

# Electrocatalysis

# Learning objectives

After this lecture you will be able to:

- Identify the difference between thermally activated and electro-catalysis
- Evaluate the influence of potential and pH on the thermodynamics in electrocatalysis
- Assess the activity of an electrocatalyst based on the limiting potential
- Explain the steps in HER and OER and the challenge in optimizing them
- Estimate currents in electrocatalysis at given (over-)potential and pH

Join at [menti.com](https://menti.com) | use code 2156 2798

 **Mentimeter**

# Think about aspects of society and technology where using electrochemistry has helped or would help sustainability

40 responses



# Why is electrochemistry becoming more and more attractive?

## Storage:

(Renewable) energy sources can be stored

## Production:

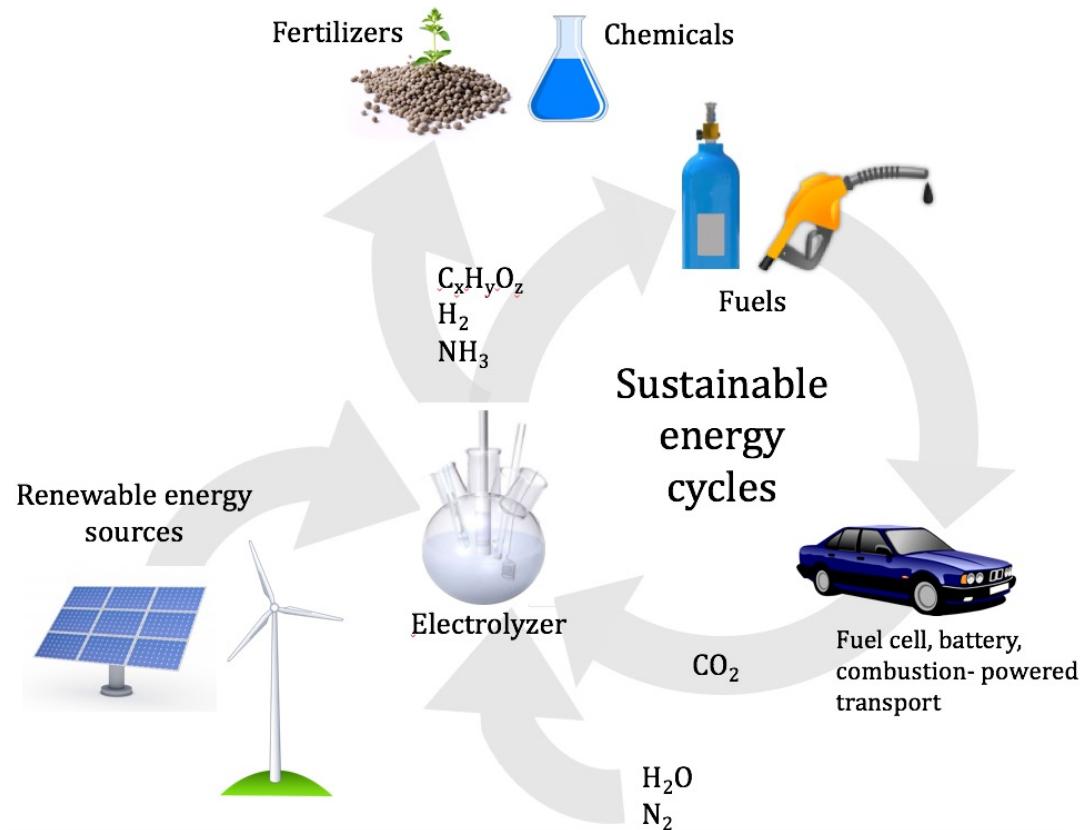
Fuels and chemicals can be produced out of waste and electrical energy

## Fuel use:

Fuels can be "burned" producing electricity instead of heat

## Decentralization:

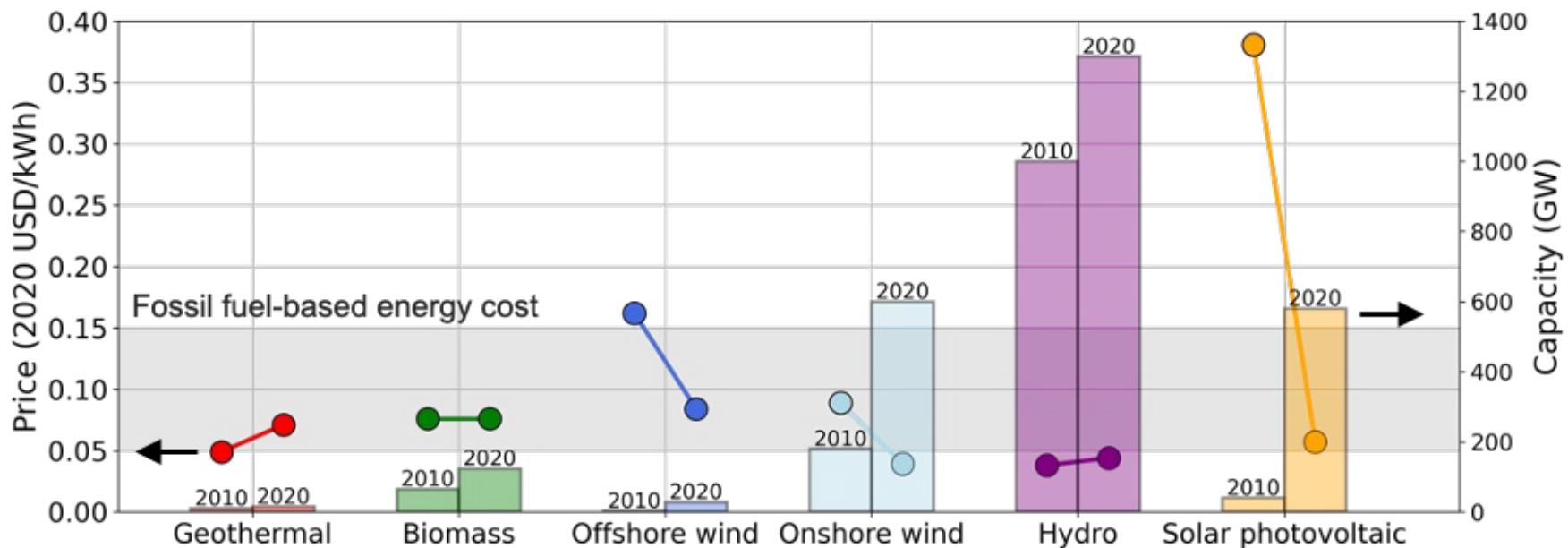
Small decentralized setups can be used rather than large thermal and pressurized plants



# Decreasing power cost from wind & solar helps electrochemistry

Both infrastructure and technology for renewable electricity is constantly upgraded!

Storing the excess energy within chemicals becomes more and more attractive!

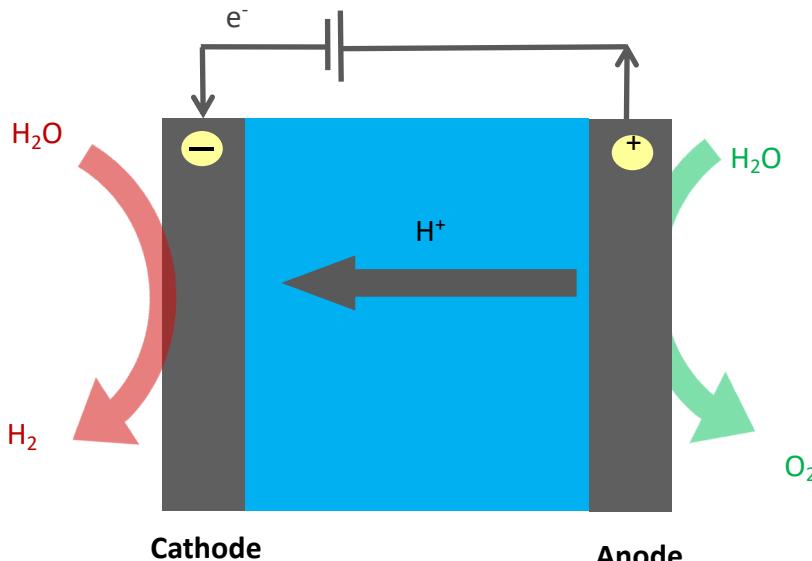


# Electrochemistry - Definition

Charge transfer reactions at the interface between an **electronic conductor (the electrode)** and an **ionic conductor (the electrolyte)**

Redox reactions can be performed on separate electrodes rather than directly, thus **we can mix any oxidation (e<sup>-</sup> are output) with any reduction (e<sup>-</sup> are input).**

The redox reactions can be directed by either **extracting (spontaneous)** or **applying (non-spontaneous)** voltage/energy



# Examples of Electrochemical Devices and Processes

## Traditional



Corrosion

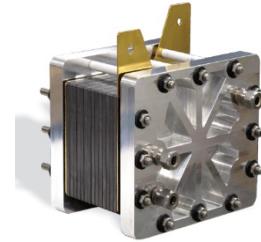


Anodization



Electroplating

## Sustainable Energy



Fuel cells



Batteries



Electrolysis

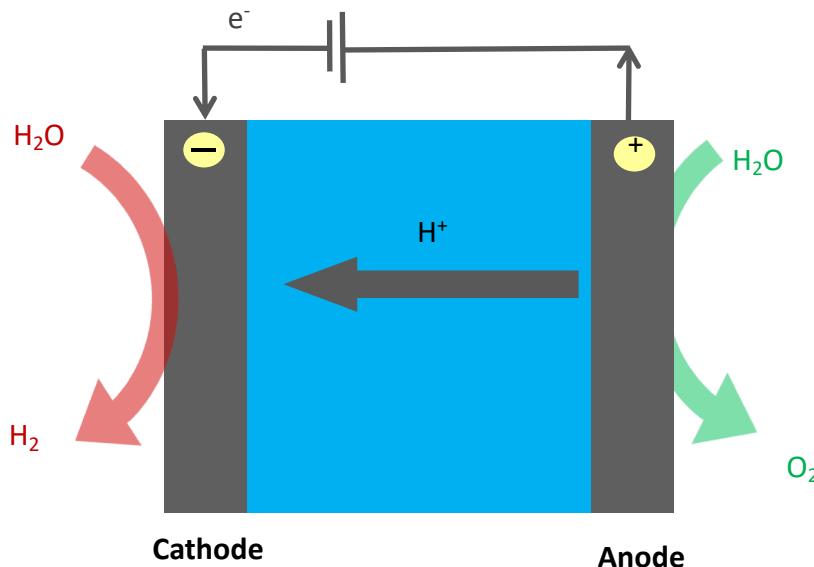
Hands up: Which devices perform electrocatalysis and why?

# Electrocatalysis - Definition

Electrocatalysis is a specialized area in electrochemistry focused on the **use of catalysts to modify the rates of electrochemical reactions**.

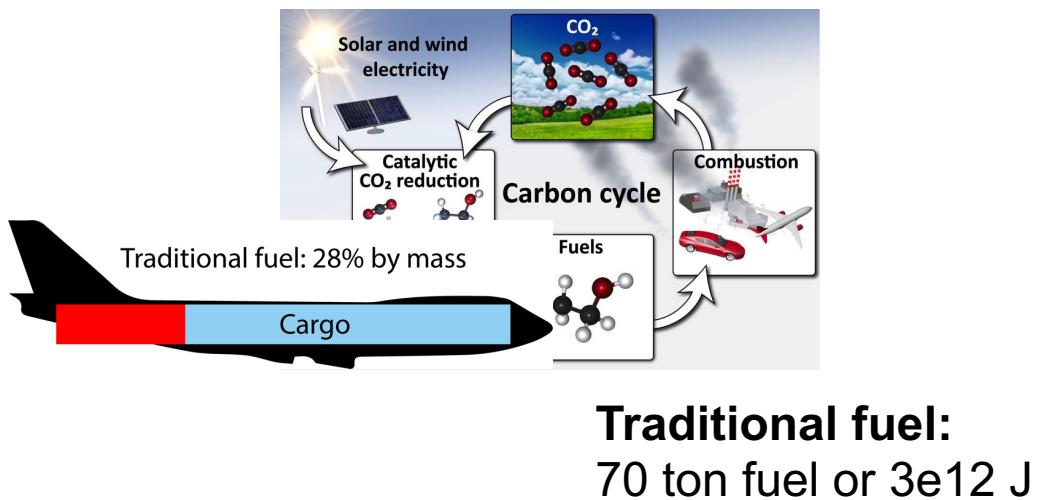
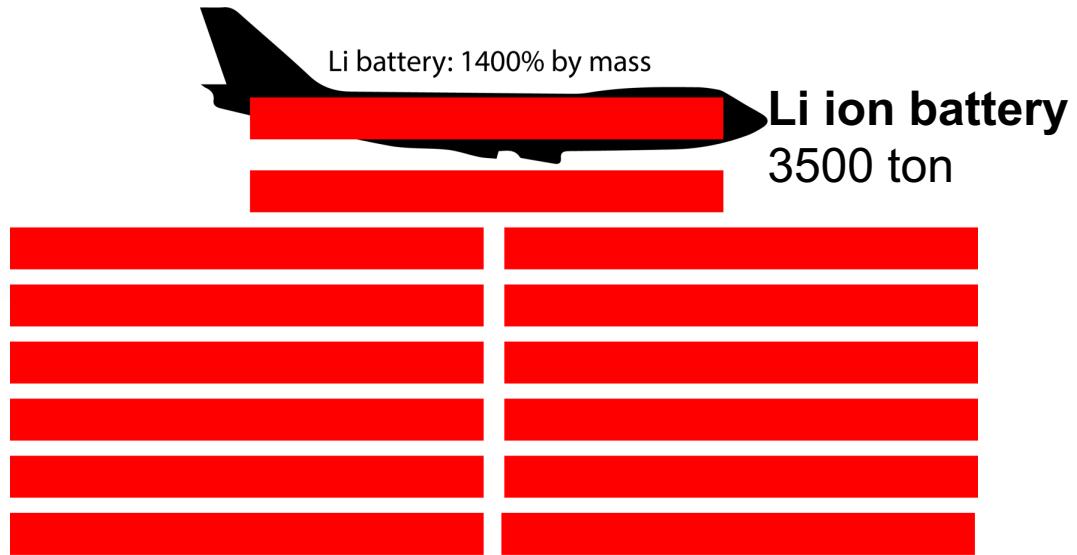
An **electrocatalyst promotes electrochemical reactions** as the electrode or being in contact with the electrode.

Electrocatalysis allows **continuous application** as the overall reactants and products are fed in and leave the catalyst surface (In contrast to battery)

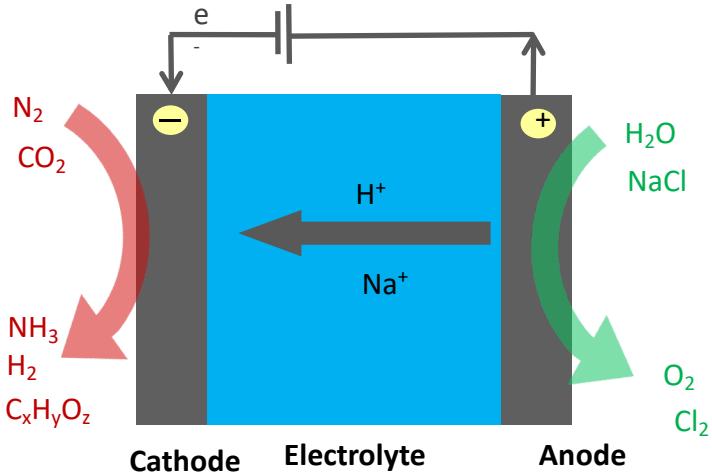


# Why not use batteries everywhere?

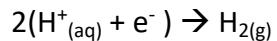
- Batteries
  - + Existing technology
  - + High efficiency
  - New infrastructure needed
  - **Low energy density**
- Synthetic fuels
  - + High energy density
  - + Existing infrastructure
  - + Basis for sustainable chemical industry
  - **Low efficiency**



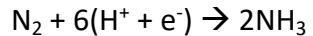
# Half reactions let us mix and match what we want!



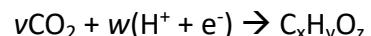
## Hydrogen evolution



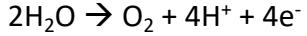
## N<sub>2</sub> reduction



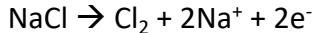
## CO<sub>2</sub> reduction



## Oxygen evolution



## Chlorine evolution



## Biomass and waste oxidation



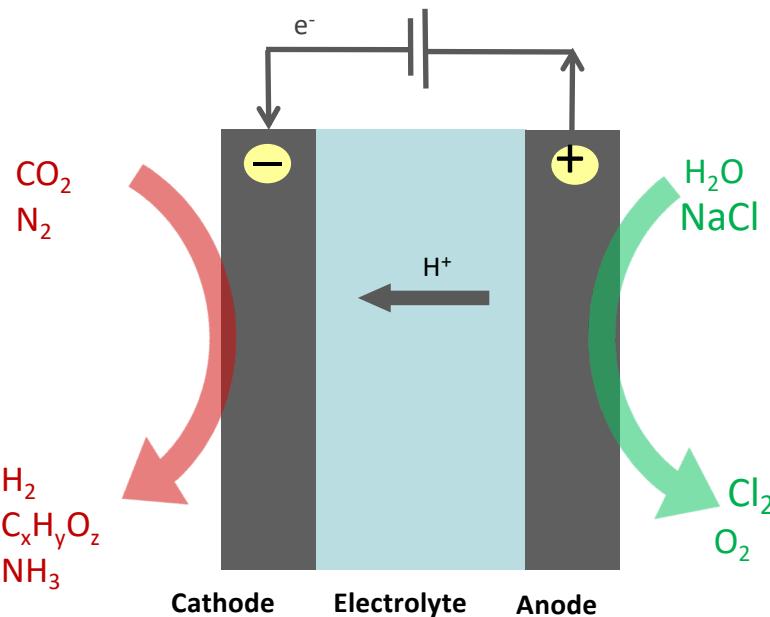
We can only combine a  
reduction (electrons are input)

and an  
oxidation (electrons are output)

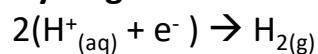
Each one of these examples need  
different working potentials.

# Electrocatalytic devices

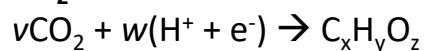
**Electrolyzers**  
for fuel and chemical production  
(Non-spontaneous.  $\Delta G > 0$ )



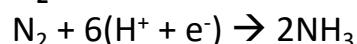
## Hydrogen evolution



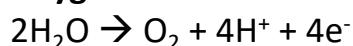
## CO<sub>2</sub> reduction



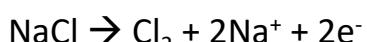
## N<sub>2</sub> reduction



## Oxygen evolution



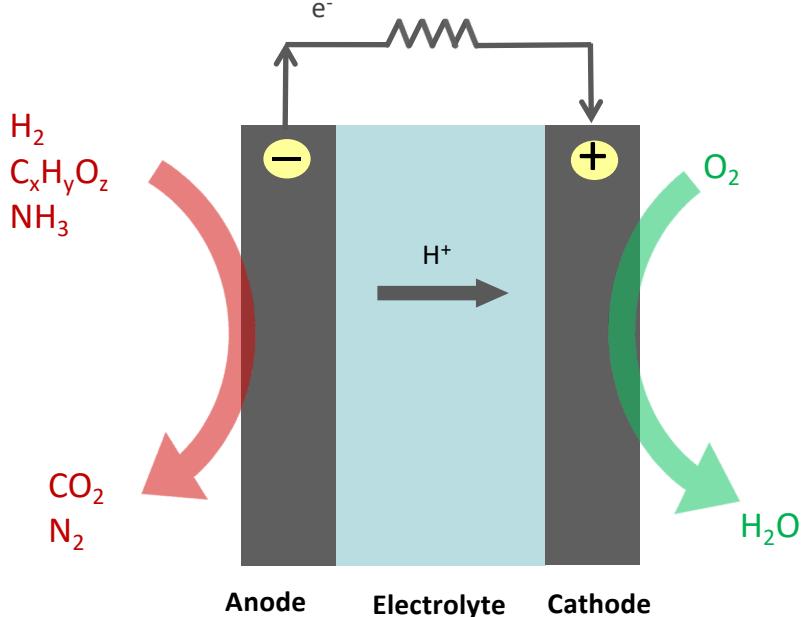
## Chlorine evolution



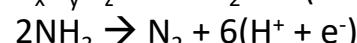
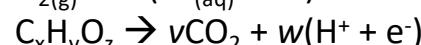
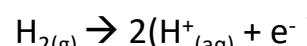
## Biomass and waste oxidation



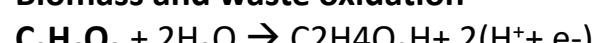
**Fuel cells**  
as energy source  
(Spontaneous,  $\Delta G < 0$ )



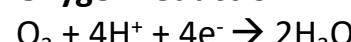
## Fuel oxidation



## Biomass and waste oxidation



## Oxygen reduction



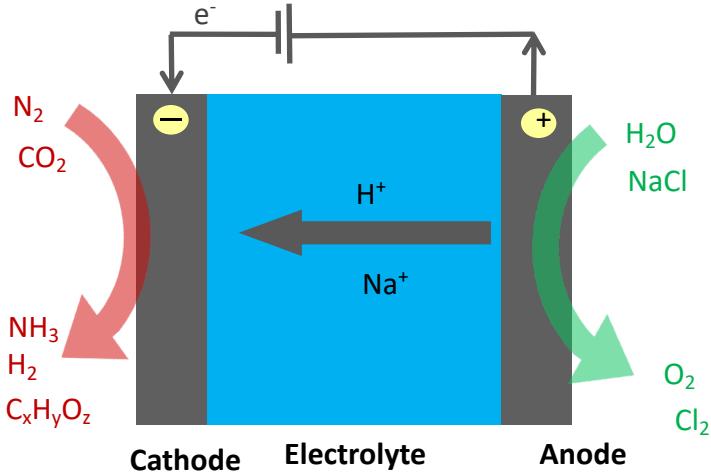
# Differences to gas-surface catalysis

What are the major differences between electrocatalysis and thermally activated catalysis?

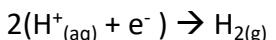
Discuss with neighbor (3min)

Your suggestions:

1.



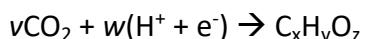
**Hydrogen evolution**



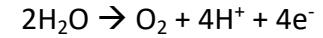
**N<sub>2</sub> reduction**



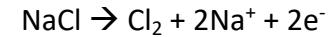
**CO<sub>2</sub> reduction**



**Oxygen evolution**



**Chlorine evolution**

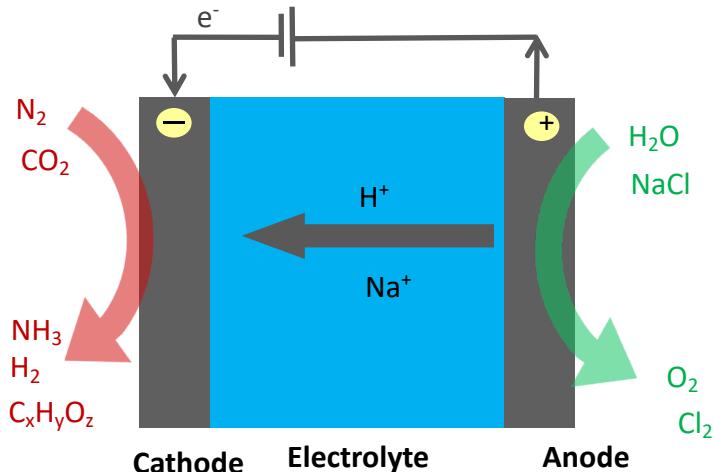


# Differences to gas-surface catalysis

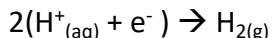
What are the major differences between electrocatalysis and thermally activated catalysis?

*My suggestions:*

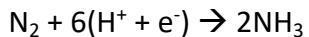
1. There is always **two reactions happening simultaneously, but spatially separated** (oxidation+ reduction)
2. **Protons and electrons** are directly involved in the reactions
3. Changes of **Voltage and pH tune activity** rather than temperature and pressure
4. Reactions happen at a **solid|electrolyte interface** rather than a solid|gas interface



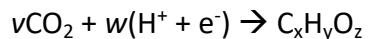
**Hydrogen evolution**



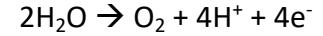
**N<sub>2</sub> reduction**



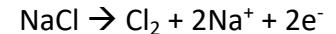
**CO<sub>2</sub> reduction**



**Oxygen evolution**



**Chlorine evolution**



# Why electro vs thermo-catalysis?

$$\Delta G_f^\circ (\text{H}_2\text{O}) = -2.46 \text{ eV}$$



$$\Delta G_f^\circ (\text{O}_2) = \Delta G_f^\circ (\text{H}_2) = 0 \text{ eV}$$

What value of  $p(\text{H}_2\text{O})$  do we need to reach equilibrium?  
( $T=300\text{K}$ ,  $p(\text{O}_2)=p^0$ ,  $p(\text{H}_2\text{O})=p^0$ ,  $p^0(\text{H}_2)=1\text{bar}$   $k_B T=0.025\text{eV}$ )

$$\Delta G = -2\Delta G_f^\circ (\text{H}_2\text{O}) + k_B T \left( \ln \left( \frac{p(\text{O}_2)}{p^0} \right) + 2 \ln \left( \frac{p(\text{H}_2)}{p^0} \right) - 2 \ln \left( \frac{p(\text{H}_2\text{O})}{p^0} \right) \right)$$

$$p(\text{H}_2\text{O}) = e^{-\frac{\Delta G_f^\circ (\text{H}_2\text{O})}{2k_B T}} = 3.5 * 10^{20} \text{ bar}$$

At room temperature, we can reach equilibrium for the reaction by either  
**increasing  $p(\text{H}_2\text{O})$  by 20 orders of magnitude**  
or  **$U=1.23\text{V}$  (less than an AA battery)**

**The electrode potential is a pretty strong driving force!**

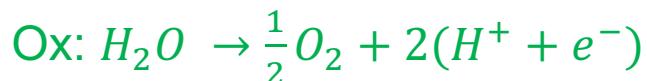
# Cell potentials

Cell potential defines the voltage gotten from batteries or needed in electrolyzers  
It is tightly bound to the thermodynamics of the overall reaction

$$U_{cell} = U^c - U^a = \frac{-\Delta G}{nF}$$

Faraday's Constant :  
 $F = 96485 \text{ C/mol}$

$\Delta G^0 > 0$ : Reaction is non – spontaneous



$$U_{cell} = -1.23 \text{ V}$$

$\Delta G^0 < 0$ : Reaction is spontaneous



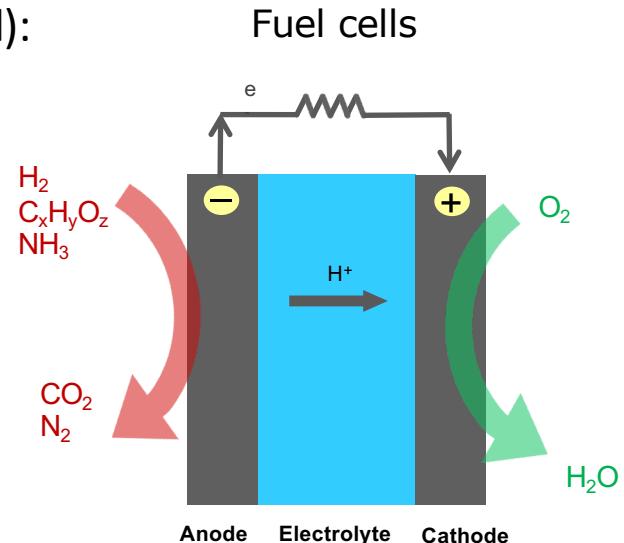
$$U_{cell} = 1.23 \text{ V}$$

# Condition for spontaneity:

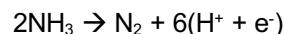
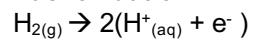
- Spontaneous e- flow (**galvanic cell, batteries, fuel cell**):

$$\Delta G < 0, U_{cell} > 0$$

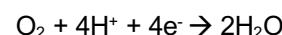
Chemical → electrical energy



Fuel oxidation



Oxygen reduction



# Condition for spontaneity:

- Spontaneous e- flow (**galvanic cell, batteries, fuel cell**):

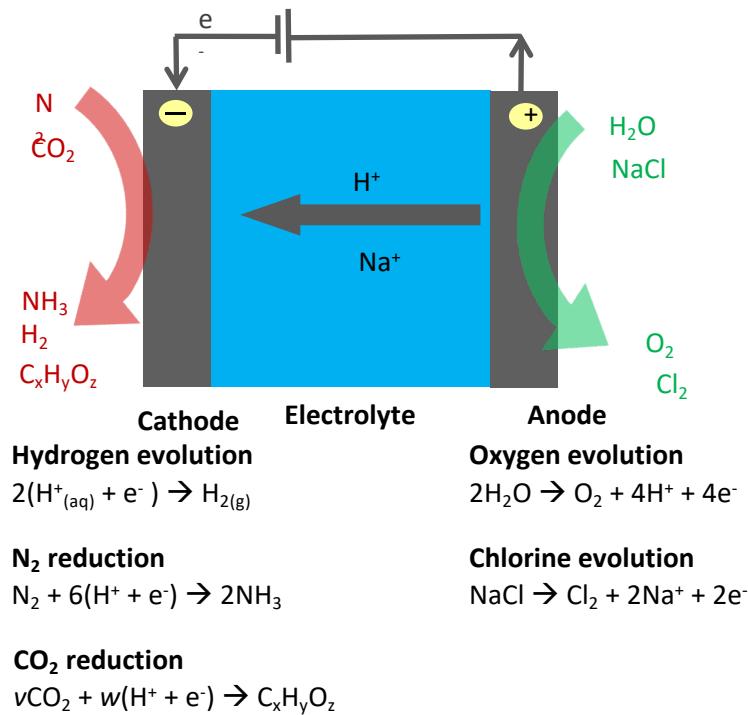
$$\Delta G < 0, U_{cell} > 0$$

Chemical → electrical energy

- Need applied voltage (**electrolytic cell**)

$$\Delta G > 0, U_{cell} < 0$$

Electrical → chemical energy





# What does it mean that protons and electrons are directly involved in reactions?

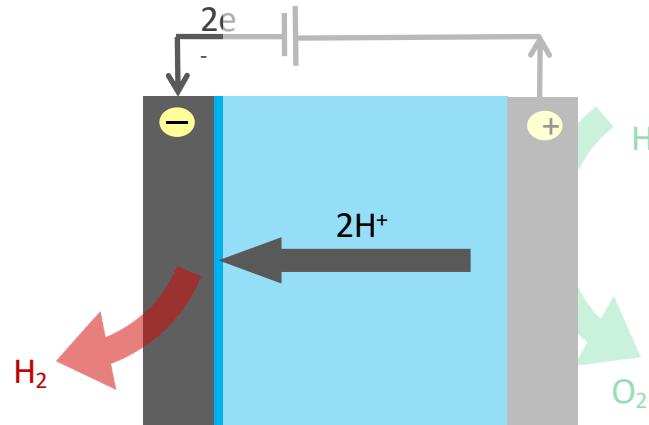
The hydrogen evolution reaction (HER):



Define the free energy change in the reaction:

$$\Delta G = \mu_{\text{H}_2} - 2(\mu_{\text{e}^-} + \mu_{\text{H}^+})$$

What defines  $\mu_{\text{e}^-}$  and  $\mu_{\text{H}^+}$  ?



$\mu_{\text{e}^-}$  is linearly proportional to the electrode potential:  $\partial \mu_{\text{e}^-} / \partial U = -1 \text{ eV/V}$

$\mu_{\text{H}^+}$  is proportional to the proton concentration, pH:  $\frac{\partial \mu_{\text{H}^+}}{\partial \text{pH}} = -\ln(10) k_B T \approx -60 \text{ meV/pH}$

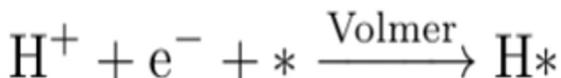
Variations in potential and pH directly change  $\Delta G$ !

$\mu$ =chemical potential=free energy per unit amount

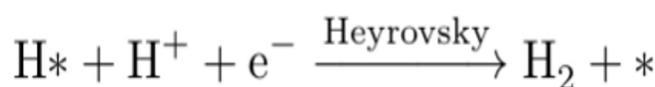
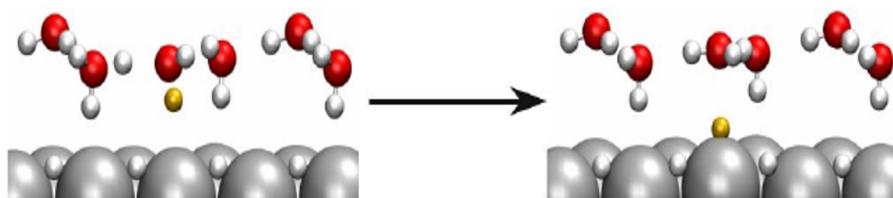
# The hydrogen evolution reaction



Catalysis happens in elementary steps



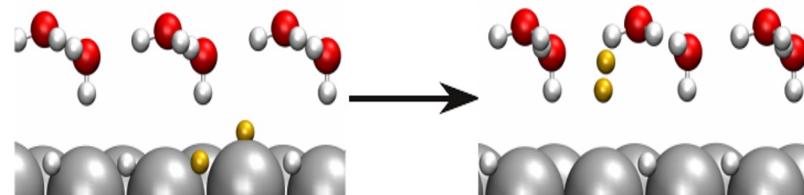
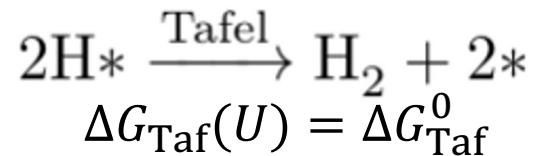
$$\Delta G_V(U) = \Delta G_V^0 + e(\textcolor{blue}{U} + k_B T \ln(10) pH)$$



$$\Delta G_{\text{Hey}}(U) = \Delta G_{\text{Hey}}^0 + e(\textcolor{blue}{U} + k_B T \ln(10) pH)$$



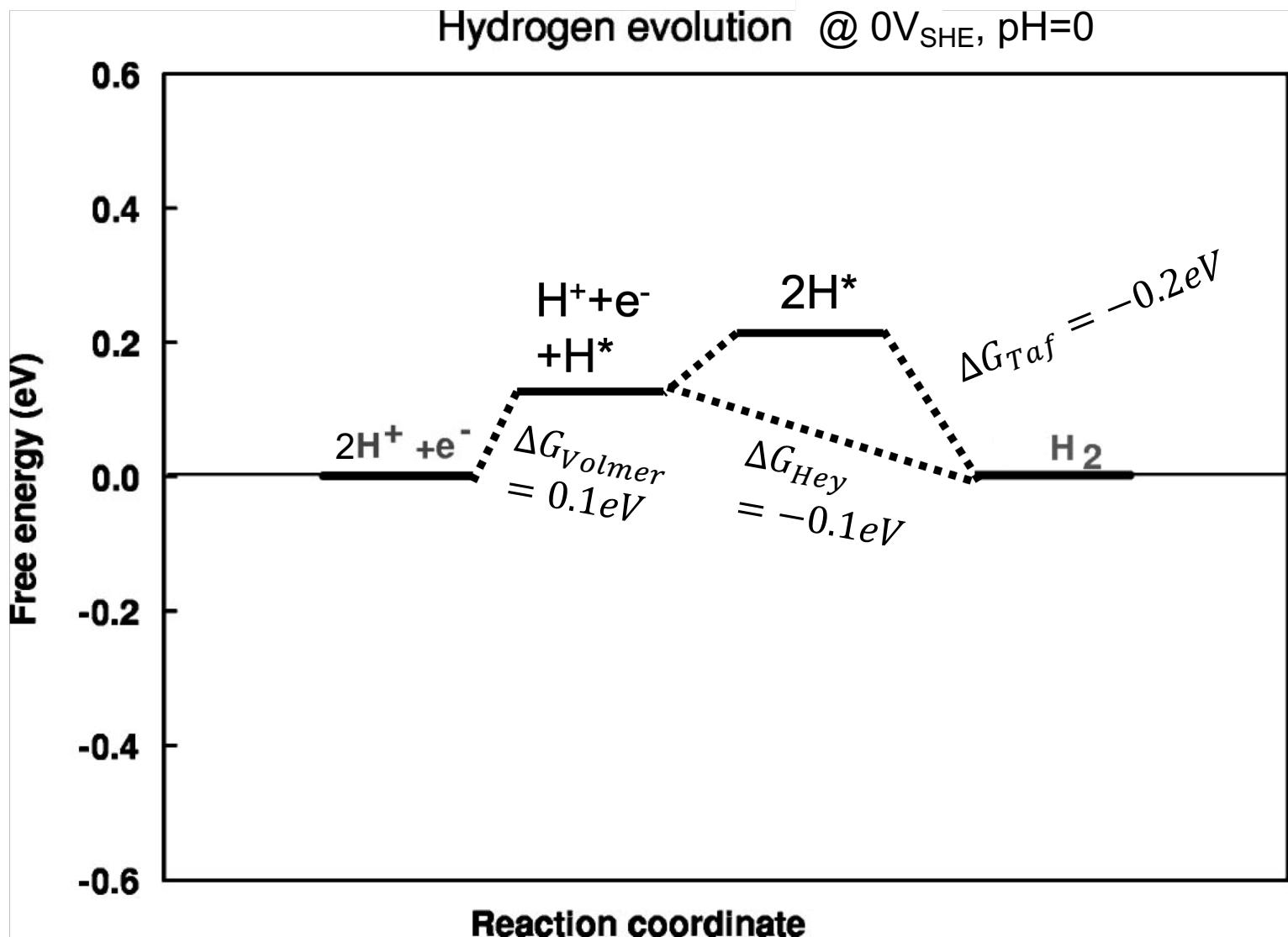
Volmer and Heyrovsky steps are  
electrochemical  
(protons and electrons are involved)



Tafel step is  
non-electrochemical  
(no electron involved)

Tafel must be preceded by  
**two** Volmer reactions

# Free energy diagram of HER



# Free energy diagram of HER

How does the FED look like at

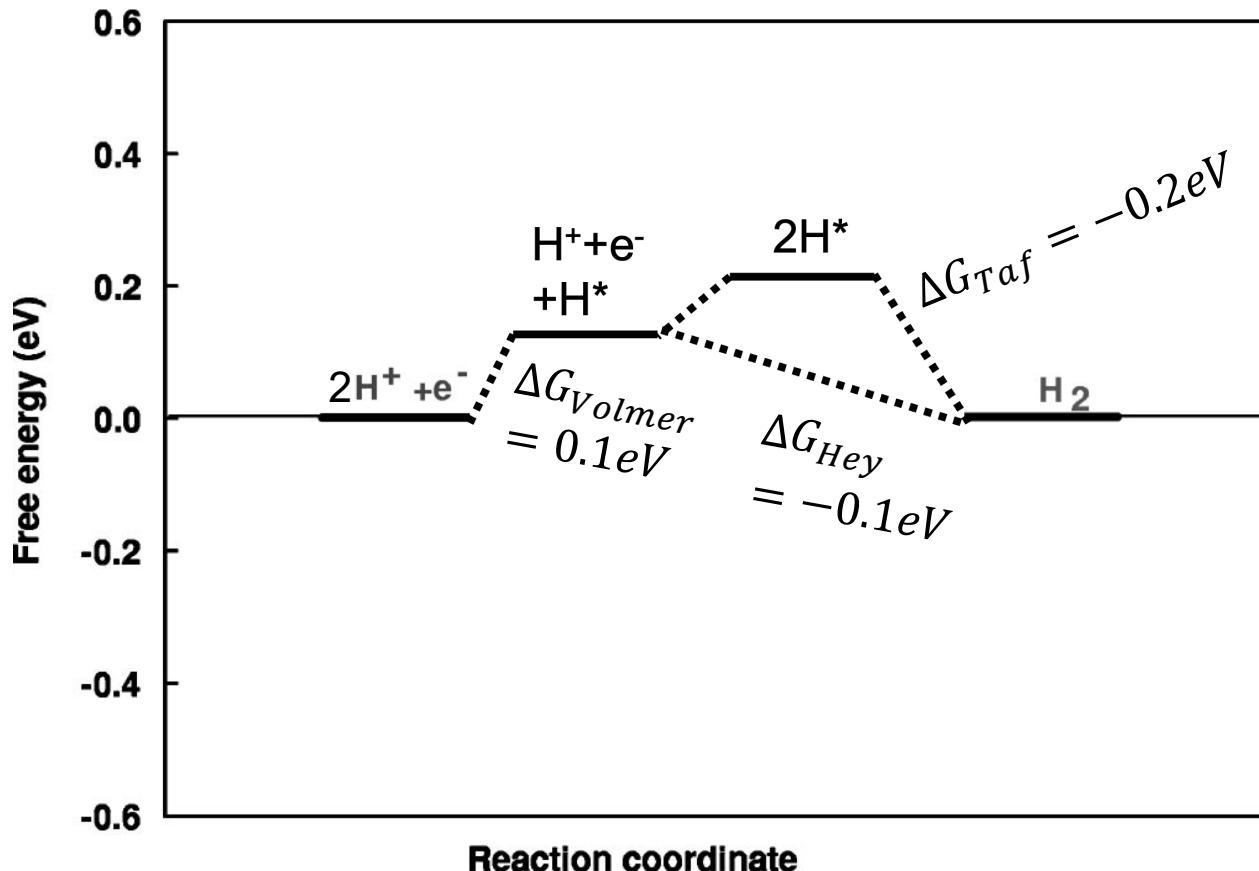
- a)  $-0.1V_{\text{SHE}}$ , pH5, b)  $-0.4V_{\text{RHE}}$ , pH=5  
(Quick math: 5 min)

Remember:

$$\frac{\partial \mu_{e^-}}{\partial U} = -1 \text{ eV/V}$$

$$\frac{\partial \mu_{H^+}}{\partial pH} \approx -60 \text{ meV/pH}$$

Hydrogen evolution @  $0V_{\text{SHE}}, \text{pH}=0$



# Free energy diagram of HER

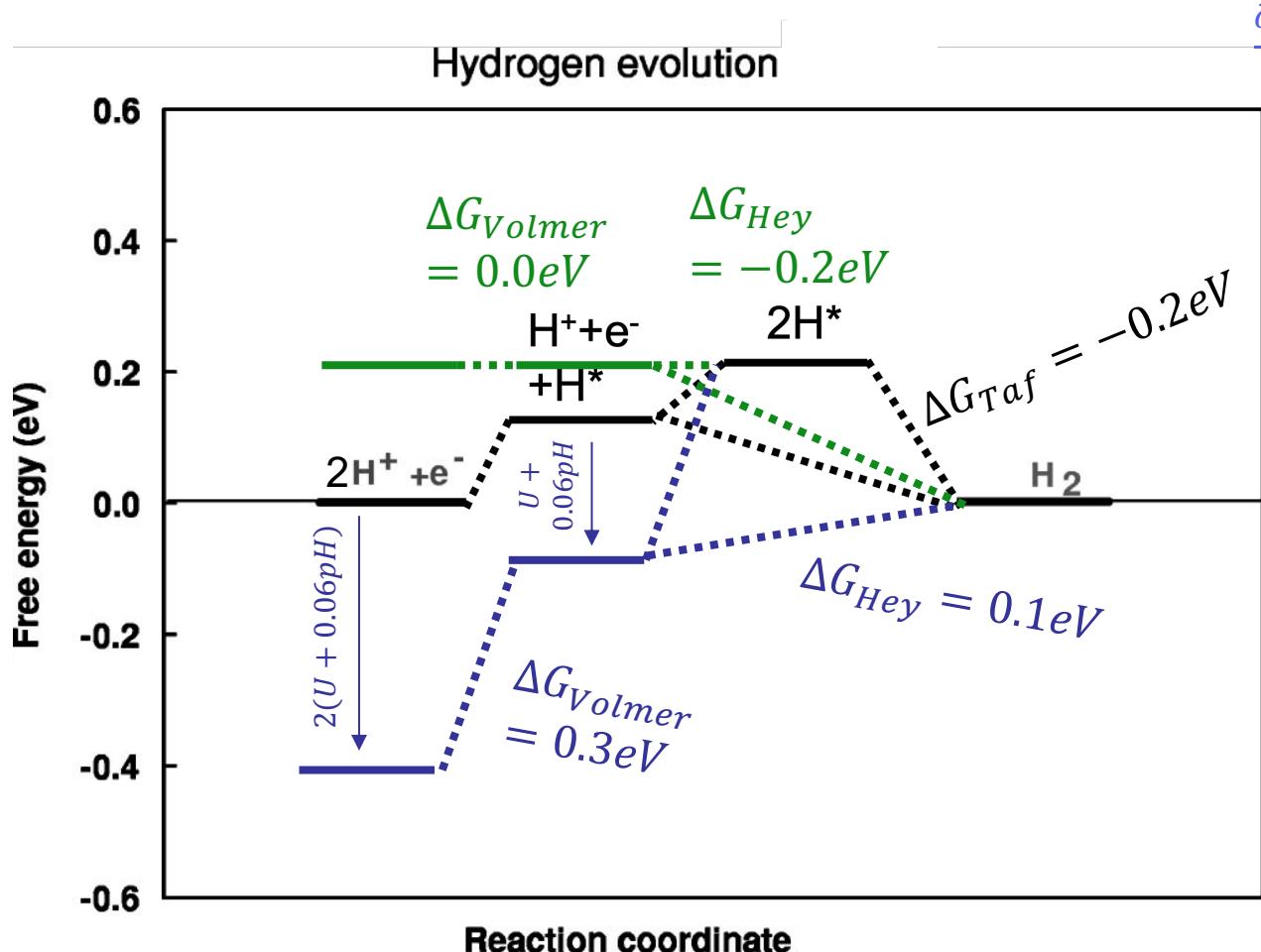
How does the FED look like at

a)  $-0.1V_{\text{SHE}}$ , pH=5, b)  $-0.4V_{\text{SHE}}$ , pH=5

Remember:

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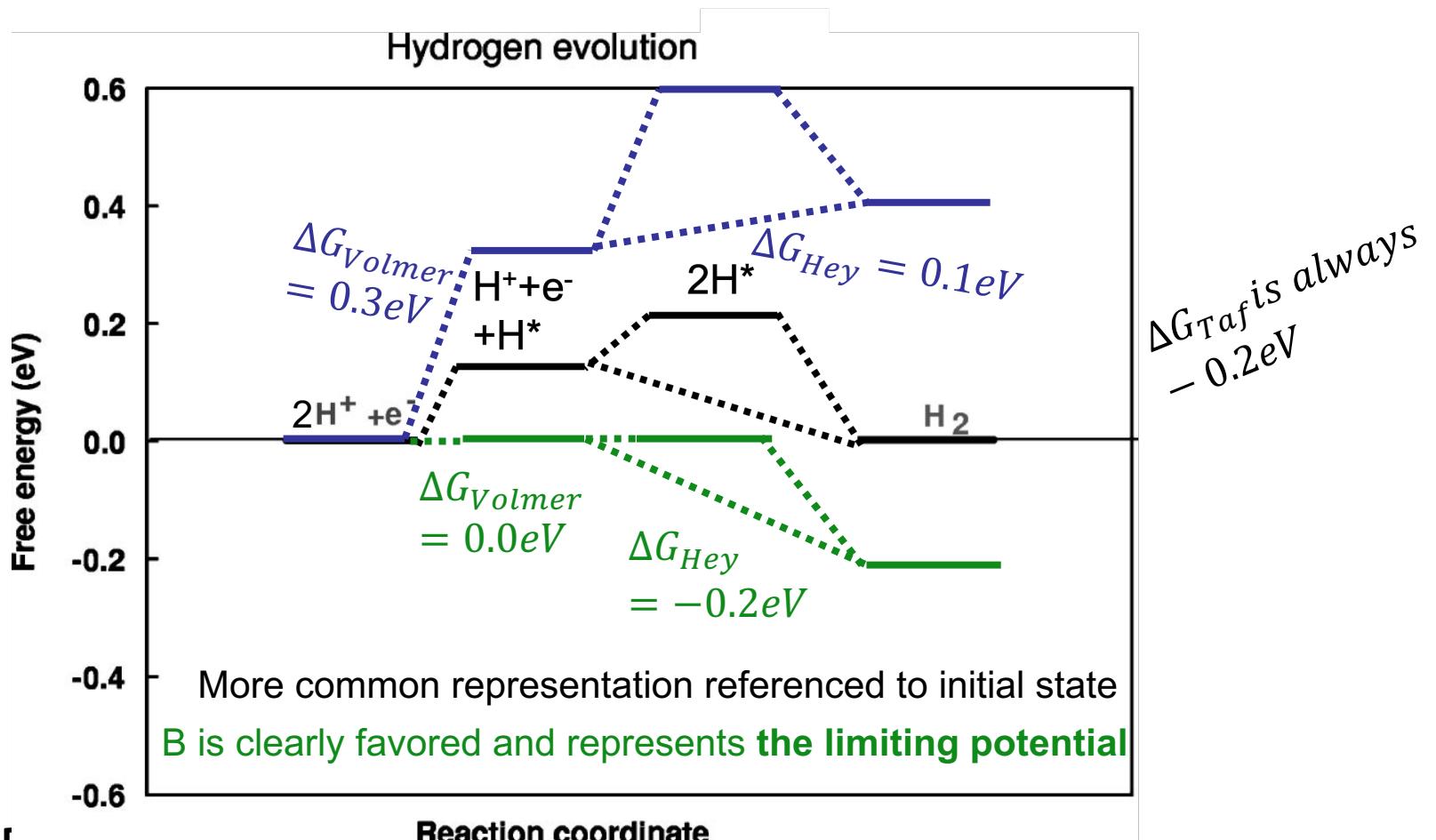


Hands up! Which conditions have better activity?

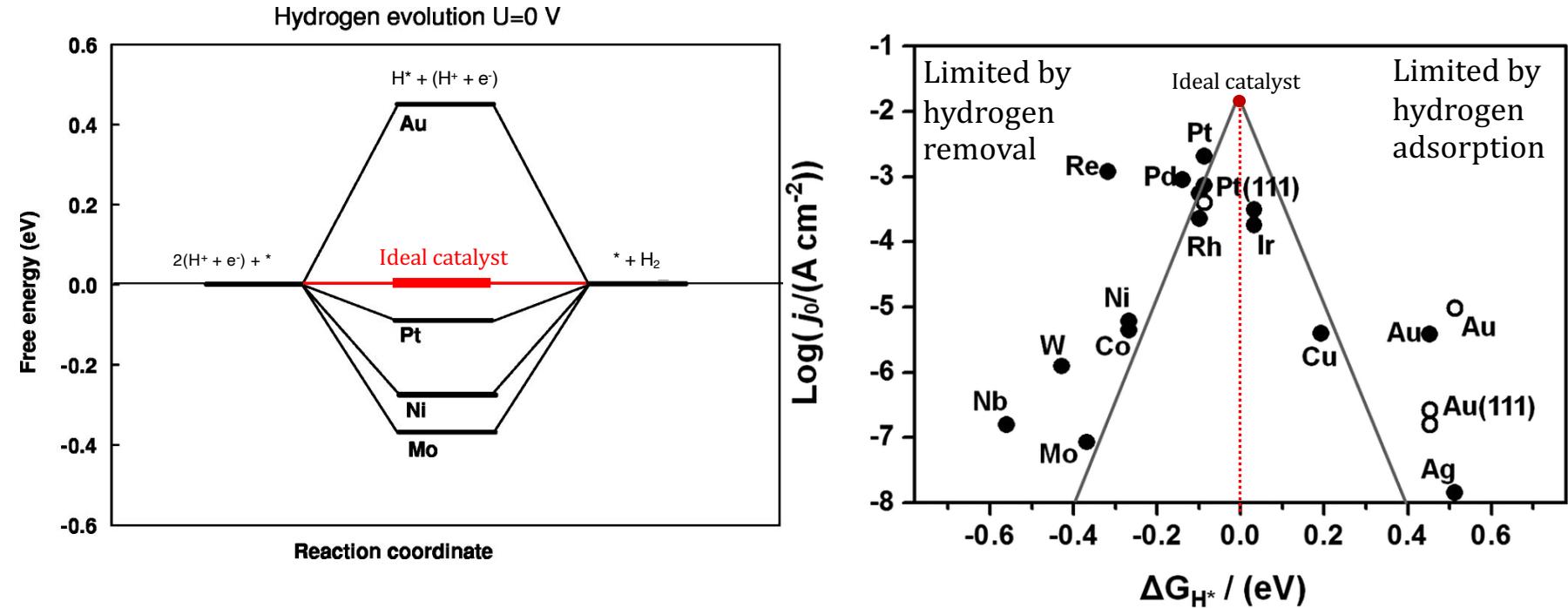
# Free energy diagram of HER

How does the FED look like at

a)  $-0.1V_{SHE}$ , pH5, b)  $-0.4V_{SHE}$ , pH=5



# The ideal electrocatalyst for HER



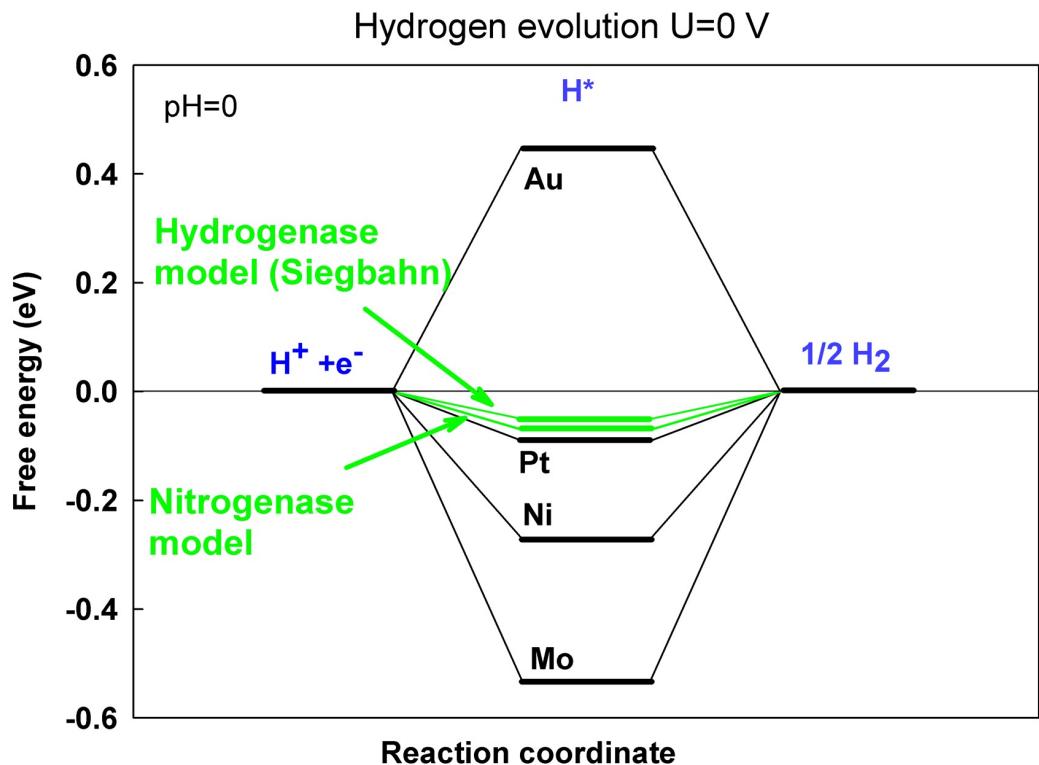
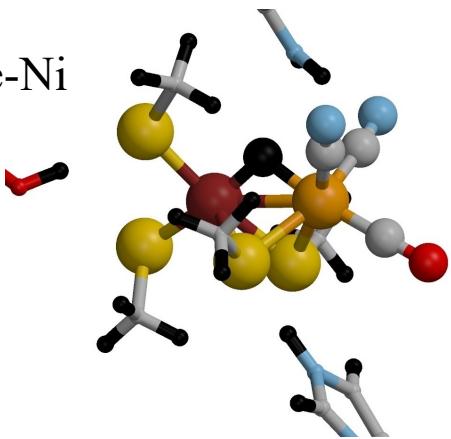
$\Delta G_H$  can be used as an activity descriptor; follows trends in experimentally determined  $j_o$   
Pt based materials near top of volcano,  $\Delta G_H \sim 0$

# Other HER catalysts

Hydrogenases:

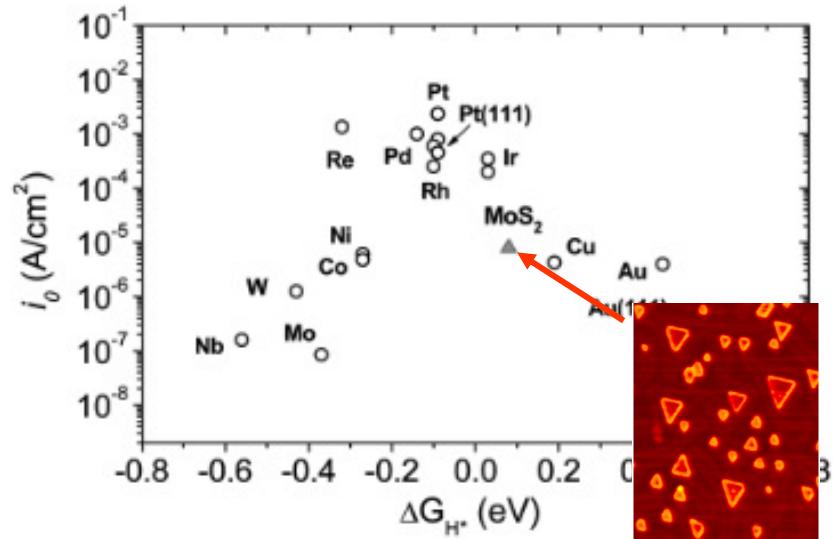
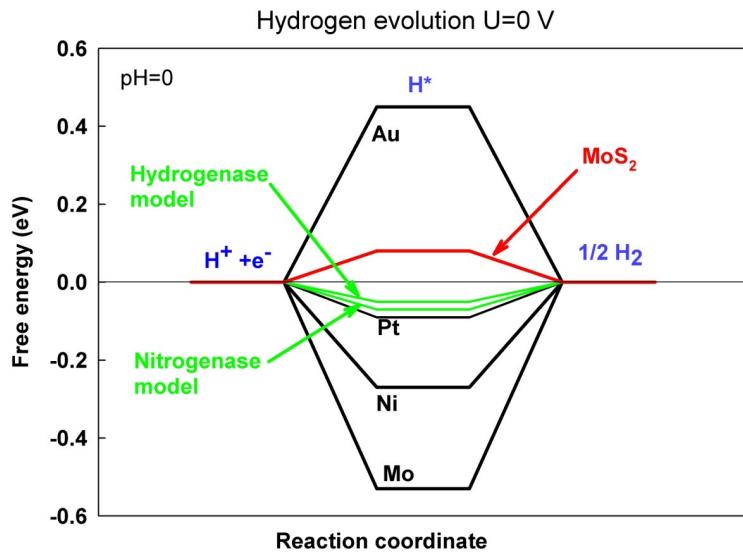
(Enzymes that produce H<sub>2</sub> out of protons and electrons):

H binds to bridging Fe-Ni site



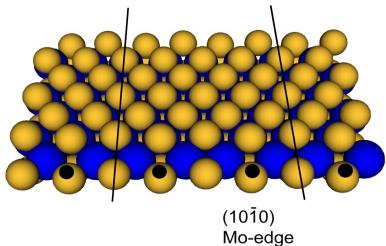
Siegbahn, Adv. Inorg. Chem. **56**, 101 (2004)  
Hinnemann, Nørskov, JACS **126**, 3920 (2004)

# Other HER catalysts



Jaramillo, Jørgensen, Bonde, Nielsen, Horch, Chorkendorff, Science **317** (2007)

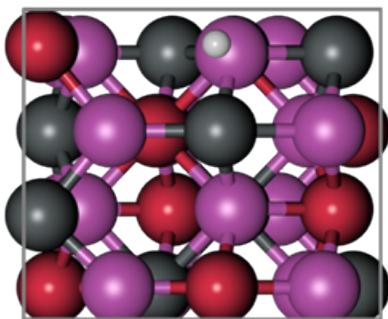
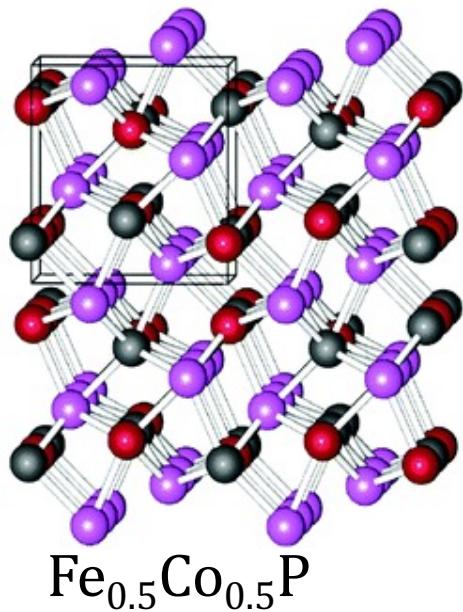
MoS<sub>2</sub>: an inorganic analogue



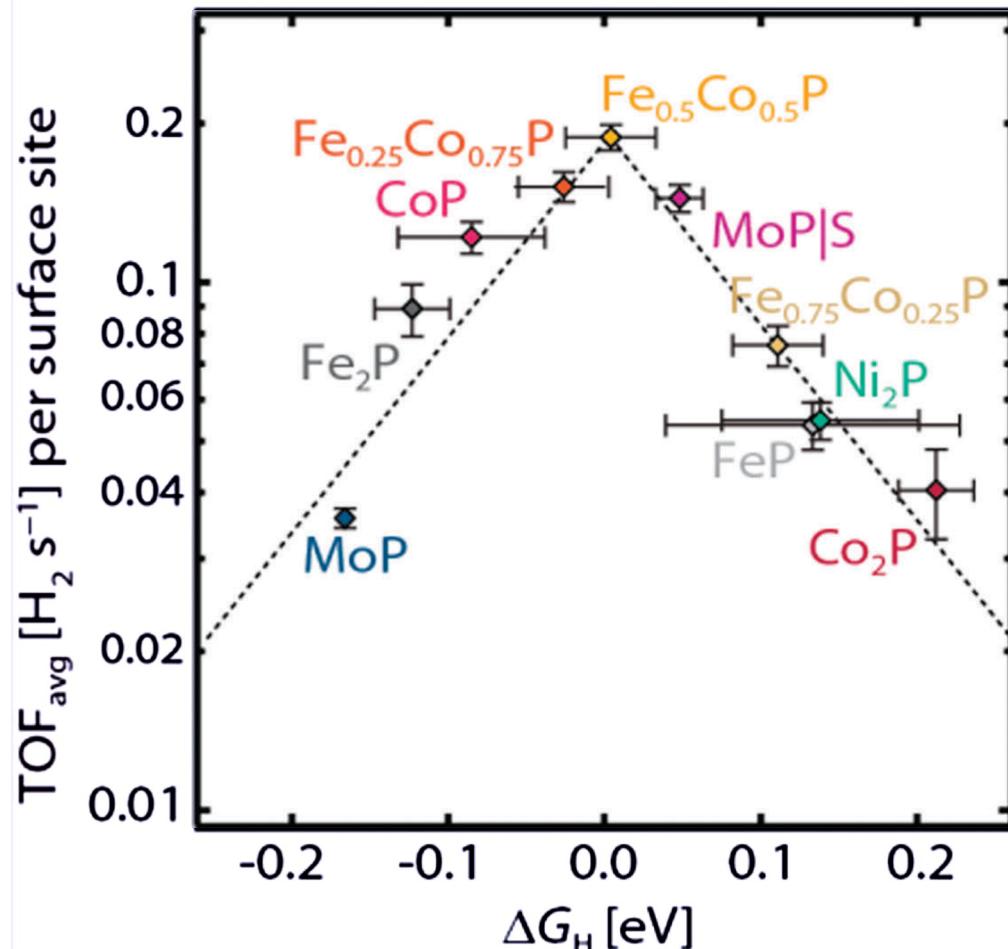
Hinnemann, Bonde, Jørgensen, Nielsen, Horch, Chorkendorff, Nørskov, JACS **127** 5308 (2005)

Bollinger, Lauritsen, Jacobsen, Nørskov, Helveg, Besenbacher, PRL **87**, 197803 (2001)

# Theory-guided design of phosphides catalysts

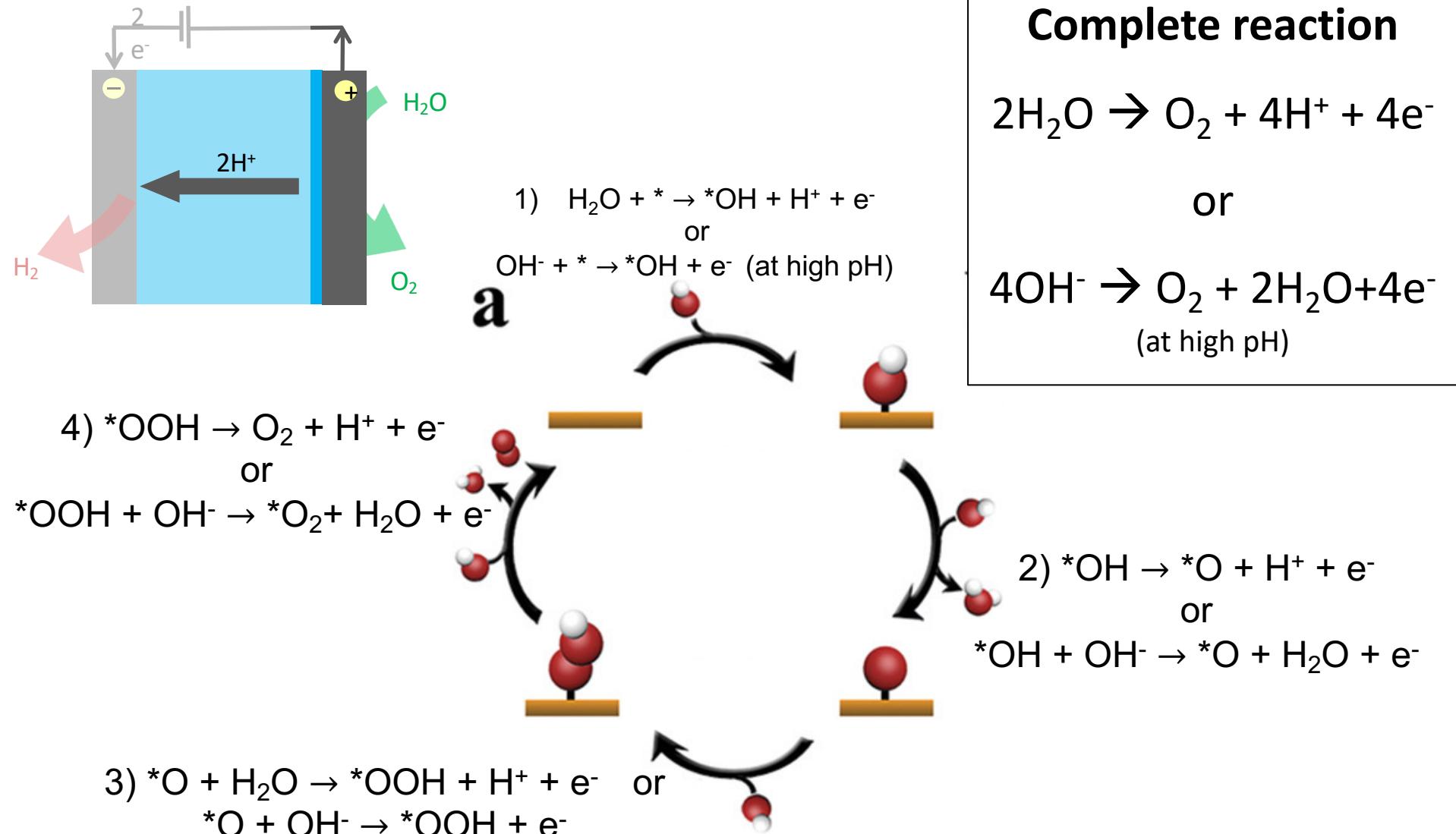


$\text{Fe}_{0.5}\text{Co}_{0.5}\text{P} (101)$





# Elementary steps in oxygen evolution (OER)



# Free energies in OER on Pt

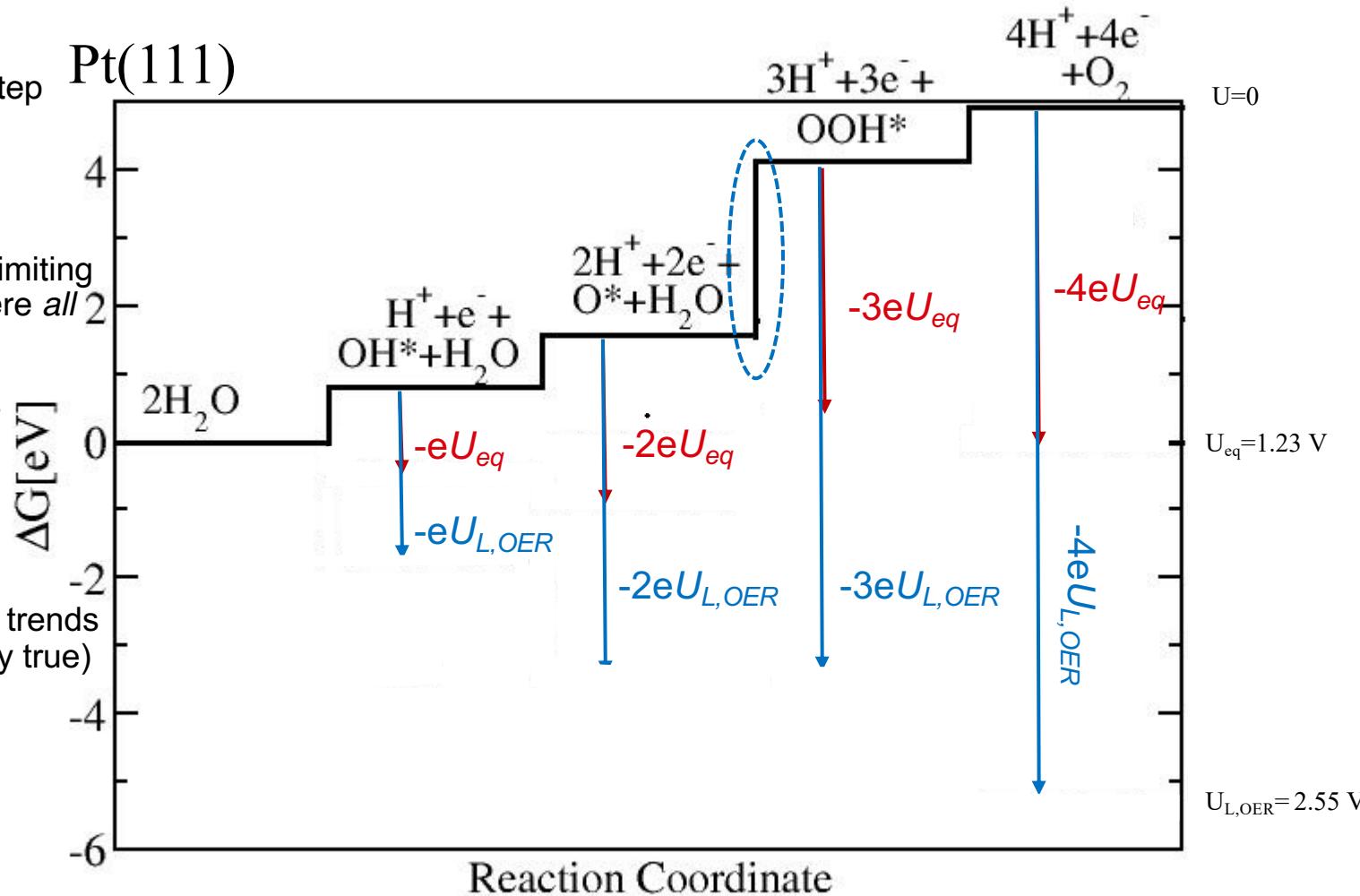
For each elementary step (oxidation):

$$\Delta G_i(U) = \Delta G_{0,i} - eU$$

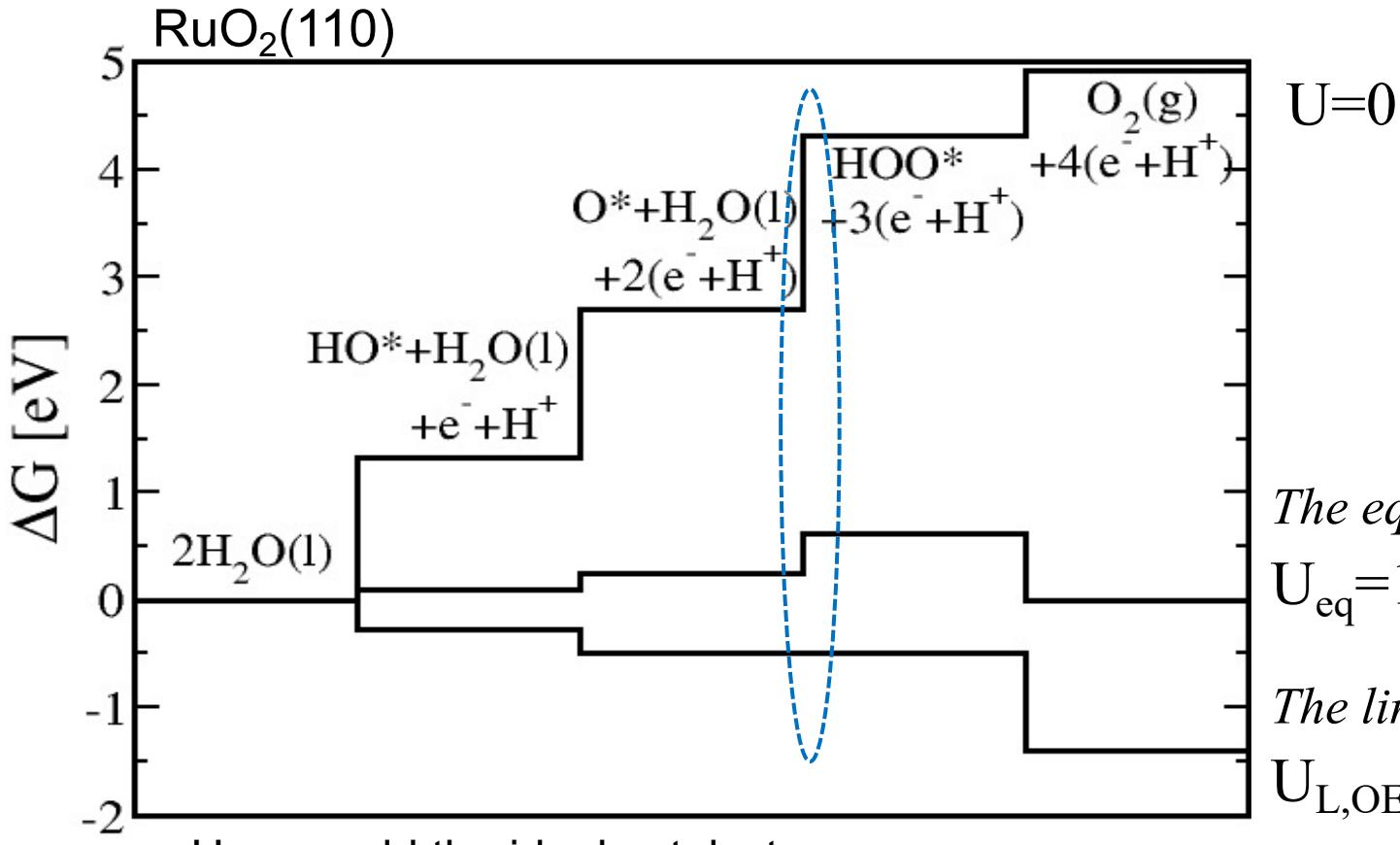
Define the theoretical limiting potential for OER, where all steps are exergonic

$$U_L = + \max(\Delta G_i(U = 0))/e$$

For OER,  $U_{L,OER}$  follow trends in activity (not generally true)



# Free energies in OER on RuO<sub>2</sub>

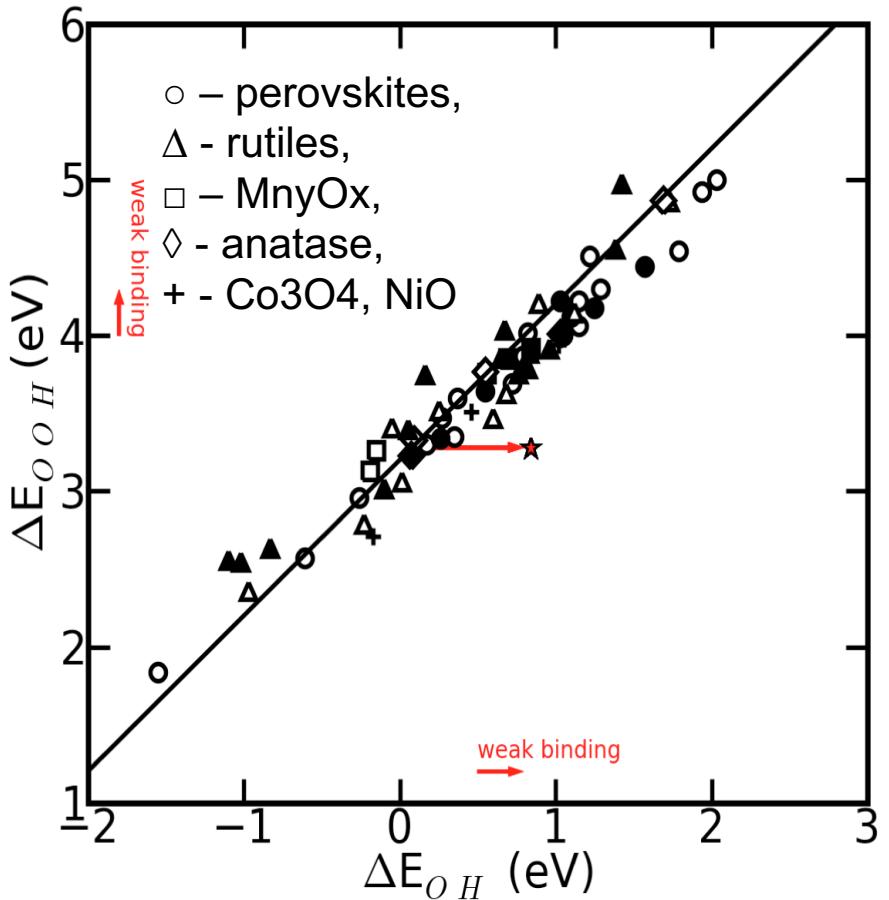


How would the ideal catalyst look like?

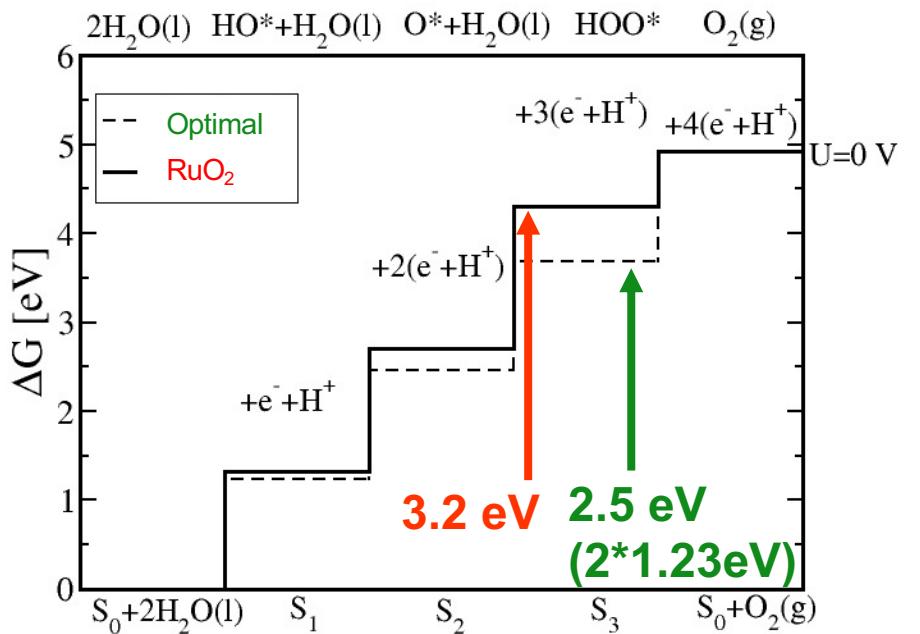
Every elementary step is 1.23eV  
uphill at 0V

*The theoretical overpotential:*  
 $\eta_{\text{theo}} = U_{\text{L}} - U_{\text{eq}} = 1.60 - 1.23 \text{ V} = 0.37 \text{ V}$

# Scaling relations



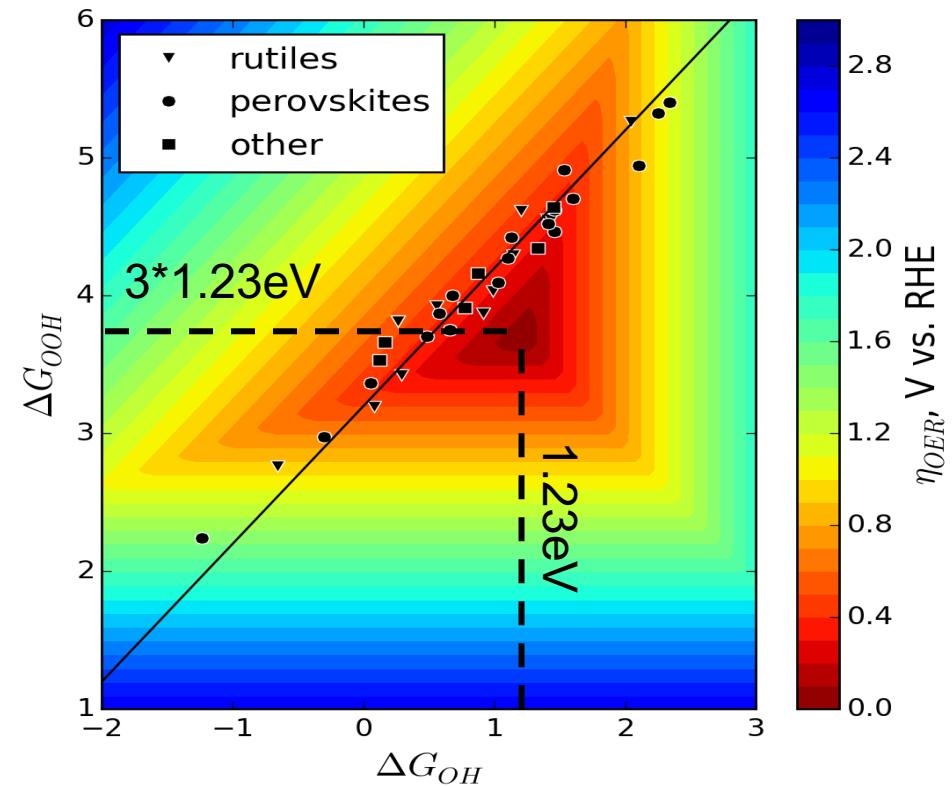
$$\Delta E_{OOH} = \Delta E_{OH} + 3.2 \text{ eV}$$



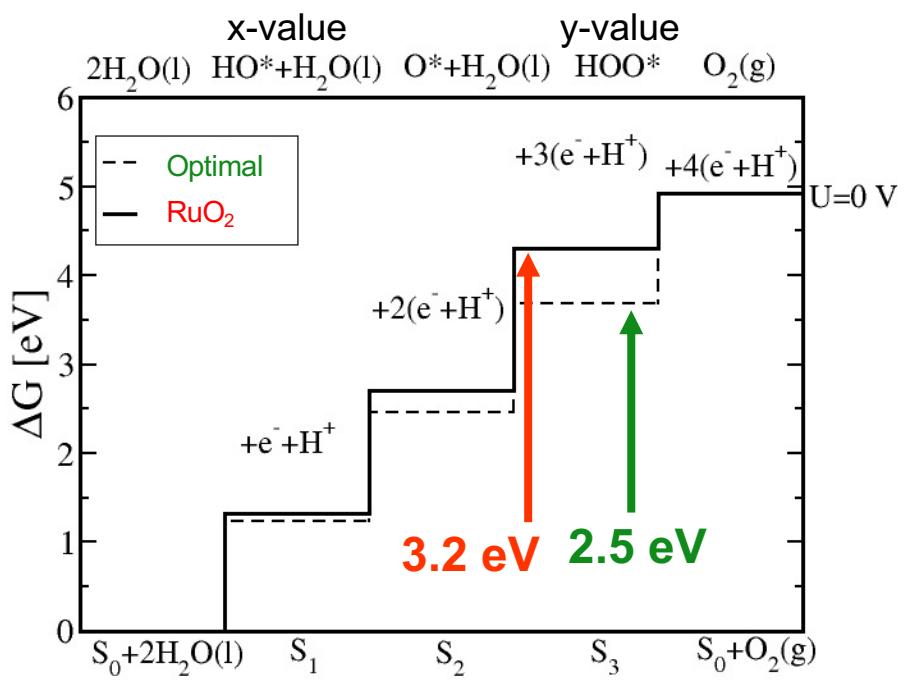
Minimum theoretical overpotential  
For catalysts following scaling:

$$(3.2 - 2.5)/2 \text{ V} = 0.35 \text{ V}$$

# Circumventing scaling



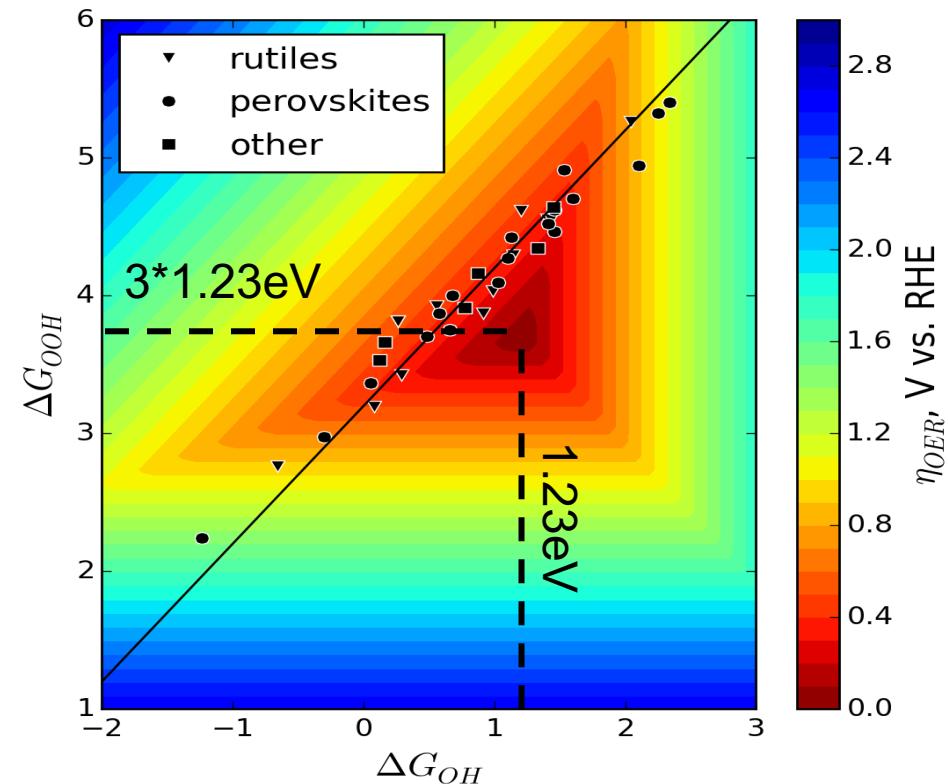
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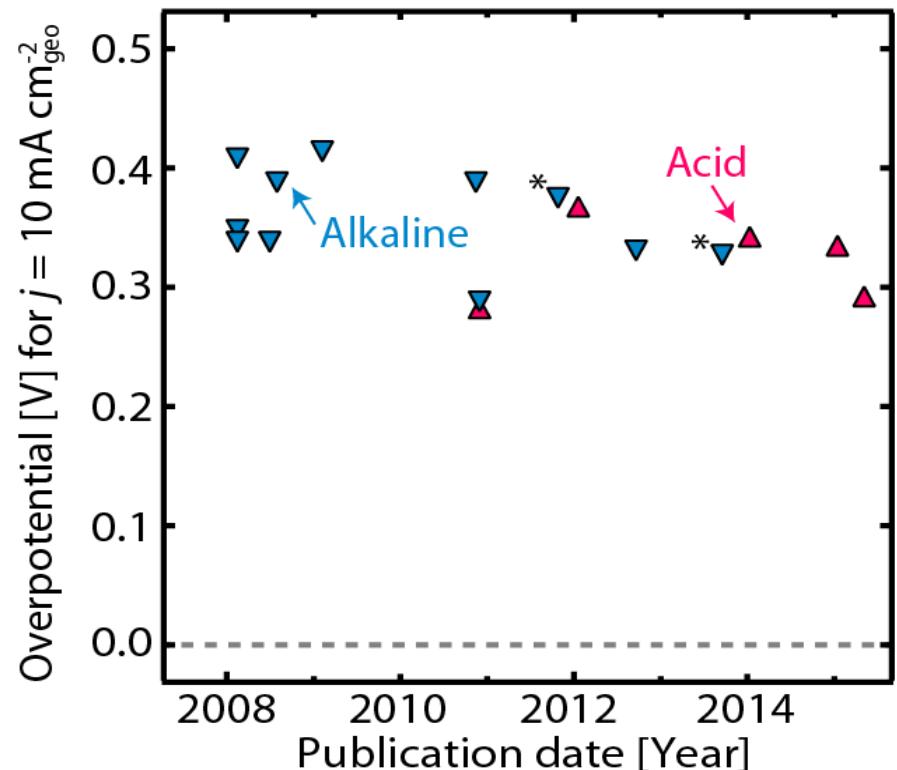
Vojvodic, Nørskov, Natl. Science Review (2015)

# Circumventing scaling

Seh, Kibsgaard, Dickins, Chorkendorff, Nørskov, Jaramillo, *Science* **355**, 146 (2017)



Vojvodic, Nørskov, Natl. Science Review (2015)



Lee, Suntivich, May, Perry, Shao-Horn, *J. Phys. Chem. Lett.* **3**, 399 (2012).

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McCrory, Jung, J. C. Peters, T. F. Jaramillo, *J. Am. Chem. Soc.* **135**, 16977 (2013)

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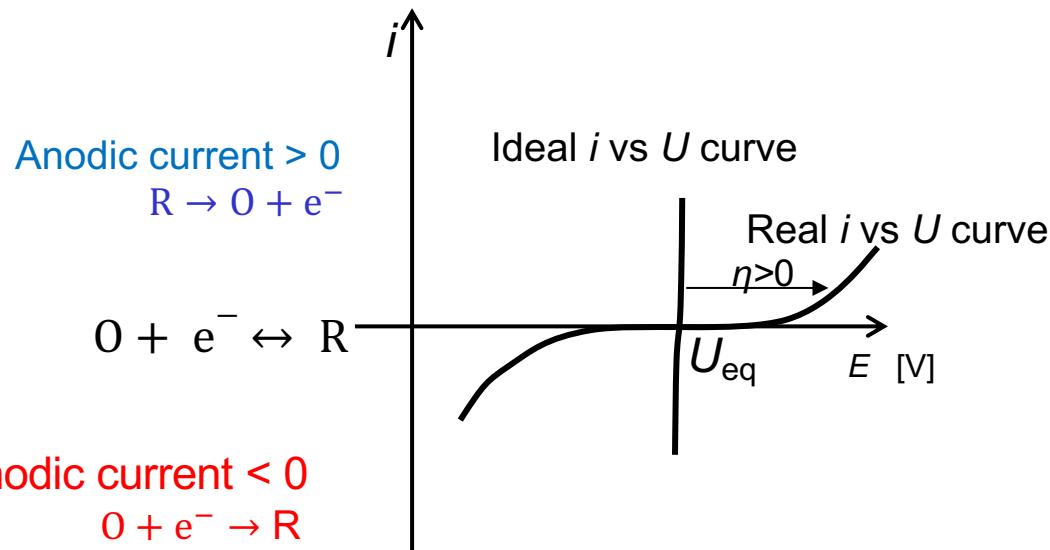
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Bajdich, Garcia-Mota, Vojvodic, Nørskov, Bell, *J. Am. Chem. Soc.* **135**, 13521 (2013)

Seitz, Dickens, Nishio, Hikita, Montoya, Doyle, Kirk, Vojvodic, Hwang, Nørskov, Jaramillo, *Science* **353**, 101 (2016)

# Kinetics: Faradaic Current densities vs. overpotential

How do we get the magnitude of current that can be gotten in an electrolyzer?



At  $E_{eq}$  both the oxidation and reduction reactions are equally fast so no net current flows

However, **we do not know how much current we get when we set a potential beyond the equilibrium potential!**

we follow the IUPAC sign convention

cathodic current <0

anodic current >0

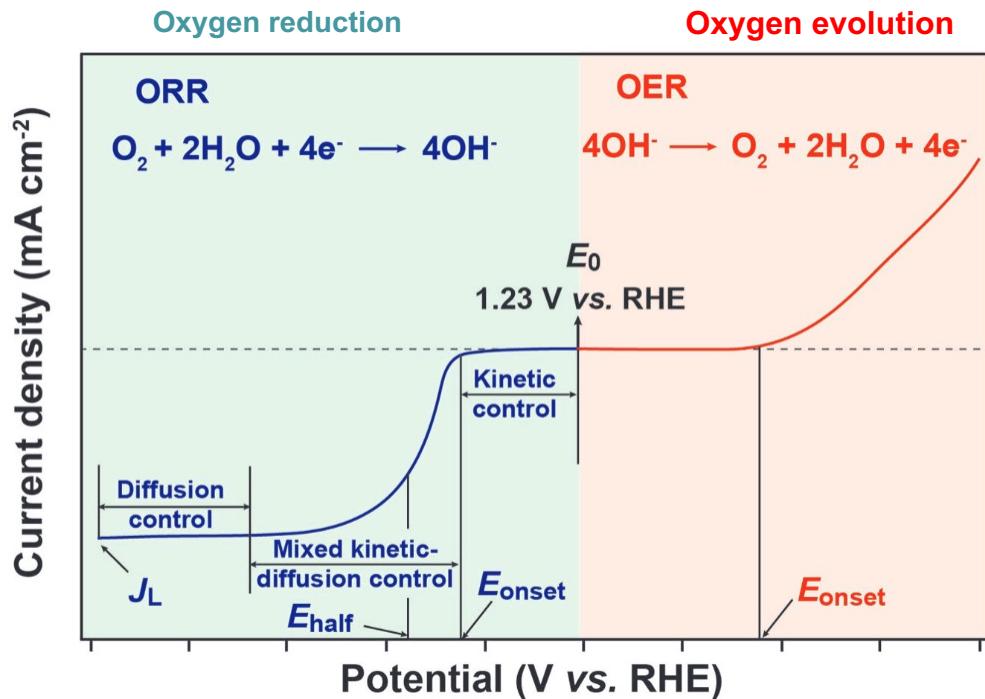
**Overpotential:**  $\eta = U - U_{eq}$

Potential beyond the equilibrium potential ( $U_{eq}$  from Nernst equation) needed to measure a defined current in a half-cell of an electrolyzer

# Kinetics: Faradaic Current densities vs. overpotential

How do we get the magnitude of current that can be gotten in an electrolyzer?

Example:



Adv. Funct. Mater. 2018, 28, 1804886

(Note in this figure U is called E)

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However, **we do not know how much current we get when we set a potential beyond the equilibrium potential!**

**Overpotential:  $\eta = U - U_{eq}$**

Potential beyond the equilibrium potential ( $U_{eq}$  from Nernst equation) needed to measure a defined current in a half-cell of an electrolyzer

# Reaction rates from chemical kinetics



Reaction rate for forward reaction (reduction, cathodic)  $\frac{dc_O}{dt} = v_f = k_f c_O$

Reaction rate for backward reaction (oxidation, anodic)  $\frac{dc_R}{dt} = \nu_b = k_b c_R$

Relate rates to current densities, since electrons are transferred:

$$\nu_f = \frac{1}{F} \frac{dq}{dt} = -\frac{j_c}{F}$$

cathodic

$$\nu_b = \frac{j_a}{F}$$

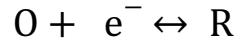
anodic

Total current density:  $j = j_a + j_c = F(v_b - v_f) = F(k_b c_R - k_f c_O)$

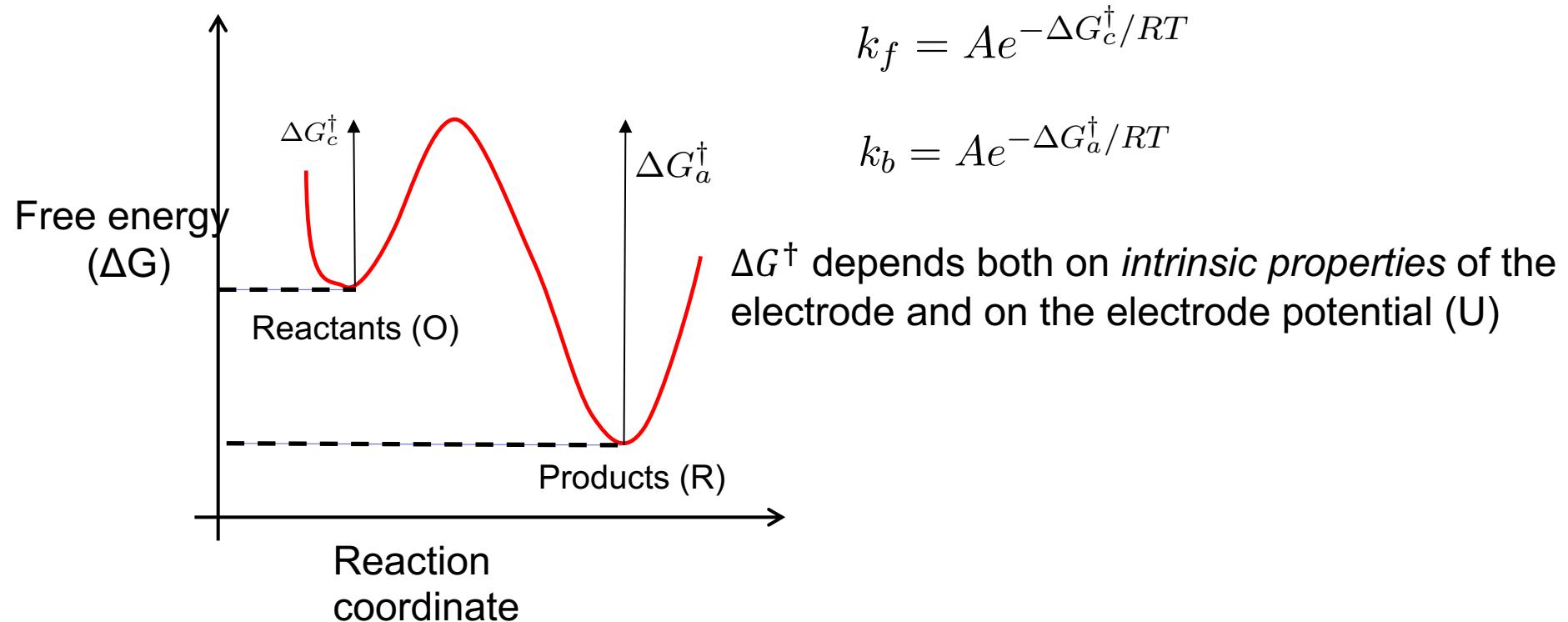
## Faraday's law:

$$q_k = \frac{\nu_{e,k}}{\nu_{p,k}} F N_{mol,k}$$

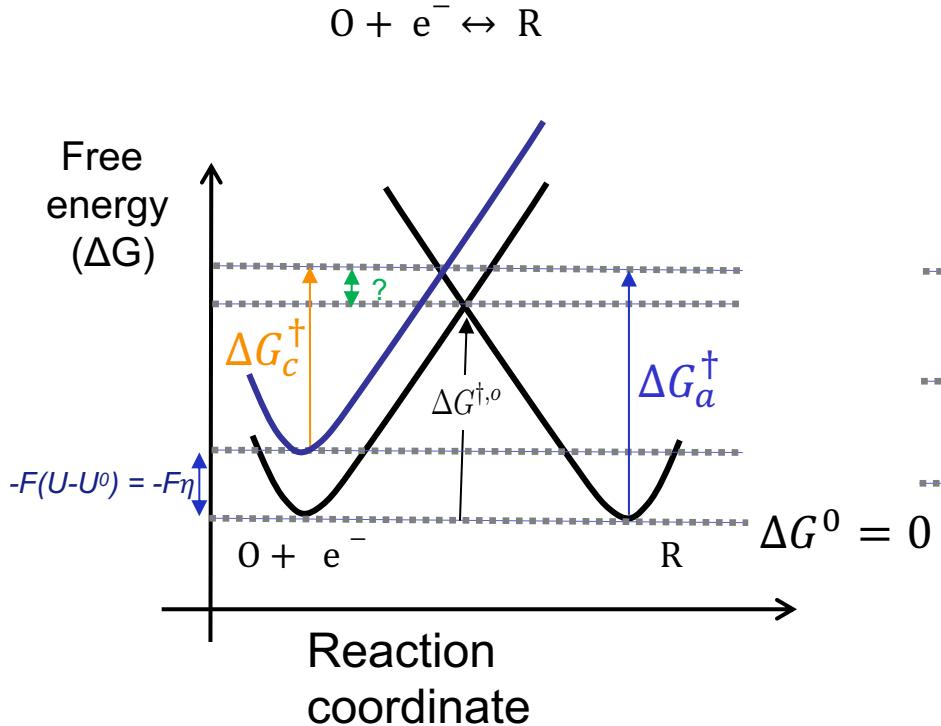
# What determines the rate constants $k_f$ , $k_b$ ?



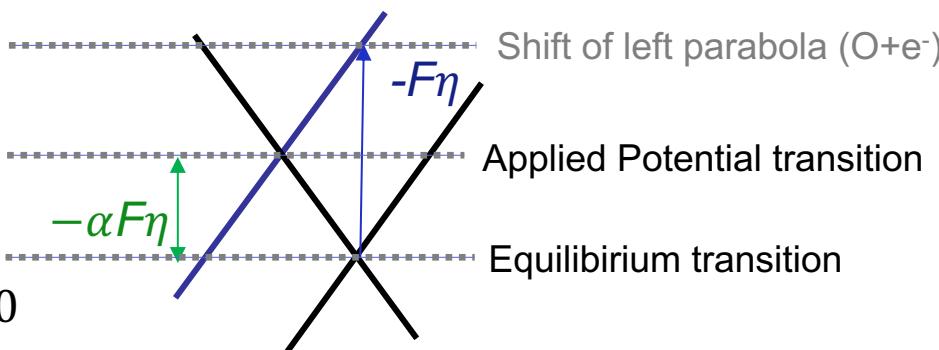
Arrhenius equation:  $k = Ae^{-\Delta G^\ddagger/RT}$



# How do the rate constants $k_f$ , $k_b$ vary with potential?



Zoom in on transition state:



Activation energy change of reduction with potential:

$$\Delta G_c^\dagger(U) = \Delta G_c^\dagger,0 - \alpha F\eta$$

$\alpha$  = charge transfer coefficient

$O$  and  $R$  are uncharged  $\rightarrow$  No reaction to potential  $e^-$  reacts to potential:  $\mu_{e^-} = \mu_{e^-}^0 - F(U-U^0) = \mu_{e^-}^0 - F\eta$   
Thus, only the left parabola reacts to the potential

# What is the transfer coefficient $\alpha$ ?

IUPAC definition:

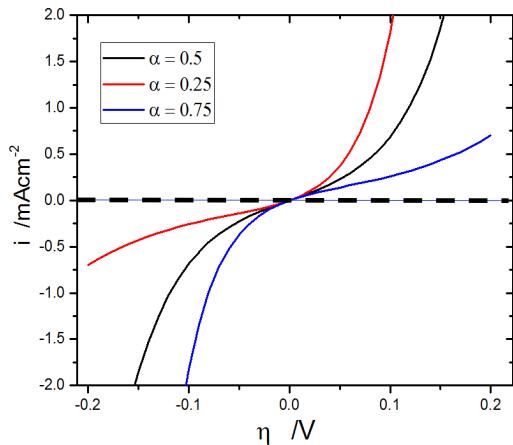
$$\alpha_a = (RT/F)(d\ln j_a / dE); \quad \alpha_c = -(RT/F)(d\ln|j_c| / dE)$$

From: Definition of the transfer coefficient in electrochemistry (IUPAC Recommendations 2014)  
Rolando Guidelli, Richard G. Compton, Juan M. Feliu, Eleizer Gileadi, Jacek Lipkowski, Wolfgang Schmickler and Sergio Trasatti  
Pure Appl. Chem. 2014; 86(2): 259–262

## In a nutshell:

$\alpha$  determines how much the current changes when the potential is changed

Variations in  $\alpha$  affect how effectively the current can increase with a change in voltage



Note: If the left side is steep the right side is flat and opposite

# Butler Volmer Equation

$$j = j_0(e^{\frac{(1-\alpha)F\eta}{RT}} - e^{-\frac{\alpha F\eta}{RT}})$$

Lets us calculate the current at any applied potential if  $j_0$  and  $\alpha$  are known.

$$j_0 = Fk_0c_O^{1-\alpha}c_R^{-\alpha} \dots \text{constant that can be fitted!}$$

Increasing both  $j_0$  and  $\alpha$  is the target in research!

However,  $\alpha$  is often defined by the reaction (scaling relations), so increasing  $j_0$  is easier.

# Learning objectives

After this lecture you will be able to:

- Identify the difference between thermally activated and electro-catalysis
- Evaluate the influence of potential and pH on the thermodynamics in electrocatalysis
- Assess the activity of an electrocatalyst based on the limiting potential
- Explain the steps in HER and OER and the challenge in optimizing them
- Estimate currents in electrocatalysis at given (over-)potential and pH

# What about the prefactor of for the exponent?

The anodic and cathodic currents do not equal 0 at equilibrium. Why?

$$j = Fk_0 \left( c_R e^{\frac{(1-\alpha)F(E-E^0)}{RT}} - c_O e^{-\frac{\alpha F(E-E^0)}{RT}} \right)$$

