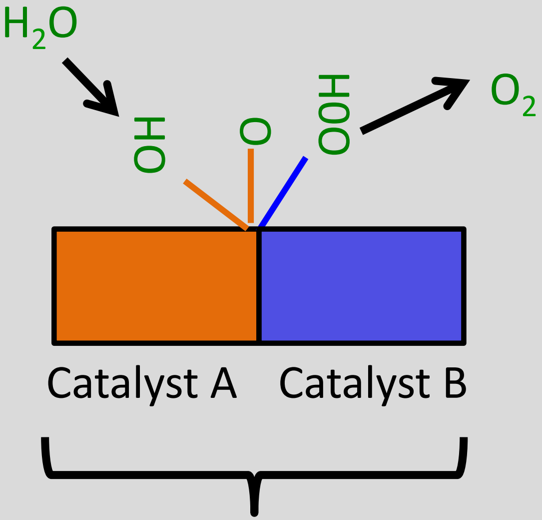
Breaking the scaling relationship

- Can we break the scaling relationship?
- It just could make the Hydrogen economy viable.
- It also would probably give you a Nobel prize.
- Discuss your ideas.



Breaking the scaling relationship

- How about making a catalyst with 2 active sites at basically the same spot.
- This would give us another parameter to optimize- 2 parameters, thus 2 ΔG optimizations.



This is an approach to break the scaling relationship

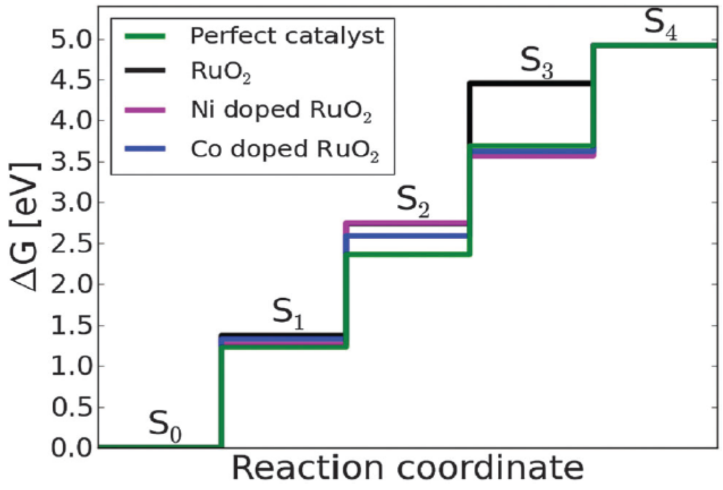
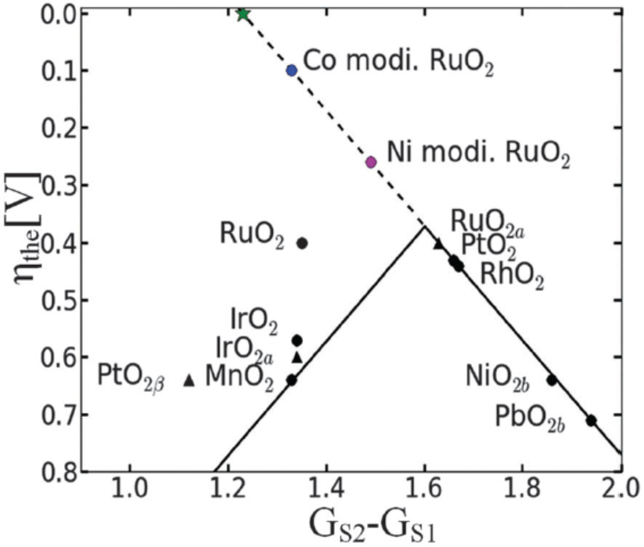


Fig. 3 Free energy diagram based on DFT calculations for conventional, Ni and Co modified ruthenia and the perfect catalyst for the four steps in

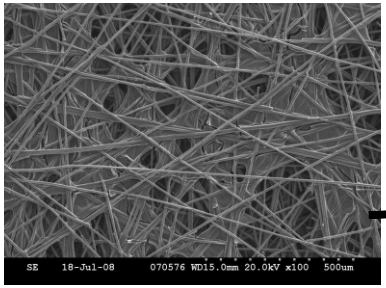


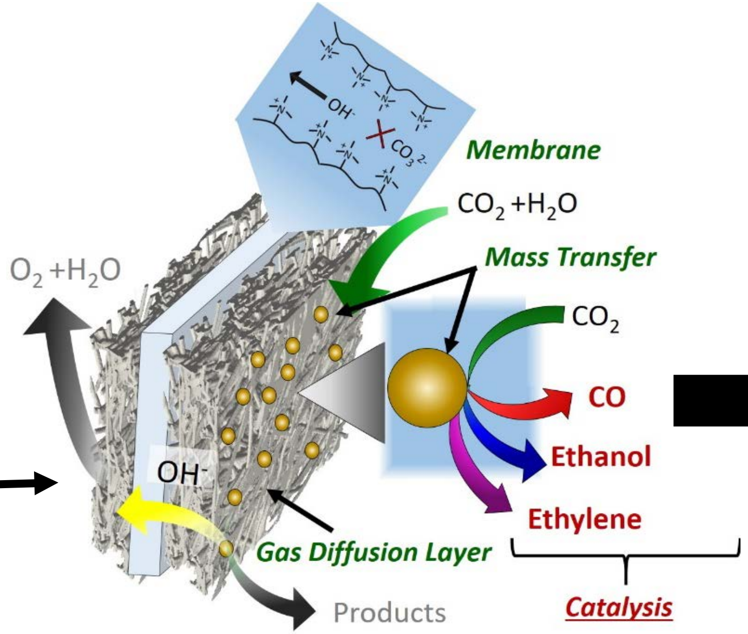
Halck, PCCP, 2014

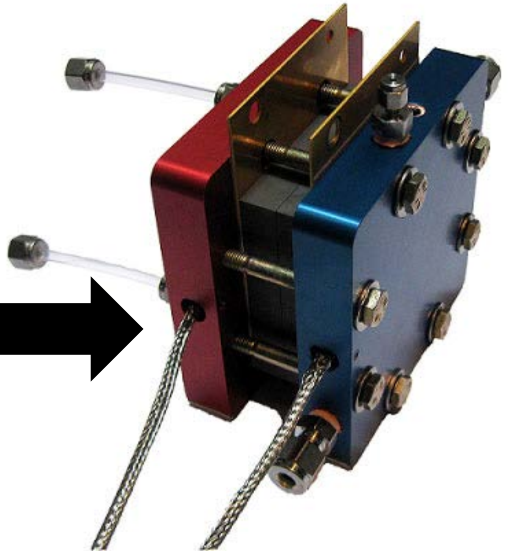
Break

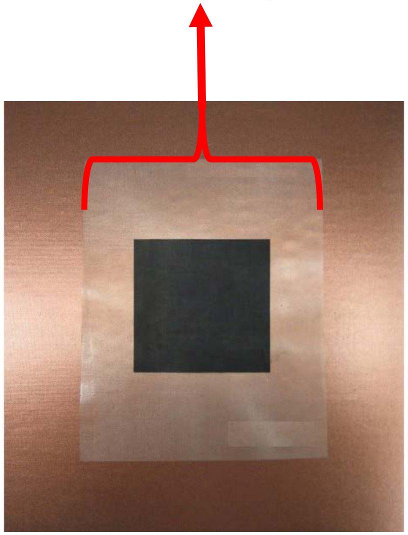
Electrochemical CO_2 reduction

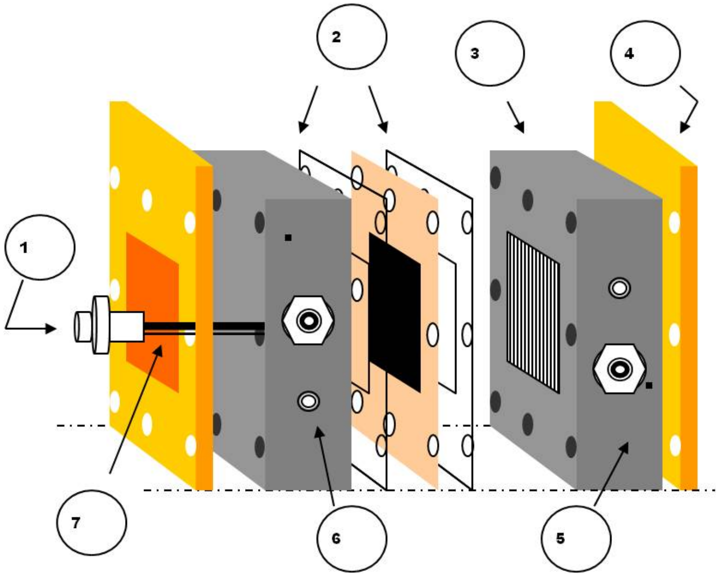
SEM Image











Water splitting

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

Cathode: $2H^+ + 2e^- \rightarrow H_2$

Overall: $H_2 + \frac{1}{2}O_2 \rightarrow H_2O$

- Water is plentiful and concentrated.
- H_2 evolution is easy.
- H_2 storage/use is difficult.

CO_2 reduction

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

$$\text{Cathode: } \begin{cases} CO_2 + H^+ + 2e^- \rightarrow HCOO^- \\ CO_2 + 2H^+ + 2e^- \rightarrow CO + 2H_2O \\ CO_2 + 8H^+ + 8e^- \rightarrow CH_4 + 2H_2O \\ 2CO_2 + 12H^+ + 12e^- \rightarrow C_2H_4 + 4H_2O \\ \text{And many more} \end{cases}$$

Overall: $H_2 + CO_2 \rightarrow C_xO_yH_z + H_2O$

- CO_2 is not concentrated (400 ppm in air)
- CO_2 is concentrated in biomass waste, cement, etc.
- CO_2 reduction competes with H_2 evolution

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 overpotential.)

Reaction	**E^0 vs. RHE**
$2H^+ + 2e^- \rightarrow H_2$	0.00 V
$CO_2 + H^+ + 2e^- \rightarrow HCOO^-$	- 0.11 V
$CO_2 + 2H^+ + 2e^- \rightarrow CO + 2H_2O$	+ 0.02 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
$2CO_2 + 12H^+ + 12e^- \rightarrow C_2H_4 + 4H_2O$	+ 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

Value of Products

- There are 2 ways to go about this:
  - Create products that are in high demand (such as energy based products)
  - Create products that are of high value (Specialty chemicals)

Material	**# of e^-**	**(\$/ton)**	**(\$/MC)**	**World Prod. (megaton)**
Hydrogen	2	1000	**0.010**	60
Carbon Monoxide	2	743	**0.11**	150
Formic Acid	2	650	**0.15**	0.8
Formaldehyde	4	530	**0.041**	10
Methanol	6	496	**0.027**	70
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

What catalyst to 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.

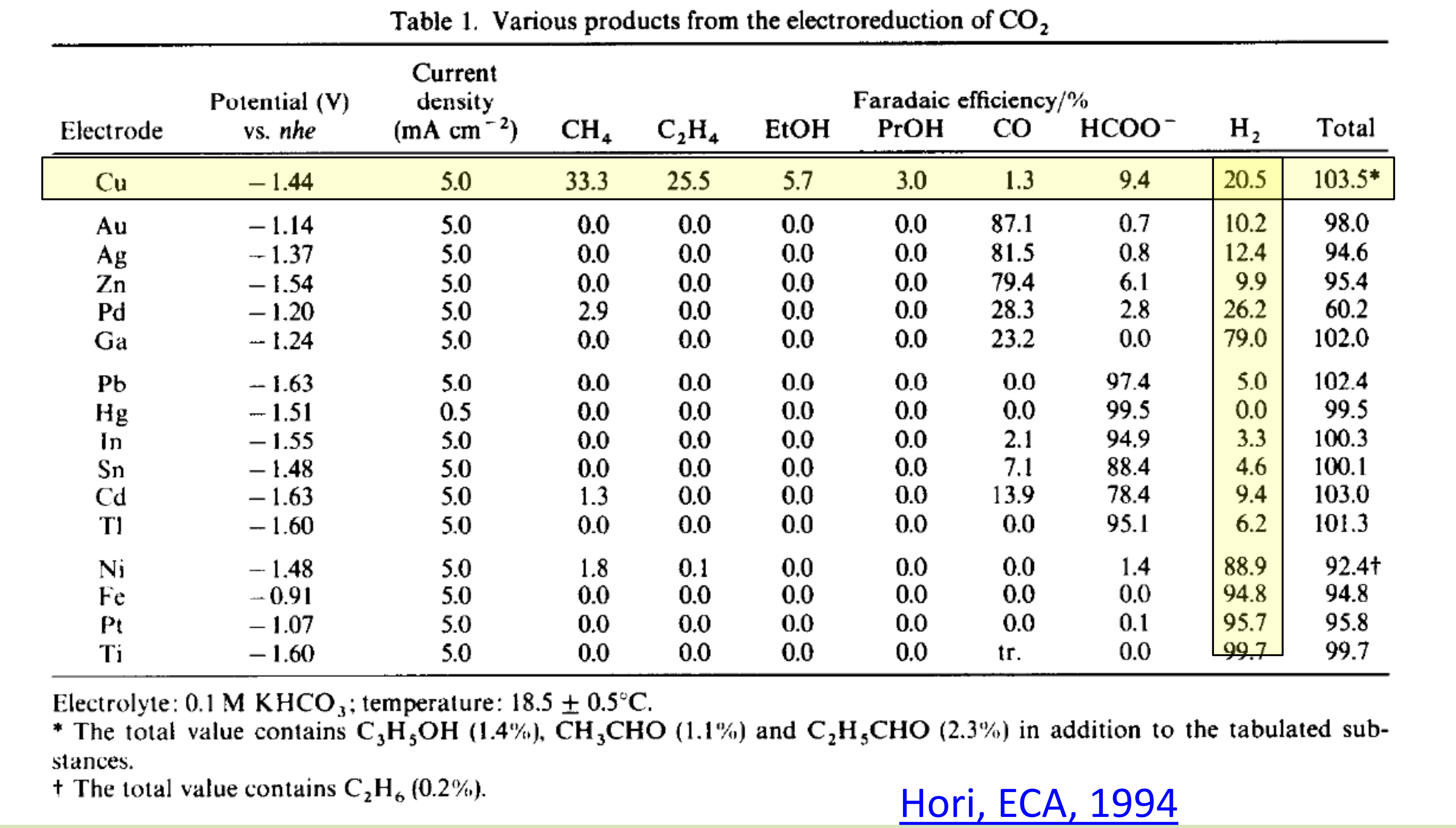


Table 1. Various products from the electroreduction of CO_2

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.

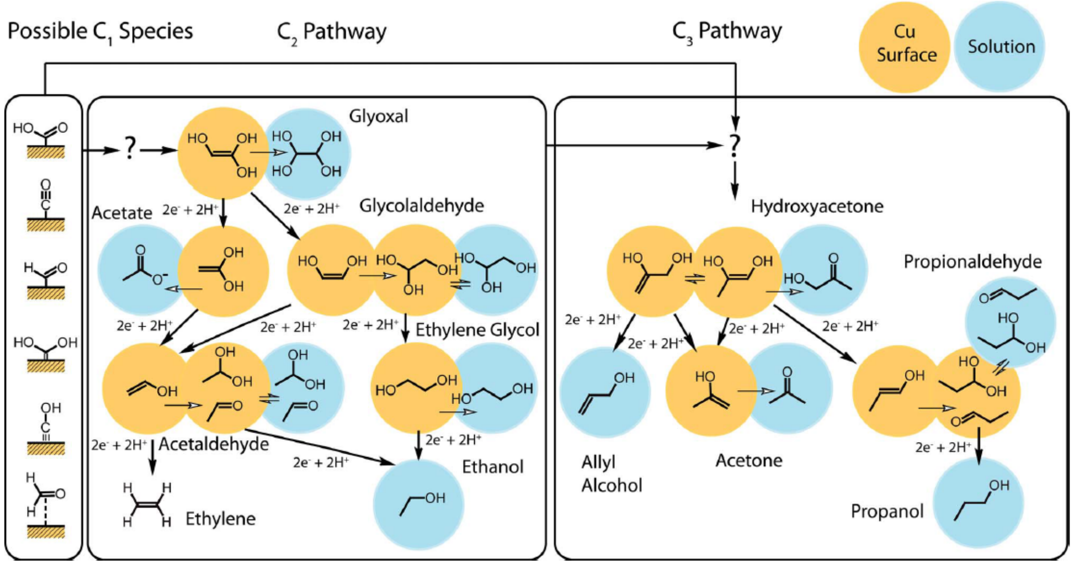
* The total value contains C_3H_5OH (1.4%), CH_3CHO (1.1%) and C_2H_5CHO (2.3%) in addition to the tabulated substances.

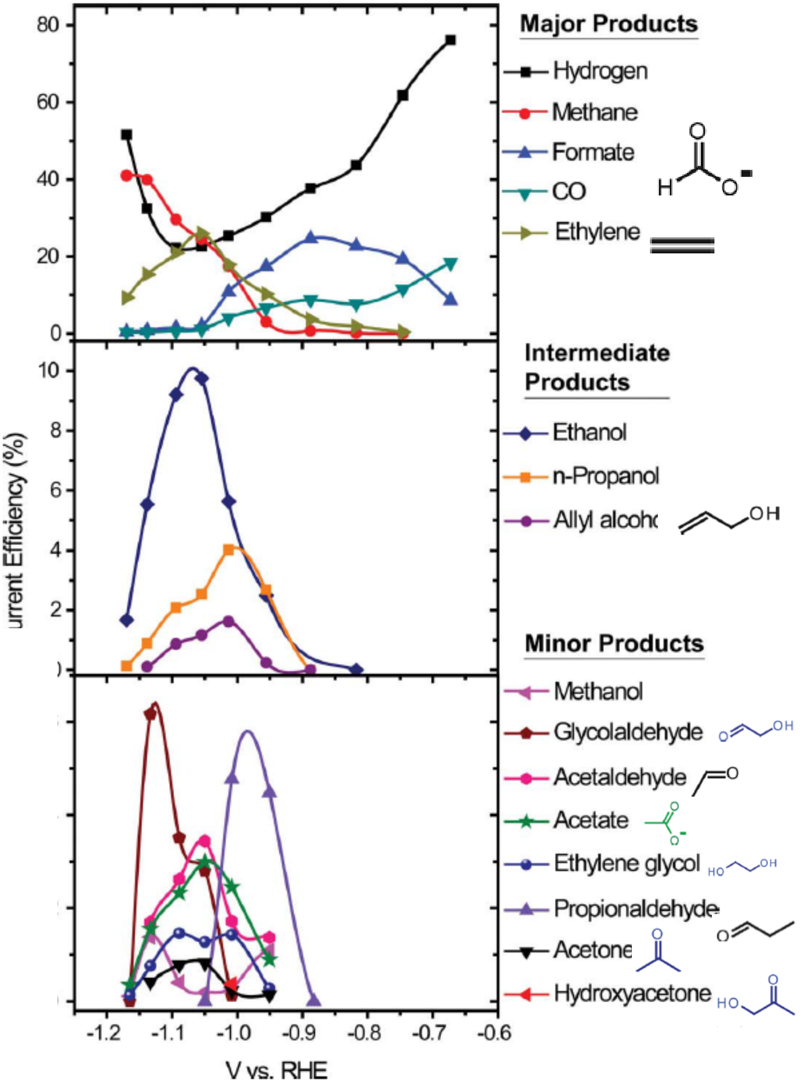
† The total value contains C_2H_6 (0.2%).

Hori, ECA, 1994

Copper as a catalyst

- Tom Jaramillo’s group showed that there are a wide variety of products coming from copper.
- They used NMR rather than the typical gas chromatograph to analyze their products.

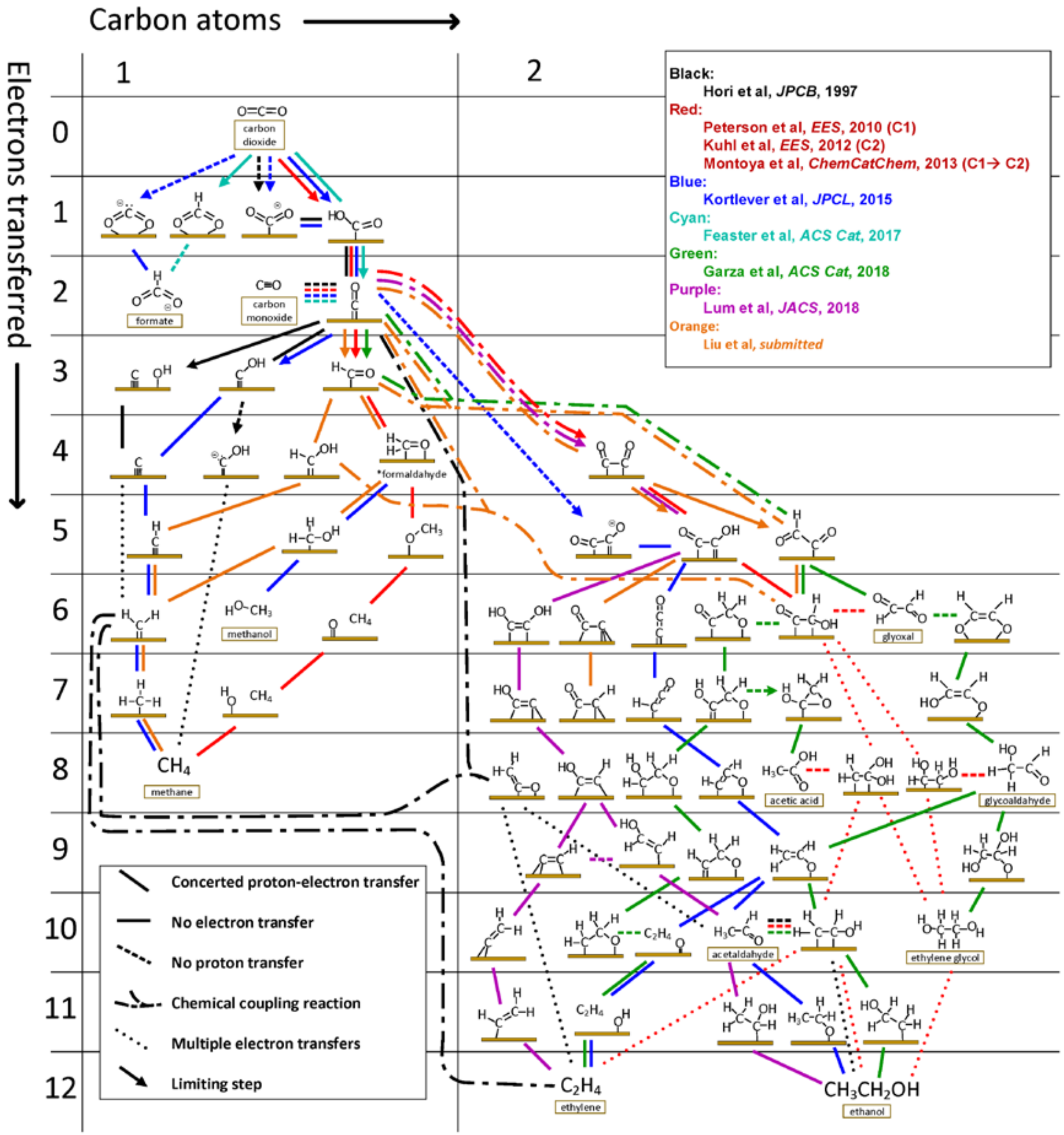




Kuhl et al., EES, 2012

Mechanisms (we think)

- Everything but formate goes through a CO intermeidate.
- Everything else is a mystery.

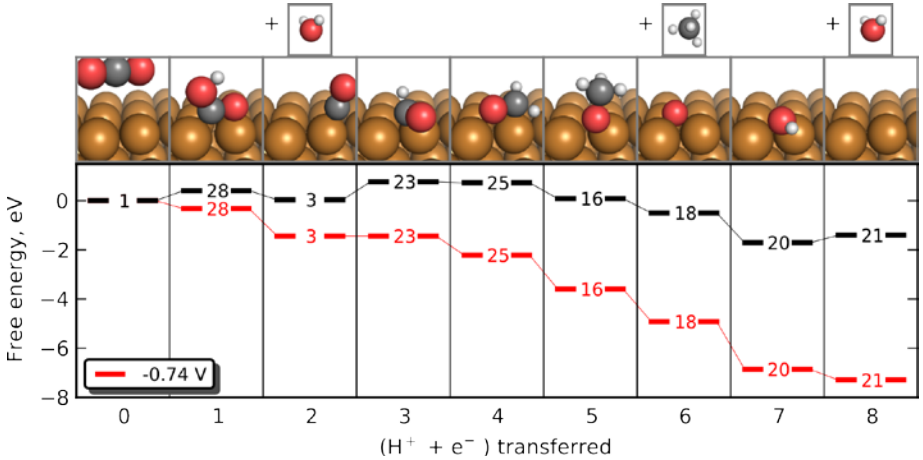


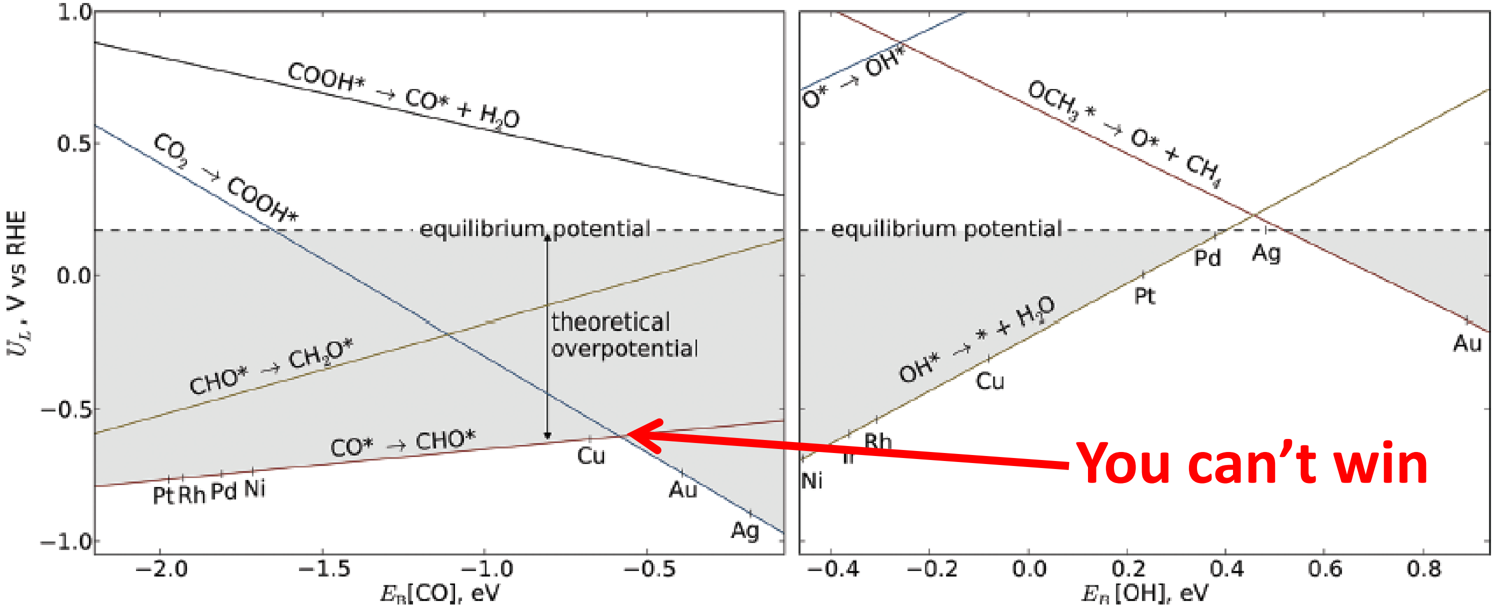
Søren Scott’s Masters Thesis

Scaling Issues? Yes

- CO_2 reduction has scaling relationship issues.
- Cu is the best candidate though.

Methane Production Cu(211)





You can't win

Peterson, Abild-Pedersen, Studt, Rossmeisl, Nørskov. ***Energy Environ Sci*** 2010
Peterson,Nørskov, *JPCL* 2012

Scaling Relationships

”It is better to avoid a scaling relationship than to fight through it”

- Common Sense

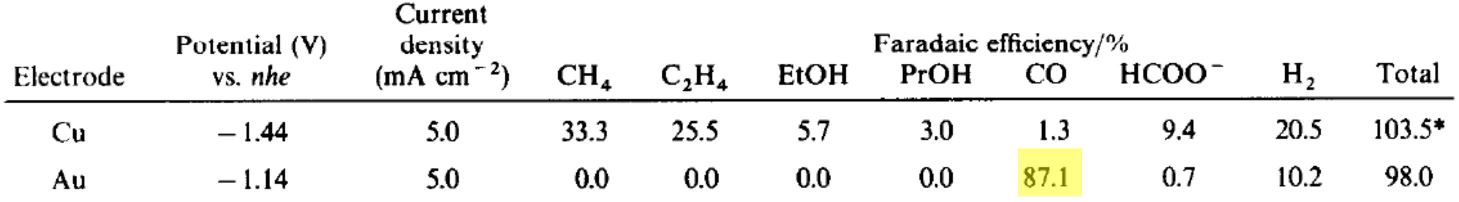
- Scaling in CO_2 reduction is slightly different than scaling in O_2 reduction/ water oxidation.
  - **CO_2 reduction has stable intermediates**
- This allows us to employ a 2-step process.

Cathode #1: $CO_2 + 2e^- + H_2O \rightarrow CO + 2OH^-$

Cathode #2: $xCO + yH^+ + ae^- + \rightarrow C_xH_yO_z$

Anode #1 & #2: $H_2O \rightarrow \frac{1}{2}O_2 + 2H^+ + 2e^-$

- We know how to take CO_2 to CO quite efficiently.

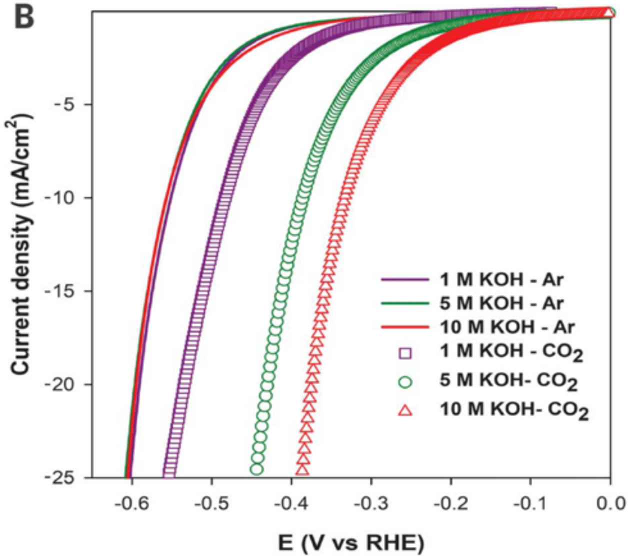


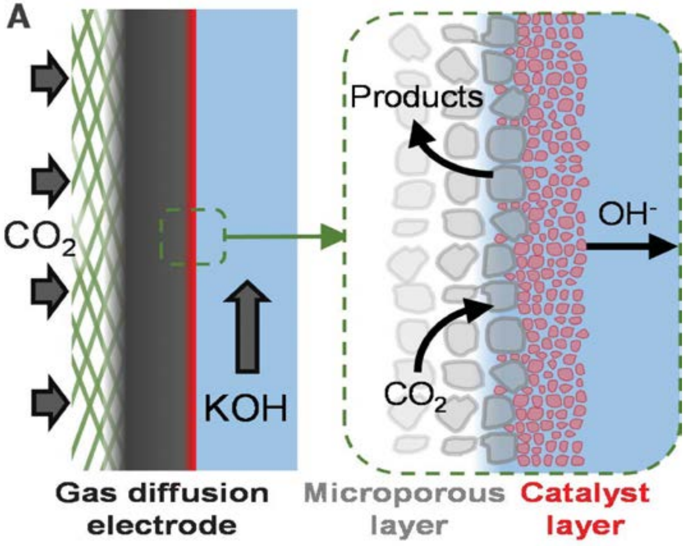
Electrode	Potential (V) vs. *nhe*	Current density (mA cm^{-2})	Faradaic efficiency/% CH_4	C_2H_4	EtOH	PrOH	CO	$HCOO^-$	H_2	Total
Cu	−1.44	5.0	33.3	25.5	5.7	3.0	1.3	9.4	20.5	103.5*
Au	−1.14	5.0	0.0	0.0	0.0	0.0	87.1	0.7	10.2	98.0

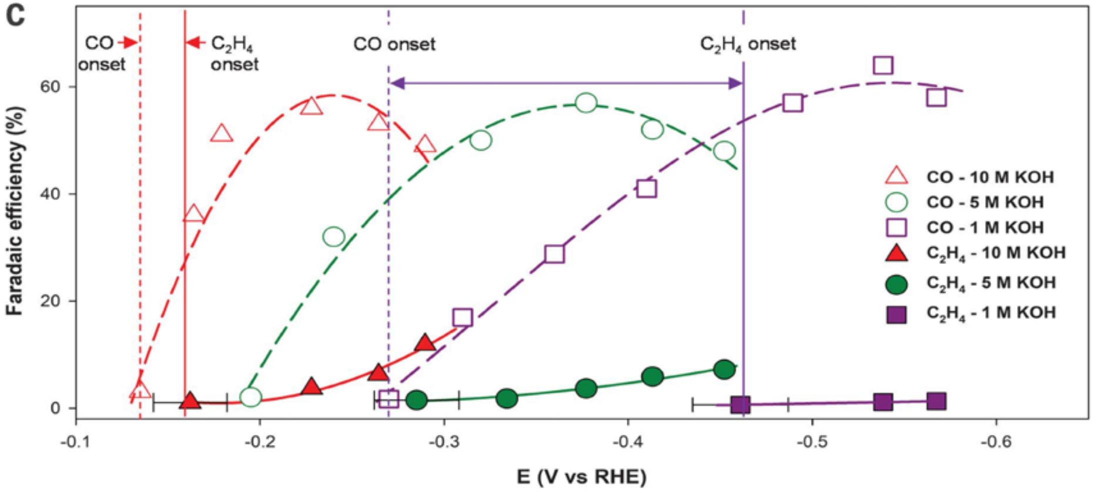
Hori, Y.; et al. Electrochim. Acta., 1994

Breakthrough in the Field

- In May 2018, a fuel cell approach was used that gave very good results.
- This approach gave:
  - Easier mass transfer
  - Eliminated H_2 side products
  - Lower overpotentials







Dingh et al., Science, 2018

Breakthrough in the Field

- CO_2 dissolves in water as carbonic acid, which sets the pH.

$$\left.\begin{array}{l} CO_2 + 2H^+ + 2e^- \rightarrow CO + 2H_2O \\[1em] CO_2 + H_2O + 2e^- \rightarrow CO + 2OH^- \end{array}\right\} \text{Equivalent Equations}$$

- However very high currents will give a basic environment.
- Our limiting step in our reaction mechanism is probably:

$$CO_2 + e^- \rightarrow COO^-$$

- Since there is no H^+/ OH^- in this step, it is pH independent. If we go to high pH, this makes H_2 evolution hard, thus favoring CO_2 reduction over H_2 evolution

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

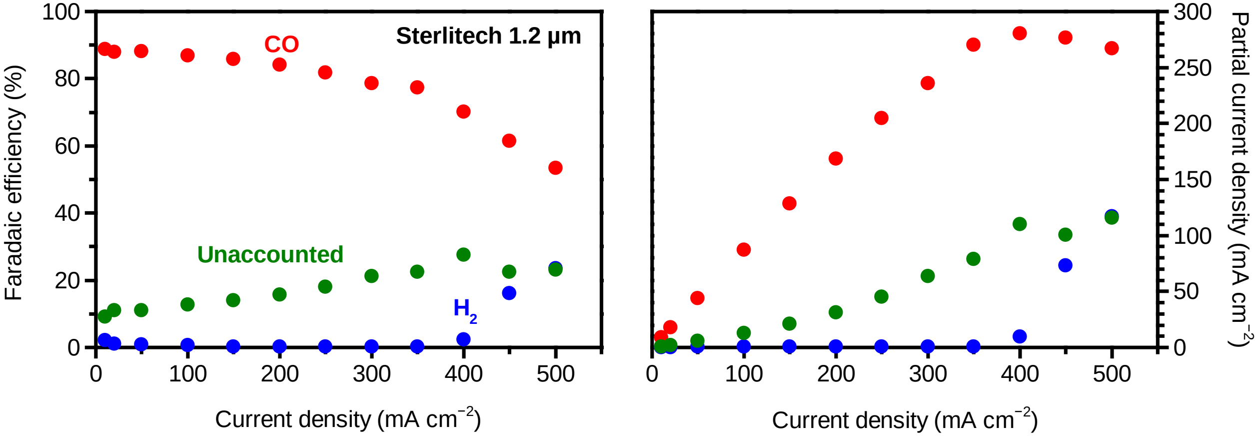
This slide is just a theory and could be wrong, so you will not be tested on it

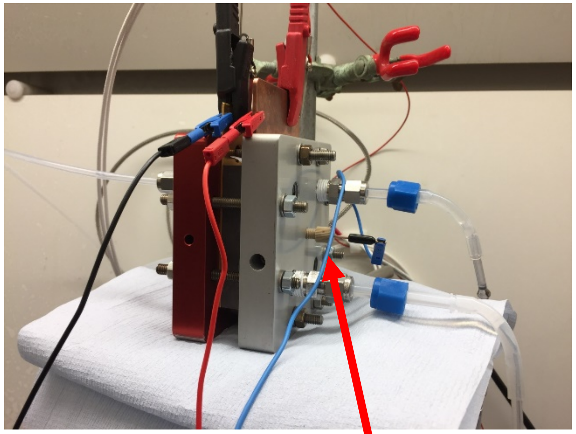
CO_2 Reduction at DTU

- We are studying this from a fundamental standpoint (mechanistically) and a scale up standpoint.

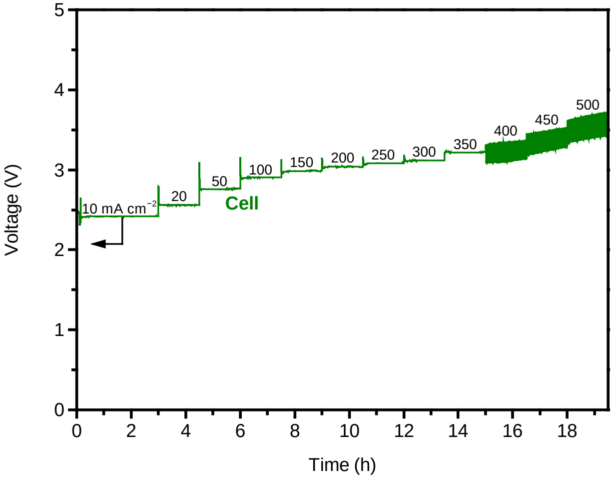
SIEMENS

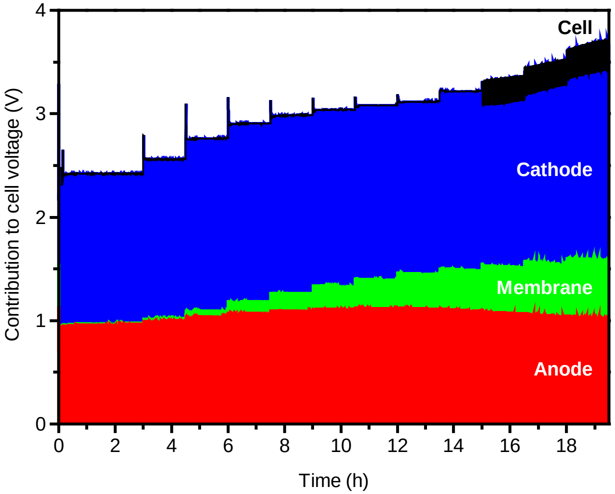
We do have Masters and Bachelor’s projects for the spring





Reference Electrode





CO_2 Reduction - Future

- The field is very active, but still very young. I lead the group at DTU / Stanford working on this.

- CO_2 to Chemicals is promising, but CO_2 to fuels is economically difficult.
- Currently the CO_2 reduction overpotential is around 0.5 V to 1 V for most products, so the efficiency is not good at all.
- Shell, Siemens, Topsoe Catalyst are all actively working in this field.

Learning Objectives

- From this lecture you should be able to understand:
  - The fundamental physics behind electrolyzers.
  - How to improve the efficiency/costs of electrolyzers.
  - The fundamental scientific principles behind CO_2 reduction.

Exercises

- If you are operating at 1 A/cm^2, what is the volumetric production rate of H_2 at 25C and 1bar pressure.
- If we have 100 GW electrolyzers that operate 80% of the time at an efficiency of 90%, how much H_2 can be produced in 1 year. If all the world's energy consumption (11.8 TW) is from electricity produced by a fuel cell (operated at 0.8V), how long can the world run solely on our annual H_2 production.

Exercises

- Let say you want to reduce CO_2 to methanol. if the O_2 evolution has 300 mV and the CO_2 reduction has 500 mV overpotential, what is your overall efficiency? Does efficiency depend on current? Explain.

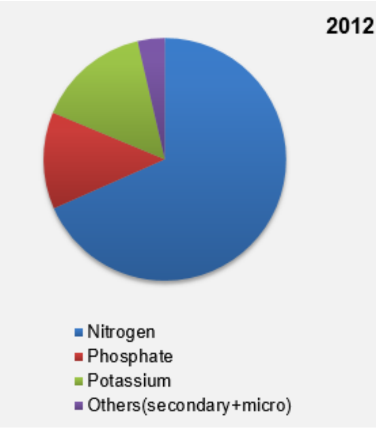
Bonus Slides

(not on test)

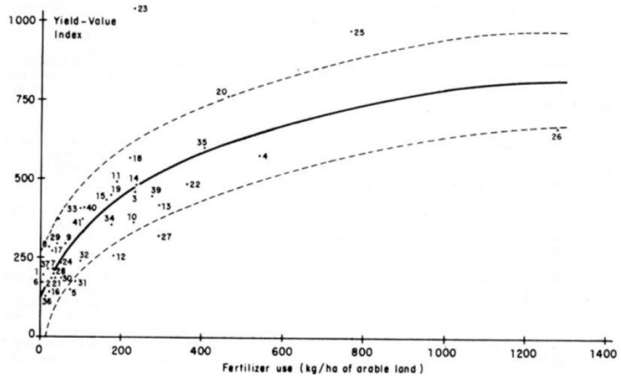
Nitrogen reduction

Fertilizers

- The majority of fertilizers are NH_3 or NH_3 based.
- Fertilizers have allowed incredible increases in productivity.
- Cheap food, allows for population growth.
- NH_3 production is based off of fossil fuels.
- 1.2 % of world's energy goes to NH_3 production.

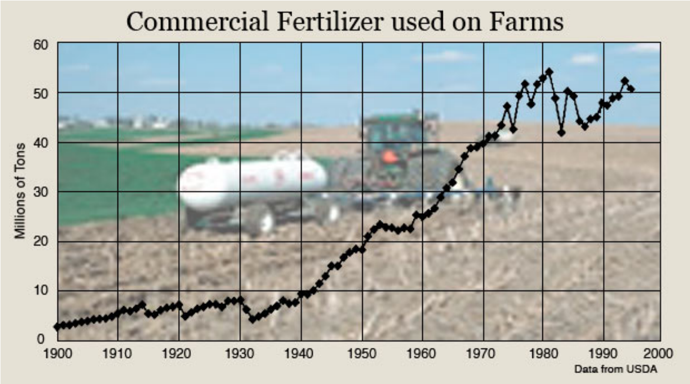


Crop Yield



Fertilizer amount

FAO, Bulletin, 1981



Based of USDA data

N_2 reduction

- Ammonia production is made almost exclusively be the Haber-Bosch process.
- This consumes 1-2 % of the world's energy.

$$N_2 + 3H_2 \rightarrow 2NH_3 \qquad \Delta\mathrm{H} = -\ 92.4\ \mathrm{kJ/mol}$$

- The reaction is thermodynamically favored, but kinetically hindered.
- N_2 has a triple bond which is very hard to break.
- This conversion is typically conducted at a pressure of 150–250 bar and a temperature of 400–500 °C.

Electrochemical N_2 reduction

- Researchers are now trying to electrochemically reduce N_2 to ammonia.

Anode: $3(H_2 \rightarrow +2H^+ \ + 2e^- \ )$

PEM fuel cell anode reaction

Cathode: $N_2 + 6e^- + 6H^+ \rightarrow 2NH_3$

Overall: $N_2 + 3H_2 \rightarrow 2NH_3$

- There have been many reports of this reaction occuring, but few (if any) have reproducable results.
- The difficulty is breaking the nitrogen triple bond.
- However the nitrogense enzyme does this reaction (albeit at 50% selectivity), so it is possible.
- We are currently working on this at DTU.