

Catalysis for Sustainable Chemicals and Energies - SS 2020

Theory in Electrocatalysis

Institute of Catalysis Research and Technology
Institute for Chemical Technology and Polymer Chemistry

what do experiments measure and how can they be modeled?

what do you want to model (current, potential, etc?)

how accurate can your models and theory be?

method of choice - density functional theory on GGA level

modeling solid liquid interface

modeling charged interfaces

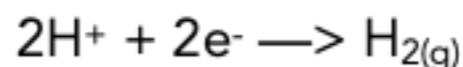
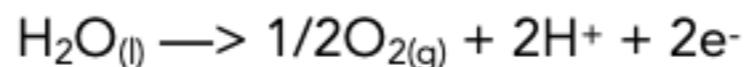
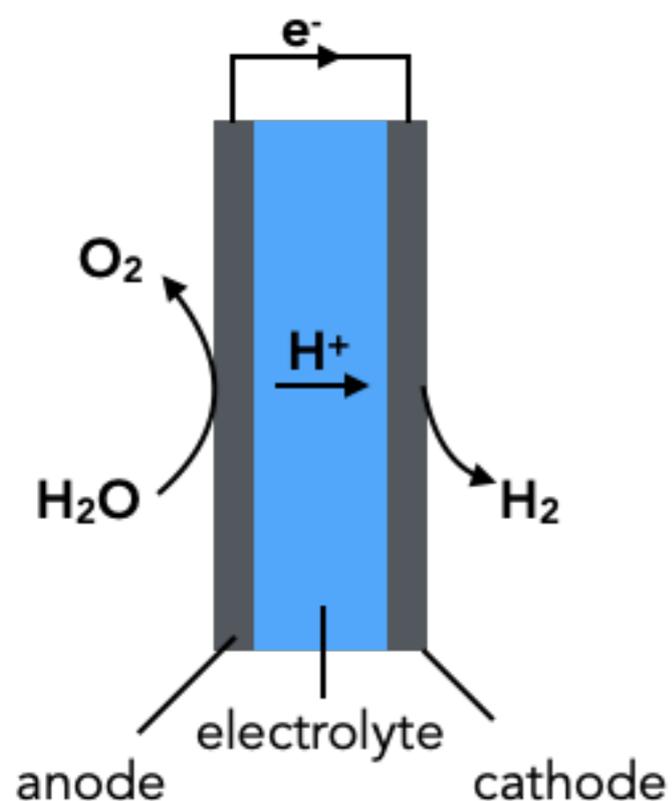
modeling varying pH in the interface

electron and proton transfer processes

approximations needed → which ones are sufficient?



electrical potential created by differences in half reactions



cell voltages (cell potentials) are differences in potential from two half-reactions that make up a complete reaction

transfer of 4 protons and electrons

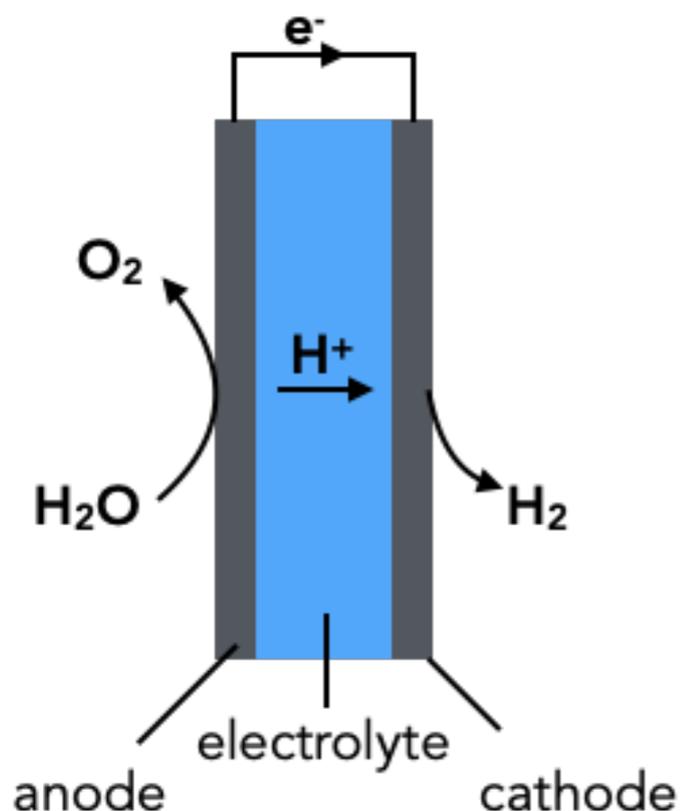
$$4.92 \text{ eV} / 4 \longrightarrow 1.23 \text{ eV}$$

$$1.23 \text{ eV} \longrightarrow \mathbf{1.23 \text{ V}} \text{ per electron}$$

a *minimum* voltage of **1.23 V** has to be applied to drive water splitting

likewise: a *maximum* voltage of **1.23 V** can be obtained through the reverse reaction





standard hydrogen electrode (SHE)

by definition 0 V at standard conditions
(298.15 K, 1 atm H₂, pH=0)

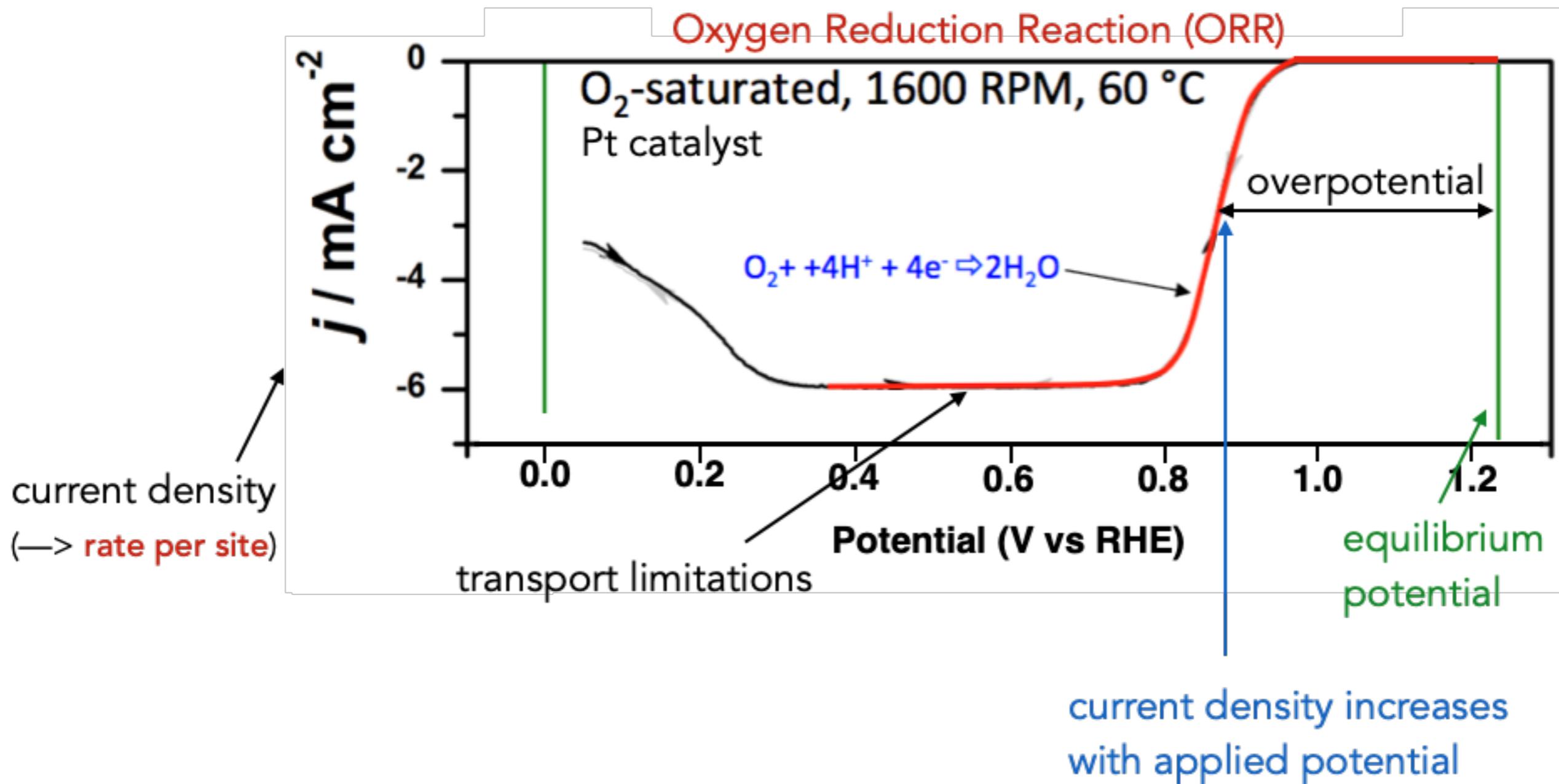
half-reaction			
oxidant		reductant	
Li ⁺ + e ⁻	⇌	Li _(s)	-3.04 V
Na ⁺ + e ⁻	⇌	Na _(s)	-2.71 V
Mg ²⁺ + 2e ⁻	⇌	Mg _(s)	-2.37 V
Zn ²⁺ + 2e ⁻	⇌	Zn _(s)	-0.76 V
Pb ²⁺ + 2e ⁻	⇌	Pb _(s)	-0.13 V
2H⁺ + 2e⁻	⇌	H_{2(g)}	0.00 V
Cu ²⁺ + 2e ⁻	⇌	Cu _(s)	+0.34 V
Ag ⁺ + e ⁻	⇌	Ag _(s)	+0.80 V
O _{2(g)} + 4H ⁺ + 4e ⁻	⇌	2H ₂ O _(l)	+1.23 V
Cl _{2(g)} + 2e ⁻	⇌	2Cl ⁻	+1.36 V

half reactions occurring at the
cathode and anode

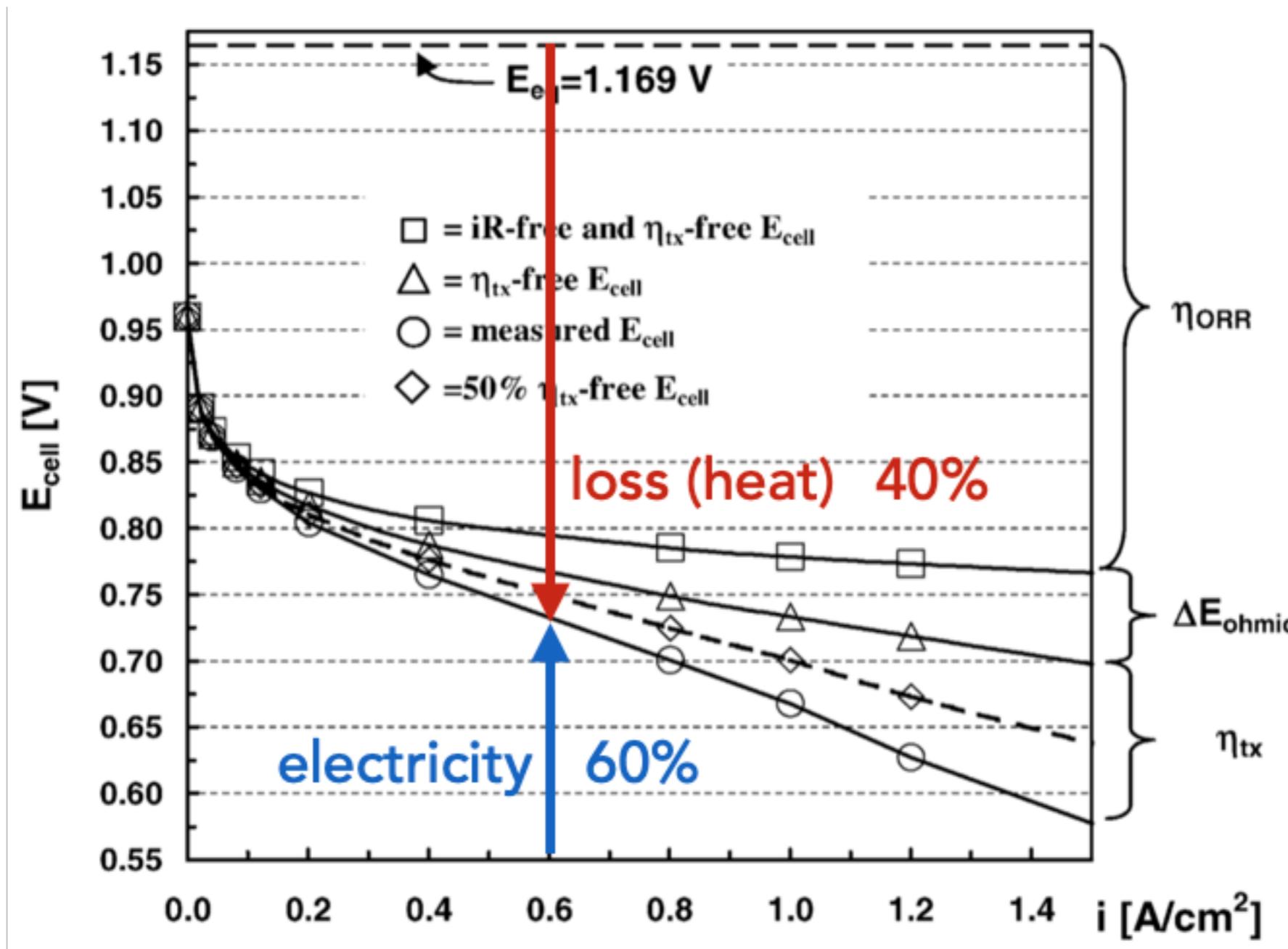
electrical potential created by
differences in half reactions

potential of half reactions
referenced to standard hydrogen
electrode (SHE)



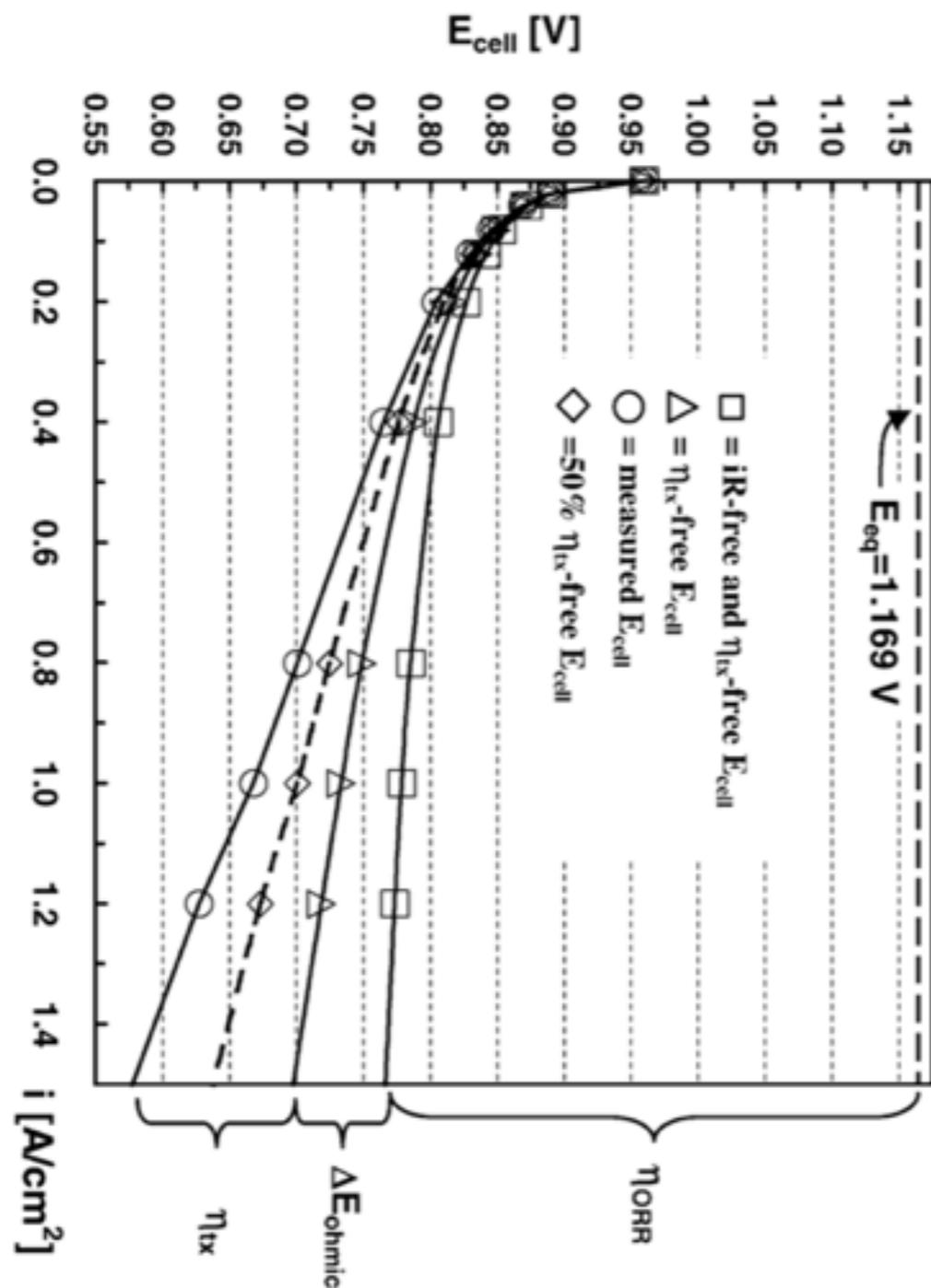


Overpotential for ORR

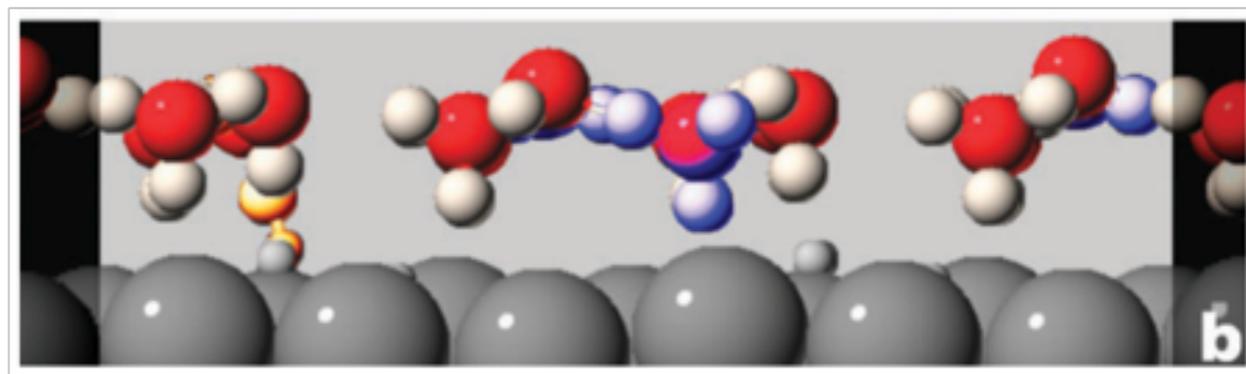


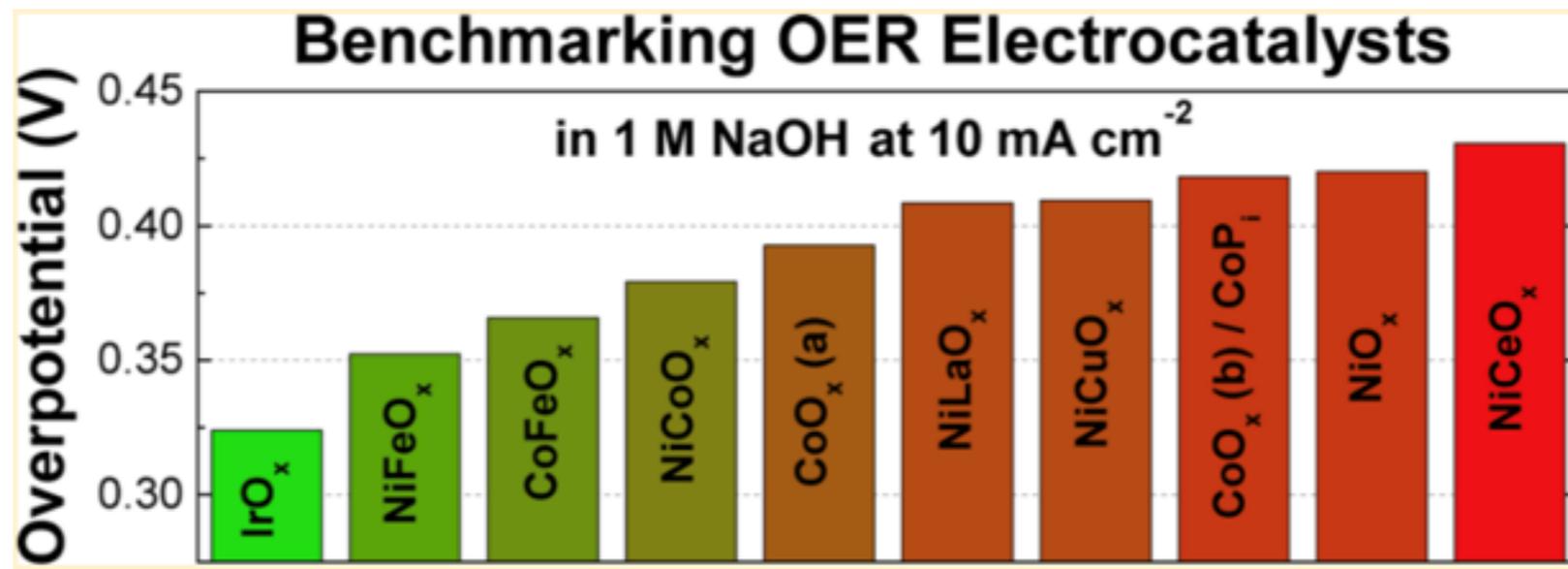
overpotential
(for Pt catalyst)
ca 33%





current relates to rate of a reaction
 how to calculate current at changing potential
 what do you calculate? overpotential?!
 overpotential depends on current density!
 electron and proton transfer processes
 (at charged interfaces, at various potentials, varying pH, ...)
 how can DFT help to understand
 electrochemical processes?

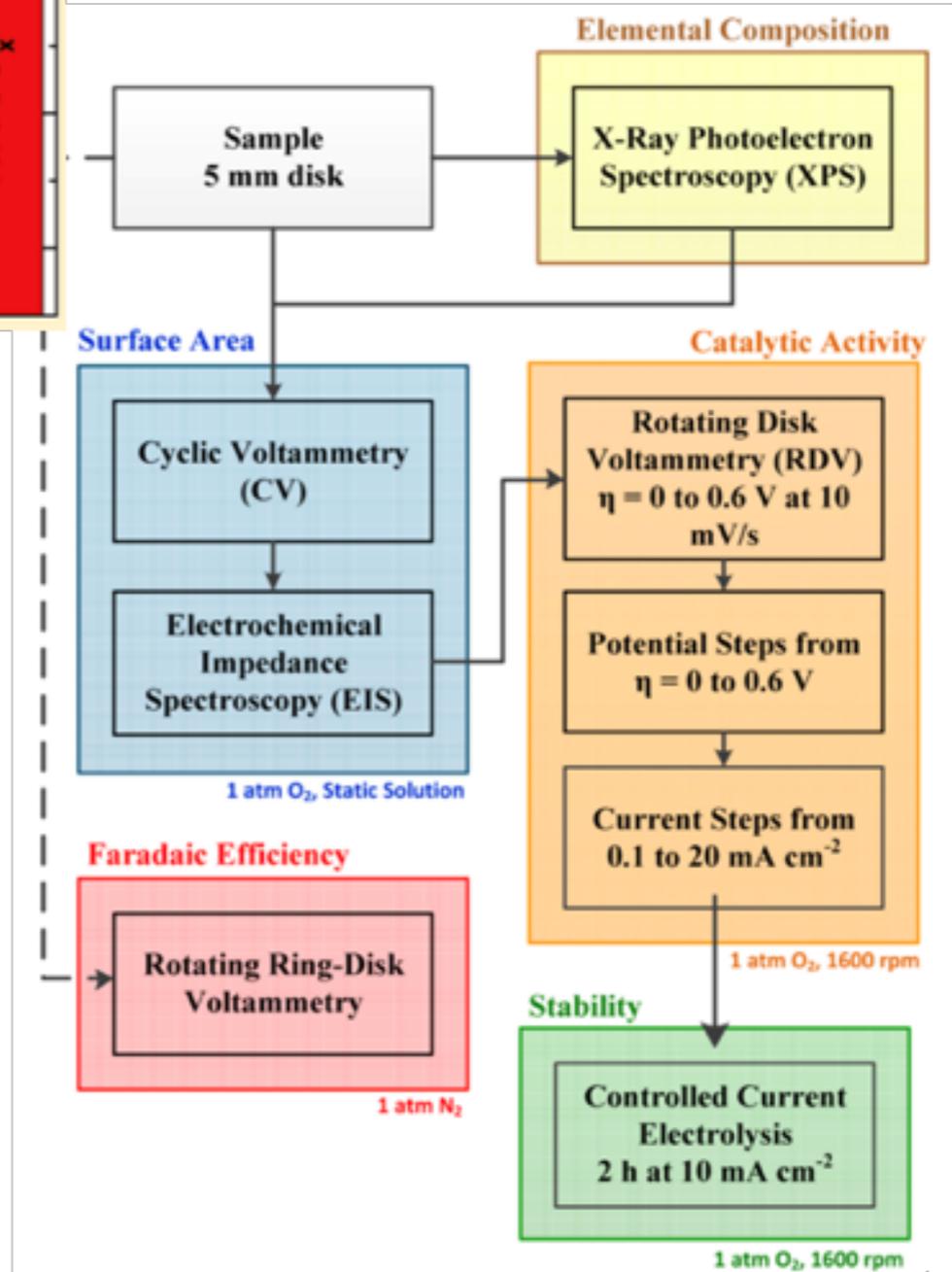




current density of 10 mA cm⁻²
(current density of app. 10% efficient solar to fuels)

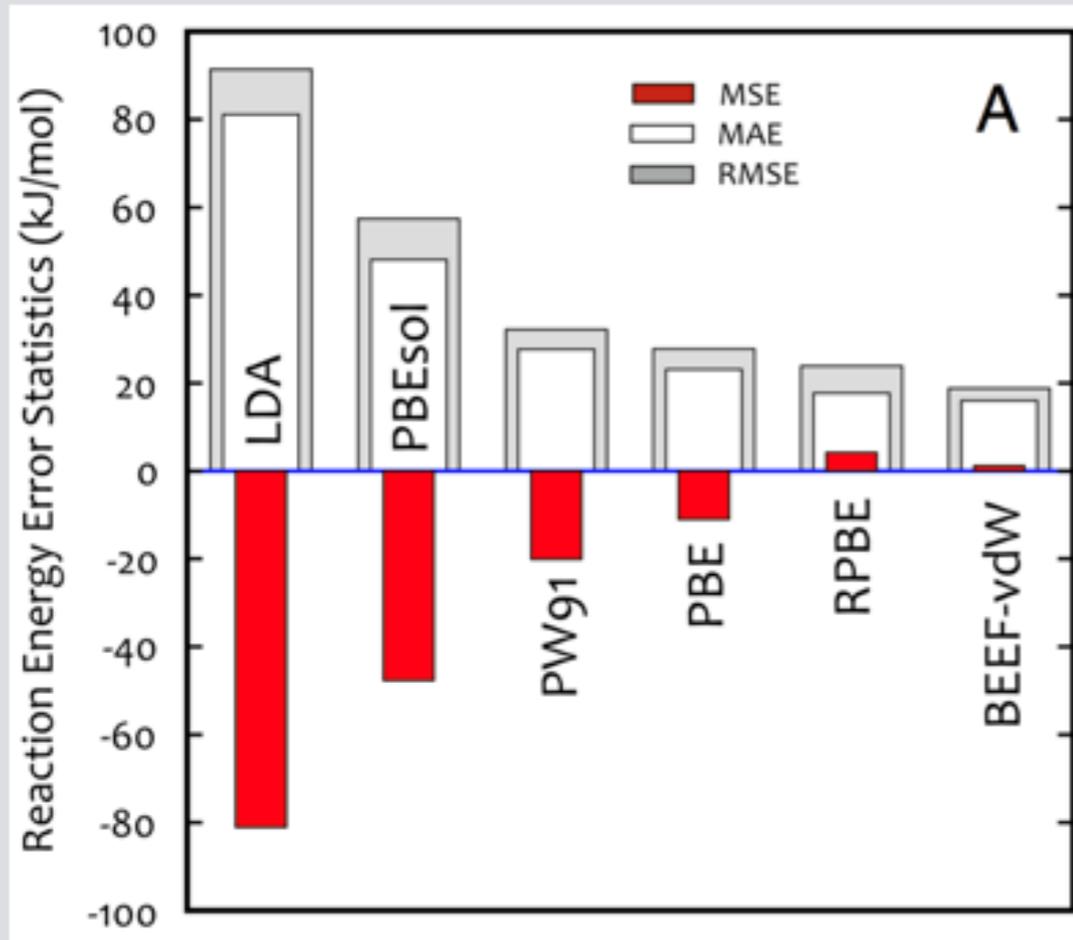
alkaline systems (1M NaOH)
(stability issues in acidic environments)

2h controlled-current electrolysis

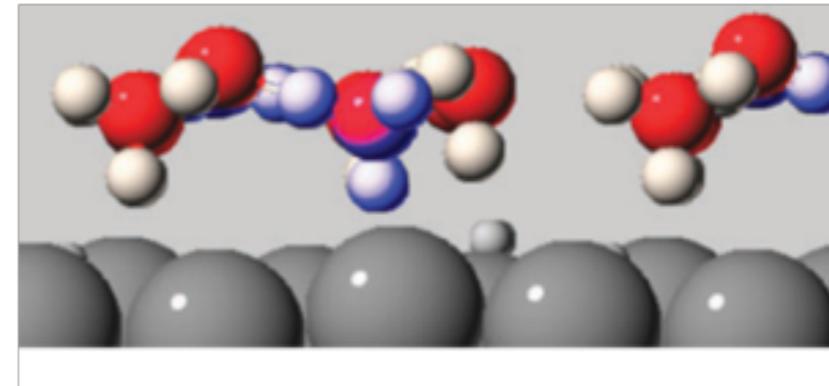


McCrary, Jung, Peters, Jaramillo, *J. Am. Chem. Soc.* **2013**, 135, 16977.

values for adsorption energies on transition metal surfaces are typically within ± 0.2 eV of experiment (depending on functional used)

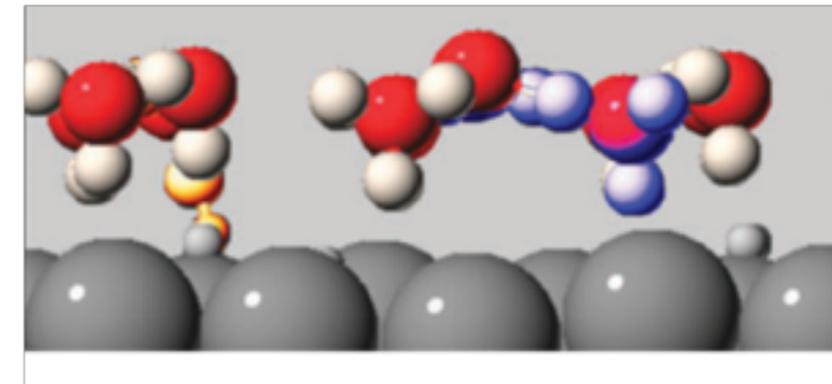


Wellendorff, Silbaugh, Garcia-Pintos, Nørskov, Bligaard, Studt, Campbell, *Surf. Sci.* **2015**, 640, 36.



Adsorption energies

~ 5h to 5d on 16 cpus



Transition state energies

~ 5d to 5w on 32 cpus

explicit solvation with water layer makes everything much more cumbersome



- how to model the electrocatalytic surface?
- H⁺ ion concentration at the electrode interface
 - only small unit cells can be modeled → high H⁺ ion concentration
 - H⁺ ion concentration might change with reaction coordinate
- calculating barriers in water surrounding very challenging
- solid-liquid interface is charged
- modeling of both electron and proton transfer
- how to model the applied potential?
- how do you calculate change in current density as function of applied potential?

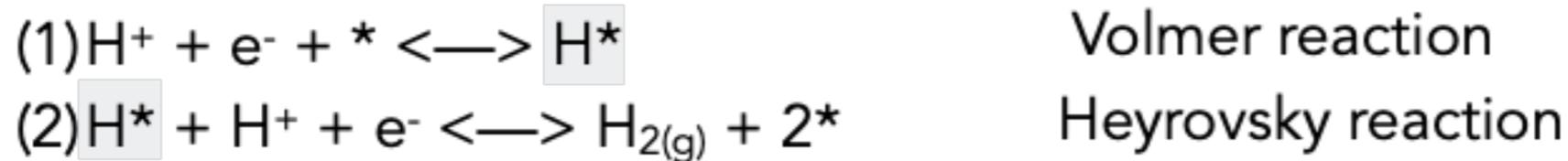


the simple approach the computational hydrogen electrode

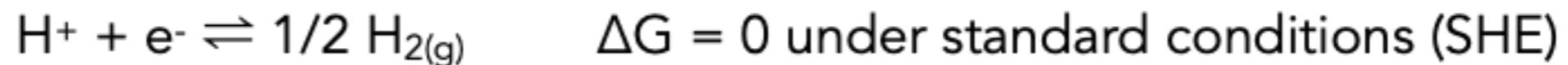


hydrogen evolution reaction (HER) $2H^+ + 2e^- \rightleftharpoons H_{2(g)}$

assumption: electron and proton transfer is coupled



H^* \rightarrow simple to calculate



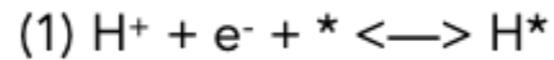
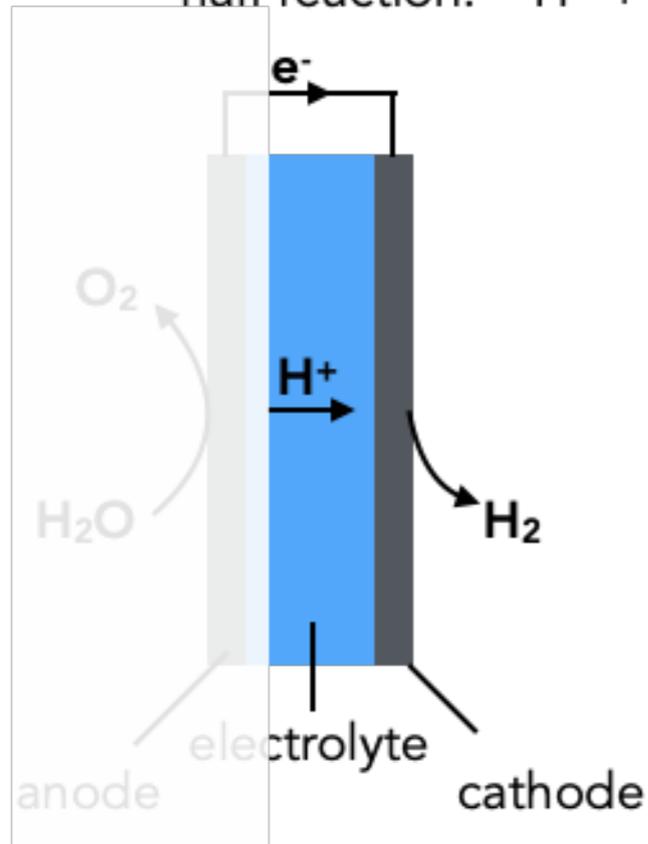
$\rightarrow H_{2(g)}$ gives reference to $H^+ + e^-$ through SHE at 0 V

computational hydrogen electrode (CHE)

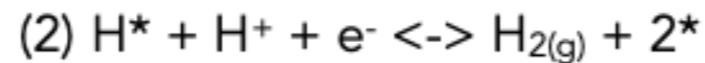


hydrogen evolution analyzed with the CHE

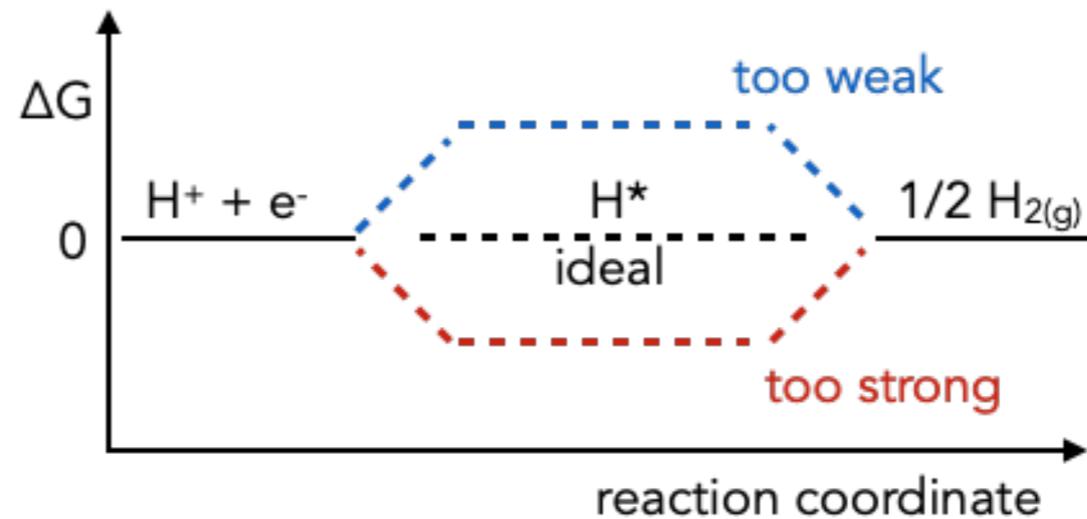
half reaction: $\text{H}^+ + \text{e}^- \rightleftharpoons 1/2 \text{H}_{2(\text{g})}$



Volmer reaction



Heyrovsky reaction



SHE: $\text{H}^+ + \text{e}^- \rightleftharpoons 1/2 \text{H}_{2(\text{g})}$ $\Delta G = 0$ under standard conditions

analysis in terms of Sabatier's principle:

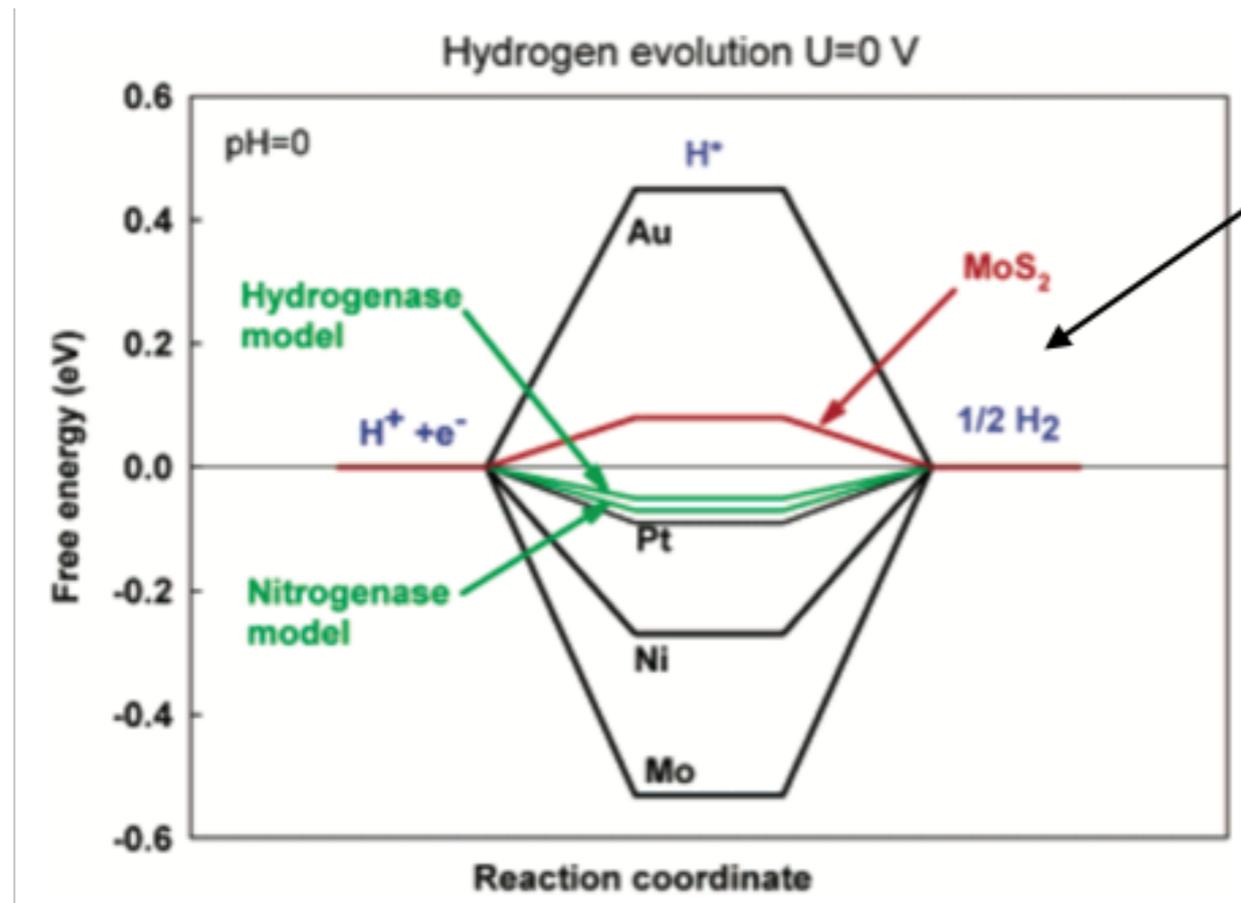
too weak adsorption energy of H^* \rightarrow **first proton transfer** to surface difficult

too strong adsorption energy of H^* \rightarrow **second proton transfer** to H^* difficult

can strength of ΔG of H^* determine overpotential required to drive HER?



hydrogen evolution analyzed with ΔG_{H^*}



calculated free energy diagram for HER at potential $U=0$ V relative to SHE

assumption according to Sabatier's principle: ΔG_{H^*} closest to zero defined as optimum

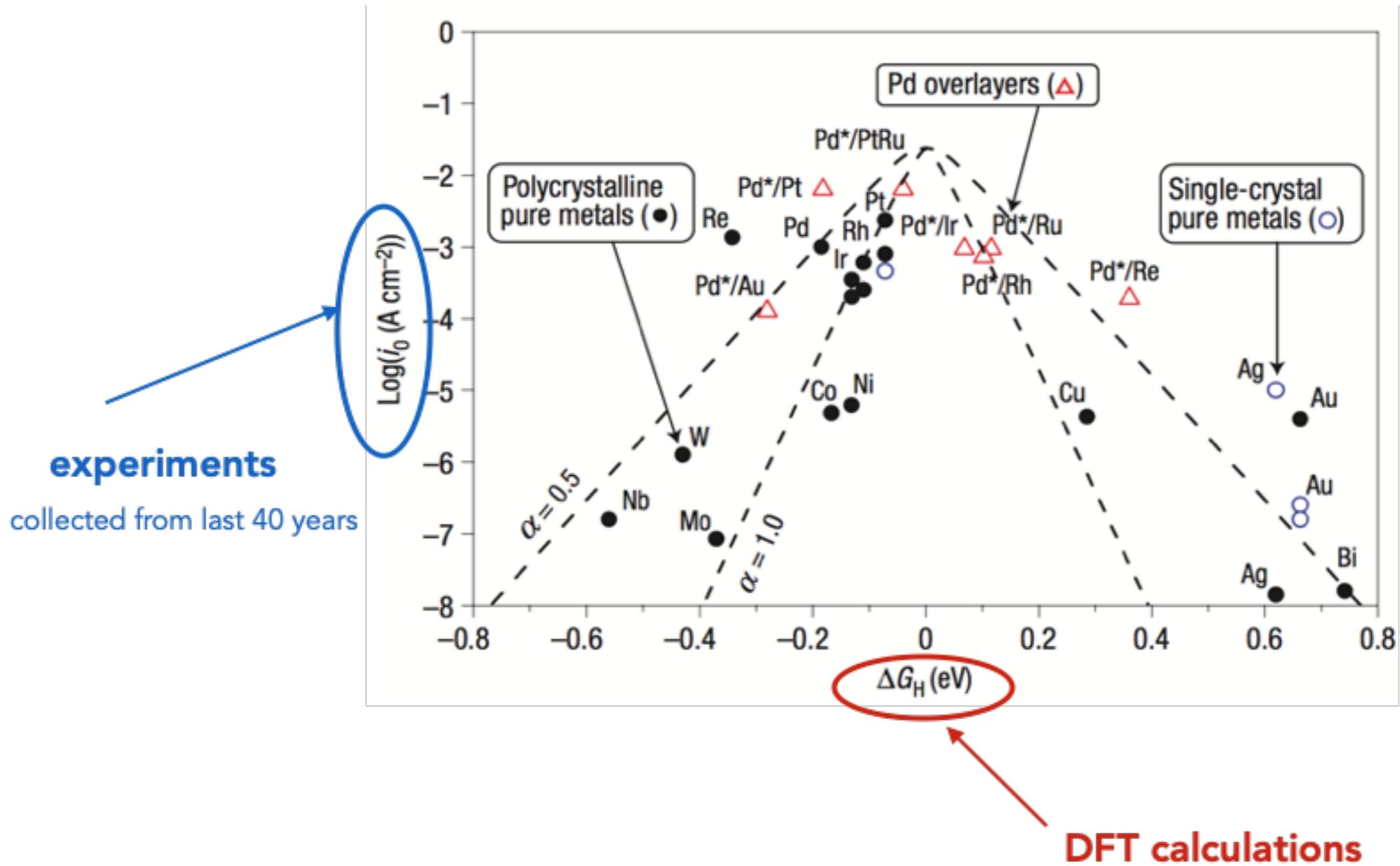
—> Pt best elemental metal

—> Hydrogenase / Nitrogenase H₂ evolving enzymes

—> MoS₂ identified through computations subsequently verified by experiments

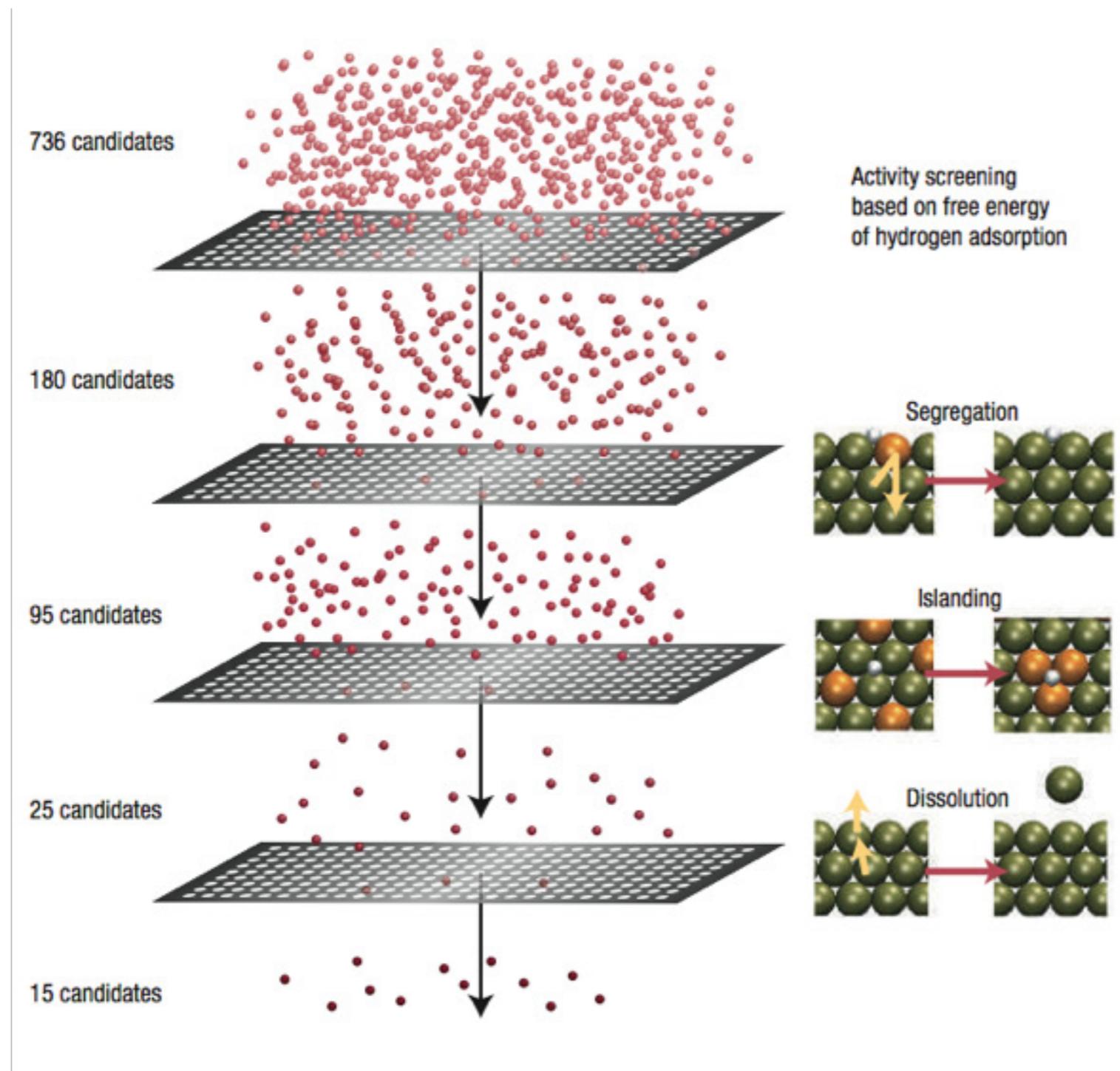


hydrogen evolution volcano



Greeley, Jaramillo, Bonde, Chorkendorff, Nørskov, *Nature Mater.* **2006**, 5, 909.





activity \rightarrow screening for ΔG_{H^*}

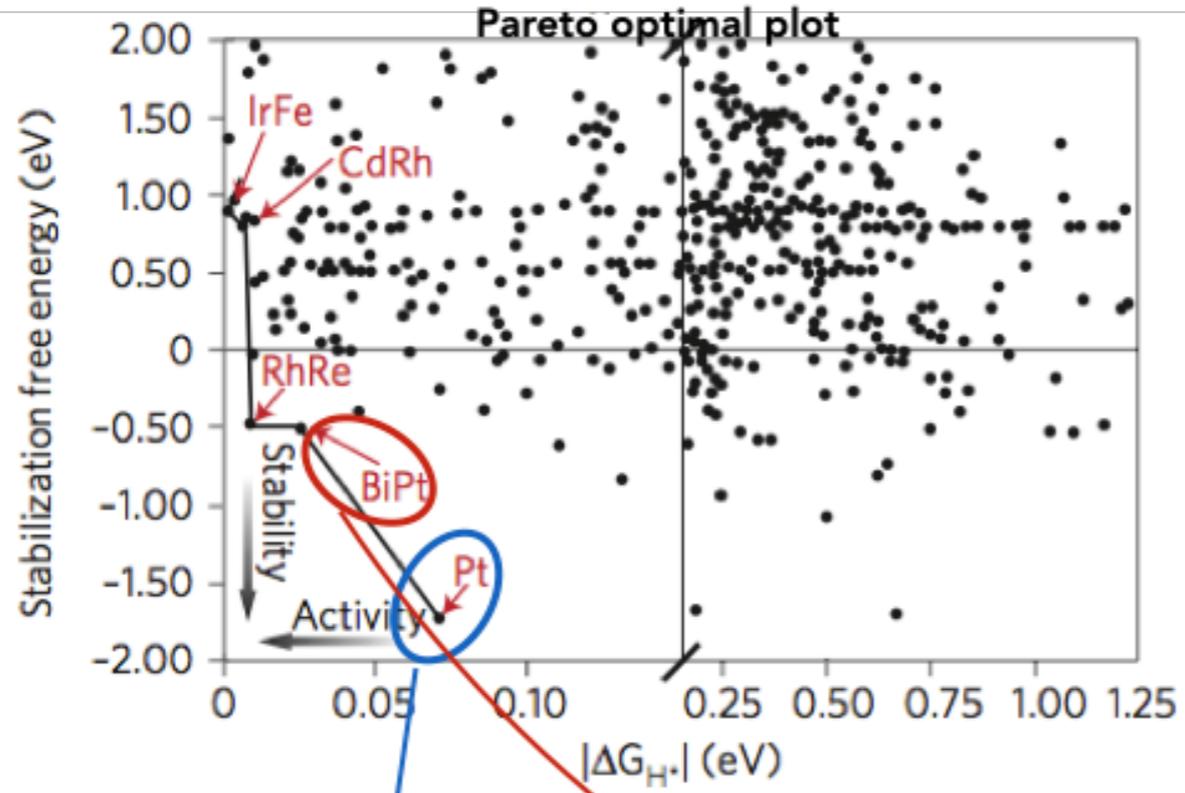
stability \rightarrow screening for:

\rightarrow segregation

\rightarrow islanding

\rightarrow dissolution

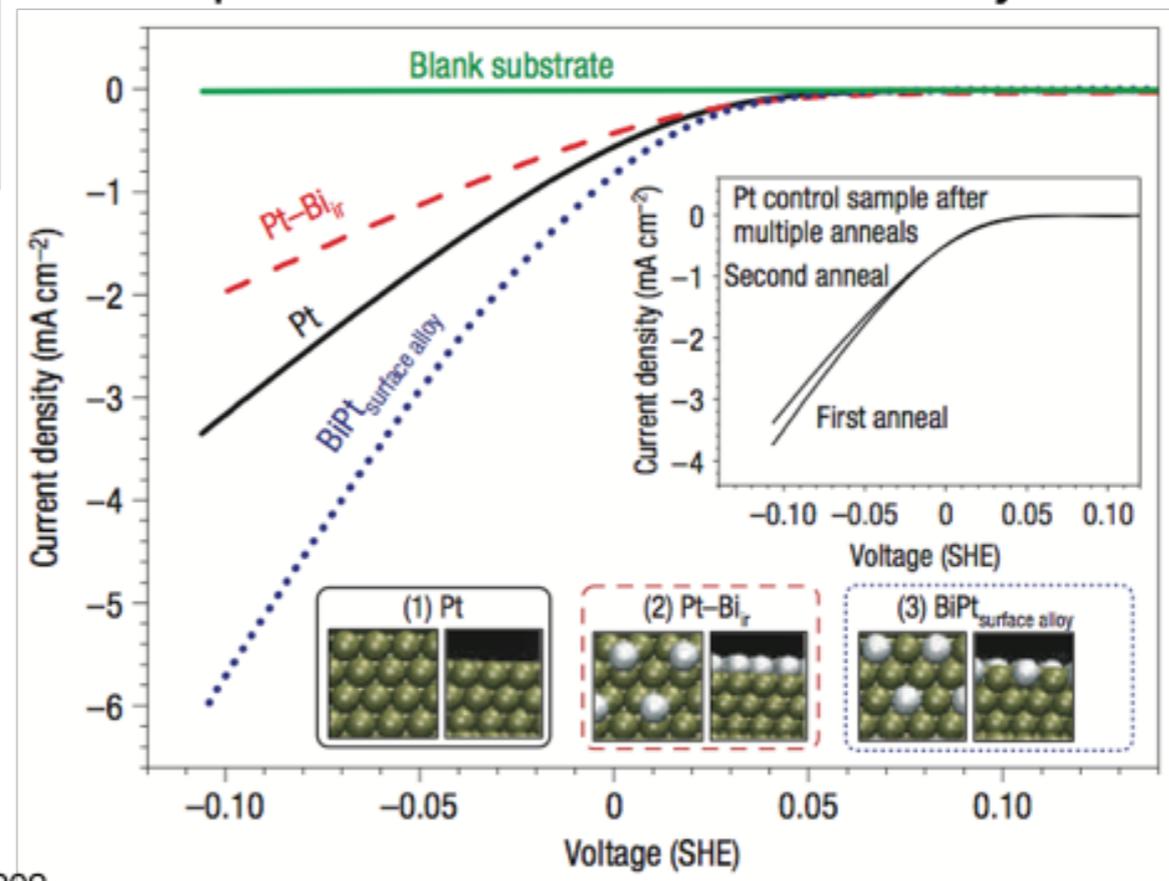




Pt stable and good

activity \rightarrow screening for ΔG_{H^*} close to 0
 stability \rightarrow screening for large ΔG_{alloy}

experimental verification of BiPt surface alloys



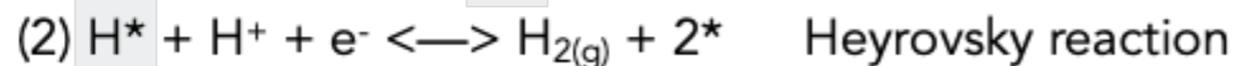
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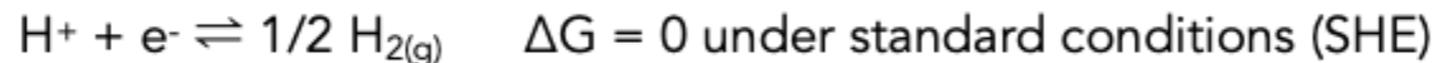
computational hydrogen electrode (CHE) model

hydrogen evolution reaction (HER) $2\text{H}^+ + 2\text{e}^- \rightleftharpoons \text{H}_{2(\text{g})}$

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H^* \rightarrow simple to calculate



$\rightarrow \text{H}_{2(\text{g})}$ gives reference to $\text{H}^+ + \text{e}^-$ through SHE at 0 V

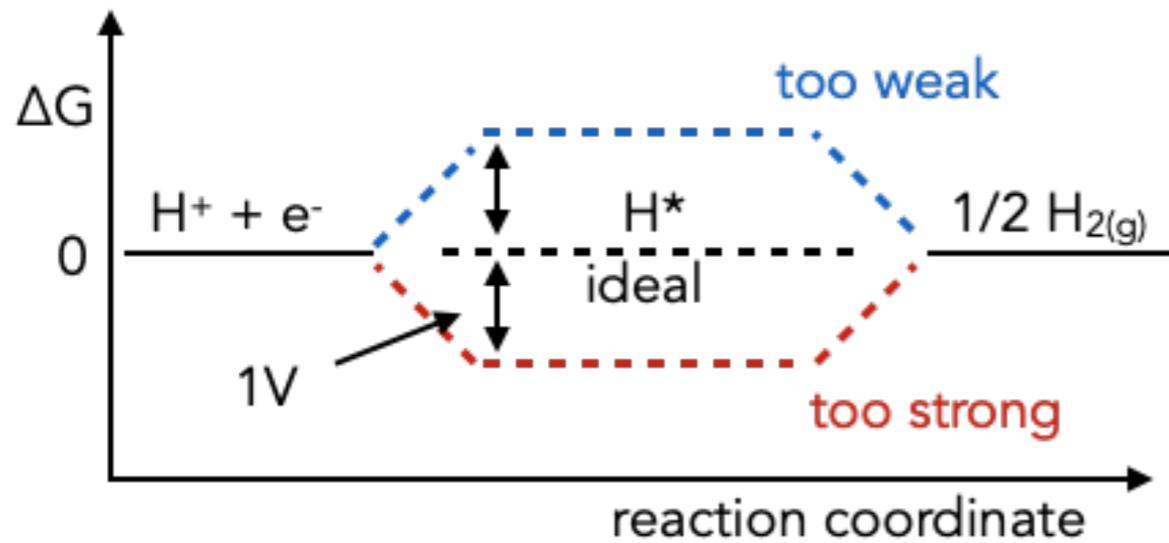
applied potential through $-neU$ (n =number of electrons, U =applied potential)

$$\Delta\text{G} = \Delta\text{H} - T\Delta\text{S} - neU$$

\rightarrow the free energy change of coupled proton/electron transfer reactions can be easily calculated and the influence of the applied potential adjusted



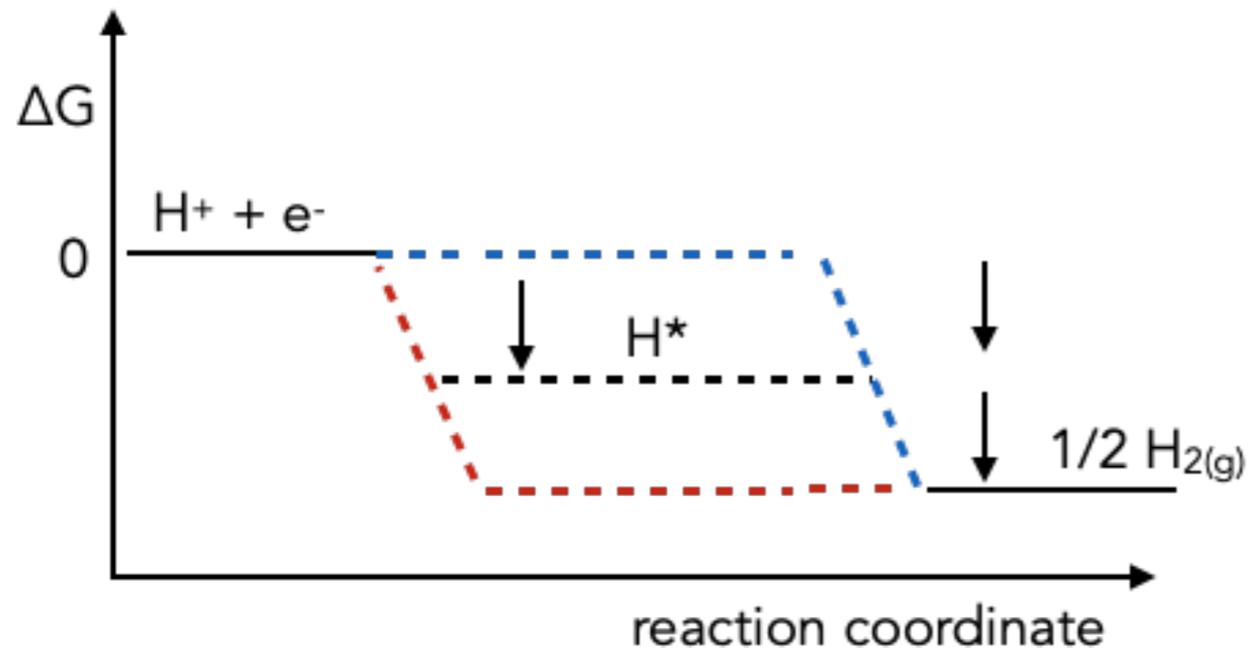
influence on applied potential on HER



$$U = 0V \quad \Delta G = \Delta G^\circ$$

apply potential through:

$$\Delta G = \Delta H - T\Delta S - neU$$



$$U = -1V \quad \Delta G_{H^*} = \Delta G_{H^*}^\circ - 1eV$$

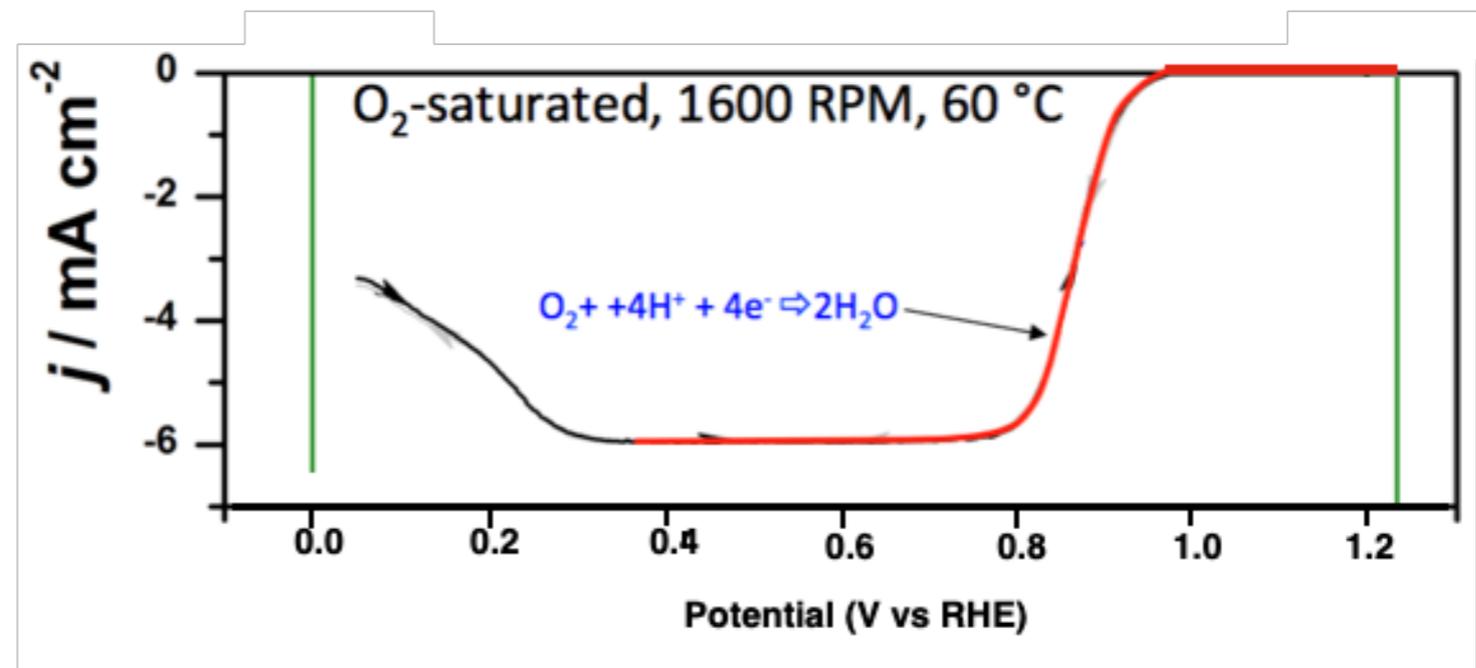
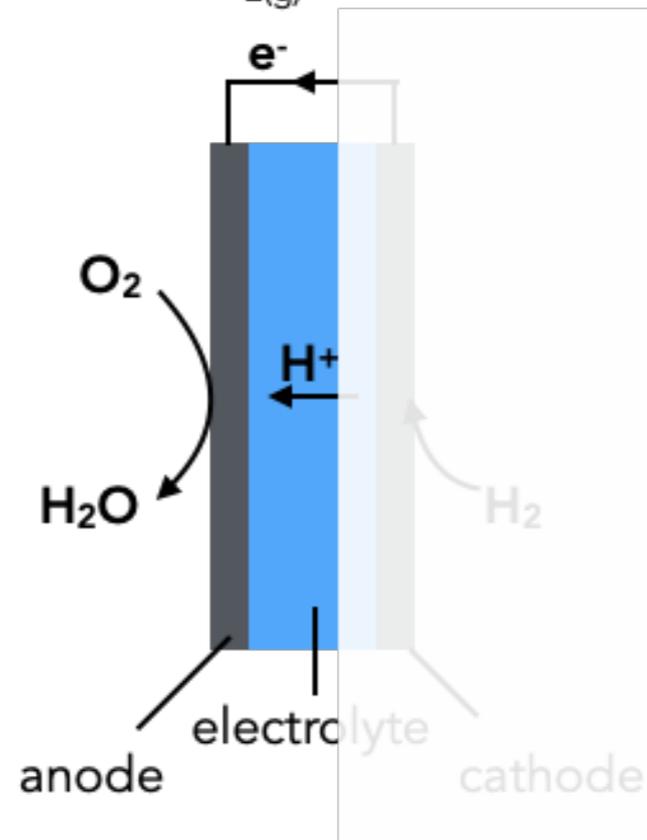
$$\Delta G_{H_{2(g)}} = \Delta G^\circ - 2eV$$

assumption: current will be sufficiently high when all reaction steps are downhill in free energy
 → *overpotential defined through necessary U*



oxygen reduction reaction (ORR)

half reaction: $\text{O}_{2(g)} + 4\text{H}^+ + 4\text{e}^- \rightleftharpoons \text{H}_2\text{O}_{(l)}$



substantial overpotential for ORR even for the best known material (Pt)

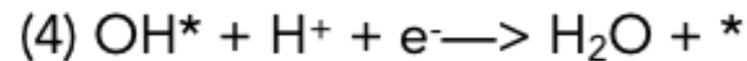
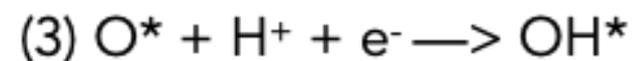
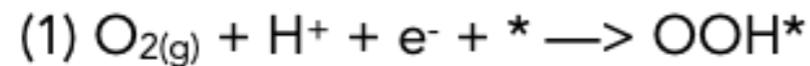
Pt rather scarce and expensive

ORR facilitated through 4 proton/electron transfers

how does ORR depend on stability of intermediates?



consider 4 consecutive proton/electron transfers to O₂



some considerations:

water environment stabilizes O* and OH*

interaction with electric field negligible (small dipole moments of adsorbates)

(bias of 1V would lead to change of app. 0.015 eV in adsorption energy for O*)

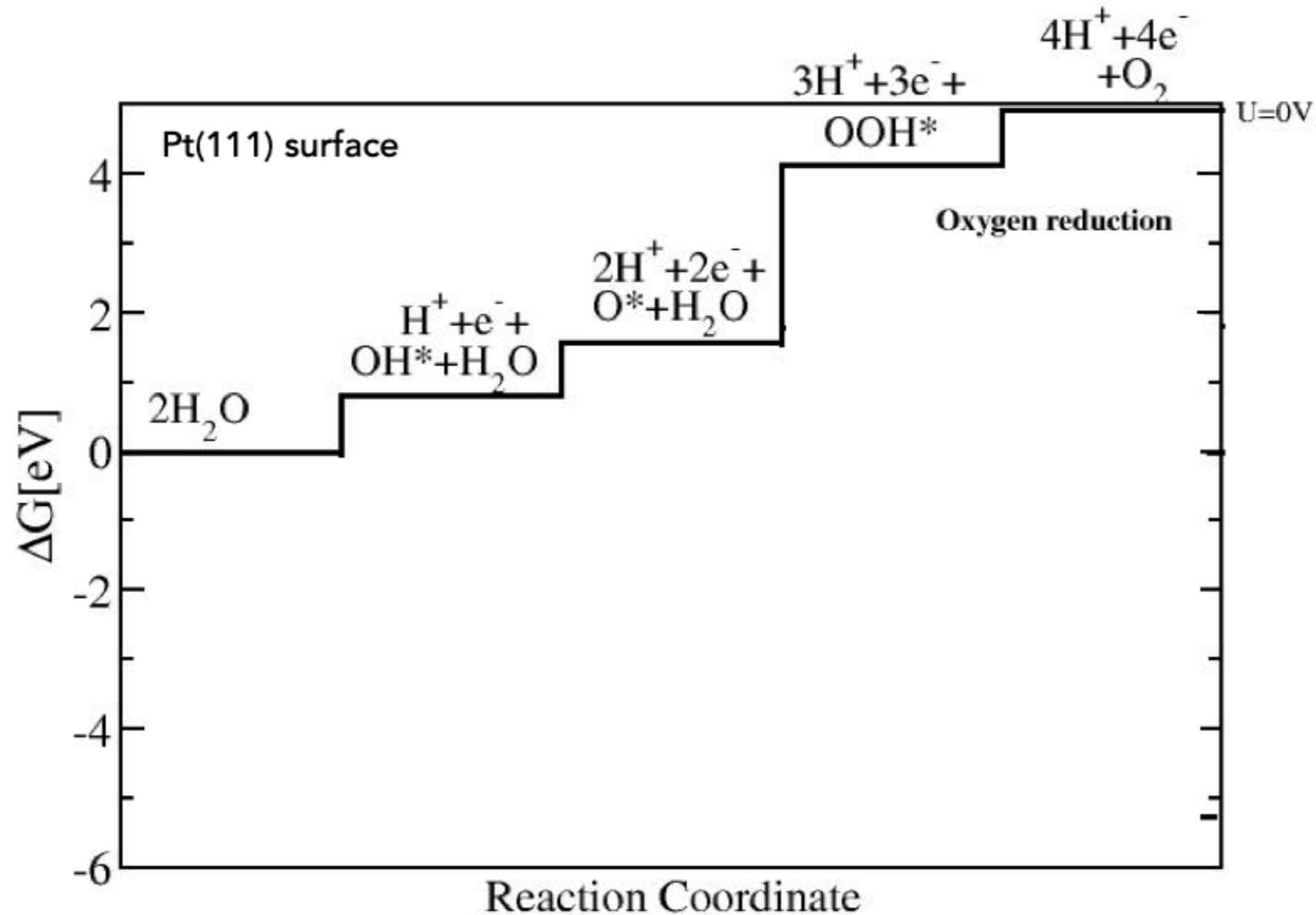
pH dependence through $G(\text{pH}) = -kT \ln[\text{H}^+] = kT \ln 10 \times \text{pH}$

O₂ molecule poorly described with DFT → use H₂O/H₂ as reference



origin of overpotential for ORR

$$\Delta G = \Delta H - T\Delta S - neU$$

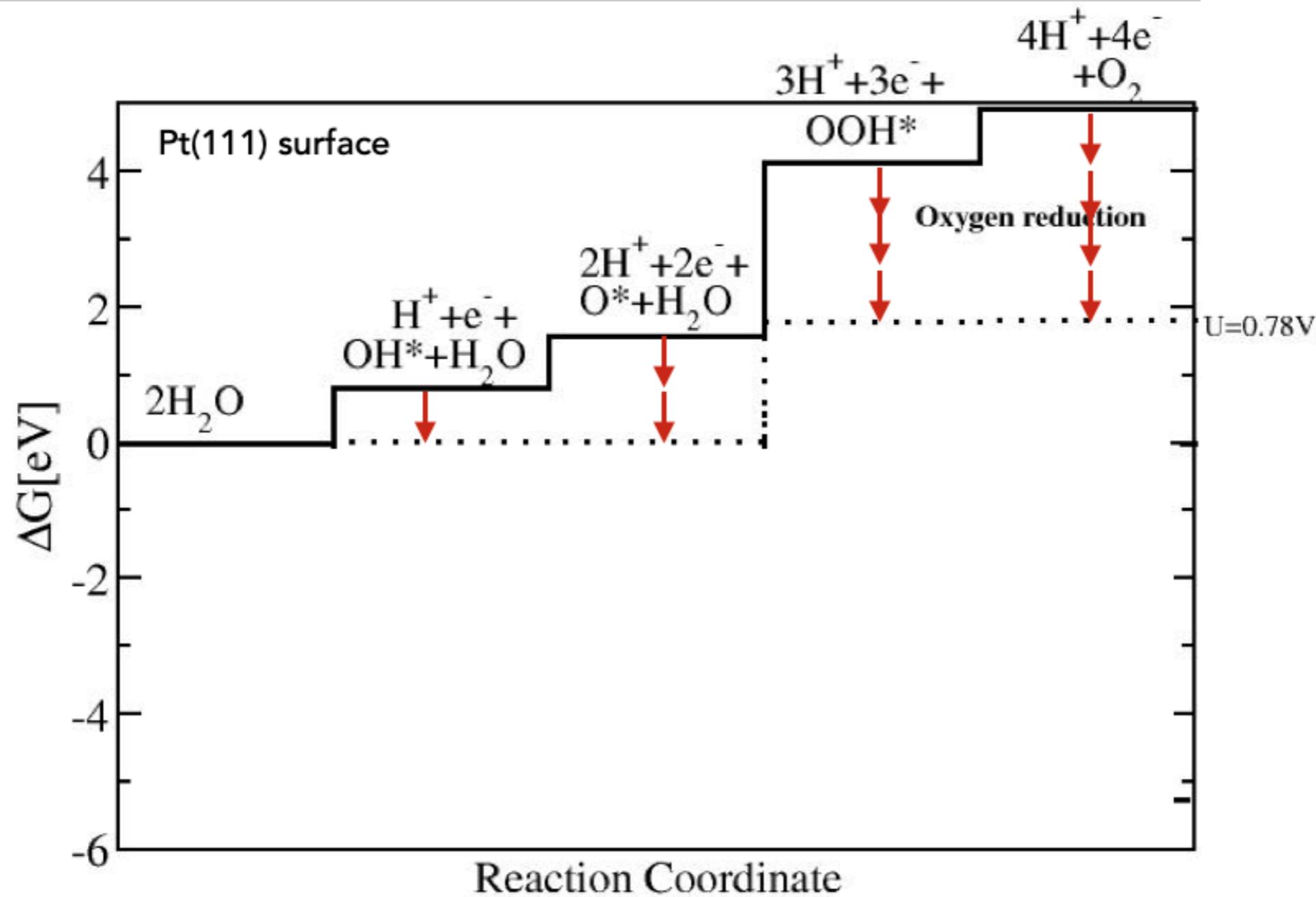


Nørskov, Rossmeisl, Logadottir, Lindqvist, Kitchin, Bligaard, Jonsson, *J. Phys. Chem. B* **2004**, *108*, 17886.



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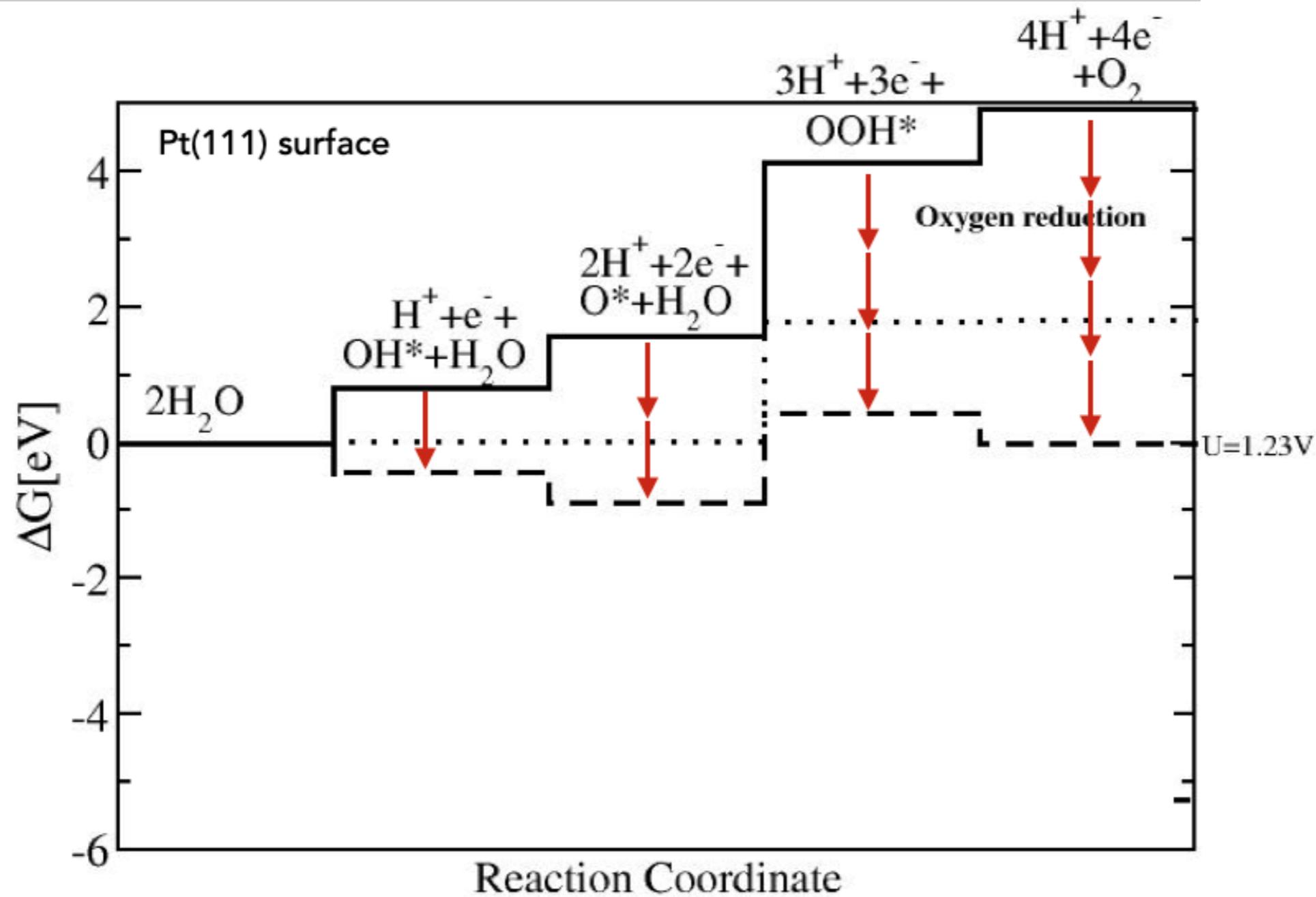


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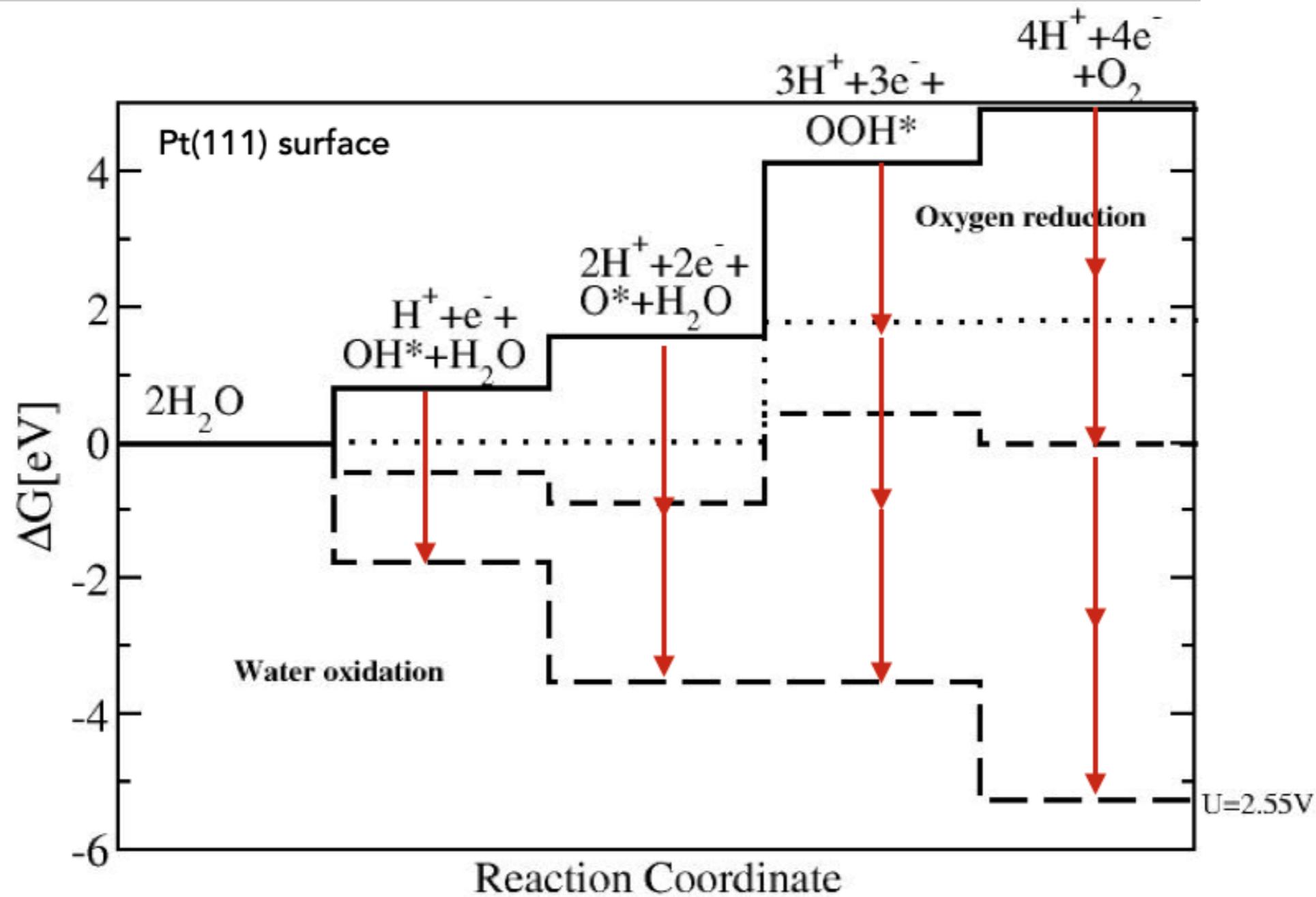


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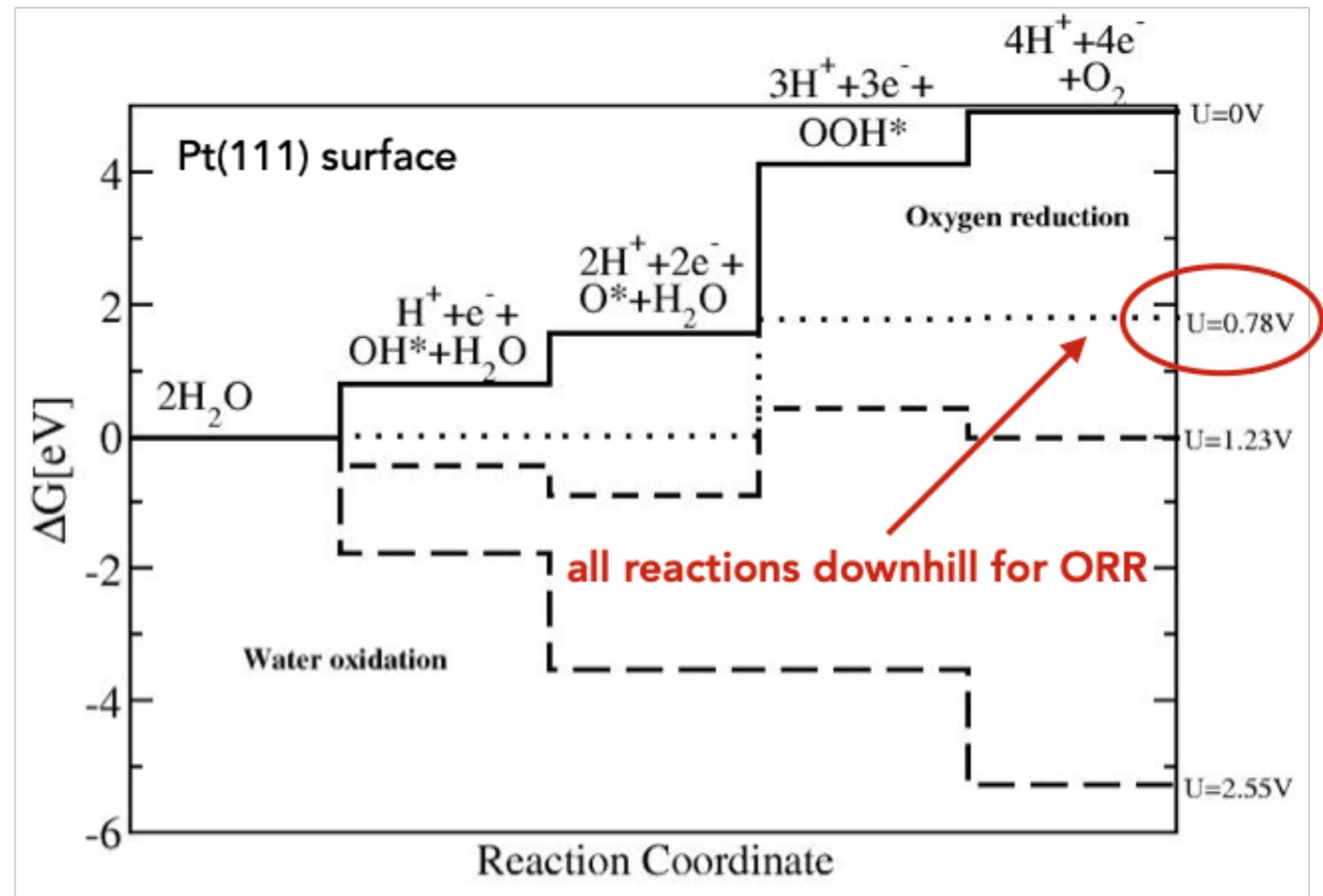
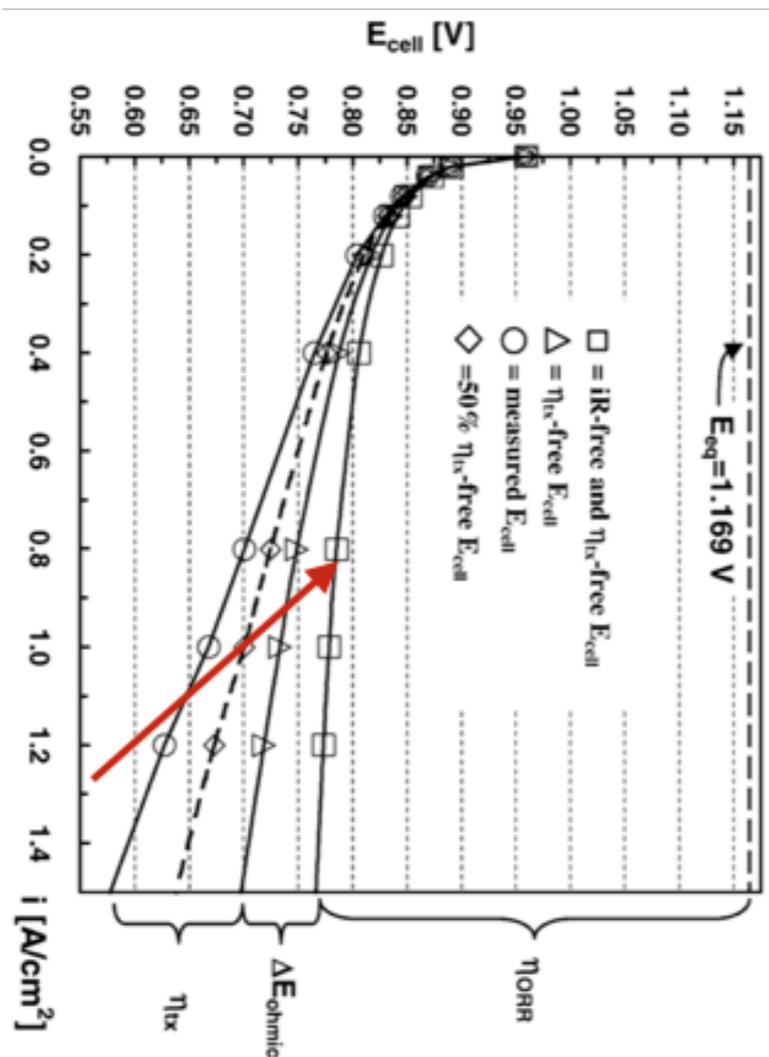


origin of overpotential for ORR

main assumption:

the overpotential is defined through applied potential where all steps are still downhill in free energy

(barriers are surmountable and give decent rate (current density))



Nørskov, Rossmeisl, Logadottir, Lindqvist, Kitchin, Bligaard, Jonsson, *J. Phys. Chem. B* **2004**, *108*, 17886.



(1) proton electron transfers are coupled

—> $\text{H}_{2(\text{g})}$ gives reference to $\text{H}^+ + \text{e}^-$ through SHE at 0 V

(2) intermediates are simply calculated on neutral surfaces

—> but: influence of e.g. water layer on adsorption energies can be calculated

(3) the overpotential is defined by flat or downhill free energy surfaces

—> rate (current density) is sufficiently high at RT for these cases

**note that both experimentally and theoretically
determined overpotentials are somewhat arbitrary**

somewhat comparison of apples and pears

—> but: is usually working for most cases!!

—> for screening purposes trends are more important anyhow



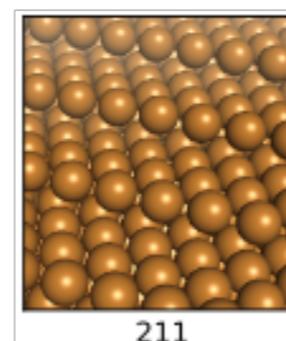
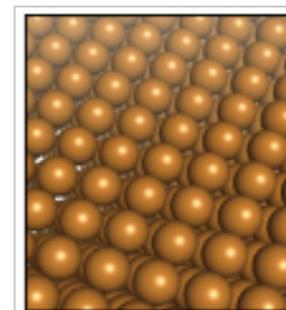
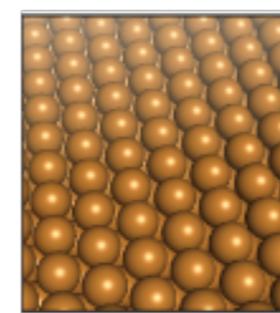
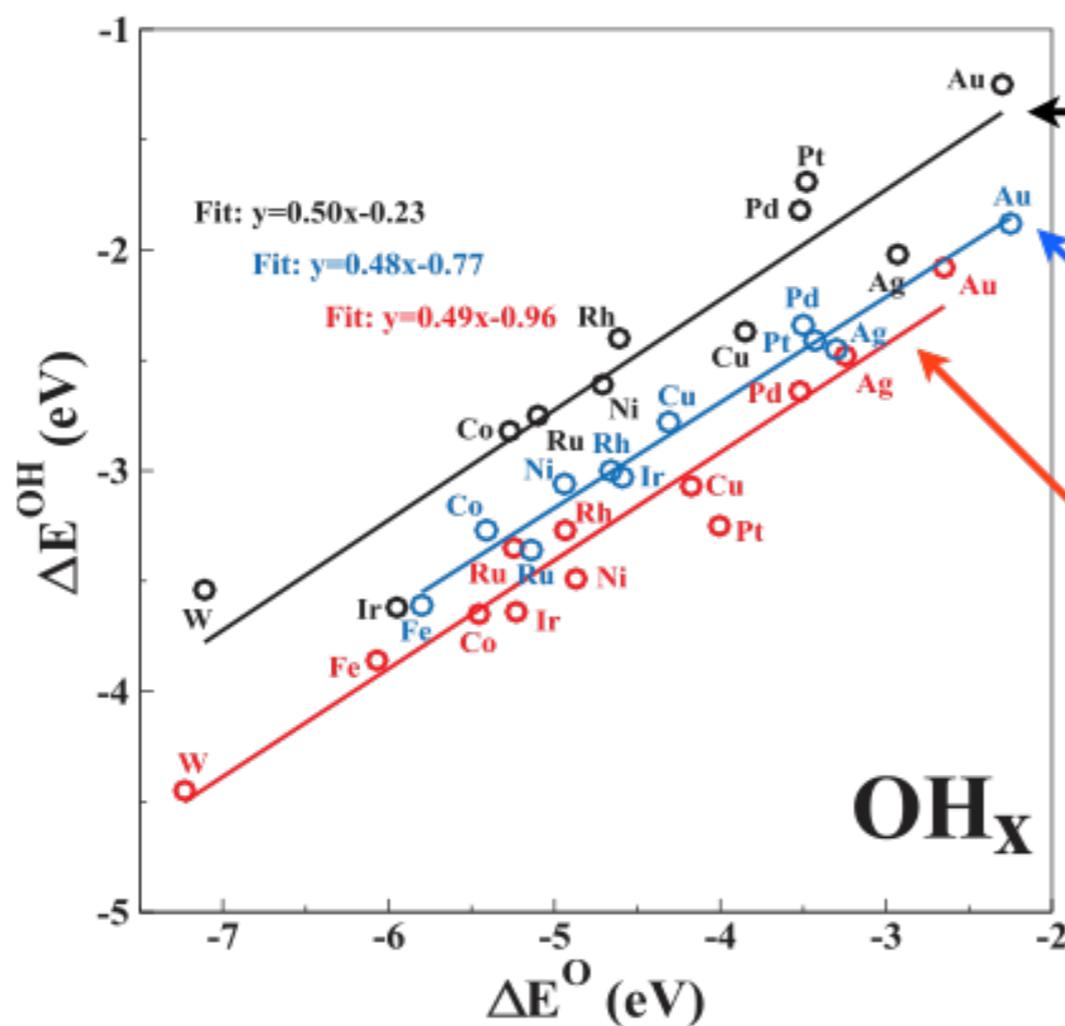
the ORR and OER volcanoes



scaling relations for adsorption energies



bond order conservation principle
 O^* two bonds, OH^* one bond
 \rightarrow slope equals 1/2



different intercepts
for different surfaces

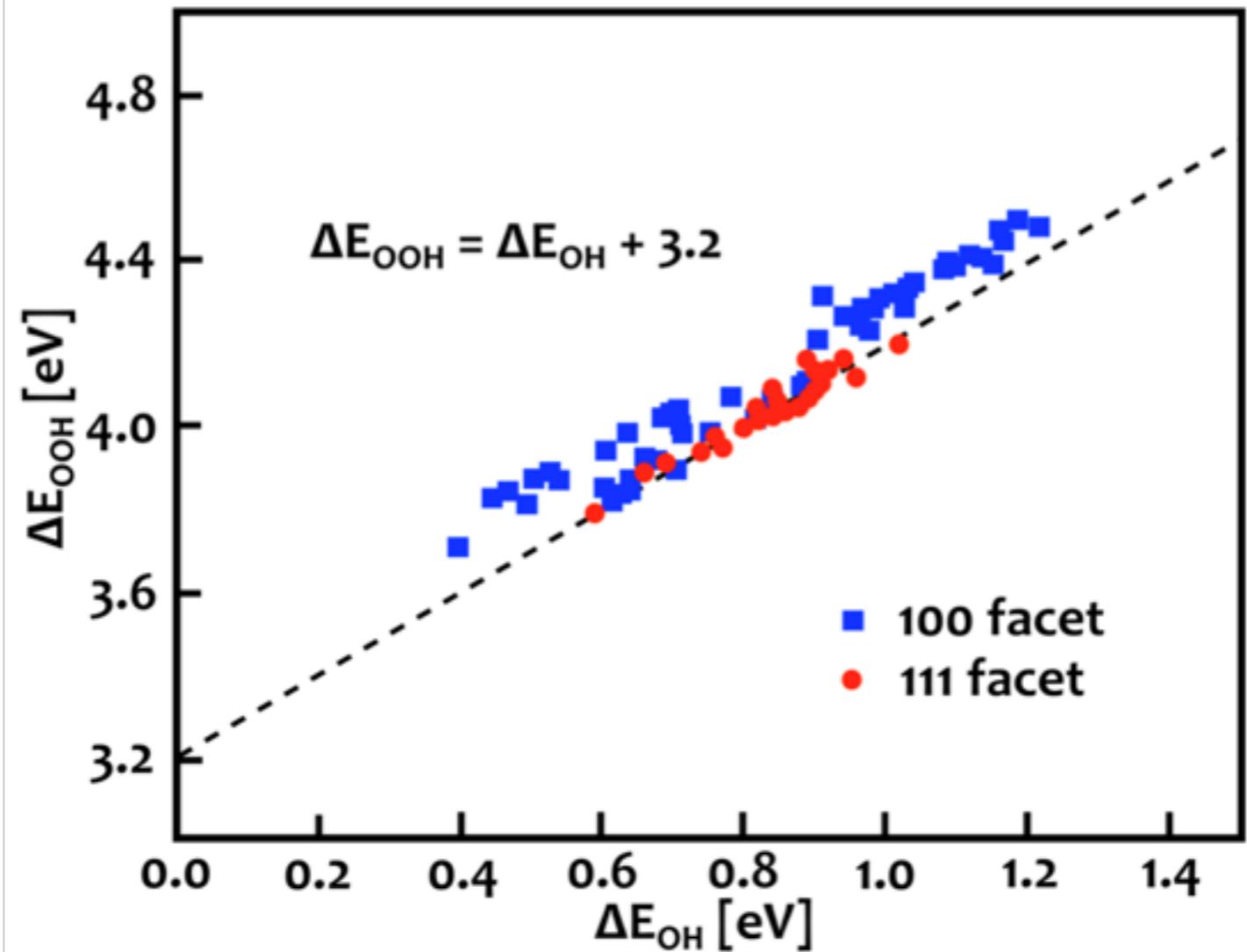




linear dependence of
 ΔE_{O} , ΔE_{OH} and ΔE_{OOH}

3D - 1D problem (e.g. ΔE_{O})

properties are not independent



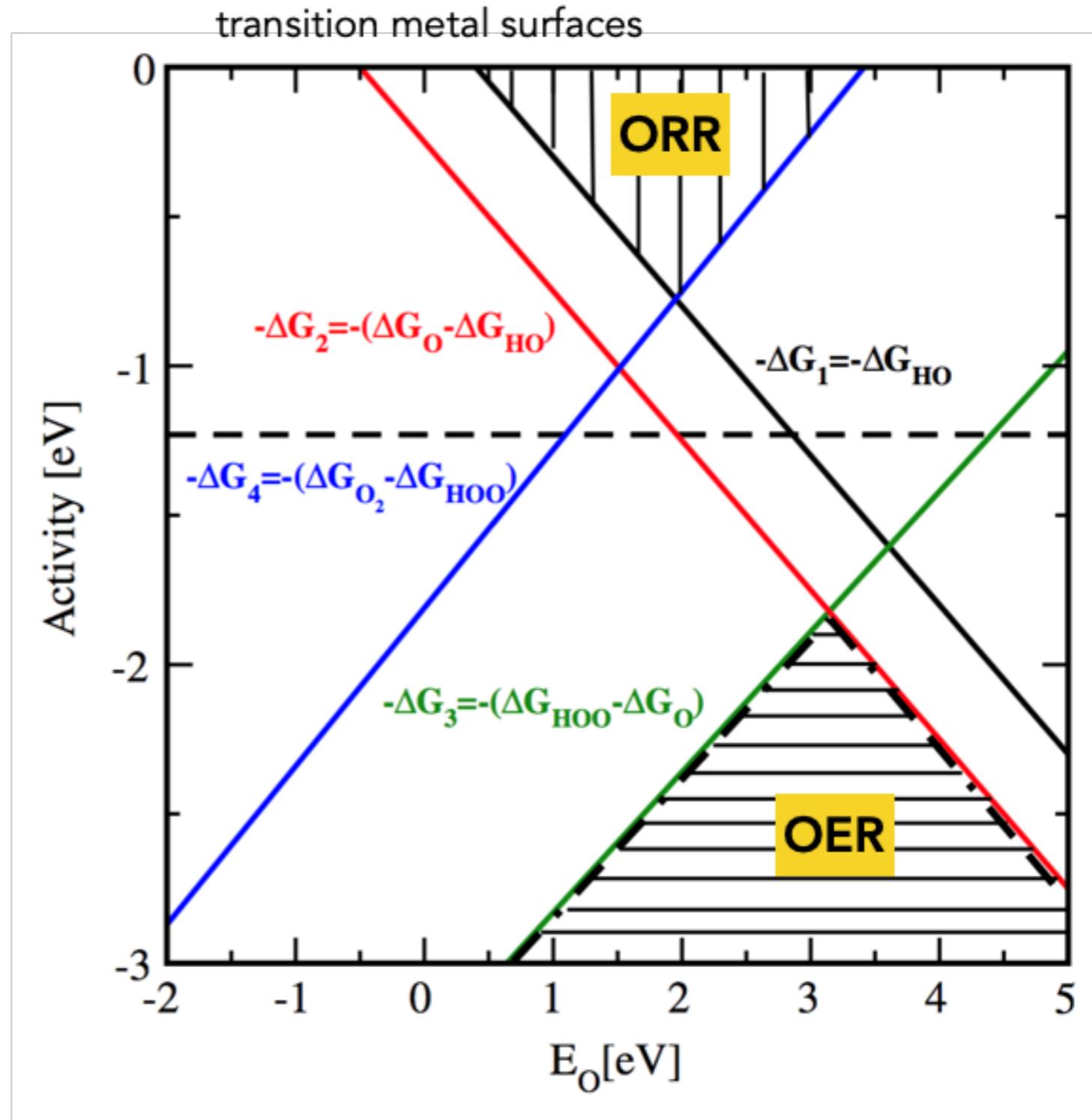
- (1) $\text{O}_{2(g)} + \text{H}^+ + \text{e}^- + * \rightarrow \text{OOH}^*$
- (2) $\text{OOH}^* + \text{H}^+ + \text{e}^- \rightarrow \text{O}^* + \text{H}_2\text{O}$
- (3) $\text{O}^* + \text{H}^+ + \text{e}^- \rightarrow \text{OH}^*$
- (4) $\text{OH}^* + \text{H}^+ + \text{e}^- \rightarrow \text{H}_2\text{O} + *$

$$-\Delta G_1 = -\Delta G_{\text{HO}}$$

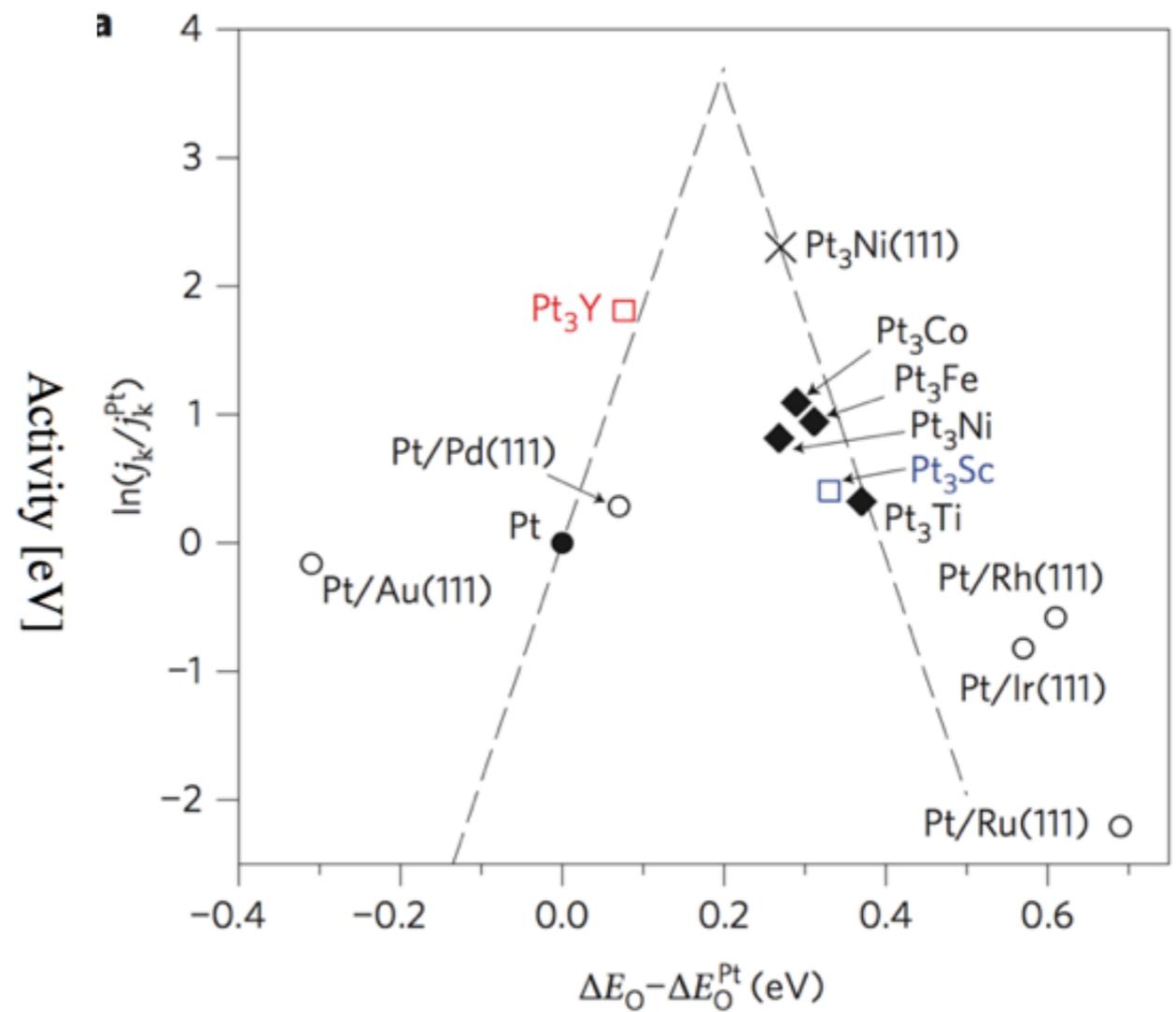
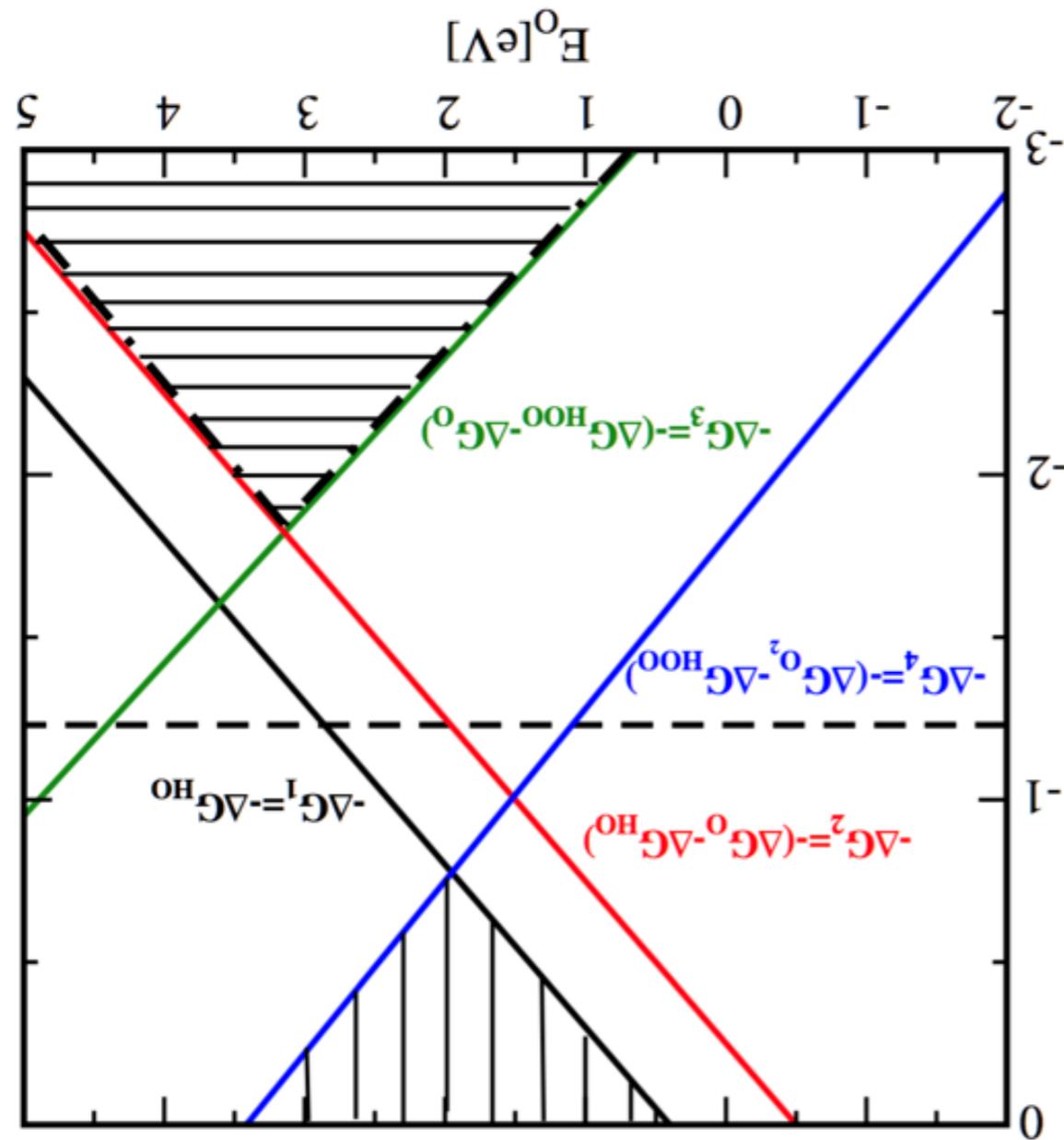
$$-\Delta G_2 = -(\Delta G_{\text{O}} - \Delta G_{\text{HO}})$$

$$-\Delta G_3 = -(\Delta G_{\text{HOO}} - \Delta G_{\text{O}})$$

$$-\Delta G_4 = -(\Delta G_{\text{O}_2} - \Delta G_{\text{HOO}})$$



ORR volcano

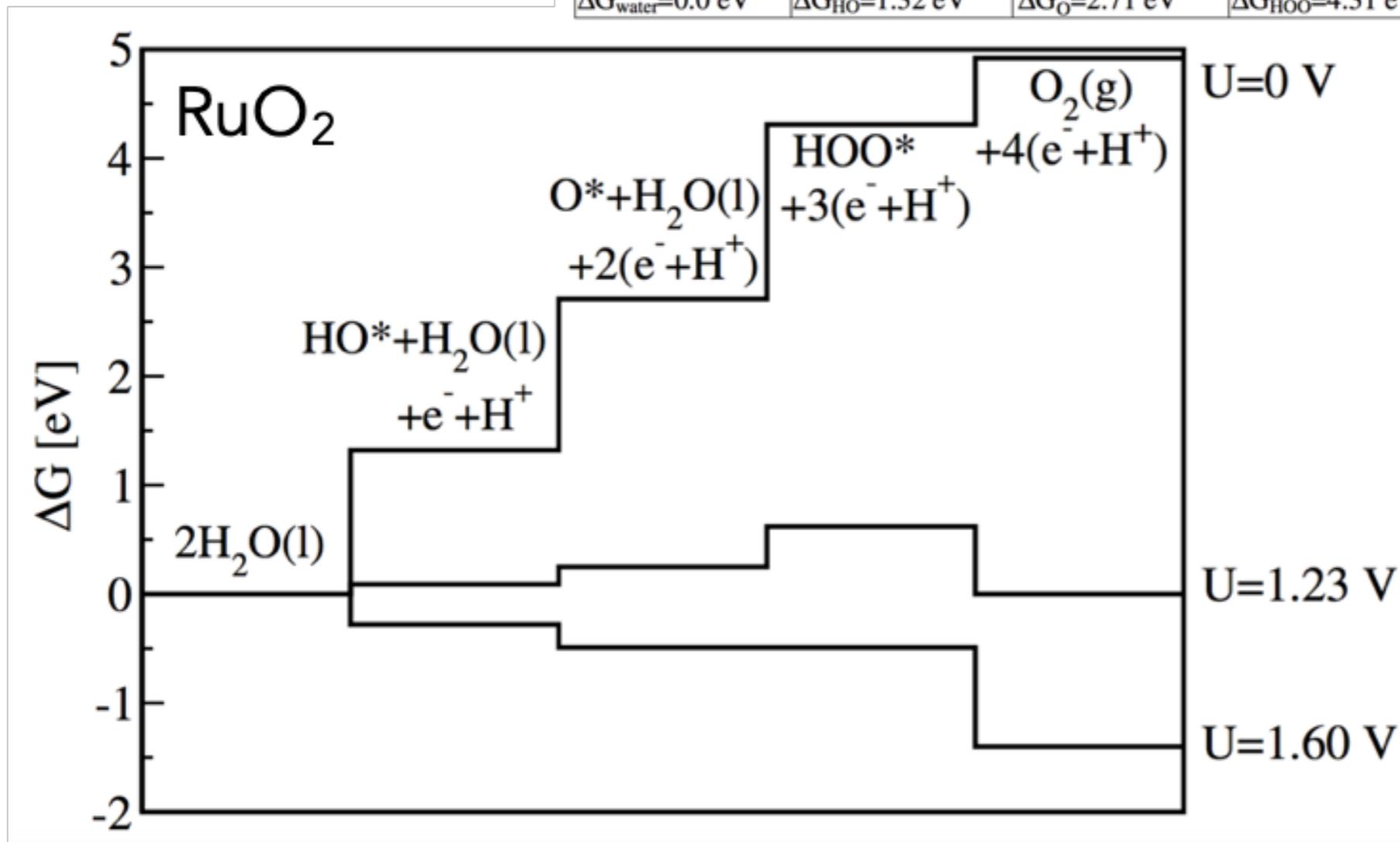
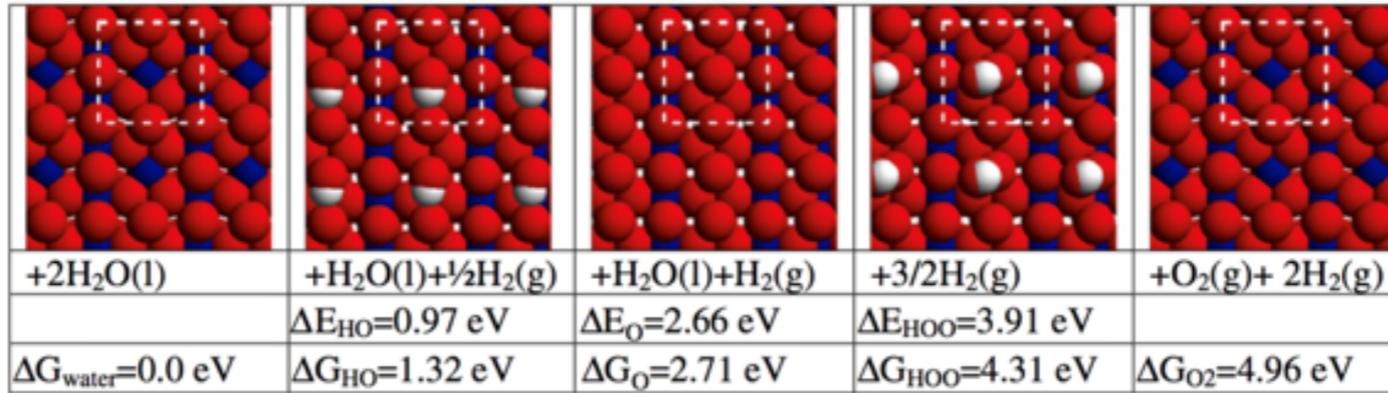


Rossmeisl, Qu, Zhu, Kroes, Nørskov, J. *Electroanal. Chem.* **2007**, *607*, 83.

Greeley, et al, *Nature Chem.* **2009**, *1*, 552.

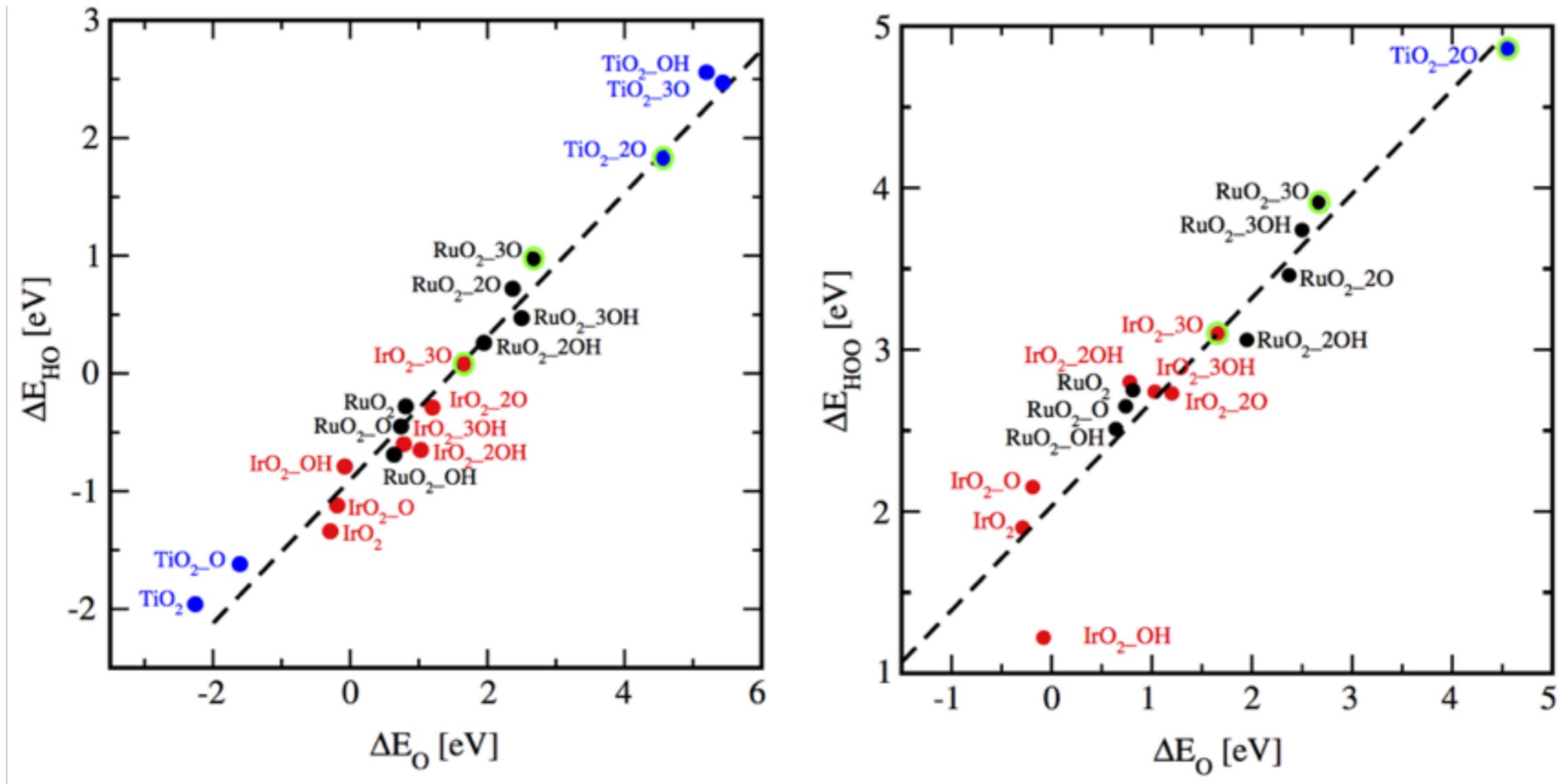


oxide surfaces

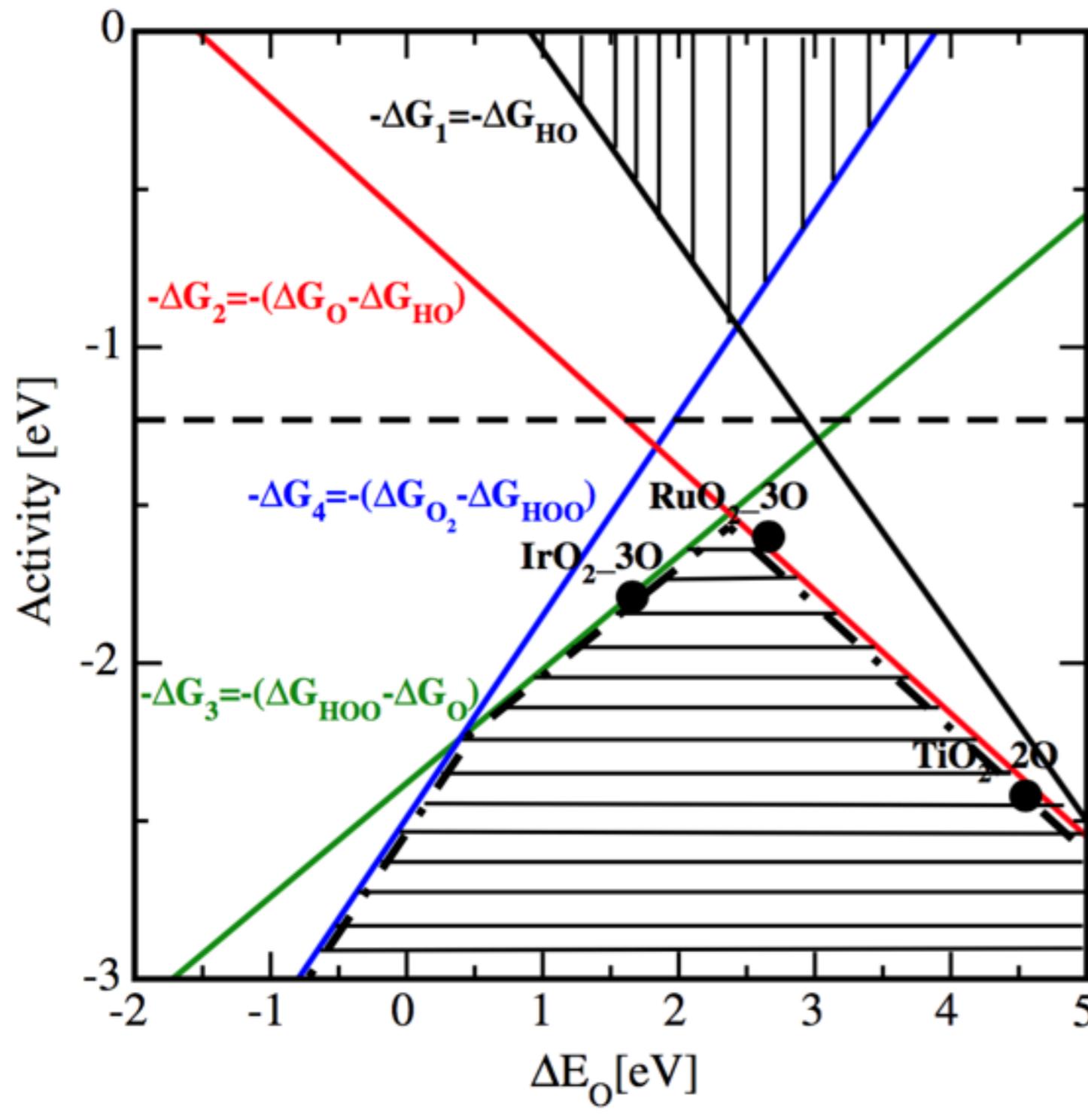


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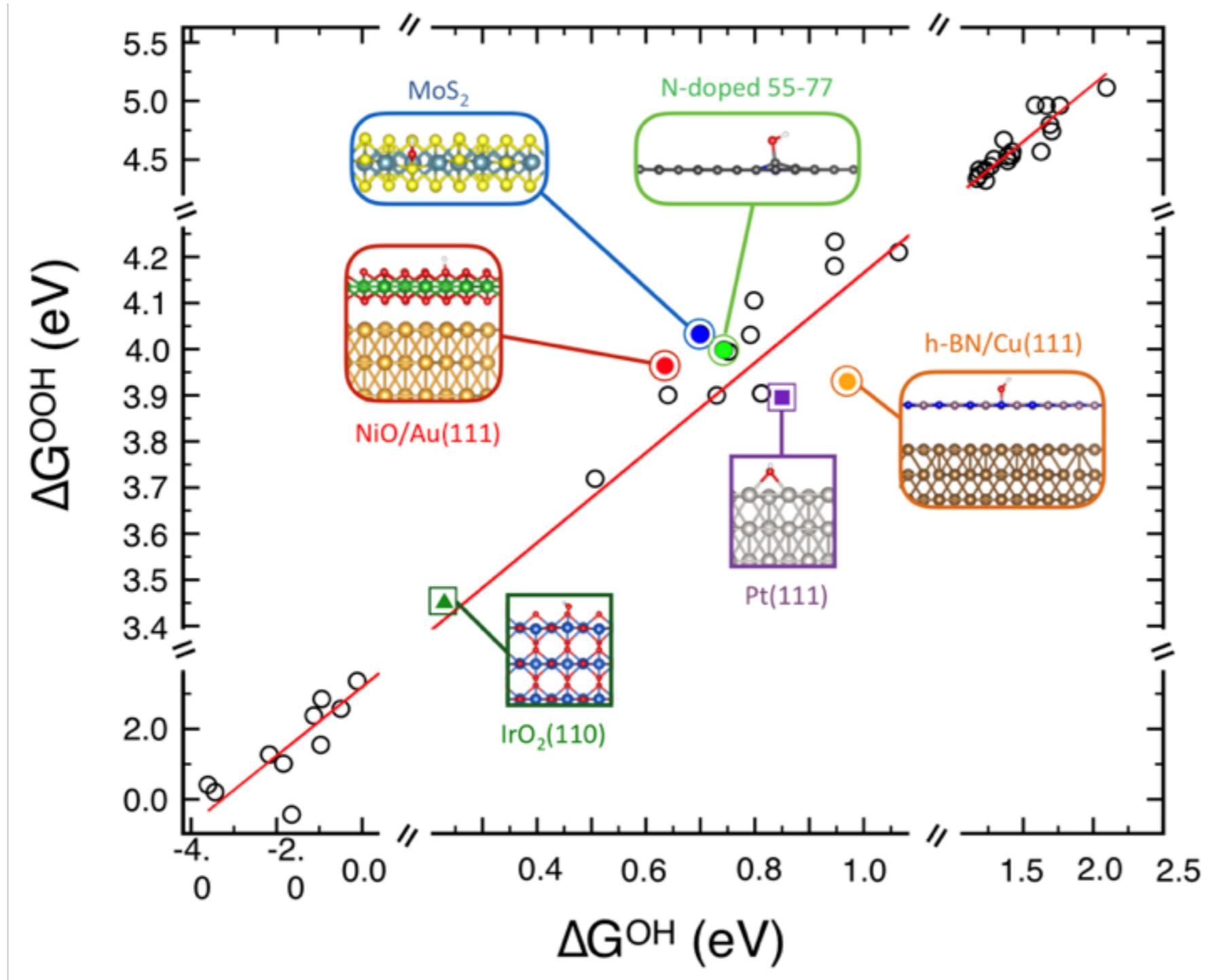


the OER volcano on oxides



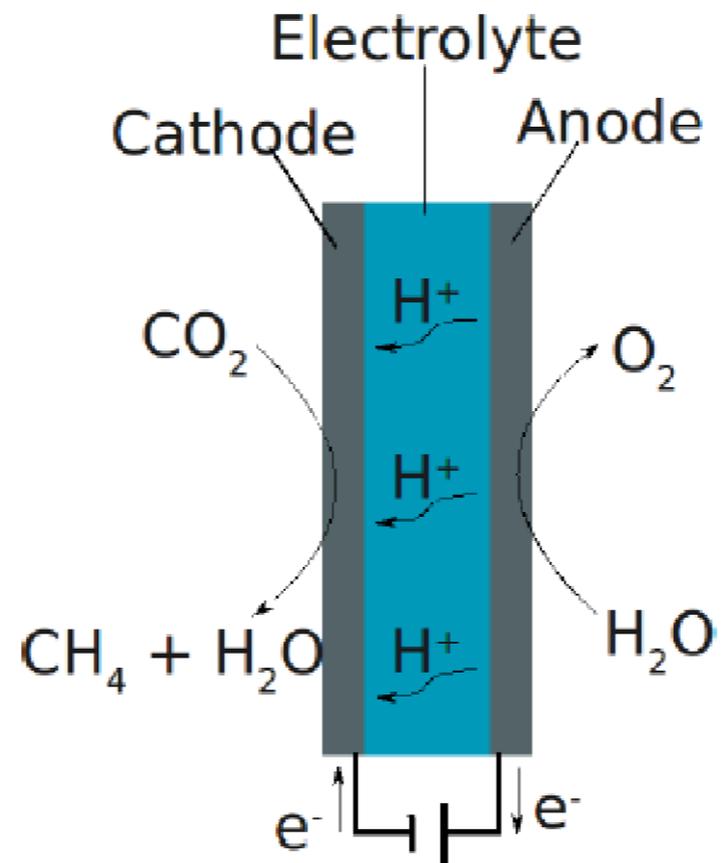
Rossmeisl, Qu, Zhu, Kroes, Nørskov, *J. Electroanal. Chem.* **2007**, 607, 83.





Siahrostami et al, *Catal. Lett.* **2016**, 146, 1917.





Electrical potential created by photon
or from a renewable electricity source.



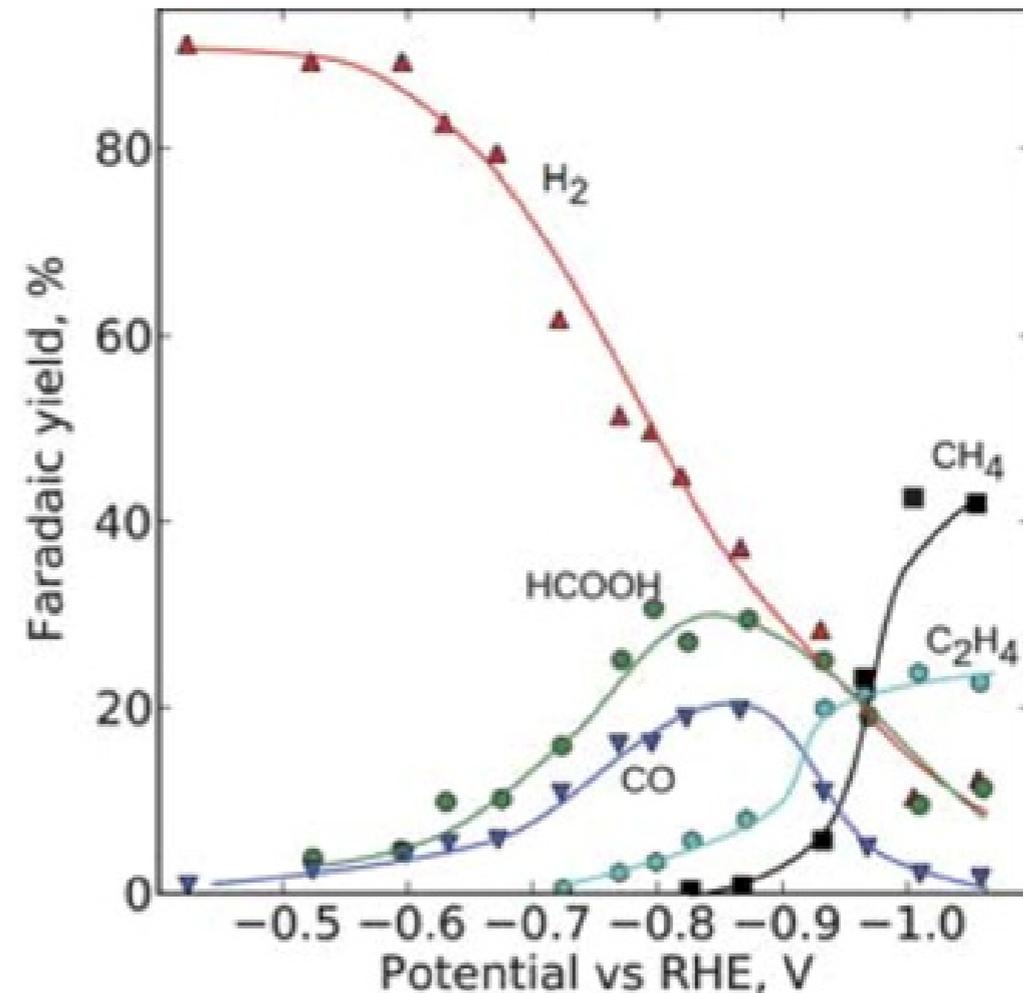
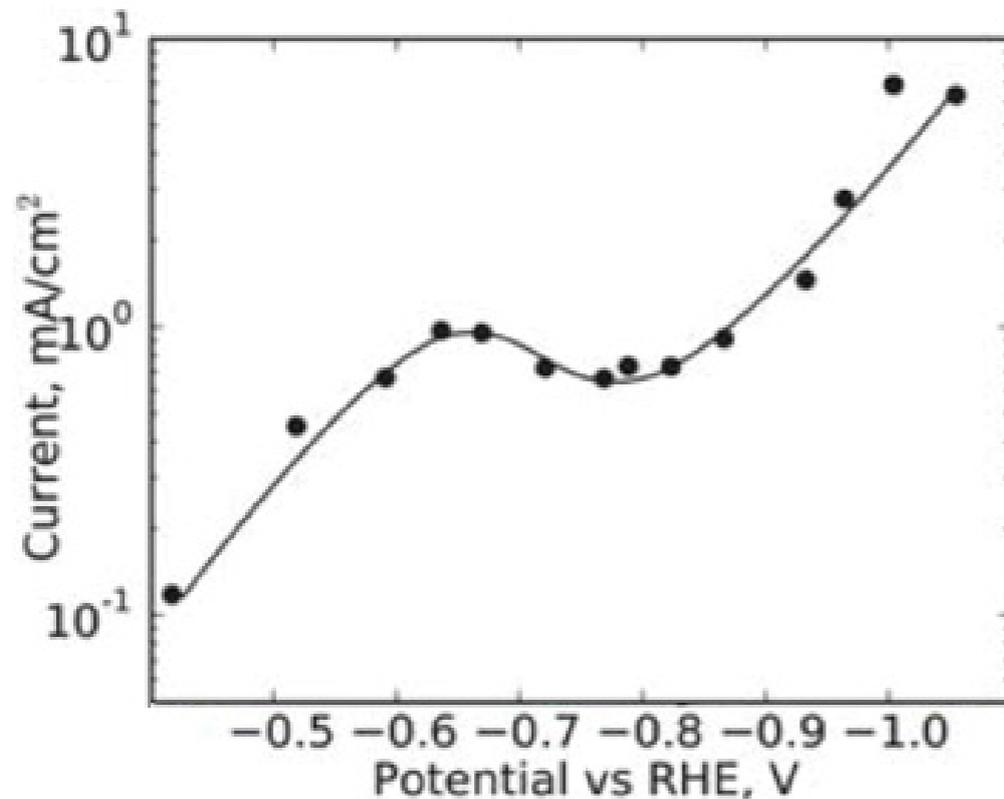
Table 3

Faradaic Efficiencies of Products in CO₂ Reduction at Various Metal Electrodes. Electrolyte: 0.1 M KHCO₃, T = 18.5 ± 0.5°C. Reprinted from Ref. 23, Copyright (1994) with Permission from Elsevier

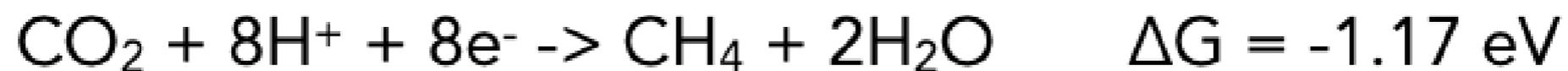
Electrode	Potential vs. SHE V	Current density mA cm ⁻²	Faradaic efficiency, %							Total
			CH ₄	C ₂ H ₄	EtOH ^a	PrOH ^b	CO	HCOO ⁻	H ₂	
Pb	-1.63	5.0	0.0	0.0	0.0	0.0	0.0	97.4	5.0	102.4
Hg	-1.51	0.5	0.0	0.0	0.0	0.0	0.0	99.5	0.0	99.5
Tl	-1.60	5.0	0.0	0.0	0.0	0.0	0.0	95.1	6.2	101.3
In	-1.55	5.0	0.0	0.0	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
Bi ^c	-1.56	1.2	-	-	-	-	-	77	-	-
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
Cu	-1.44	5.0	33.3	25.5	5.7	3.0	1.3	9.4	20.5	103.5 ^d
Ni	-1.48	5.0	1.8	0.1	0.0	0.0	0.0	1.4	88.9	92.4 ^e
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

^aethanol; ^bn-propanol; ^cthe data are taken from Hori et al.²³ except Bi which is read from an illustration in a paper by Kunugi et al.¹¹⁷; ^dthe total value contains C₃H₅OH(1.4%), CH₃CHO(1.1%), C₂H₅CHO(2.3%) in addition to the tabulated substances; ^ethe total value contains C₂H₆(0.2%)





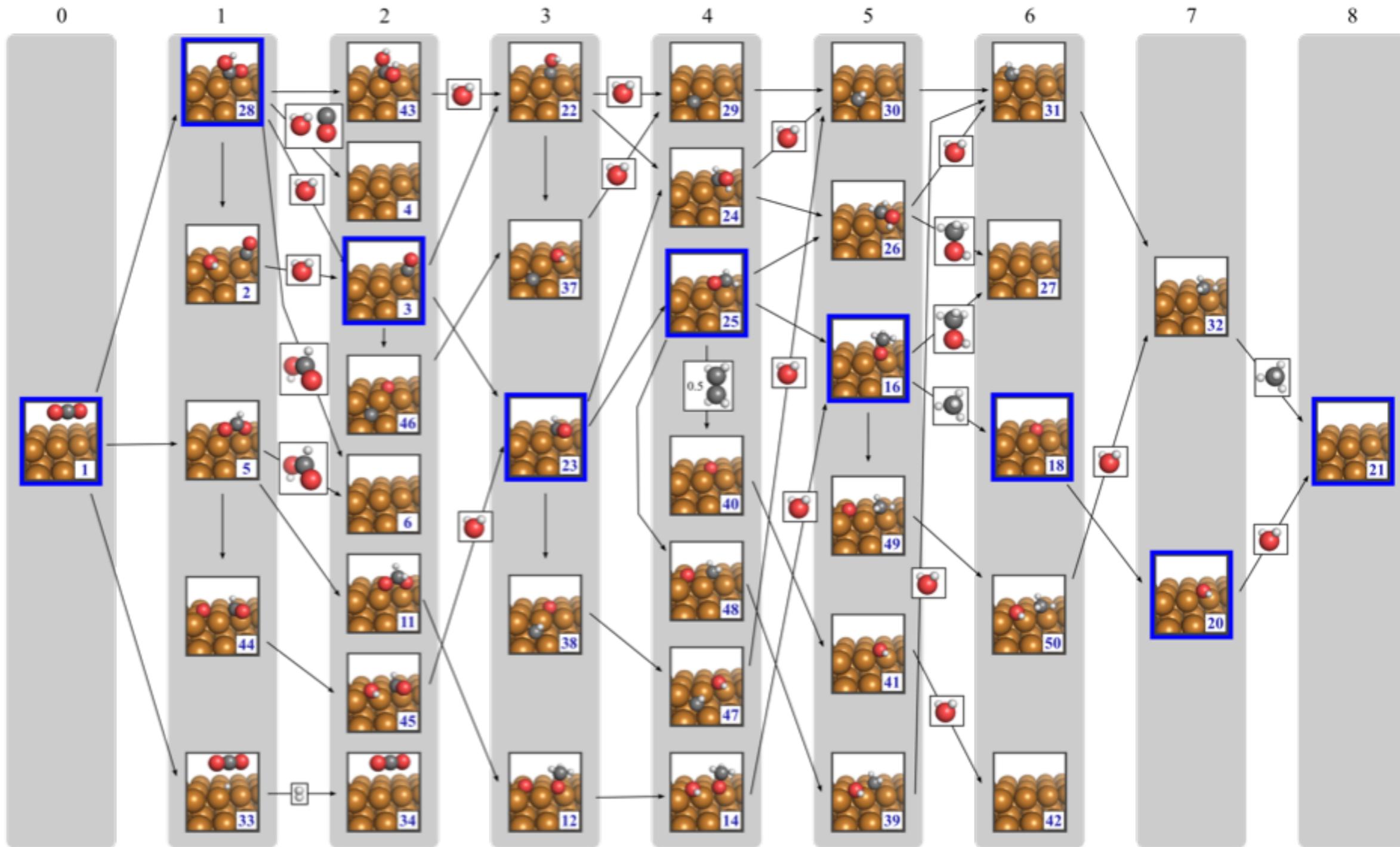
methane formation



+0.15 V vs RHE should be sufficient!

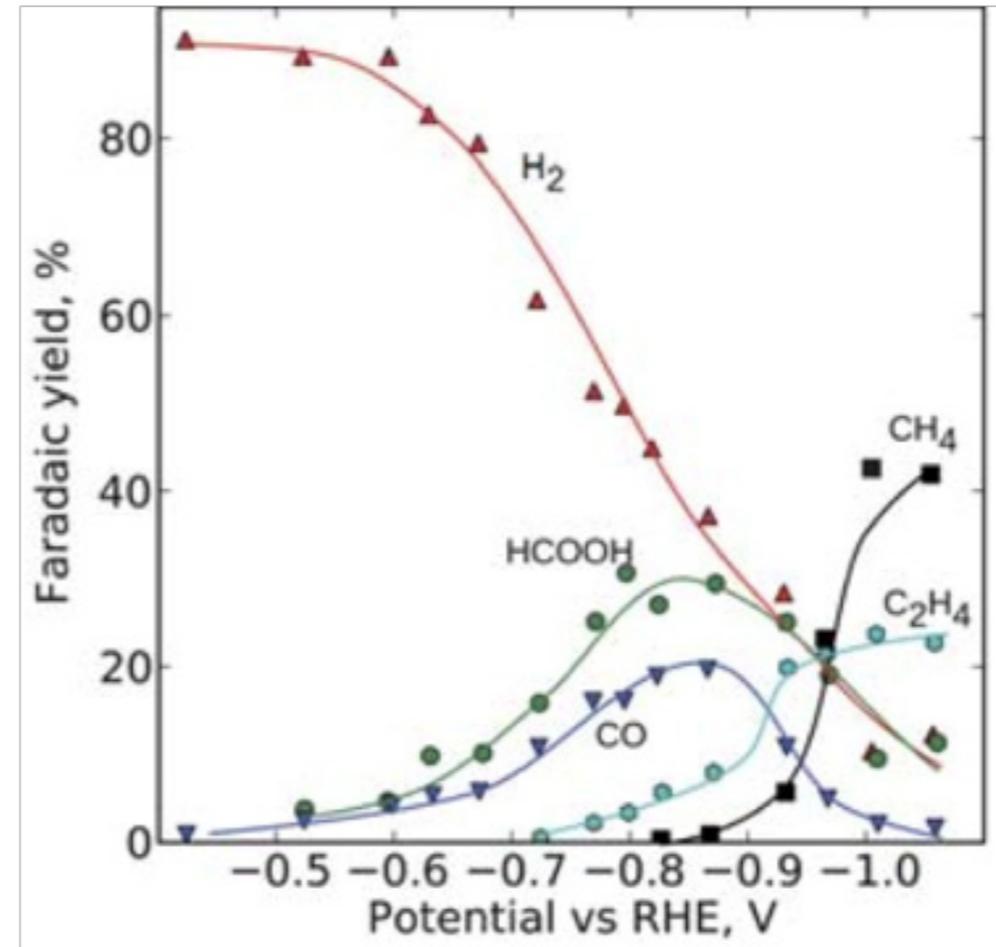
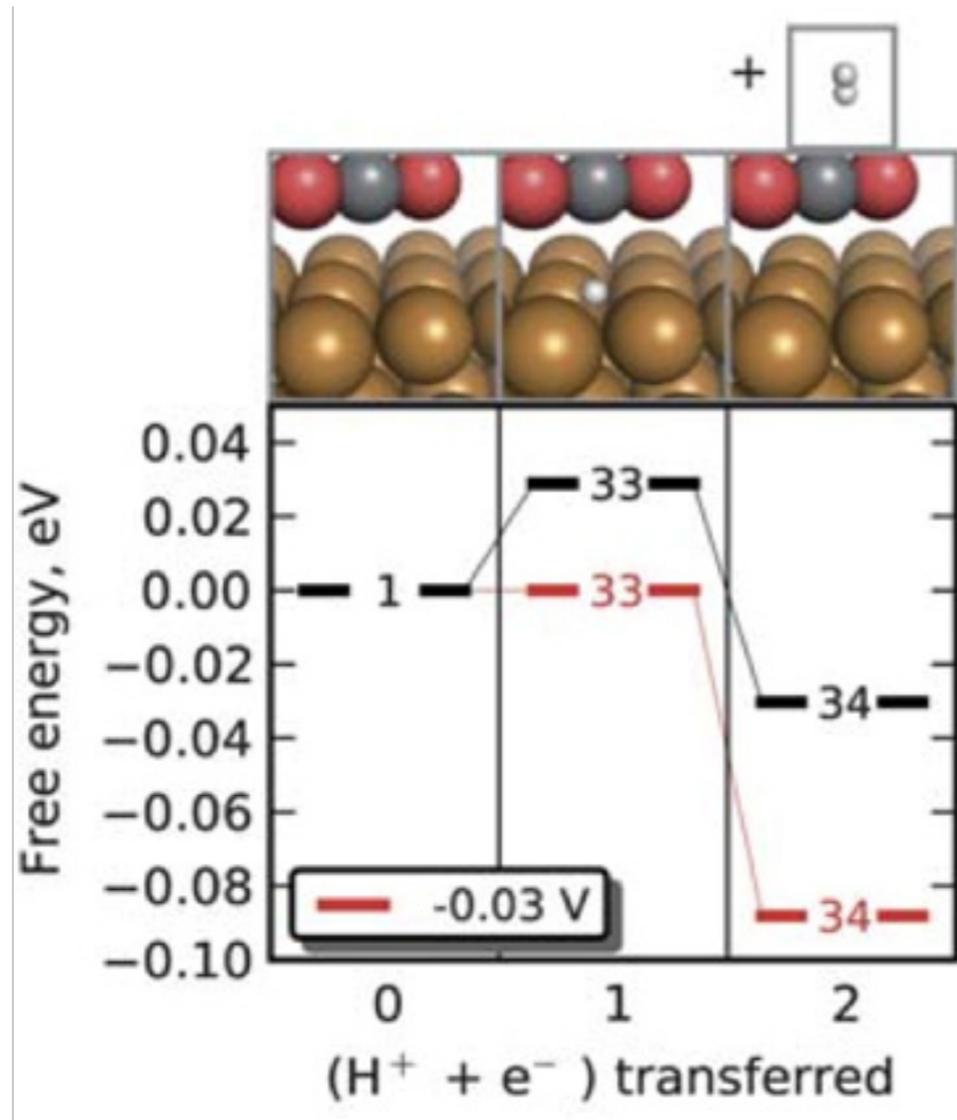


CO₂ reduction intermediates



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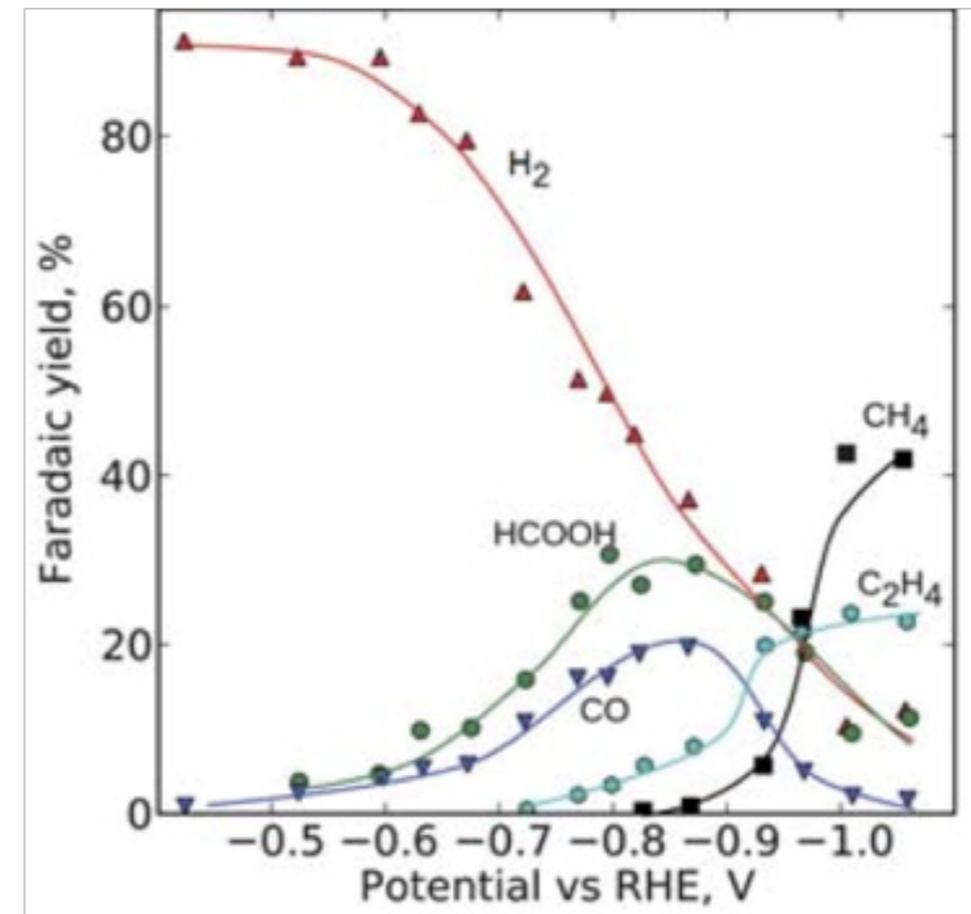
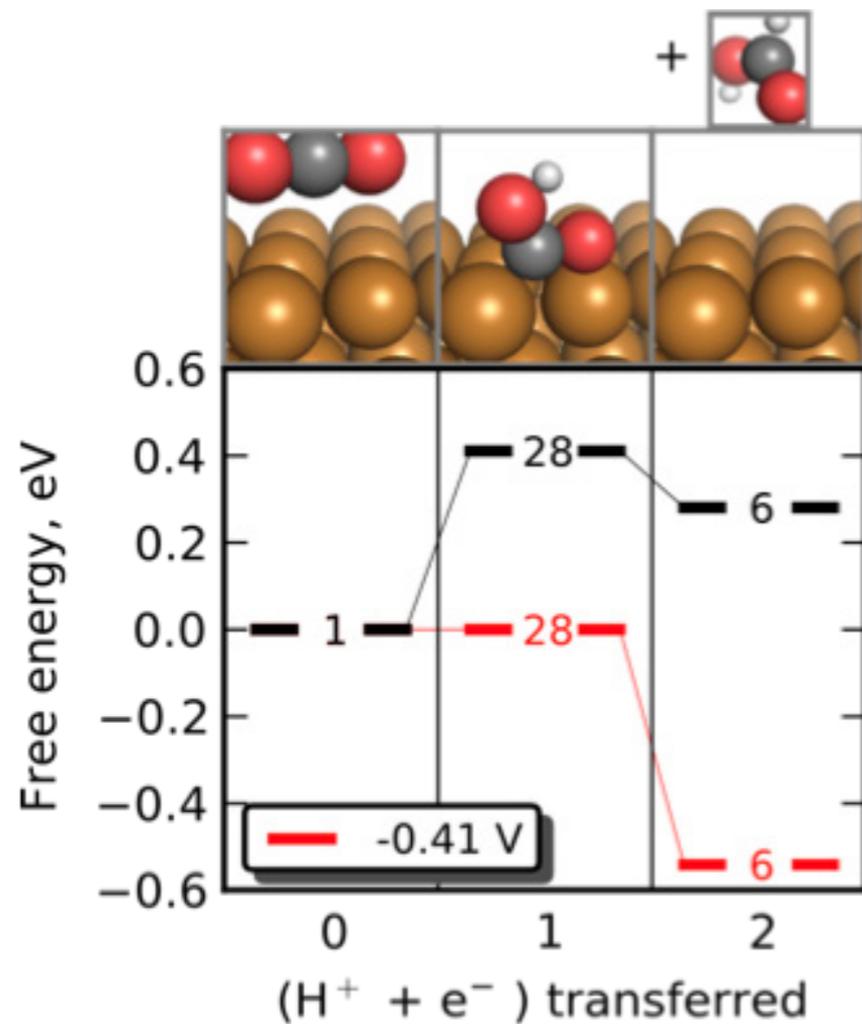




experiments: onset potential ~ - 0.4 V

possible reason: oxidation of surface → -0.3 V to clear adsorbed OH

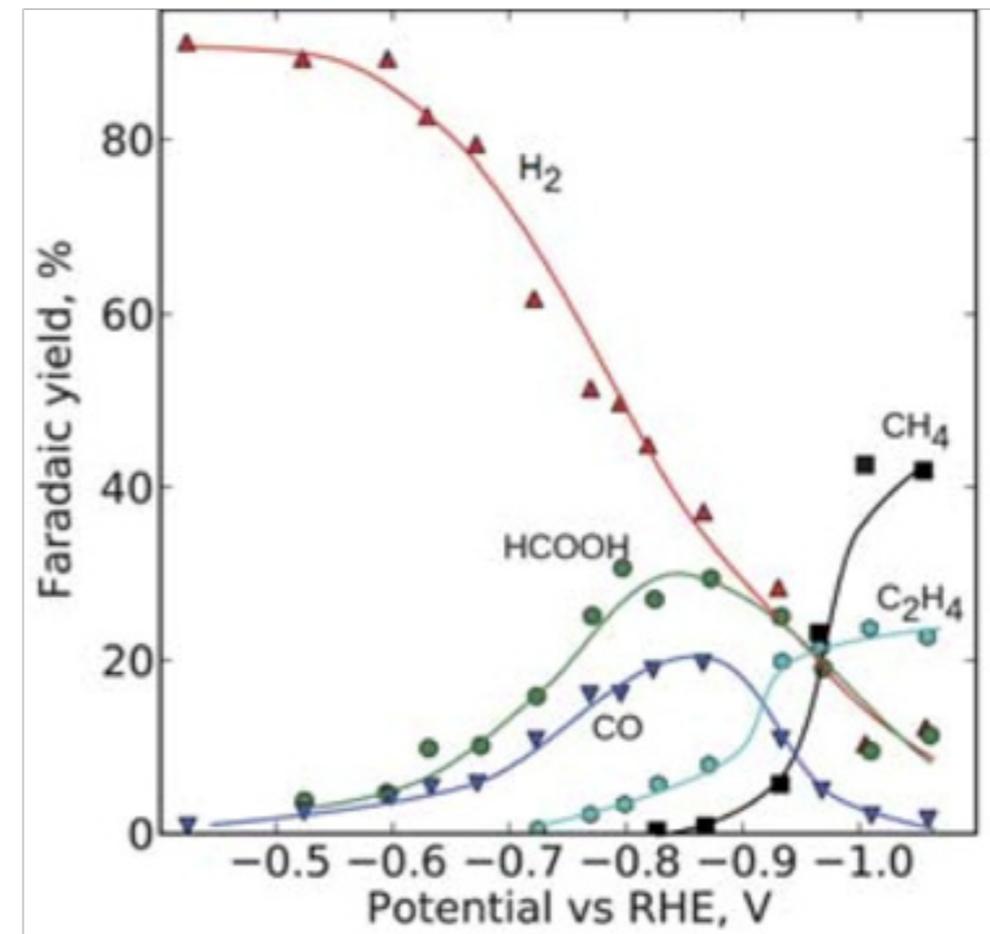
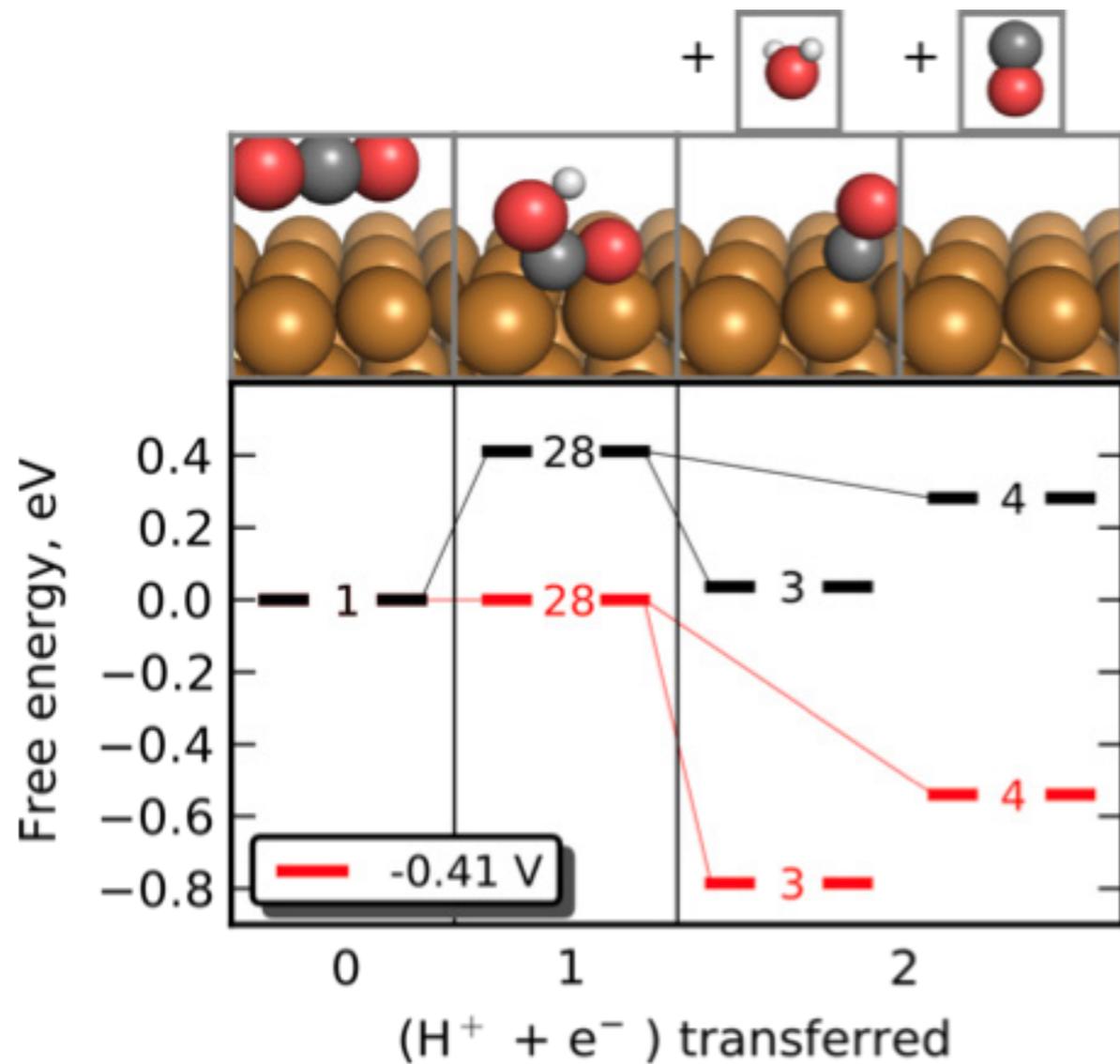




second pathway through formate possible at more negative potentials
formate bystander -> might poison the surface



CO₂ to CO

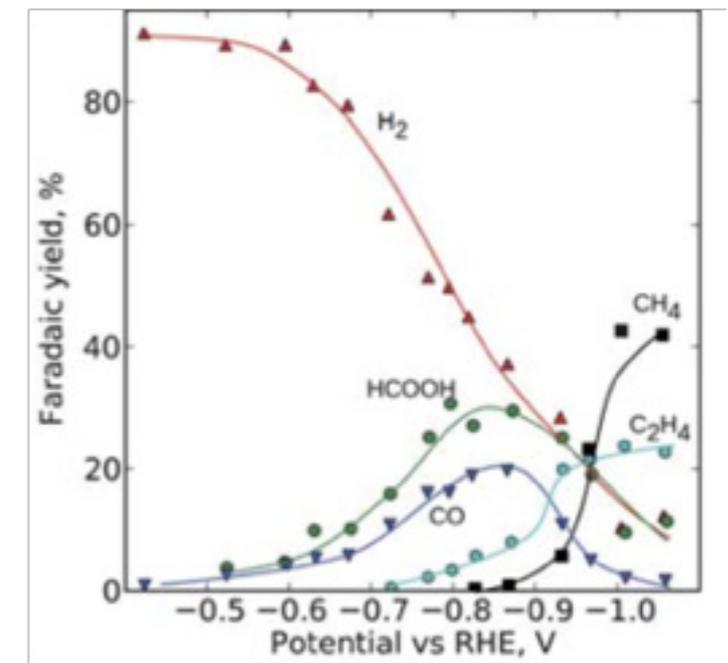
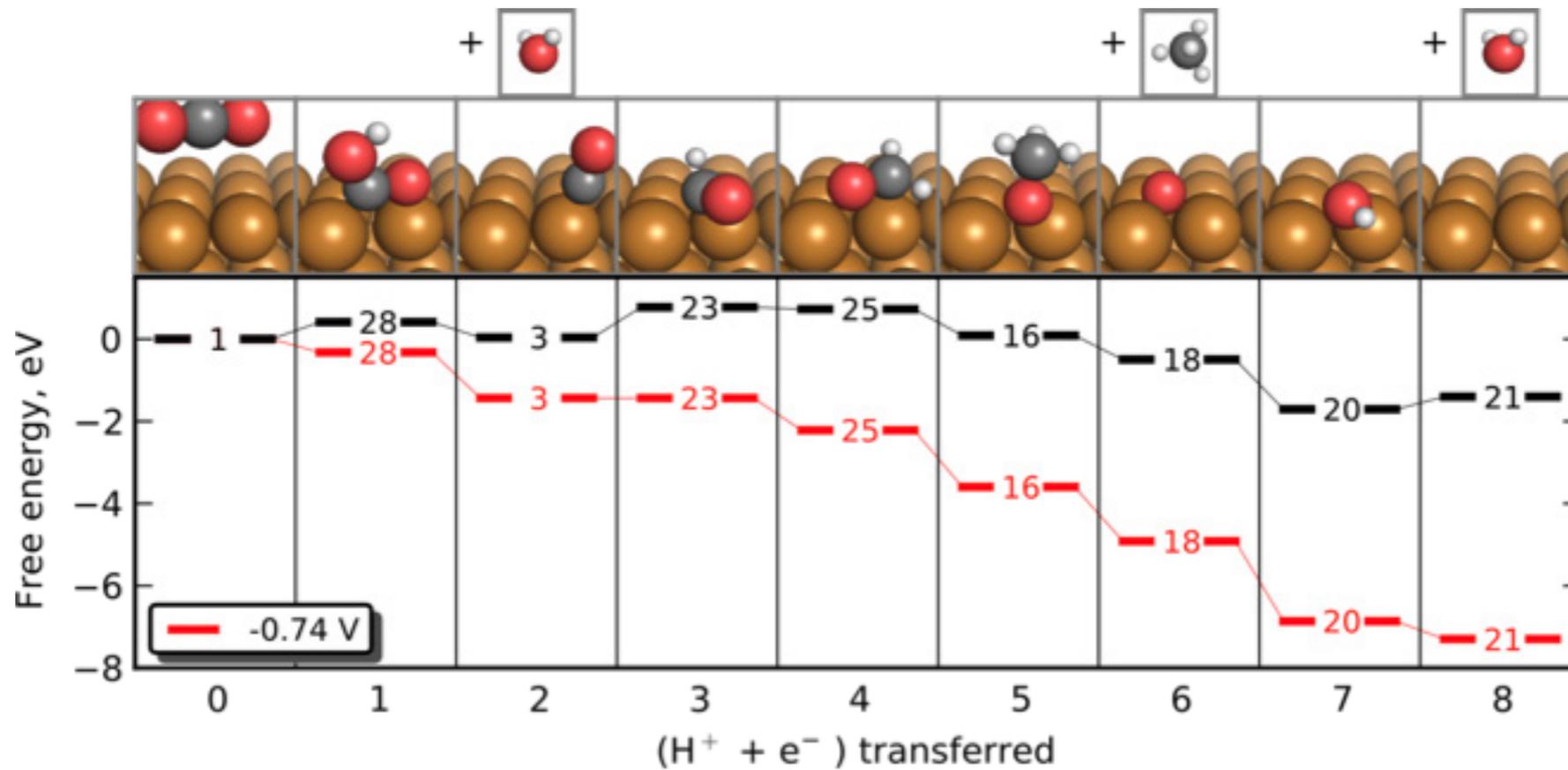


same intermediate as formic acid production -> same onset potential

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CO₂ to CH₄

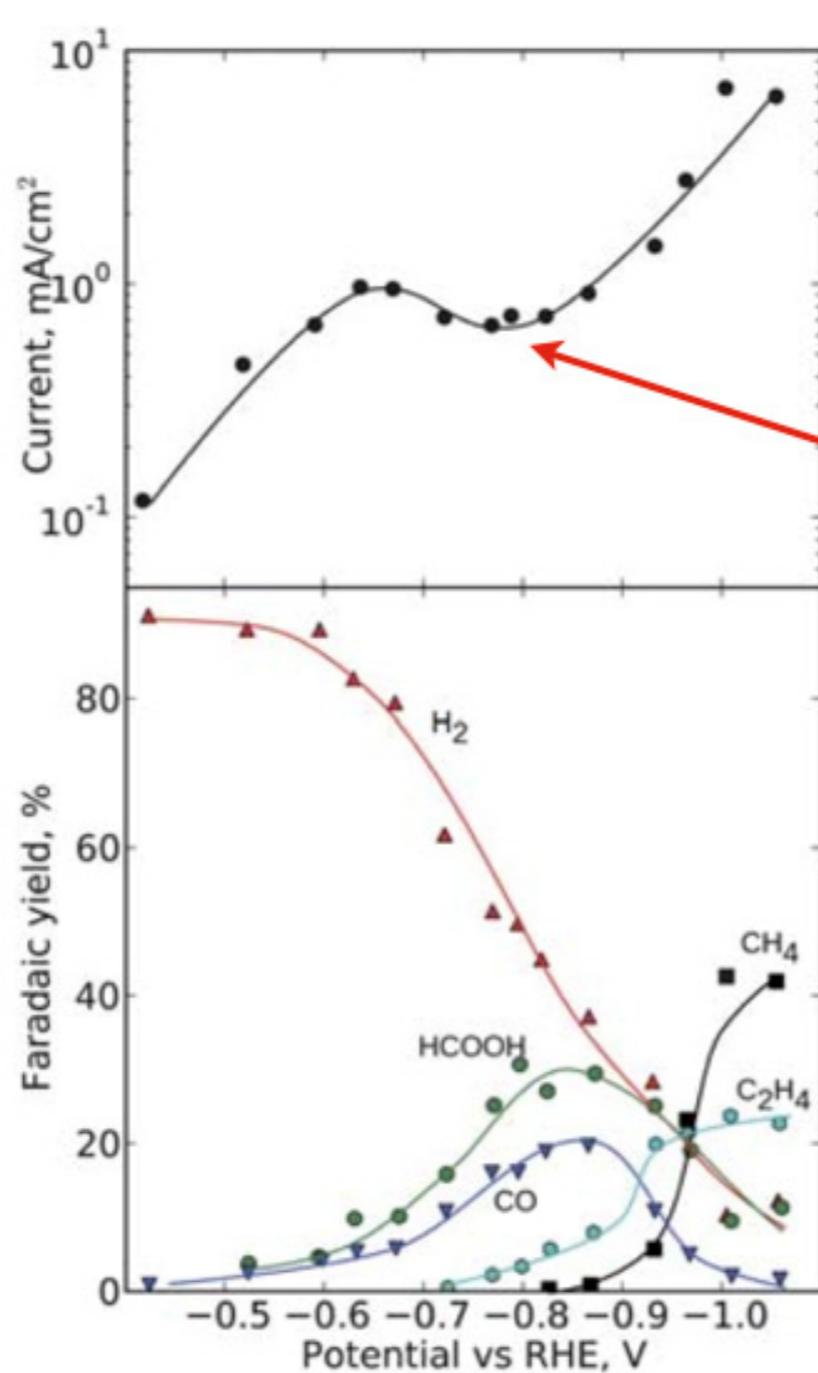


CO → HCO potential limiting step

OCH₃ + H⁺/e⁻ gives methane and O*

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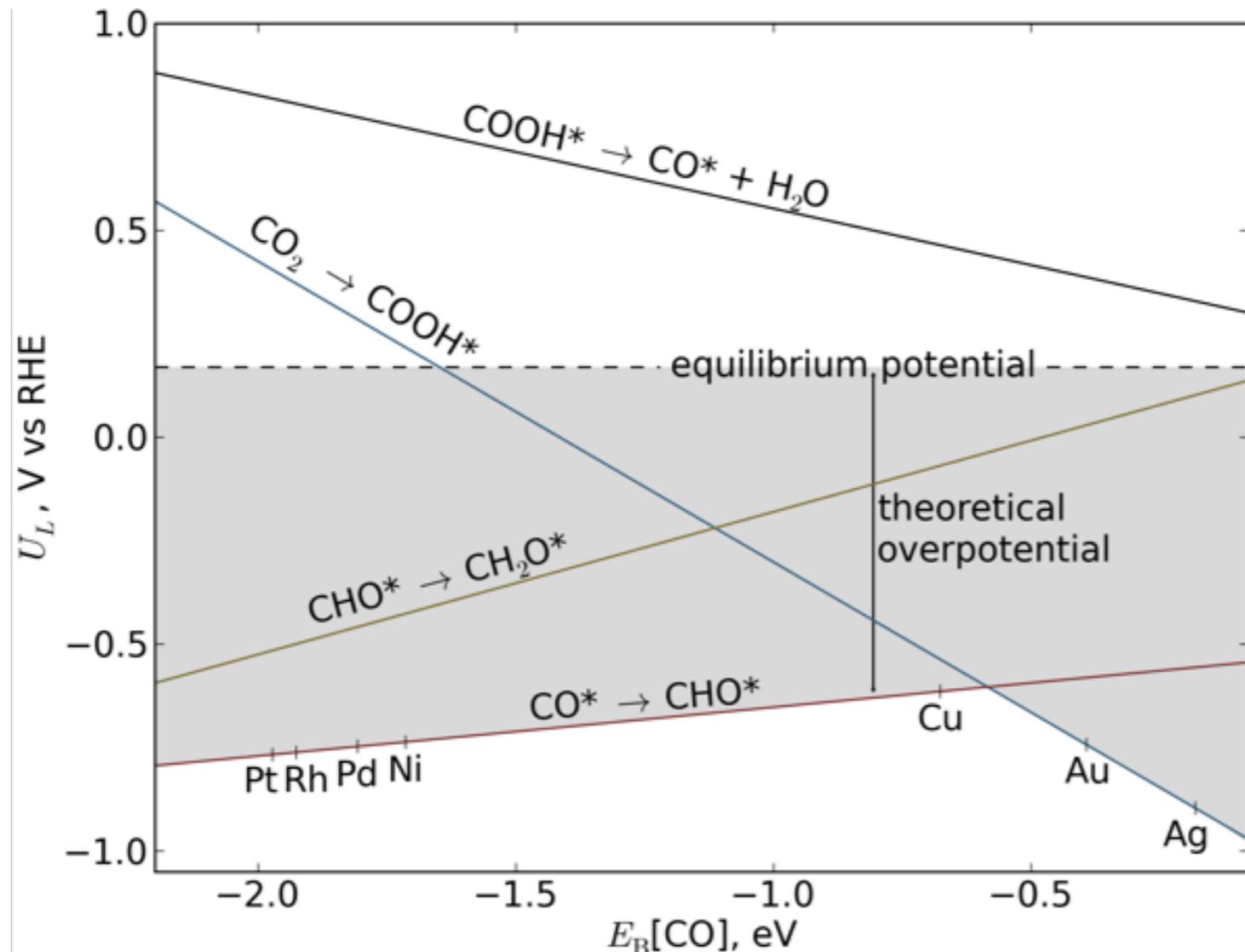


CO*/HCOO* poisoning

- 0.30 V H₂ (OH* clearance)
- 0.41 V Formic acid + CO
- 0.74 V Methane



CO₂ reduction as function of ΔE_{CO}



like ORR and OER:
minimum overpotential dictated
through scaling relations

often problem for reactions with
> 2H⁺/2e⁻ transfers



2 proton/electron transfer processes
—> zero overpotential achievable

multi proton/electron transfer processes
—> overpotential unavoidable!?

H₂ evolution —> 2 proton/electron transfer

O₂ reduction —> 4 proton/electron transfer
—> ~ 0.4 V overpotential

CO₂ reduction:

—> CO : 2 proton/electron transfer

—> HCOOH : 2 proton/electron transfer

—> CH₄ : 8 proton/electron transfer

—> C₂₊ : 12+ proton/electron transfer

