



**GLOBAL CLIMATE AND ENERGY PROJECT
STANFORD UNIVERSITY**



Energy Tutorial: Electrocatalysis 101

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GLOBAL CHALLENGES – GLOBAL SOLUTIONS – GLOBAL OPPORTUNITIES

Outline for this tutorial

- Introduction
- Fundamentals of electrochemistry & electrocatalysis
 - Thermodynamics
 - Kinetics
 - Methods in electrocatalysis research
 - Figures of merit for electrocatalyst development
- Applications – two examples
 - The hydrogen evolution reaction (HER)
 - The carbon dioxide reduction reaction (CO₂RR)



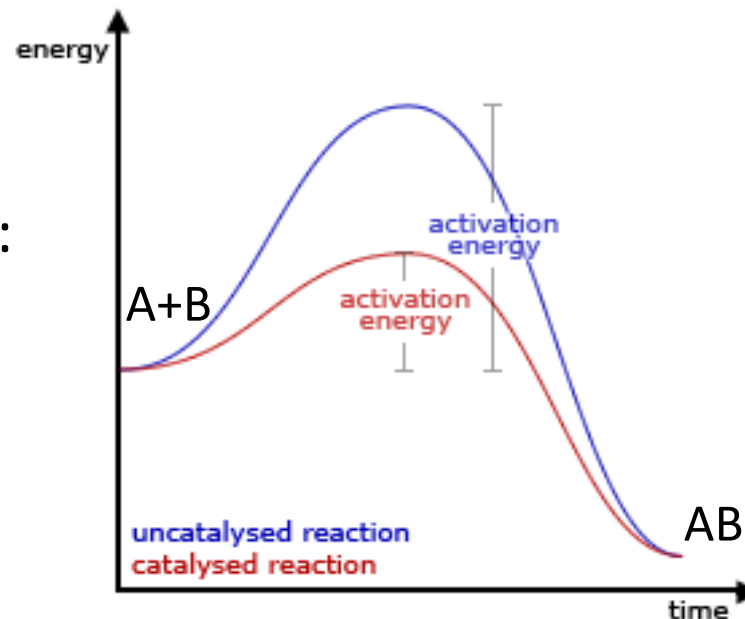
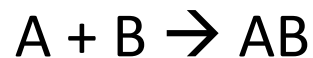
What is a catalyst?

cat·a·lyst *noun* \ˈkɑ-tə-ləst\

1: a substance that enables a chemical reaction to proceed at a usually faster rate or under different conditions (as at a lower temperature) than otherwise possible.

2: an agent that provokes or speeds significant change or action.

Elementary chemical reaction:

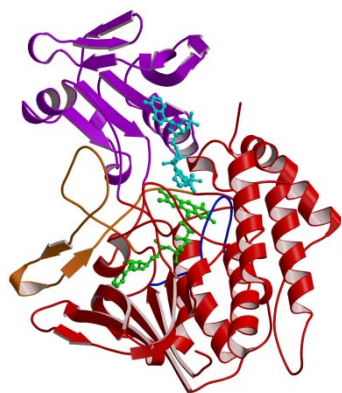


www.m-w.com

www.newworldencyclopedia.org



Five broad classes of catalysis research

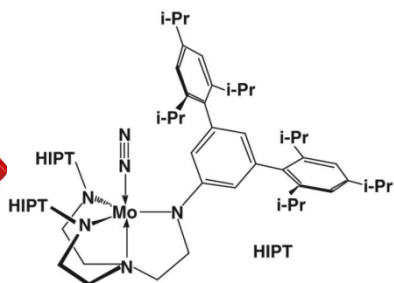


Biocatalysts

e.g. enzymes

H₂O oxidation in photosynthesis

H⁺ and e⁻ transfers
Ambient Temp
Ambient Pressure
Liquid (aqueous)

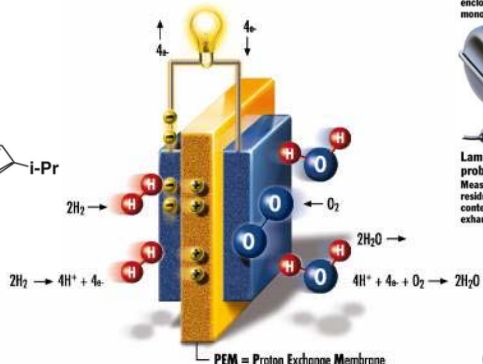


Homogeneous Catalysts

e.g. transition metal complexes

Fine chemicals
Olefin metathesis

H⁺/e⁻, thermochemical
Low-Intermediate T's
Wide range P's
Liquid (aq. or non-aq.)

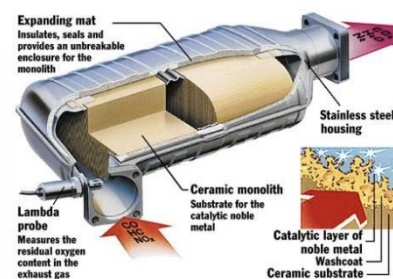


Electrocatalysts

e.g. Pt nanoparticles

Fuel Cells
Water electrolysis

H⁺/e⁻, thermochemical
Wide range of Temps
Wide range P's
Liquid (aq. or non-aq.)

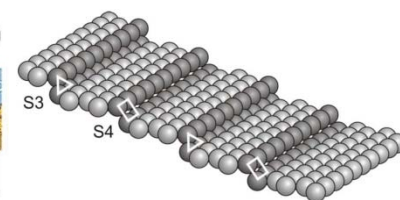


Conventional Heterogeneous Catalysts

e.g. Rh nanoparticles

Catalytic converters
NH₃ synthesis

Thermochemical
Wide range of Temps
Wide range of P's
Gas or liquid-phase



Ultra-high Vacuum (UHV) Surface Science

e.g. Ru(109)

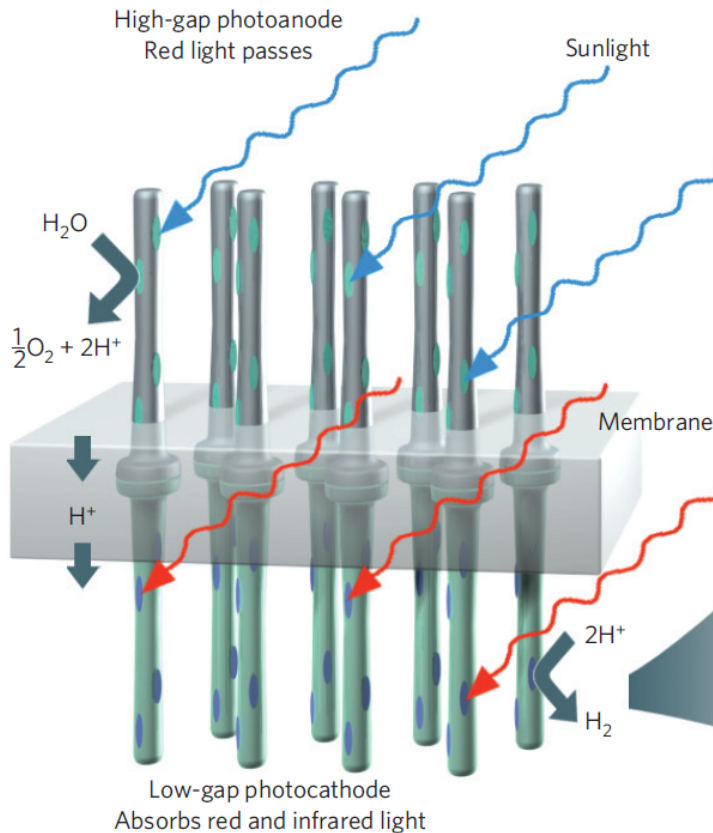
Fundamental studies
Adsorption, desorption, reaction

Thermochemical
Wide range of Temps
Very low P (vacuum)
Gas-on-surface



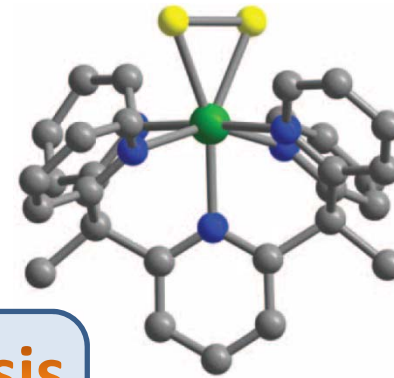
Electrocatalysis comes in different forms

Photocatalysts



Y. Hu et. al. *Nature Materials* (2011)

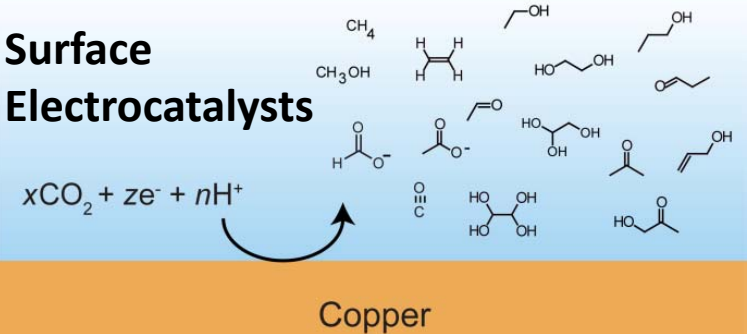
Solution-phase Electrocatalysts



H.I. Karunadasa et. al. *Science* (2012)

Electrocatalysis

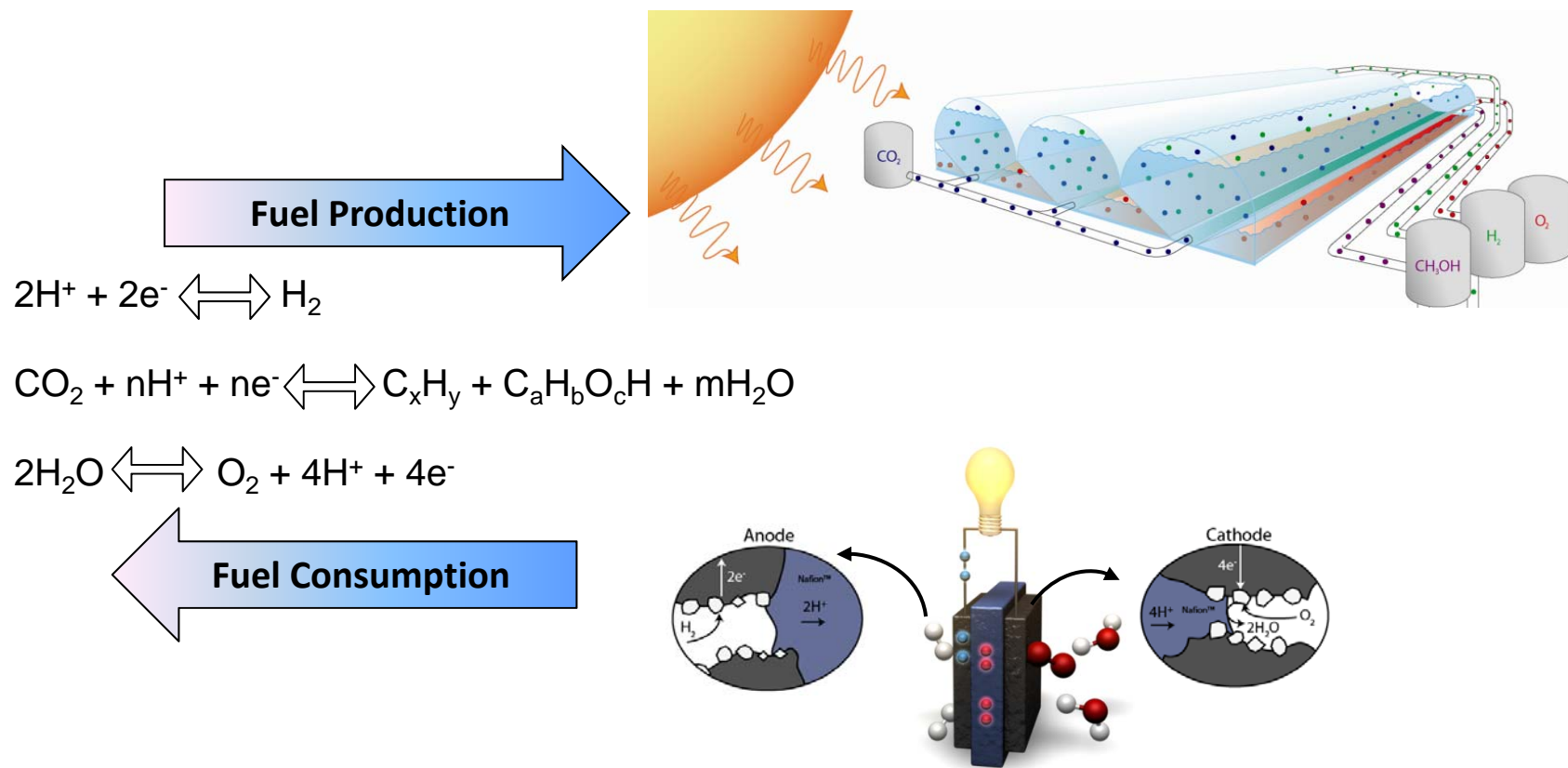
Surface Electrocatalysts



K.P. Kuhl et. al. *Energy & Environmental Science* (2012)



Three key energy conversion reactions in need of improved electrocatalysts



Key terms in electrochemistry

What is oxidation? What is reduction?

Losing Electrons is **O**xidation.

Gaining Electrons is **R**eduction.

Just remember: “**LEO** the lion goes **GERRRR....**”

What is a cathode? What is an anode?

Reduction happens at the **C**athode.

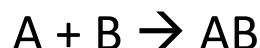
Oxidation happens at the Anode.

Just remember to think of a “**Red Cat.**”

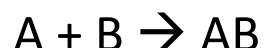


Chemistry → Electrochemistry

Equilibrium Thermodynamics



$$\Delta G = -100 \text{ kJ/mol}$$



$$\Delta G^\circ = -100 \text{ kJ/mol} = -nFE^\circ_{\text{cell}}$$

Where: n = # of electrons transferred (overall rxn)

F = Faraday's constant = 96,485 C/mol

$E^\circ_{\text{cell}} = \Delta E^\circ \dots$ can be confusing!

See next slides on how to use tables of standard electrochemical potentials to calculate this.



Equilibrium Potentials

OXIDISING AGENTS (Oxidants)	Redox table - list of reduction potentials measured under standard conditions (25°C, 1 atmosphere pressure, 1 mol/L solution)	REDUCING AGENTS (Reductants)
Weakest oxidising agents	$\text{Li}^+ + \text{e}^- \rightleftharpoons \text{Li(s)} \quad -3.04 \text{ V}$ $\text{K}^+ + \text{e}^- \rightleftharpoons \text{K(s)} \quad -2.92 \text{ V}$ $\text{Ba}^{2+} + 2\text{e}^- \rightleftharpoons \text{Ba(s)} \quad -2.90 \text{ V}$ $\text{Ca}^{2+} + 2\text{e}^- \rightleftharpoons \text{Ca(s)} \quad -2.87 \text{ V}$ $\text{Na}^+ + \text{e}^- \rightleftharpoons \text{Na(s)} \quad -2.71 \text{ V}$ $\text{Mg}^{2+} + 2\text{e}^- \rightleftharpoons \text{Mg(s)} \quad -2.36 \text{ V}$ $\text{Al}^{3+} + 3\text{e}^- \rightleftharpoons \text{Al(s)} \quad -1.66 \text{ V}$ $\text{Zn}^{2+} + 2\text{e}^- \rightleftharpoons \text{Zn(s)} \quad -0.76 \text{ V}$ $\text{Fe}^{2+} + 2\text{e}^- \rightleftharpoons \text{Fe(s)} \quad -0.41 \text{ V}$ $\text{Sn}^{2+} + 2\text{e}^- \rightleftharpoons \text{Sn(s)} \quad -0.14 \text{ V}$ $\text{Pb}^{2+} + 2\text{e}^- \rightleftharpoons \text{Pb(s)} \quad -0.13 \text{ V}$ $\text{Fe}^{3+} + 3\text{e}^- \rightleftharpoons \text{Fe(s)} \quad -0.02 \text{ V}$ $\text{H}^+ + \text{e}^- \rightleftharpoons 1/2\text{H}_2(\text{g}) \quad 0.00 \text{ V}$ $\text{SO}_4^{2-} + 2\text{e}^- + 4\text{H}^+ \rightleftharpoons \text{SO}_2(\text{g}) + 2\text{H}_2\text{O} \quad 0.21 \text{ V}$ $\text{Cu}^{2+} + 2\text{e}^- \rightleftharpoons \text{Cu(s)} \quad 0.34 \text{ V}$ $1/2\text{I}_2(\text{s}) + \text{e}^- \rightleftharpoons \text{I}^- \quad 0.54 \text{ V}$ $1/2\text{I}_2(\text{aq}) + \text{e}^- \rightleftharpoons \text{I}^- \quad 0.62 \text{ V}$ $\text{Fe}^{3+} + \text{e}^- \rightleftharpoons \text{Fe}^{2+} \quad 0.77 \text{ V}$ $\text{Ag}^+ + \text{e}^- \rightleftharpoons \text{Ag(s)} \quad 0.80 \text{ V}$ $1/2\text{O}_2(\text{g}) + 2\text{H}^+ + 2\text{e}^- \rightleftharpoons \text{H}_2\text{O} \quad 1.23 \text{ V}$ $1/2\text{Cl}_2(\text{g}) + \text{e}^- \rightleftharpoons \text{Cl}^- \quad 1.36 \text{ V}$ $\text{MnO}_4^- + 5\text{e}^- + 8\text{H}^+ \rightleftharpoons \text{Mn}^{2+} + 4\text{H}_2\text{O} \quad 1.51 \text{ V}$ $1/2 \text{F}_2(\text{g}) + \text{e}^- \rightleftharpoons \text{F}^- \quad 2.87 \text{ V}$	Strongest reducing agents
Strength of oxidising agents increases down table		Strength of reducing agents decreases down table
Strongest oxidising agents	<p>The higher the reduction potential, (e.g. F_2), the more easily the substance is reduced (and thus the greater its oxidising power).</p> <p style="text-align: center;">http://hsc.csu.edu.au</p>	Weakest reducing agents

- Mainly the study of half-reactions
- Thermodynamics of half-reactions defined on an absolute potential (E^0) scale, $G^0 = -nFE^0$
- Potential scale can be shifted for convenience
 - e.g. $E_{vac} = E_{SHE} - 4.44 \text{ V}$
- Cell voltages (ΔE^0 a.k.a. cell potential E^0_{cell}) are differences in potential from two half-reactions that make up a complete reaction.



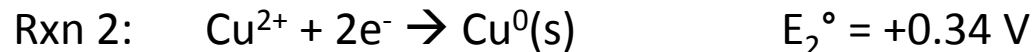
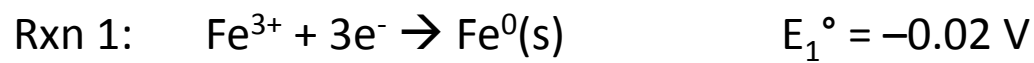
Calculating Cell Potentials: The Statue of Liberty



1886 2012

Important: We are using a standard **reduction** table from the preceding slide.

Step 1: Identify the relevant red-ox reactions. In this example, the relevant reactions are red-ox reactions involving Fe and Cu:

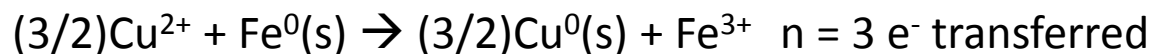


Step 2: Choose one reaction to be the oxidation, and one to be the reduction (an arbitrary decision). For this example, let's choose Rxn 1 to be the oxidation rxn.

Step 3: $E^\circ_{\text{cell}} = E^\circ_{\text{cathode}} - E^\circ_{\text{anode}}$. The minus sign arises because we are using tabulated data from **reduction** tables. And since oxidation is what occurs at the anode, the sign must be reversed since the reaction runs in the reverse direction.

$$E^\circ_{\text{cell}} = E_2^\circ - E_1^\circ = +0.34 \text{ V} - (-0.02 \text{ V}) = +0.36 \text{ V}.$$

Step 4: Balance the overall equation (cathode rxn + anode rxn) and then calculate ΔG° .



$$\Delta G^\circ = -(3)(96,485 \text{ C/mol})(+0.36 \text{ V}) = -104,204 \text{ J/mol} = -104.2 \text{ kJ/mol}.$$

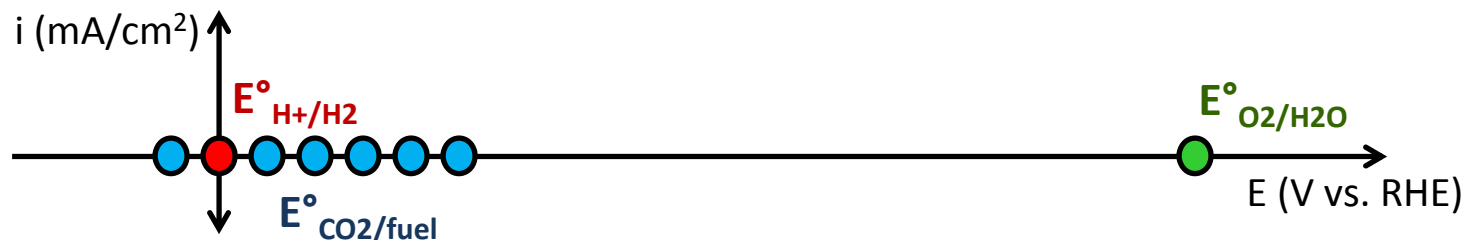
Key result: ΔG° is **negative** so the overall rxn is **spontaneous as-written**.



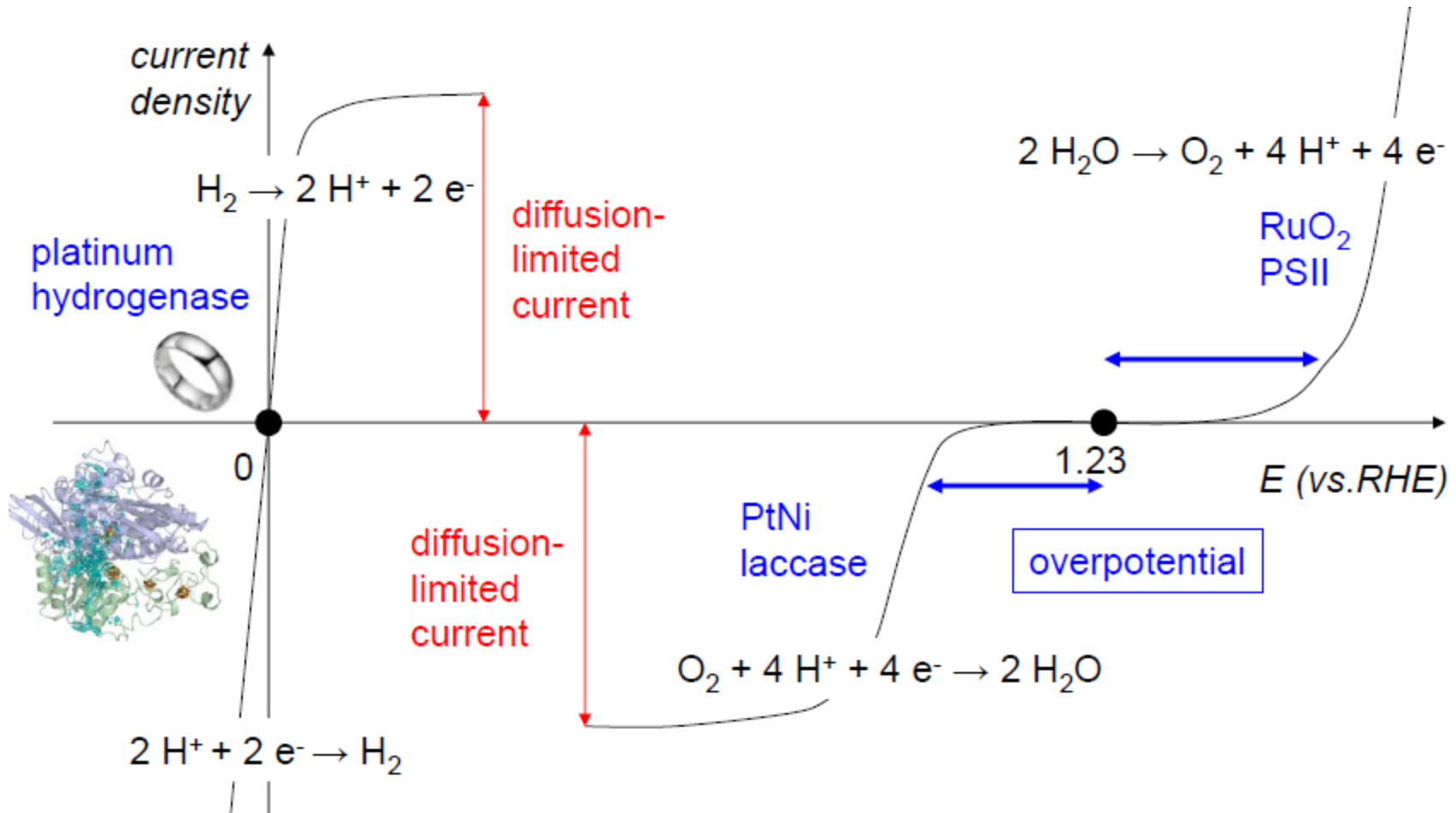
Thermodynamic considerations for electrocatalytic conversions related to energy

Y. Hori, "Electrochemical CO₂ reduction on metal electrodes" *Modern Aspects of Electrochemistry*, Number 42, edited by C. Vayenas et. al., Springer, NY (2008)

	E^0 vs. RHE	
$2\text{H}^+ + 2\text{e}^- \leftrightarrow \text{H}_2$	0.00 V	
$\text{CO}_2 + 2\text{H}^+ + 2\text{e}^- \leftrightarrow \text{CO} + \text{H}_2\text{O}$	- 0.11 V	All values are close to the H ₂ evolution potential (0.00 V).
$\text{CO}_2 + 6\text{H}^+ + 6\text{e}^- \leftrightarrow \text{CH}_3\text{OH} + \text{H}_2\text{O}$	+ 0.02 V	
$\text{CO}_2 + 8\text{H}^+ + 8\text{e}^- \leftrightarrow \text{CH}_4 + 2\text{H}_2\text{O}$	+ 0.16 V	
$2\text{CO}_2 + 12\text{H}^+ + 12\text{e}^- \leftrightarrow \text{C}_2\text{H}_4 + 4\text{H}_2\text{O}$	+ 0.07 V	
$2\text{CO}_2 + 12\text{H}^+ + 12\text{e}^- \leftrightarrow \text{C}_2\text{H}_5\text{OH} + 3\text{H}_2\text{O}$	+ 0.08 V	
$3\text{CO}_2 + 18\text{H}^+ + 18\text{e}^- \leftrightarrow \text{C}_3\text{H}_7\text{OH} + 5\text{H}_2\text{O}$	+ 0.09 V	
$\text{O}_2 + 4\text{H}^+ + 4\text{e}^- \leftrightarrow 2\text{H}_2\text{O}$	+ 1.23 V	



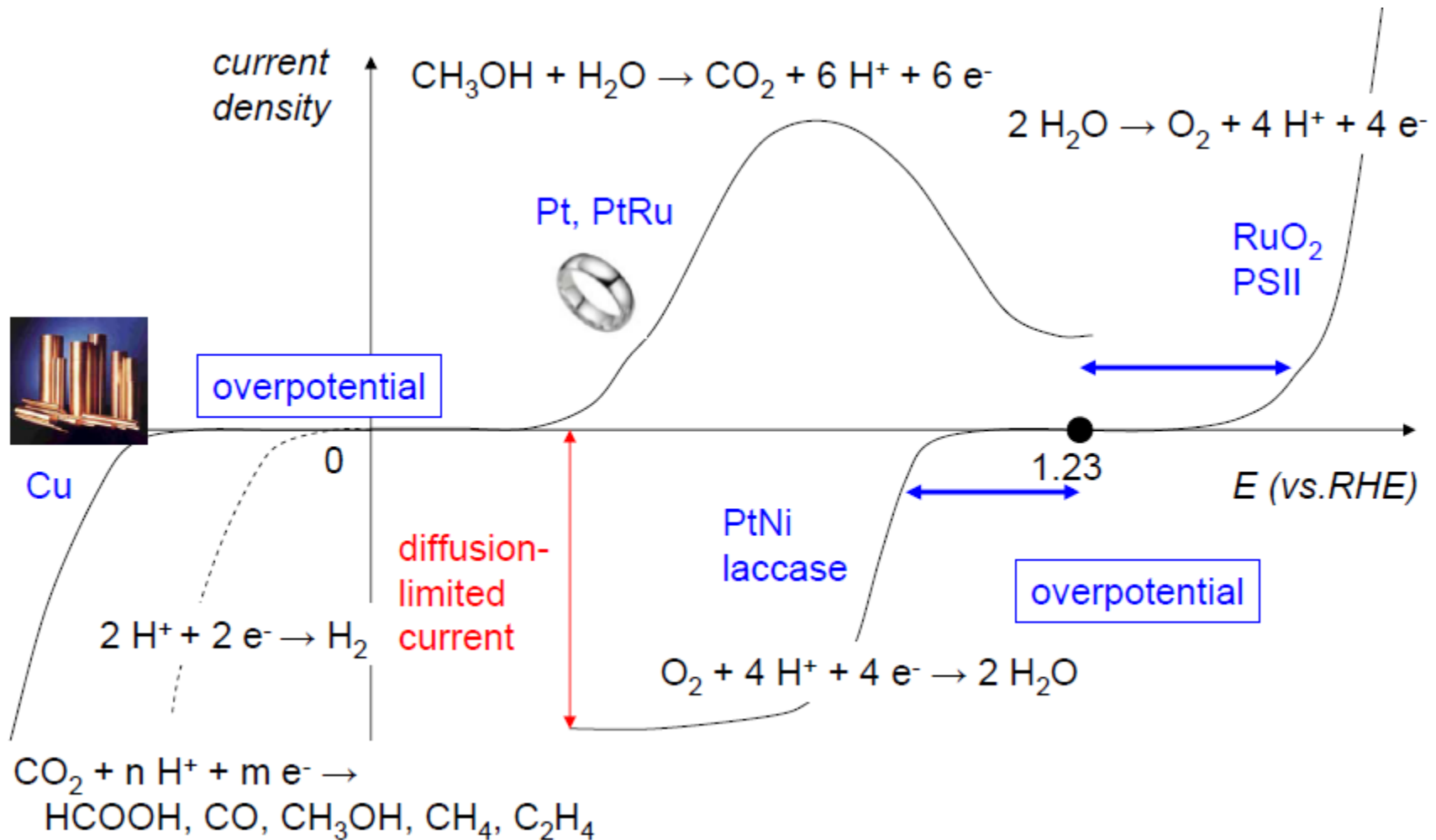
Reaction kinetics involving H₂O-H₂-O₂



M.T.M. Koper, H.A. Heering, in "Fuel Cell Science", Eds. A. Wieckowski, J.K. Nørskov, Wiley (2010), p. 71-110



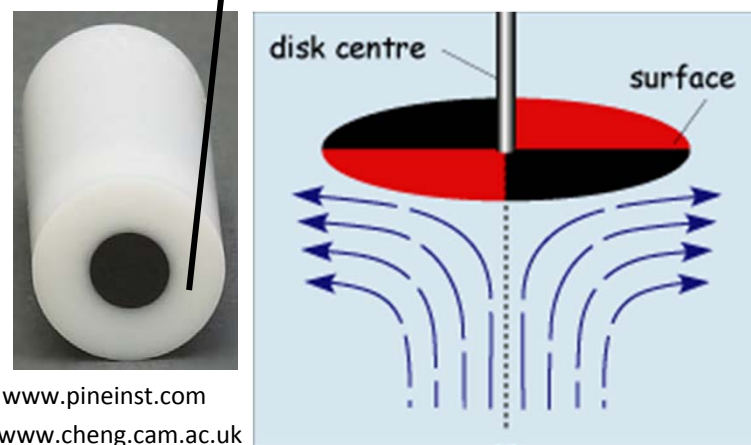
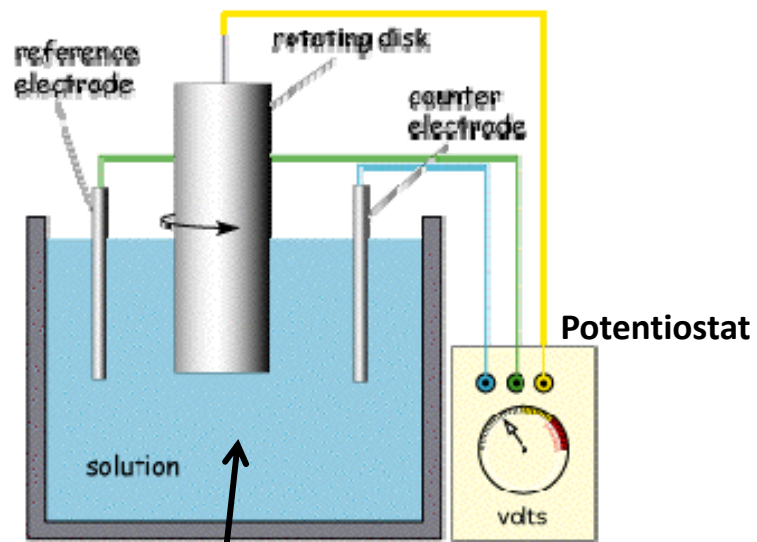
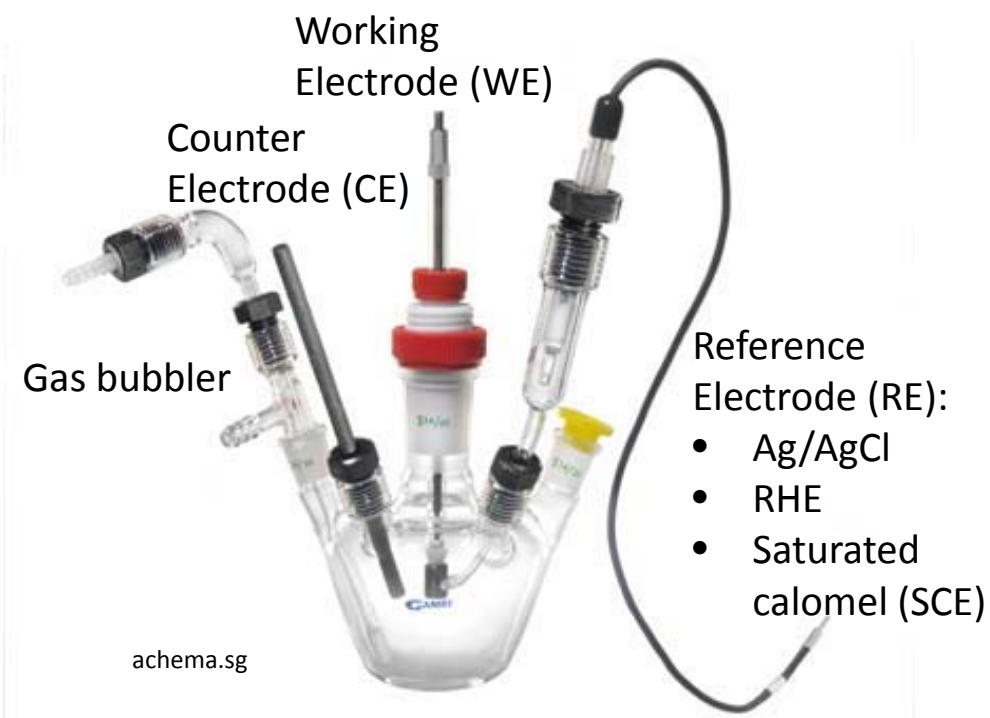
Reaction kinetics involving fuels-CO₂



M.T.M. Koper, H.A. Heering, in "Fuel Cell Science", Eds. A. Wieckowski, J.K. Nørskov, Wiley (2010), p. 71-110



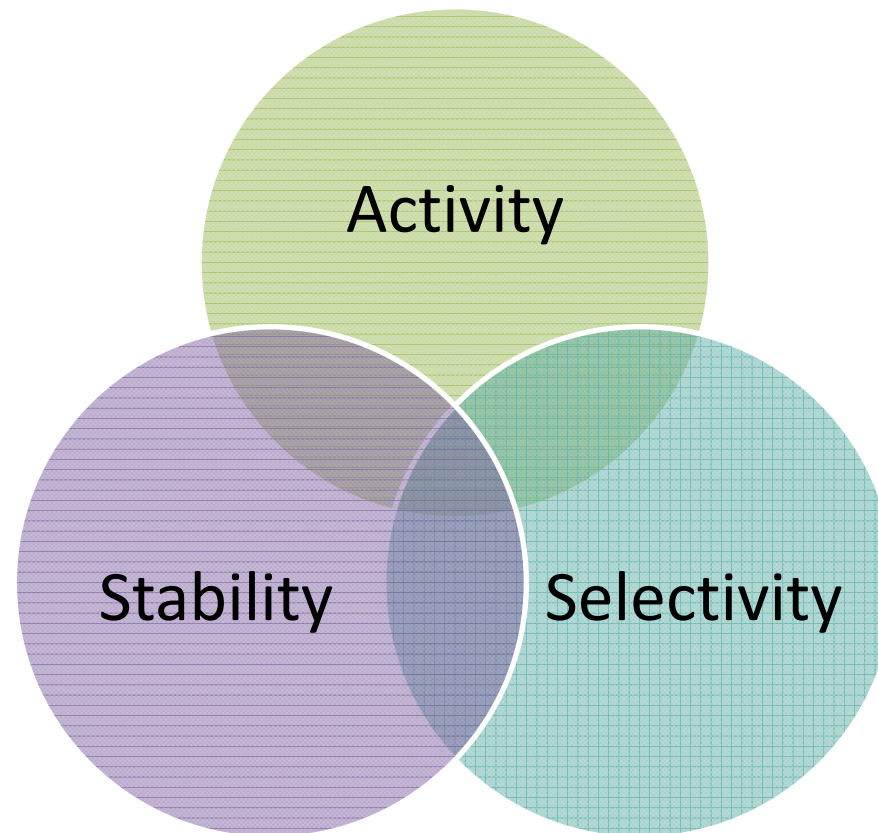
Electrochemical methods (3 electrode cell)



Hydrodynamic methods (e.g. rotating disk electrode) are particularly useful for cases where **mass transfer** is being studied and/or may be problematic (e.g. low concentration of dissolved gases or gas bubble formation on the electrocatalyst surface).



Three primary figures of merit for catalysts



Q: Which of these is most critically needed in catalyst development?

A: All three! But every reaction has different needs for catalyst development.



Electrochemical reaction kinetics

The big question: How much current do I achieve for the amount of overpotential that I apply?

Depends on two major factors (as with any chemical reaction):

- (1) The inherent kinetics of the reaction.
- (2) Effects of mass-transfer.

The Butler-Volmer Equation

$$i = i_o \left\{ \underbrace{\exp\left[\frac{\alpha_a n F \eta}{RT}\right]}_{\text{anodic term}} - \underbrace{\exp\left[-\frac{\alpha_c n F \eta}{RT}\right]}_{\text{cathodic term}} \right\}$$

$$i = i_a + i_c$$

i = current density
 i_o = exchange current density
 n = # of electrons transferred
 α = transfer coefficient (anodic or cathodic)
 F = Faraday's constant: 96,485 C/mol
 η = $(E - E_{\text{equil}})$ = overpotential
 R = gas constant
 T = temperature

- Assumes only one step is rate-determining
- If near equilibrium, both terms are important.
- If farther from equilibrium, one term dominates... can use the Tafel Equation!

$$i_a = i_o \exp\left(\frac{\eta}{b}\right)$$

$$i_c = -i_o \exp\left(-\frac{\eta}{b}\right)$$

where b = Tafel slope



Electrocatalyst activity: Figures of merit

Four primary figures of merit for electrocatalyst activity:


- Exchange current density, i_o (mA/cm^2)
- Tafel slope, b (mV/decade)
- Current density at a given overpotential:

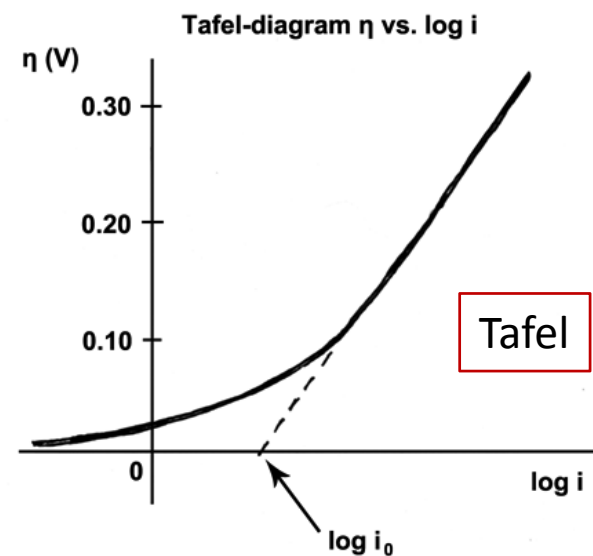
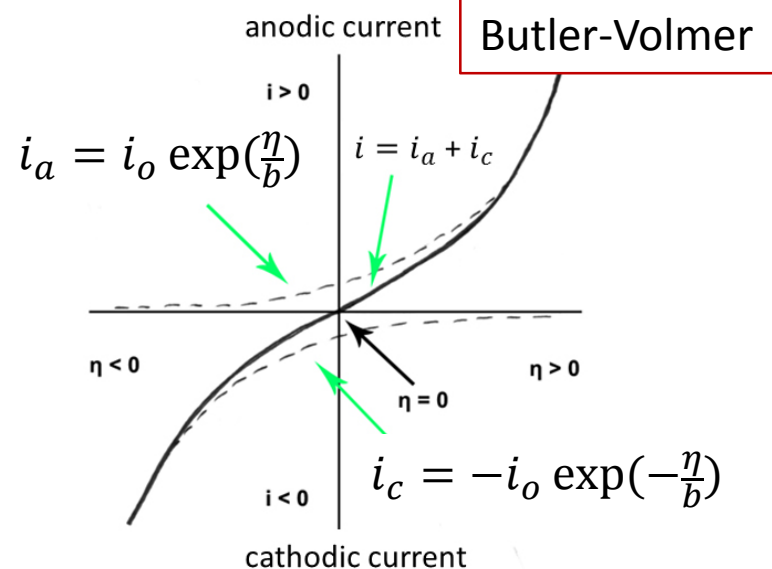
$$i_{E(\text{V vs. RHE})} (\text{mA}/\text{cm}^2)$$
- Overpotential needed to reach a given current density:

$$\eta_{i=10\text{mA}/\text{cm}^2} (\text{mV})$$

Three ways to report current densities:

- Per geometric area (cm^2_{geo})
- Per surface area ($\text{cm}^2_{\text{real}}$)
- Per electrochemically active surface area ($\text{cm}^2_{\text{ECSA}}$)
 - Closest to a true Turnover Frequency (TOF)

Easy/Practical

 Difficult/Useful



Recapping the fundamentals

- Thermodynamics
- Kinetics
- Methods in electrocatalysis research
- Figures of merit for electrocatalyst development

Four primary figures of merit for electrocatalyst activity:

- Exchange current density, i_o (mA/cm^2)
- Tafel slope, b (mV/decade)
- Current density at a given overpotential:

$$i_{E(\text{V vs. RHE})} (\text{mA}/\text{cm}^2)$$

- Overpotential needed to reach a given current density:

$$\eta_{i=10\text{mA}/\text{cm}^2} (\text{mV})$$

10 mA/cm²

Three ways to report current densities:

- Per geometric area (cm^2_{geo})
- Per surface area ($\text{cm}^2_{\text{real}}$)
- Per electrochemically active surface area ($\text{cm}^2_{\text{ECSA}}$)
 - This is the closest to providing a true Turnover Frequency (TOF)



**Relevant metric
for solar fuels**

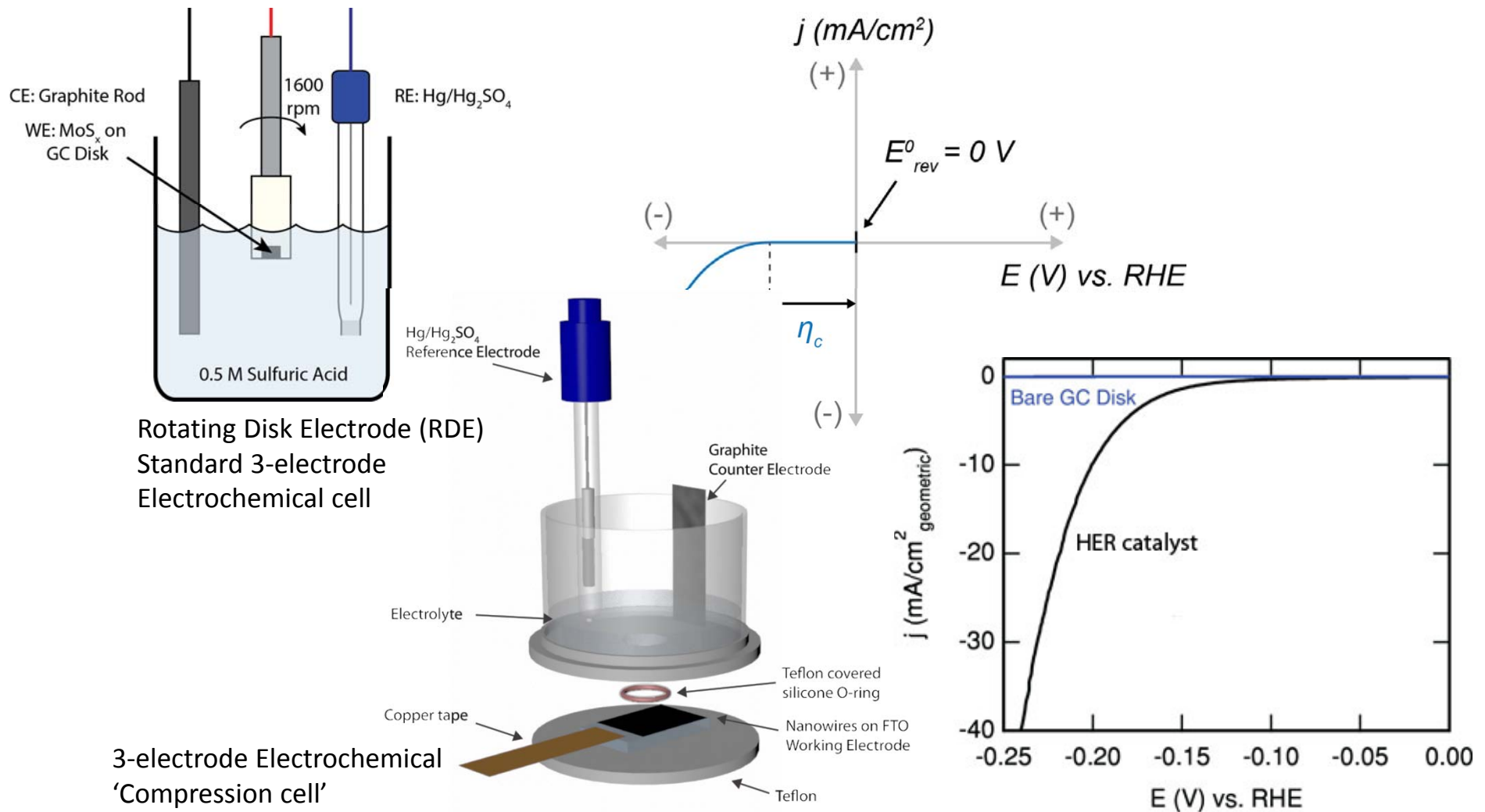


Now that we have covered the fundamentals, let us examine some examples of electrocatalyst development.

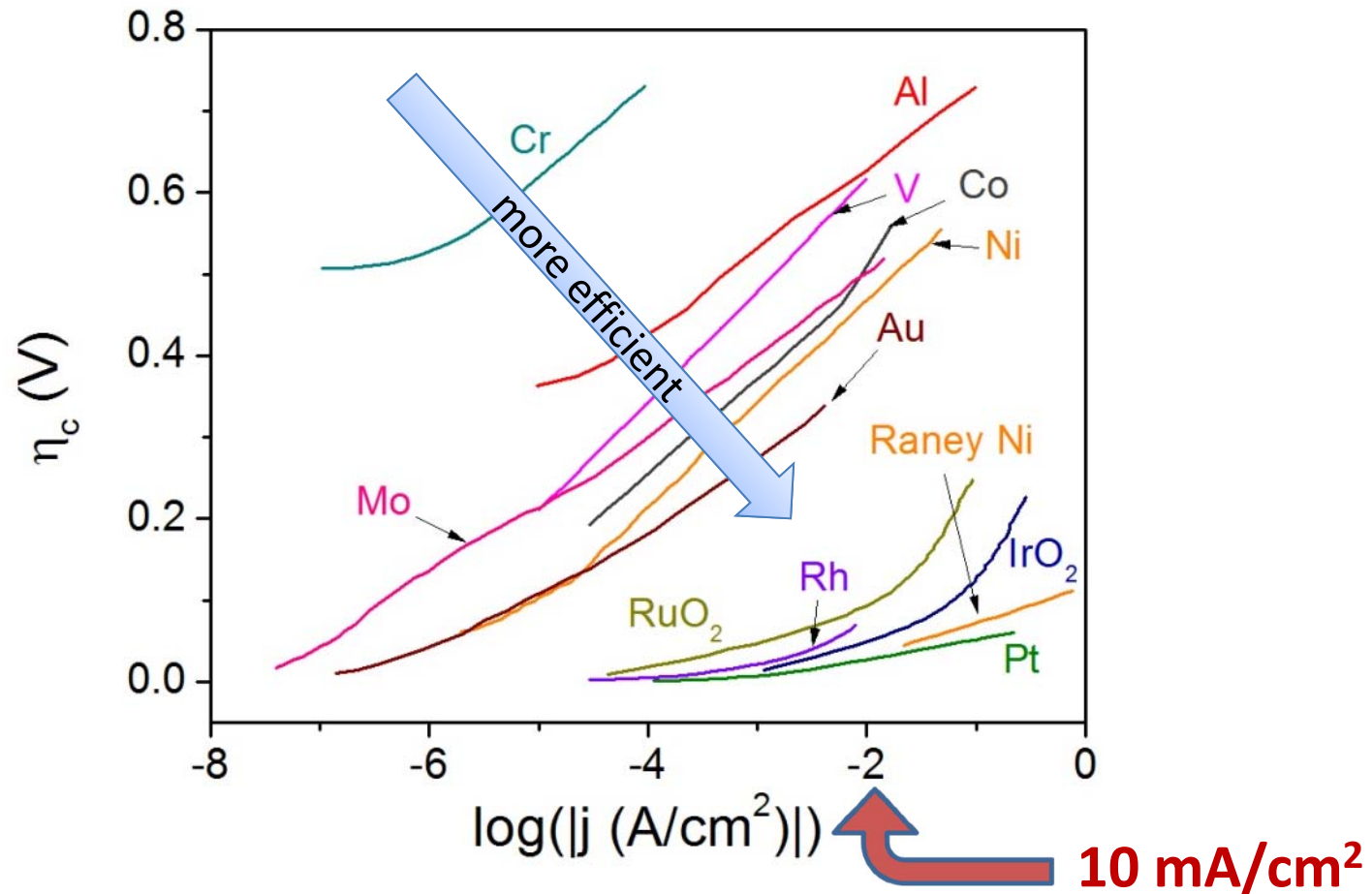
- H₂ evolution
- CO₂ reduction to fuels and chemicals



The hydrogen evolution reaction (HER): Experimental methodology



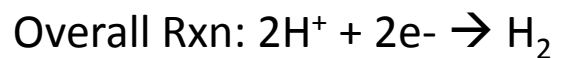
Tafel Plots for various HER catalysts



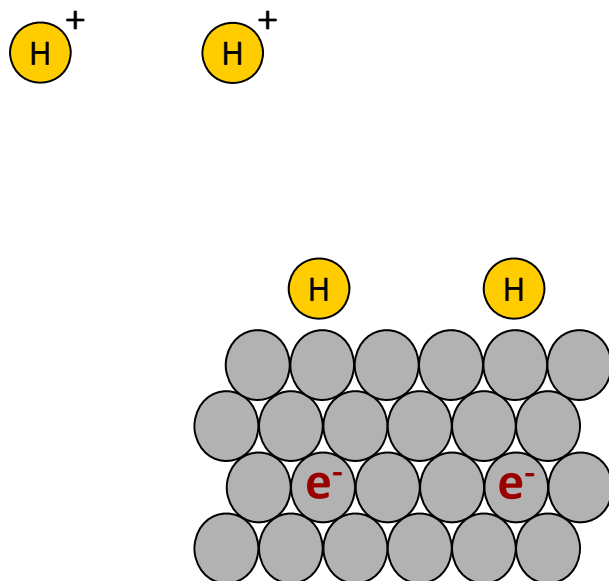
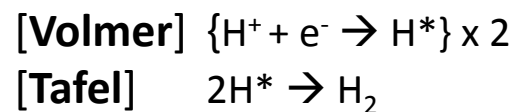
Chen Z, Jaramillo T.F., et al. *NanoLetters* 11, 10 (2011)



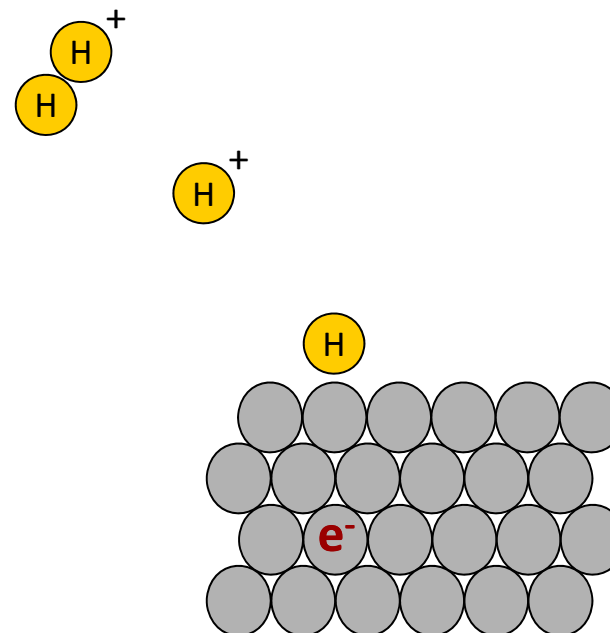
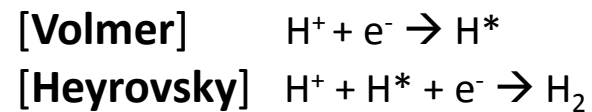
A molecular scale-view: H₂ evolution mechanisms



Volmer-Tafel
(i.e. Langmuir-Hinshelwood)



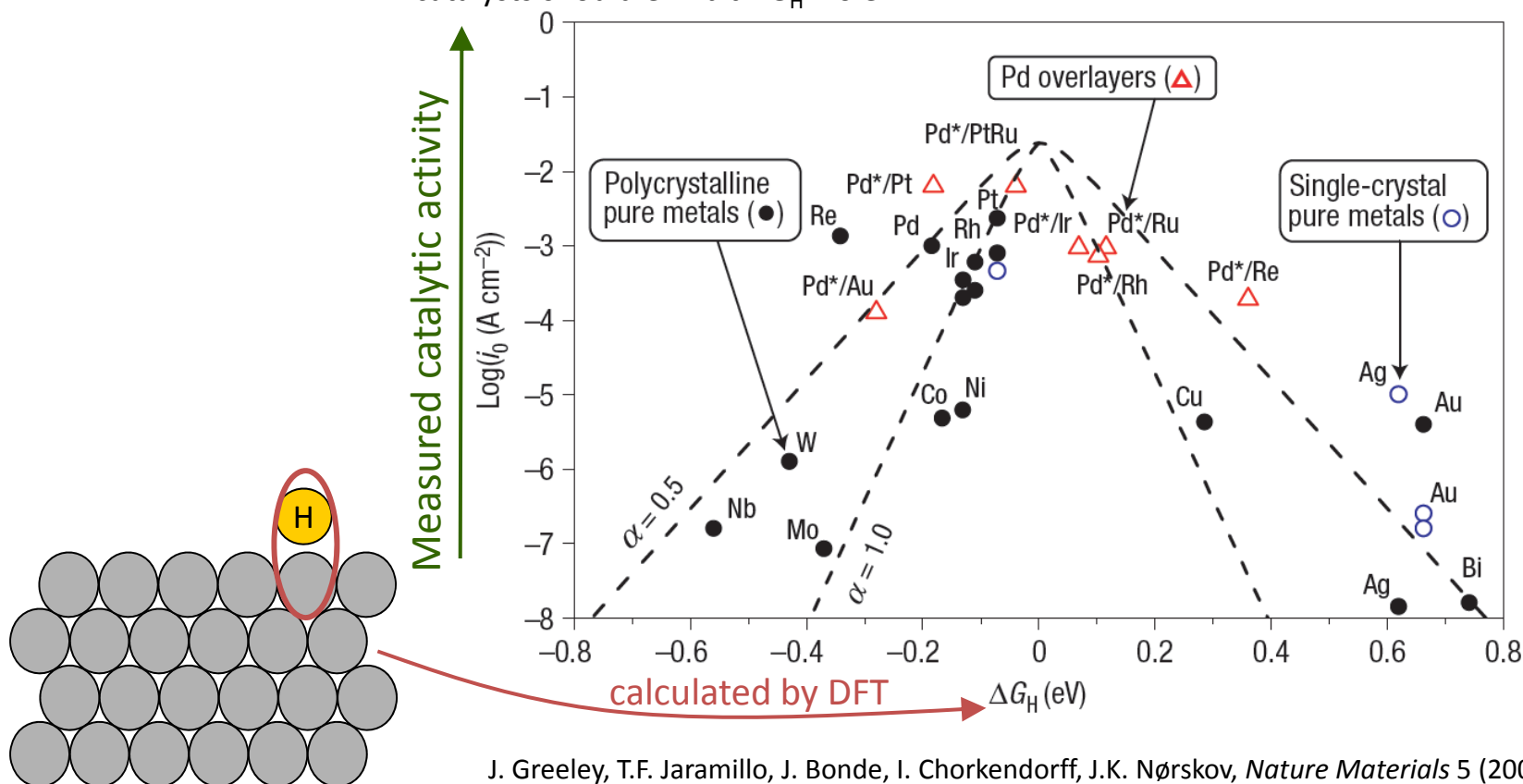
Volmer-Heyrovsky
(i.e. to Eley-Rideal)



Towards quantitative 'descriptors' for catalysis

Paul Sabatier (1911): An optimal catalyst will bind reaction intermediates moderately on its surface; not too strongly nor too weakly.

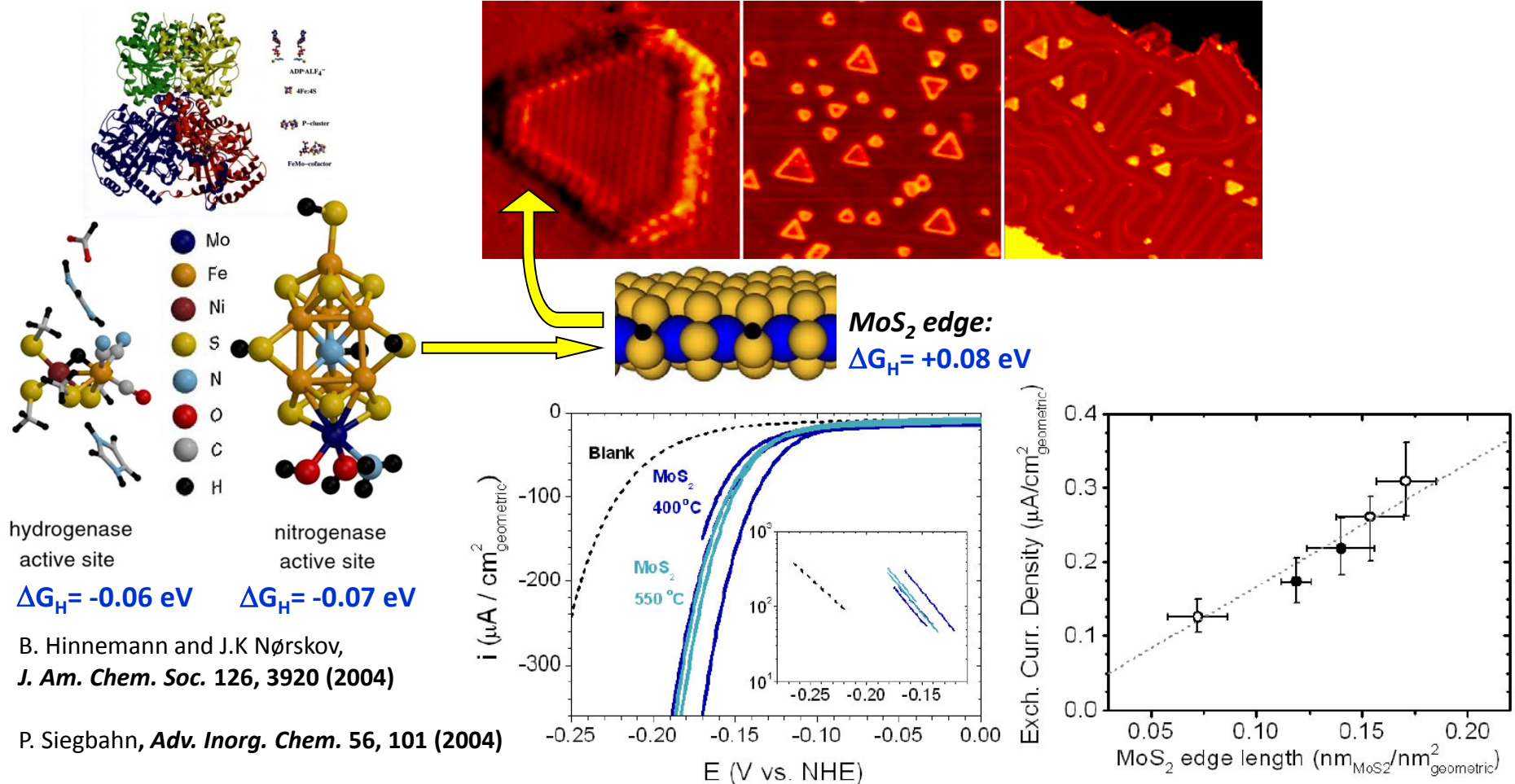
Roger Parsons (1957): The first 'qualitative' volcano in electrocatalysis, indicating that the best HER catalysts should exhibit $\Delta G_H \approx 0$ eV.



J. Greeley, T.F. Jaramillo, J. Bonde, I. Chorkendorff, J.K. Nørskov, *Nature Materials* 5 (2006) 909-913.



A bio-inspired approach



B. Hinnemann and J.K Nørskov,
J. Am. Chem. Soc. **126**, 3920 (2004)

P. Siegbahn, *Adv. Inorg. Chem.* **56**, 101 (2004)

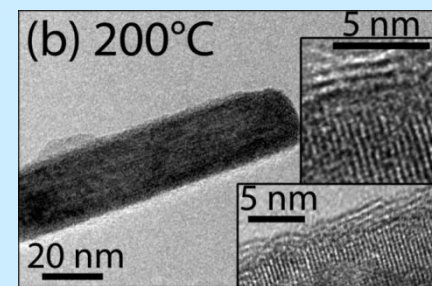
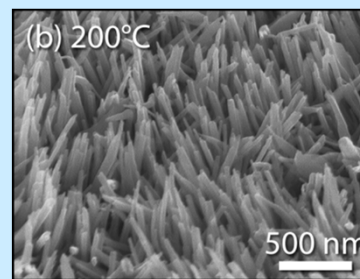
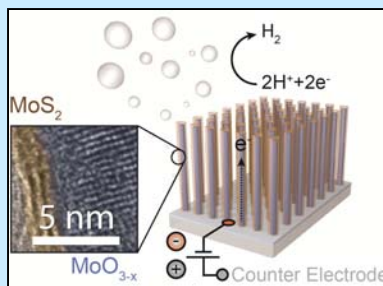
B. Hinnemann, P.G. Moses, J. Bonde, K.P. Jørgensen, J. H. Nielsen, S. Horch,
 I. Chorkendorff, J.K. Nørskov, *J. Amer. Chem. Soc.* **127** (2005) 5308-5309.

T.F. Jaramillo, K.P. Jørgensen, J. Bonde, J.H. Nielsen,
 S. Horch, I. Chorkendorff; *Science* **317** (2007) 100.

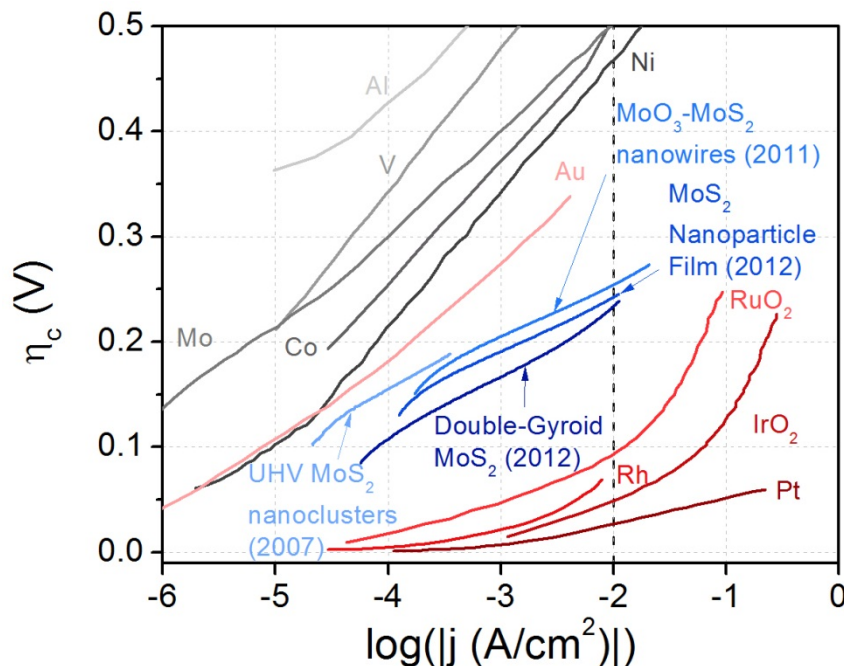


A family of nanostructured MoS₂ catalysts for the HER

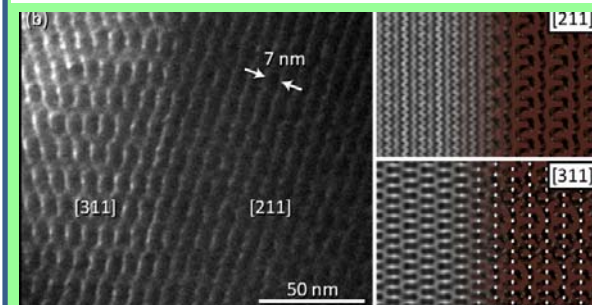
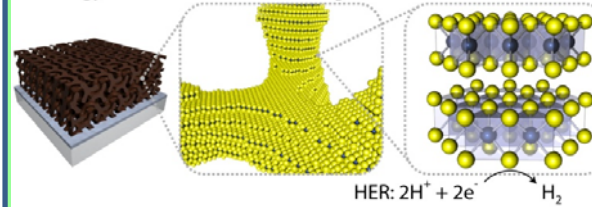
Core-shell MoO₃-MoS₂ nanowires



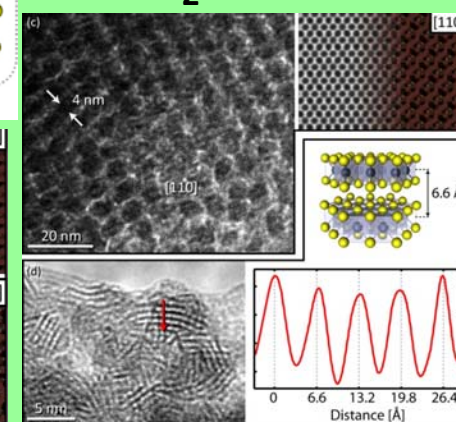
Z. Chen, D. Cummins, B.N. Reinecke, E. Clark, M.K. Sunkara, T.F. Jaramillo, *Nano Letters*, v11 (2011) 4168-4175.



Double gyroid meso-structured MoS₂



Double-gyroid MoS₂ thin films



J. Kibsgaard, Z. Chen, B.N. Reinecke, T.F. Jaramillo, *Nature Materials* [advance online publication Oct 7, 2012, DOI: 10.1038/NMAT3439].



Current state of catalyst development for H₂ evolution

Catalyst	Advantages	Disadvantages
Precious metals (Pt, Pd)	Best known catalysts.	Expensive (\$65/gram for Pt).
Common metals (Al, V)	Inexpensive.	Poor activity.
Nickel alloys (NiMo, NiAl)	Inexpensive, stable in base, very active.	Lower activity than precious metals, unstable in acidic electrolyte.
Molybdenum sulfides (MoS ₂)	Inexpensive, stable in acid, very active.	Lower activity than precious metals, unstable in base.



A molecular-scale view of CO₂ reduction

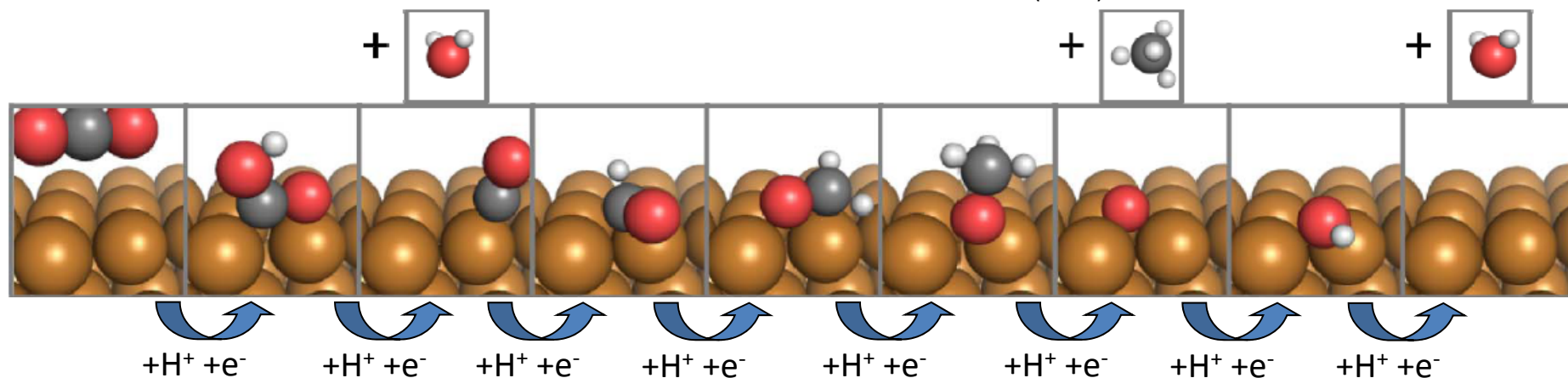
Y. Hori, "Electrochemical CO₂ reduction on metal electrodes"

E⁰ vs. RHE

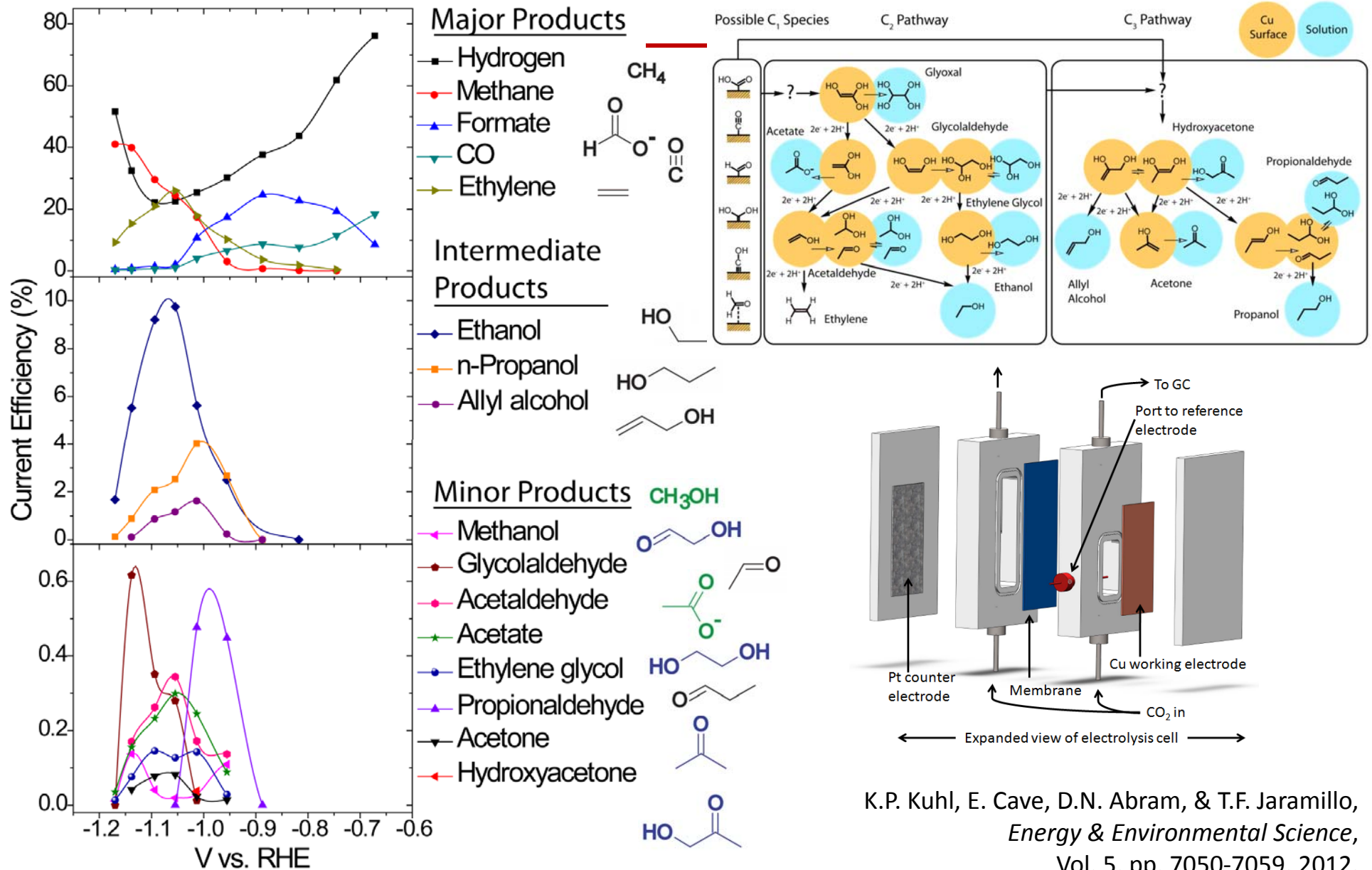
$2\text{H}^+ + 2\text{e}^-$	$\leftrightarrow \text{H}_2$	0.00 V
$\text{CO}_2 + 2\text{H}^+ + 2\text{e}^-$	$\leftrightarrow \text{CO} + \text{H}_2\text{O}$	- 0.11 V
$\text{CO}_2 + 8\text{H}^+ + 8\text{e}^-$	$\leftrightarrow \text{CH}_4 + 2\text{H}_2\text{O}$	+ 0.16 V
$2\text{CO}_2 + 12\text{H}^+ + 12\text{e}^-$	$\leftrightarrow \text{C}_2\text{H}_4 + 4\text{H}_2\text{O}$	+ 0.07 V
$2\text{CO}_2 + 12\text{H}^+ + 12\text{e}^-$	$\leftrightarrow \text{C}_2\text{H}_5\text{OH} + 3\text{H}_2\text{O}$	+ 0.08 V
$3\text{CO}_2 + 18\text{H}^+ + 18\text{e}^-$	$\leftrightarrow \text{C}_3\text{H}_7\text{OH} + 5\text{H}_2\text{O}$	+ 0.09 V

All values are close to the H₂ evolution potential (0.00 V).

A. Peterson, F. Abild-Pederson, F. Studt, J. Rossmeisl, J.K. Nørskov, *Energy & Environmental Science* v3 (2010) 1311-1315.



CO₂ electro-reduction on copper



K.P. Kuhl, E. Cave, D.N. Abram, & T.F. Jaramillo,
Energy & Environmental Science,
 Vol. 5, pp. 7050-7059, 2012.

Summary

- Introduction
 - The role of electrocatalysis and how it relates to energy conversion
- Electrochemistry fundamentals
 - Anodes, cathodes, redox chemistry
- Thermodynamics
 - Equilibrium potentials and reaction energetics
- Kinetics
 - Key equations: Butler-Volmer and Tafel
 - Primary figures of merit in determining electrocatalyst activity
- Methods in electrocatalysis research
 - 3-electrode electrochemical cells and the rotating disk electrode (RDE)
- Figures of merit for electrocatalyst evaluation and development
- Applications & examples: A molecular-scale view of electrocatalysis
 - The hydrogen evolution reaction (HER)
 - The carbon dioxide reduction reaction (CO₂RR)
- References
 - A.J. Bard & L. Faulkner, *Electrochemical Methods: Fundamentals and Applications*, Wiley, 2000.
 - J.O'M. Bockris & S.U.M. Khan, *Surface Electrochemistry: A Molecular-Level Approach*, Springer, 1993.
 - J. Newman & K.E. Thomas-Alyea, *Electrochemical Systems*, Wiley, 2004.

