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Workshop on New Materials for Renewable Energy

17 - 21 October 2011

First-principles modeling of electrochemical reactions for solar-to-fuel energy storage

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ICTP-SISSA Workshop on New Materials for Renewable Energy
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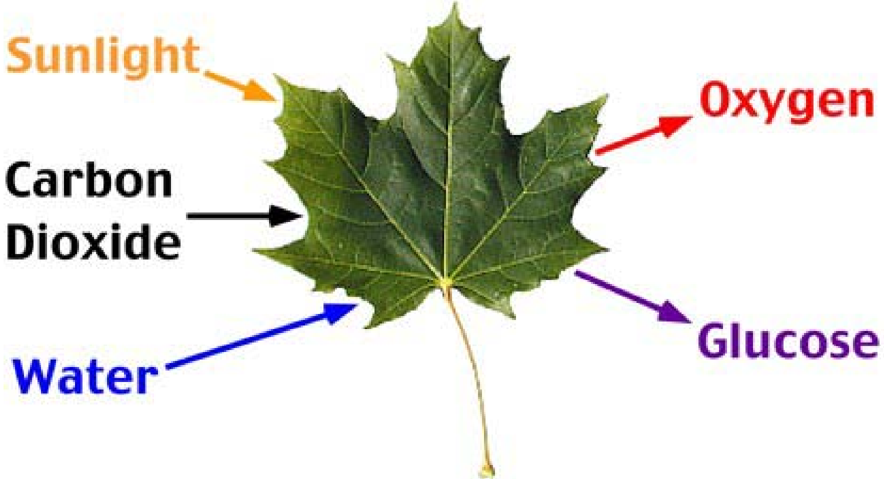
Artificial photosynthesis: using light to make fuels



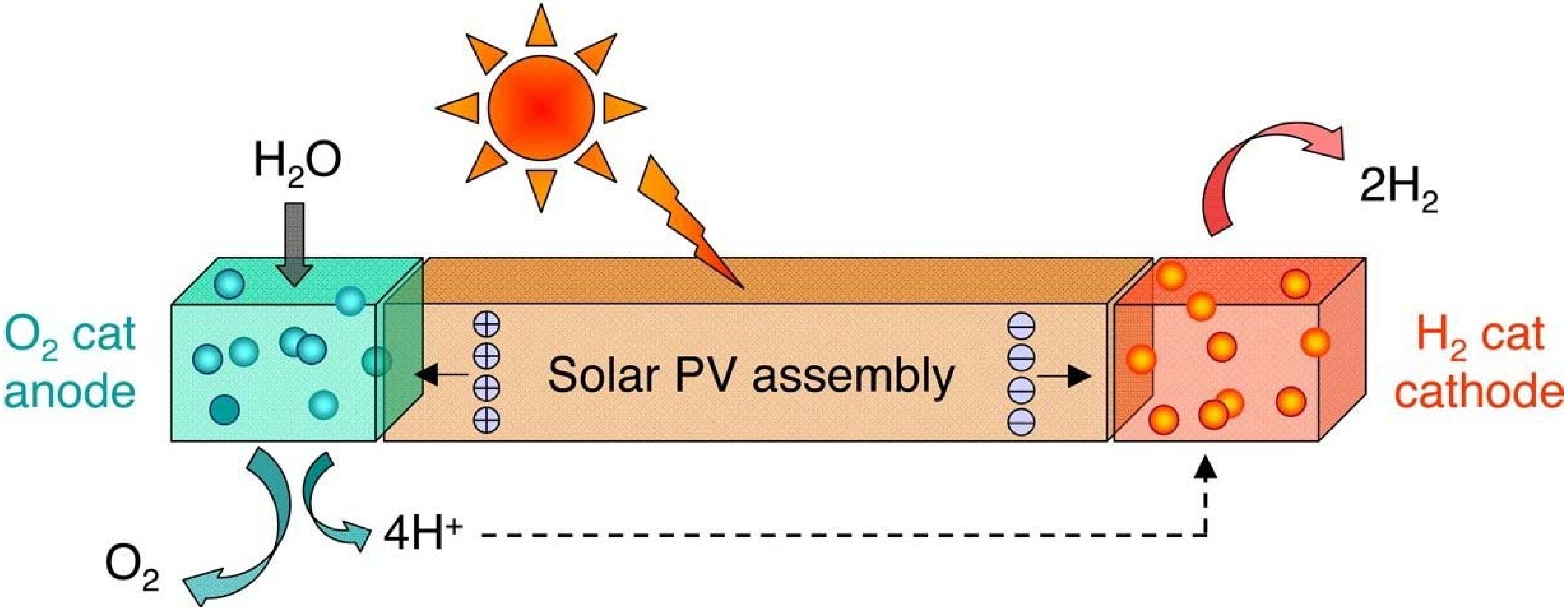
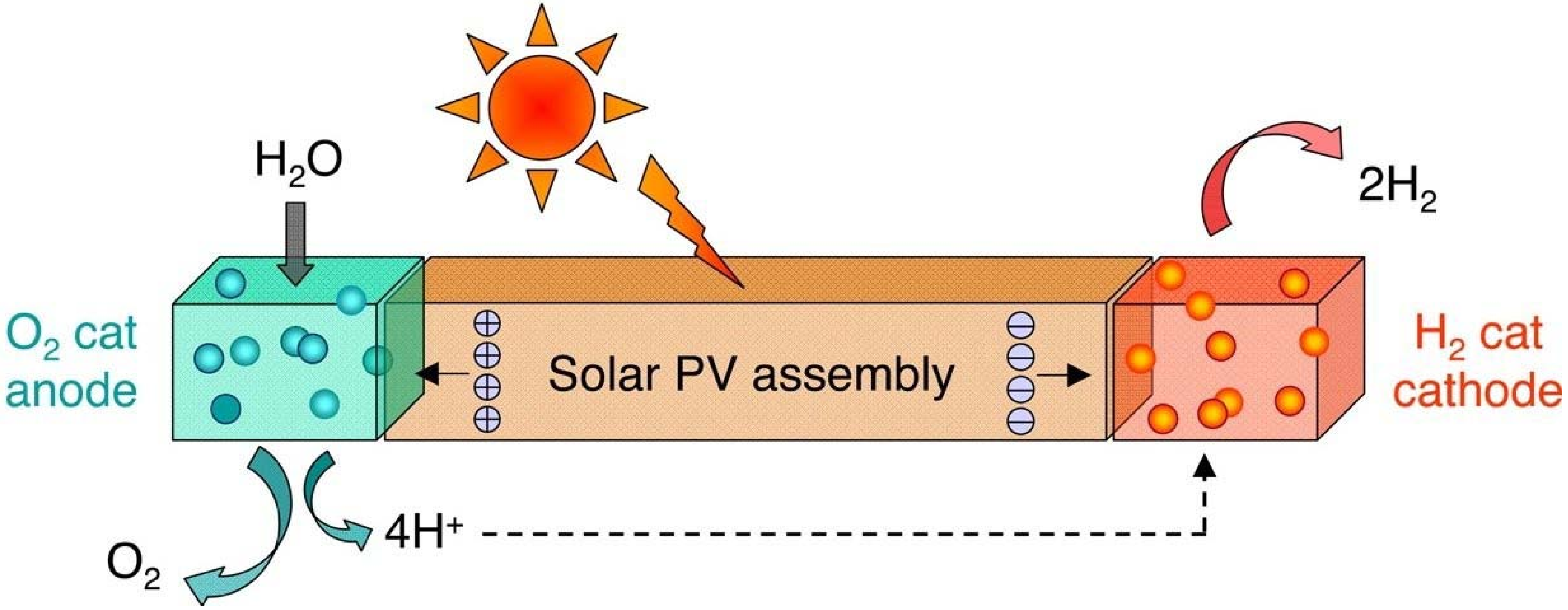


Figure from: Lewis and Nocera, PNAS **103**, 15729 (2006)

Artificial photosynthesis: using light to make fuels



Overall reaction: $2H_2O \rightarrow O_2 + 2H_2$ $(\Delta G^0 = 4.92\ \text{eV}, E^0 = -1.23\ \text{V})$

Oxidation: $2H_2O \rightarrow O_2 + 4H^+ + 4e^-$ $(E^0 = 1.23\ \text{V})$

Reduction: $2H^+ + 2e^- \rightarrow H_2$ $(E^0 = 0.00\ \text{V})$

Figure from: Lewis and Nocera, PNAS **103**, 15729 (2006)

Outline

- Reduction potentials, free energies, reference electrodes … :
a quick overview of electrochemistry

- Lessons from the oxygen evolving complex in PSII

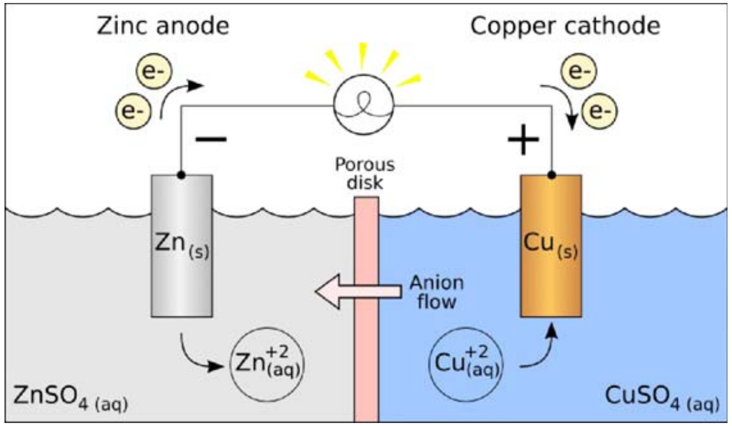
- Theoretical approaches for modeling electrochemical reactions:

    (a) Nørskov's approach

    (b) Applications to OER on metal and metal-oxide surfaces

Electrochemistry: a quick overview

Galvanic cell



$Cu^{2+}(aq) + Zn(s) \rightarrow Cu(s) + Zn^{2+}(aq)$

Cathode (Red): $Cu^{2+}(aq) + 2e^- \rightarrow Cu(s)$

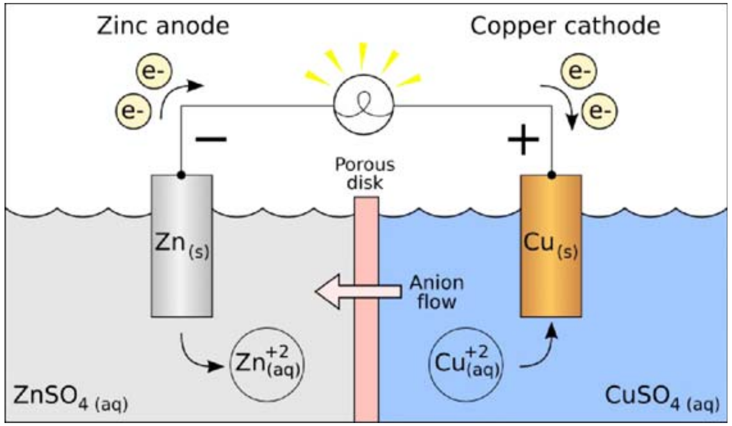
Anode (Ox): $Zn(s) \rightarrow Zn^{2+}(aq) + 2e^-$

Zn is oxidized
(e^- removed from Zn)

Cu is reduced
(e^- donated to Cu)

Electrochemistry: a quick overview

Galvanic cell



$Cu^{2+}(aq) + Zn(s) \rightarrow Cu(s) + Zn^{2+}(aq)$

Cathode (Red): $Cu^{2+}(aq) + 2e^- \rightarrow Cu(s)$

Anode (Ox): $Zn(s) \rightarrow Zn^{2+}(aq) + 2e^-$

E^0 : standard reduction potential

$Cu^{2+}(aq) + 2e^- \rightarrow Cu(s)$ $E^0 = 0.34$ V

$Zn^{2+}(aq) + 2e^- \rightarrow Zn(s)$ $E^0 = -0.76$ V

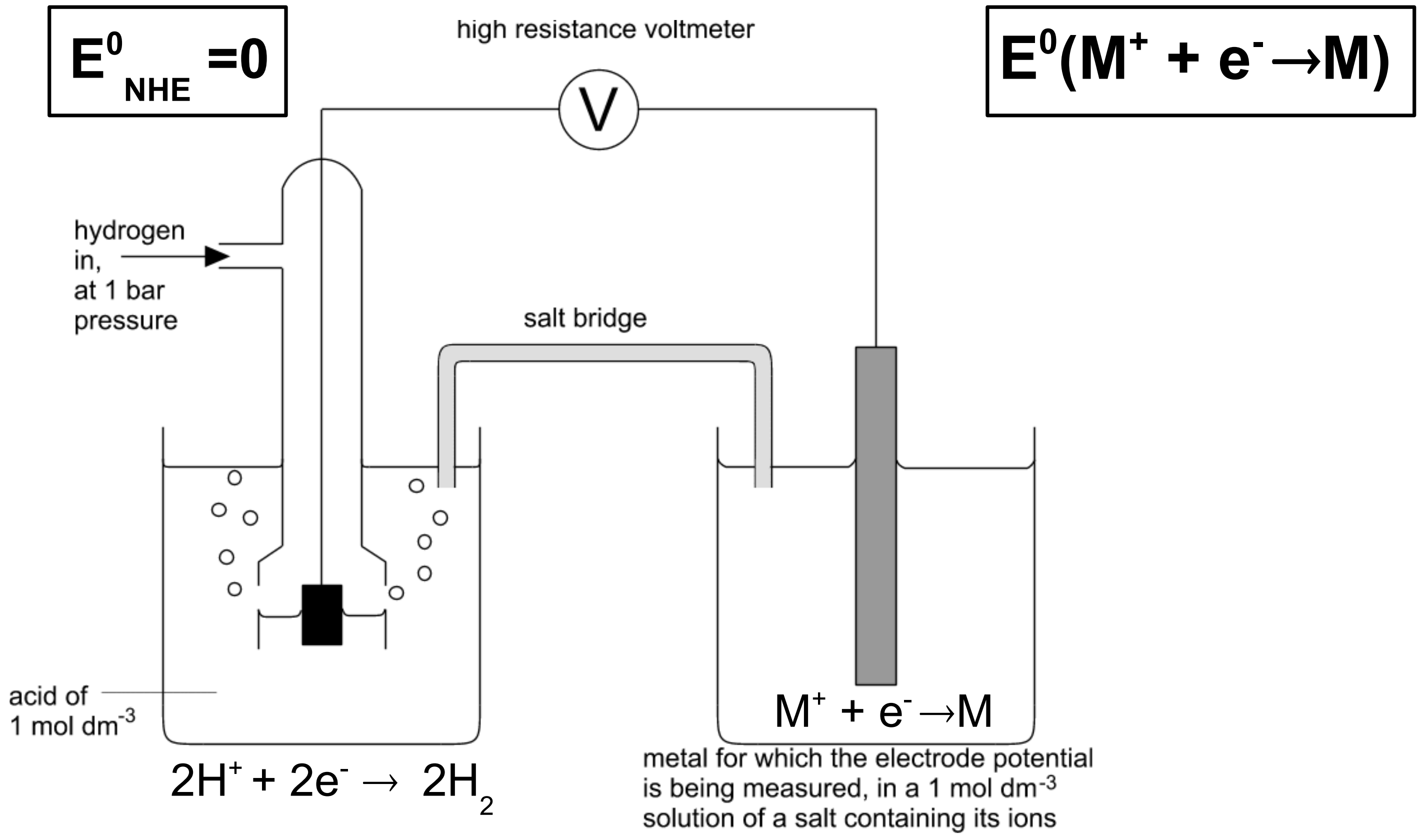
$E^0 = 0.34 - (-0.76) = 1.10$ V

$$-nFE^0 = \Delta G^0$$

Higher E^0 : reduction

Lower E^0: oxidation

Normal (Standard) Hydrogen Electrode (NHE)



$E^0_{NHE} = 0$

$E^0(M^+ + e^- \rightarrow M)$

Electrochemistry: a quick overview

ORR/OER

$O_2 + 4H^+ + 4e^- \rightarrow 2H_2O$ $E^0 = 1.23$ V

$2H^+ + 2e^- \rightarrow H_2$ $E^0 = 0.00$ V

Higher E^0 : reduction
Lower E^0: oxidation

$-nFE^0 = \Delta G^0$

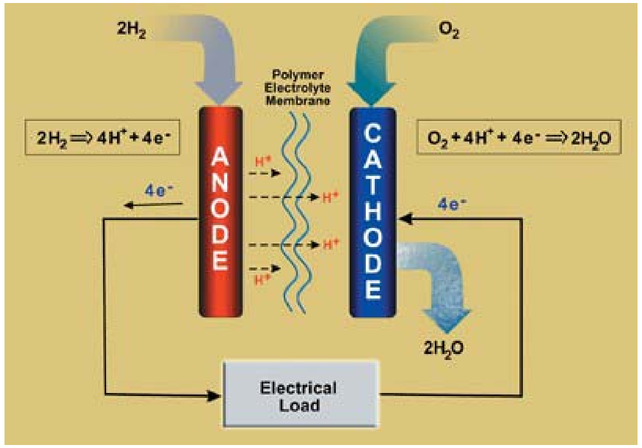
$O_2 + 4H^+ + 4e^- \rightarrow 2H_2O$ **ORR**

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

$\mathbf{O_2 + 2H_2 \rightarrow 2H_2O}$ $\Delta G^0 = -4.92$ eV

$E^0 = 1.23$ V

PEM Fuel cells



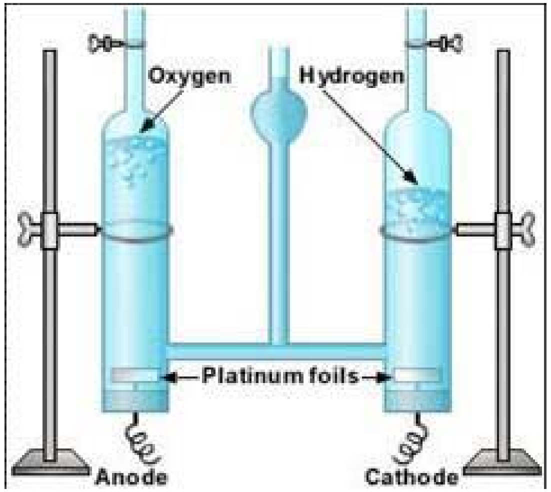
$2H_2O \rightarrow O_2 + 4H^+ + 4e^-$ **OER**

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

$\mathbf{2H_2O \rightarrow O_2 + 2H_2}$ $\Delta G^0 = 4.92$ eV

$E^0 = -1.23$ V

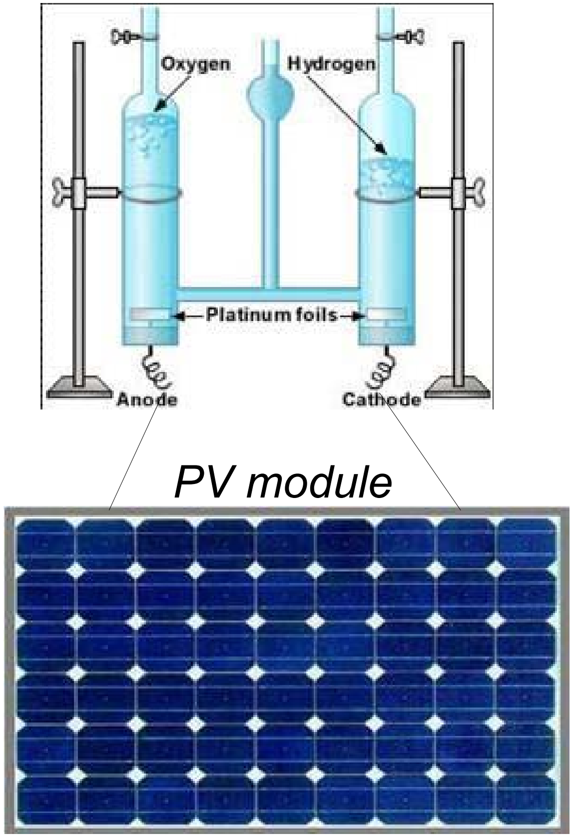
Electrolysis



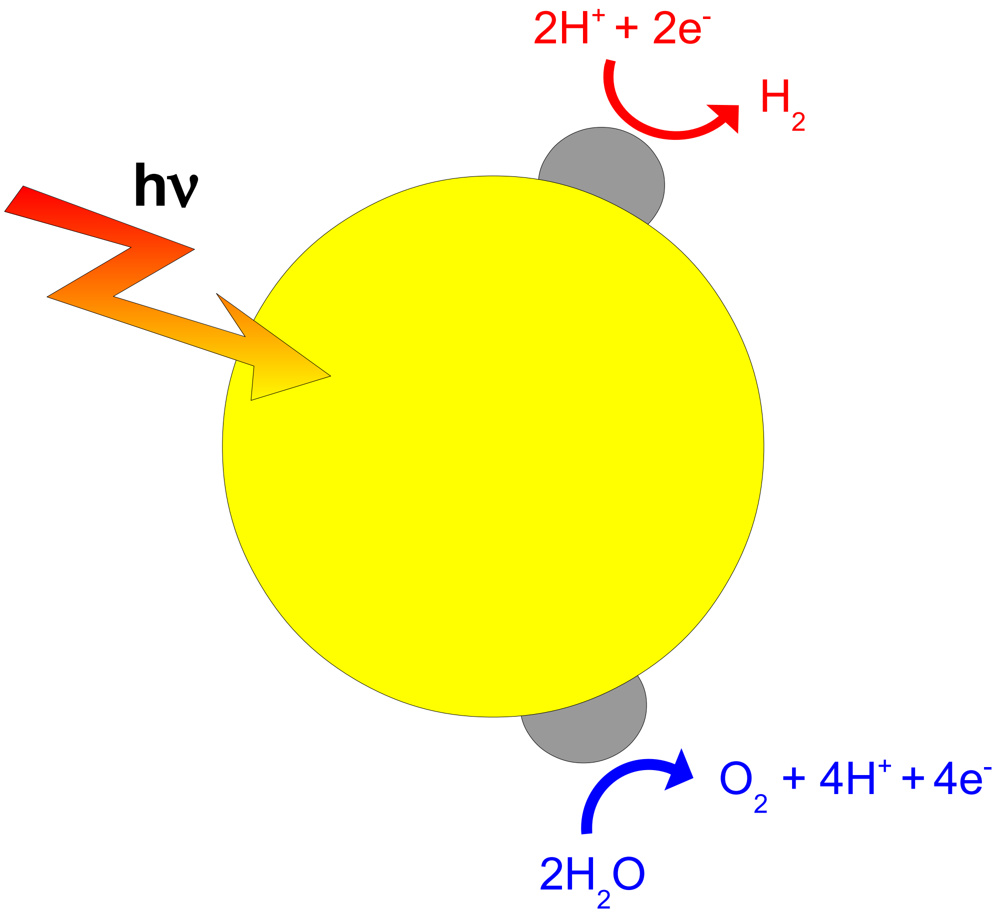
Artificial photosynthesis: using light to make fuels

Goal: storing solar energy through water splitting

Electrolyzer



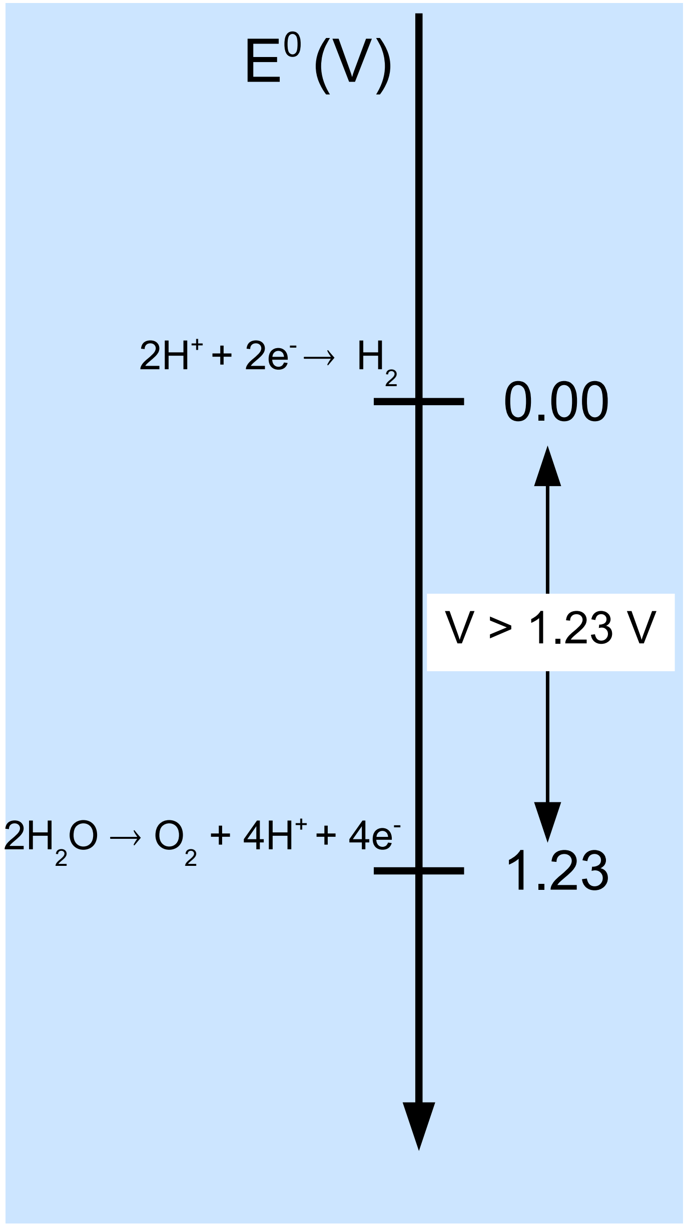
Integrated photo-catalyst



Energy level alignment

Higher E^0 : reduction
Lower E^0: oxidation

$-nFE^0 = \Delta G^0$



E^0 (V)

$2H^+ + 2e^- \rightarrow H_2$ 0.00

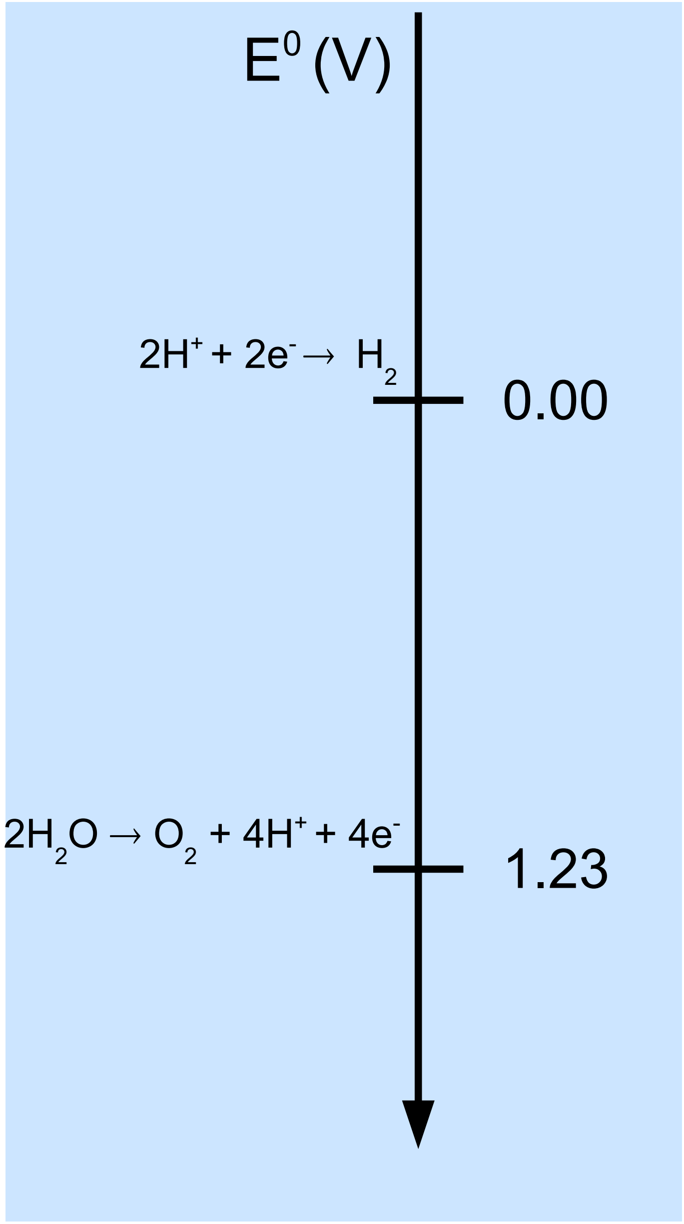
$2H_2O \rightarrow O_2 + 4H^+ + 4e^-$ 1.23

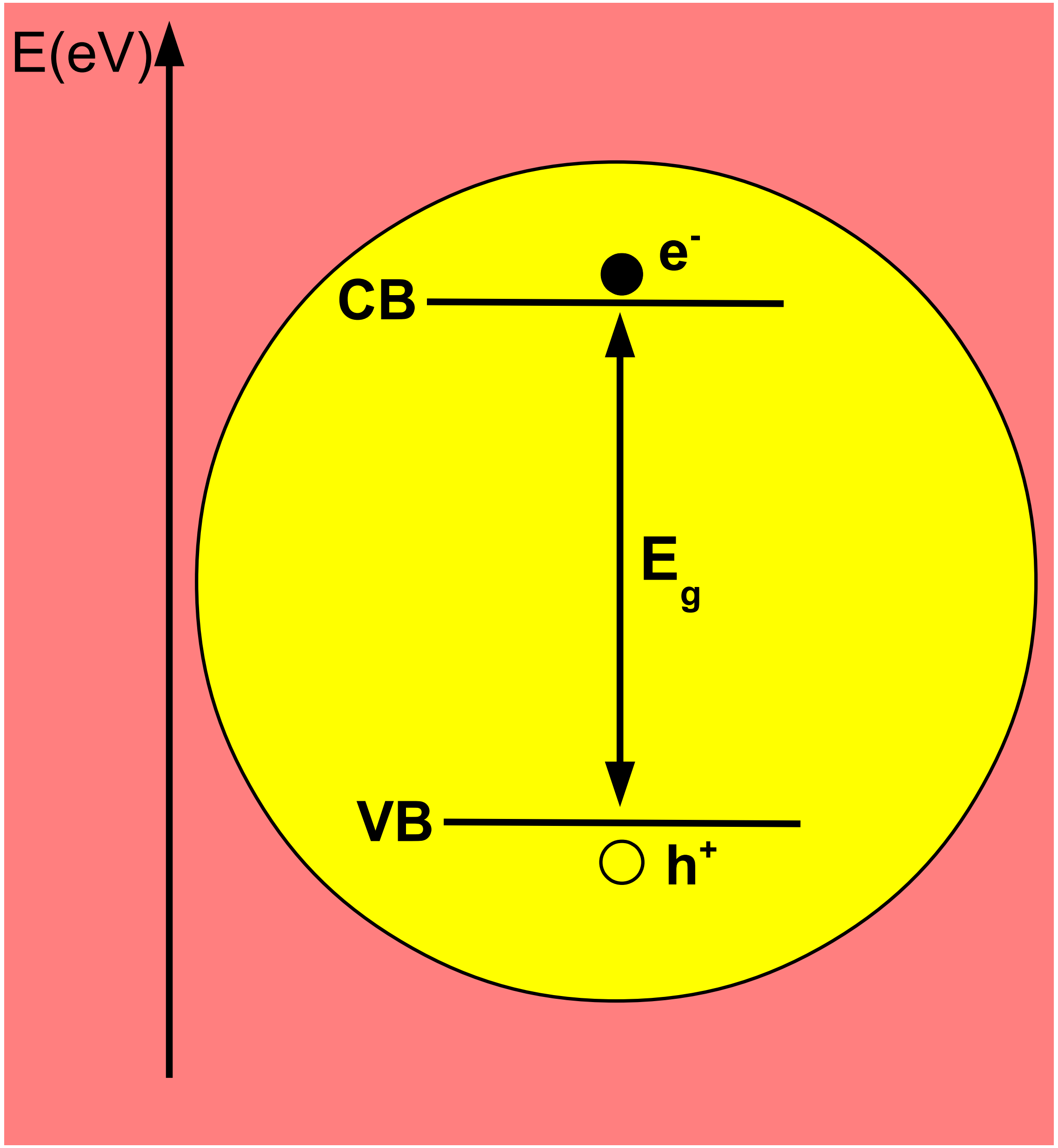
V > 1.23 V

Energy level alignment

Higher E^0 : reduction
Lower E^0: oxidation

$-nFE^0 = \Delta G^0$





Energy level alignment

Higher E^0 : reduction
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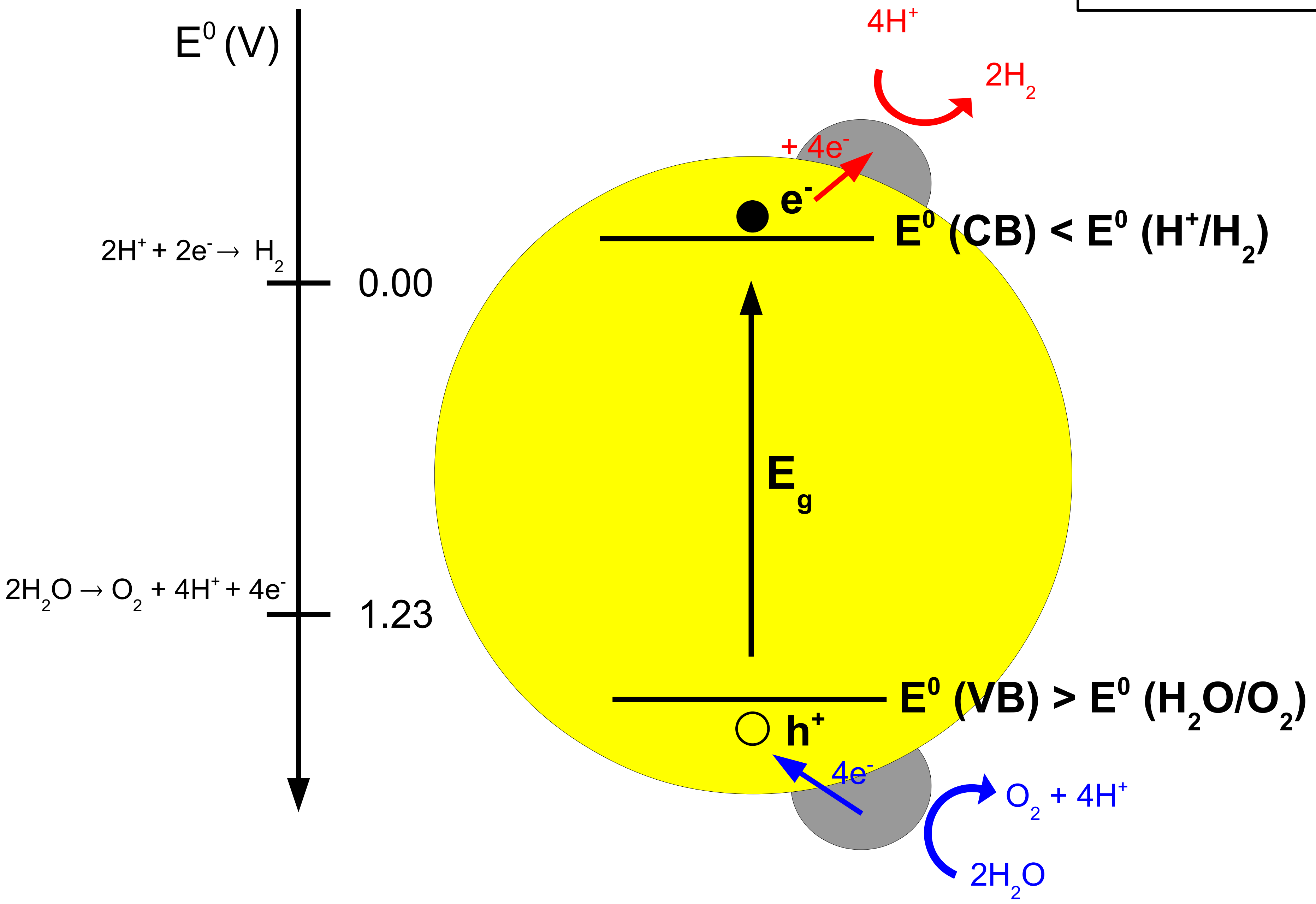
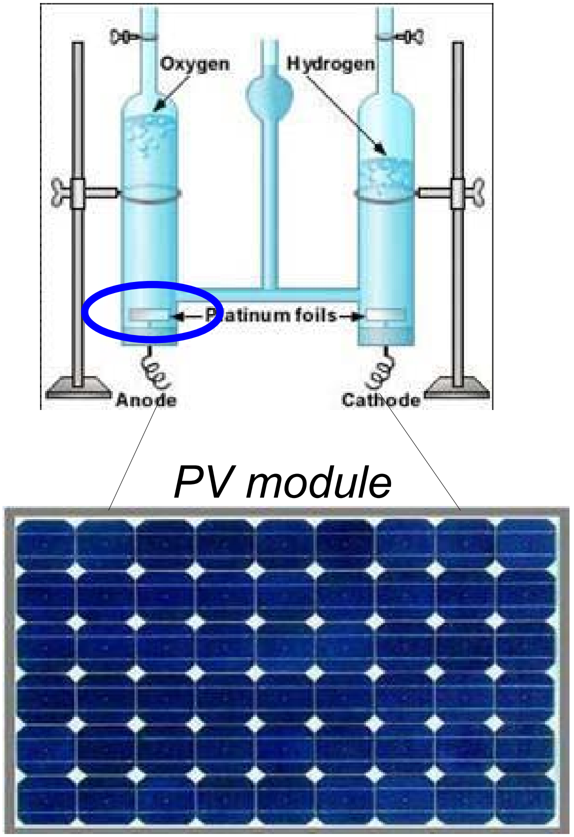
$-nFE^0 = \Delta G^0$



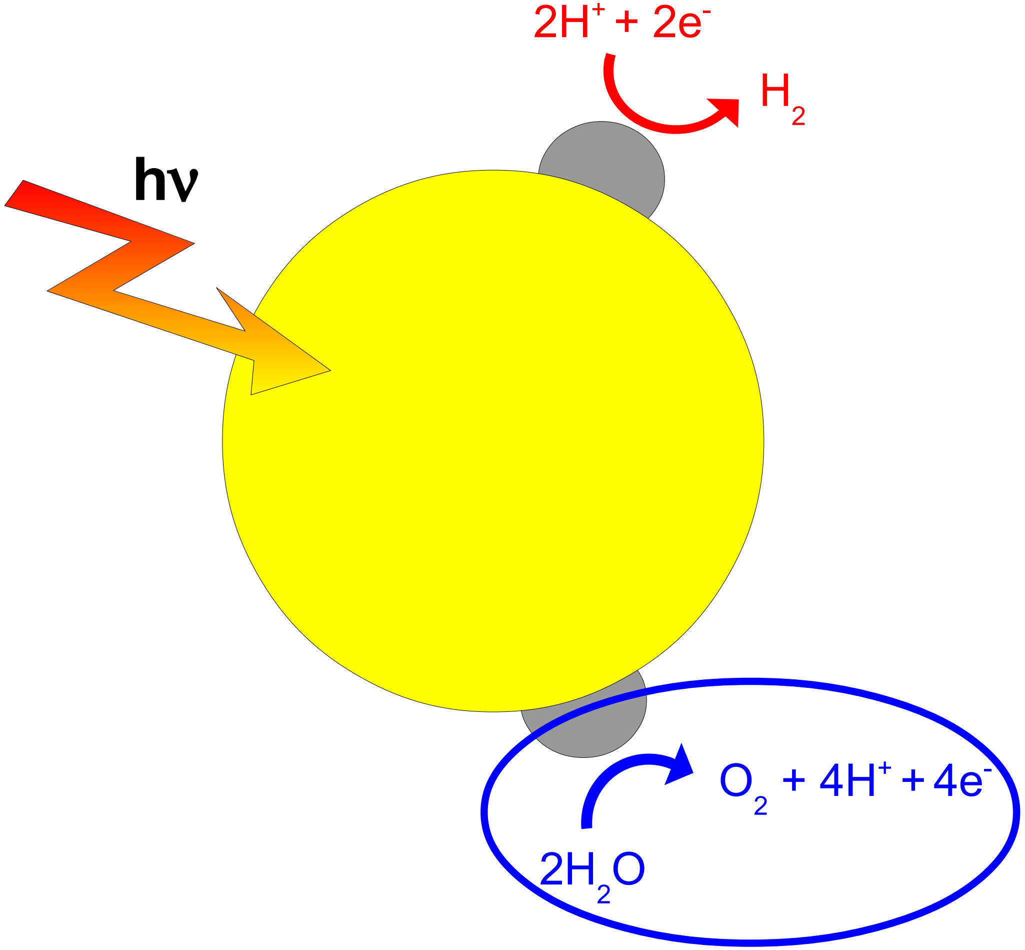
Artificial photosynthesis: using light to make fuels

Electrolyzer



PV module

Integrated photo-catalyst



$2H^+ + 2e^-$

H_2

hν

$O_2 + 4H^+ + 4e^-$

$2H_2O$

Water oxidation: a 4 electron reaction

$2H_2O \rightarrow O_2 + 4H^+ + 4e^-$ $(E^0 = 1.23\ V)$

- Oxidizing water is thermodynamically demanding

- This reaction involves a 4-electron mechanism: 1- and 2-electron intermediates need to be avoided

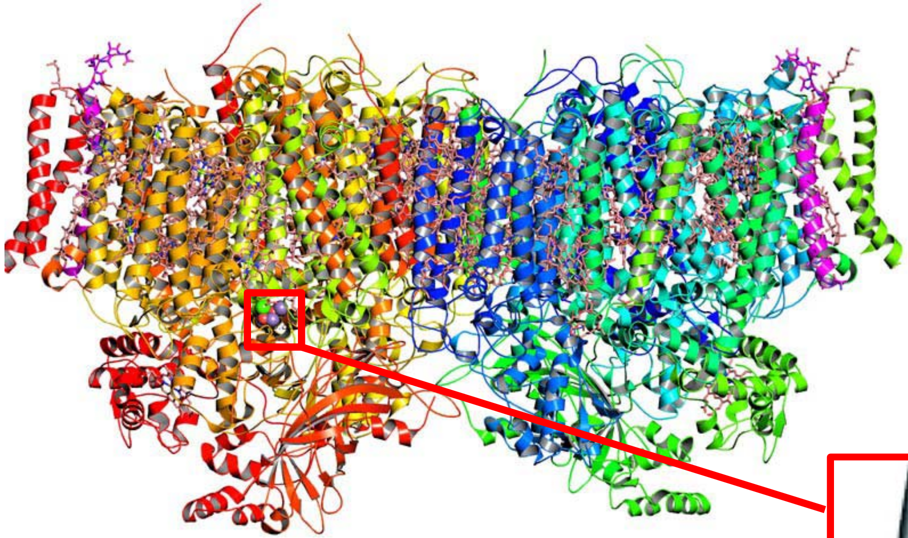
1-electron mechanism: $H_2O \rightarrow OH^\bullet + H^+ + e^-$ $(\Delta G^0 = 2.31\ V)$

2-electron mechanism: $2H_2O \rightarrow H_2O_2 + 2H^+ + 2e^-$ $(\Delta G^0 = 1.78\ V)$

4-electron mechanism: $2H_2O \rightarrow O_2 + 4H^+ + 4e^-$ $(\Delta G^0 = 1.23\ V)$

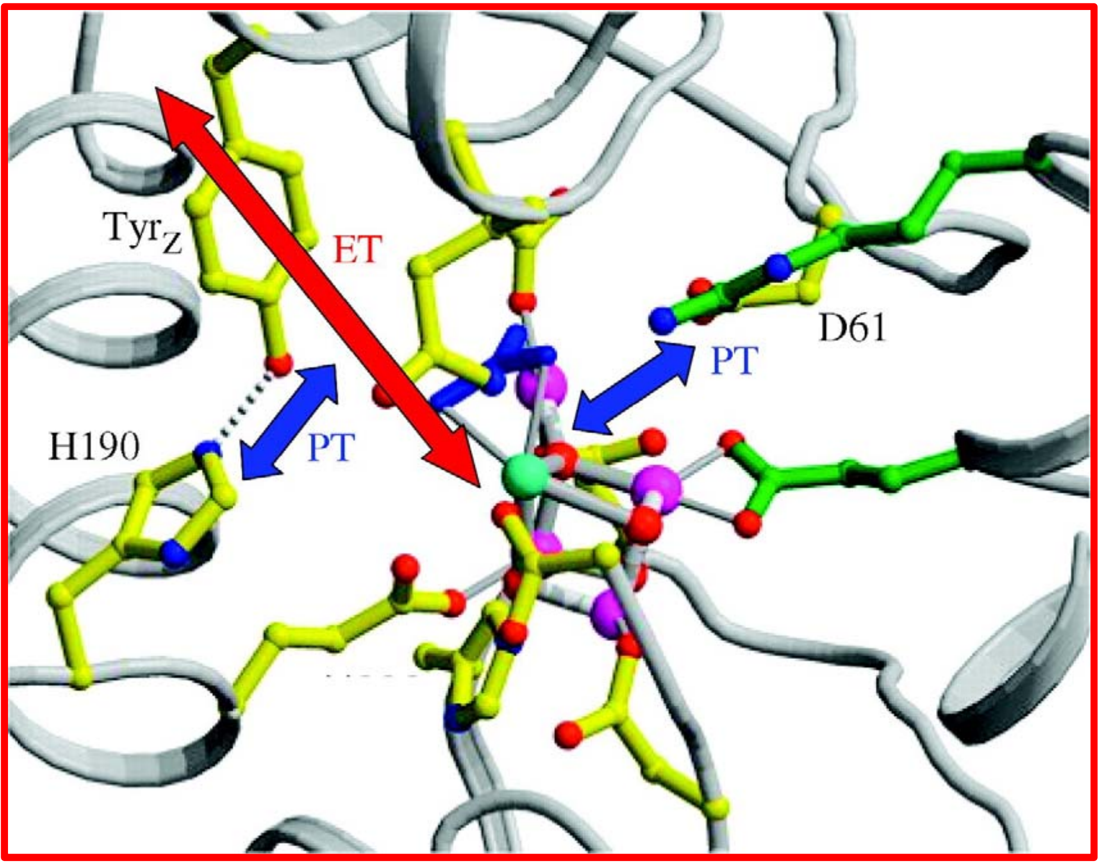
- We need **catalysts** that efficiently promote the 4-electron mechanism

Oxygen evolving complex in PSII

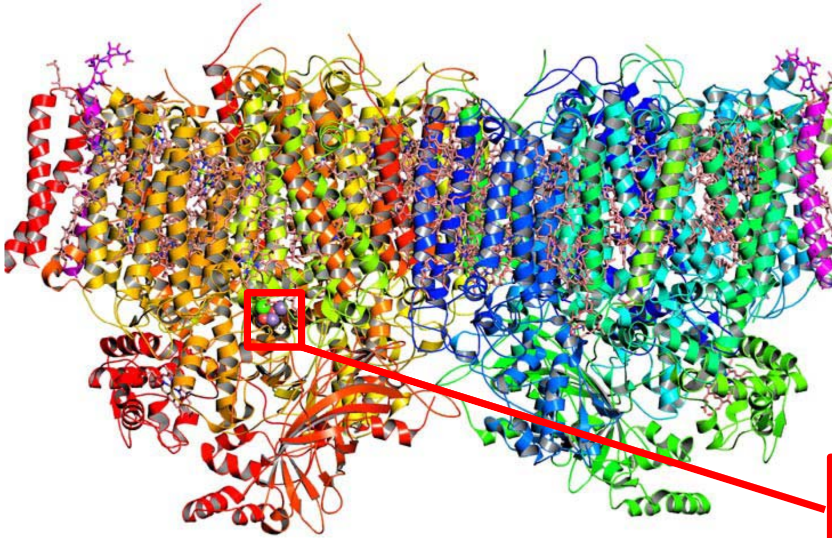


Photosystem II

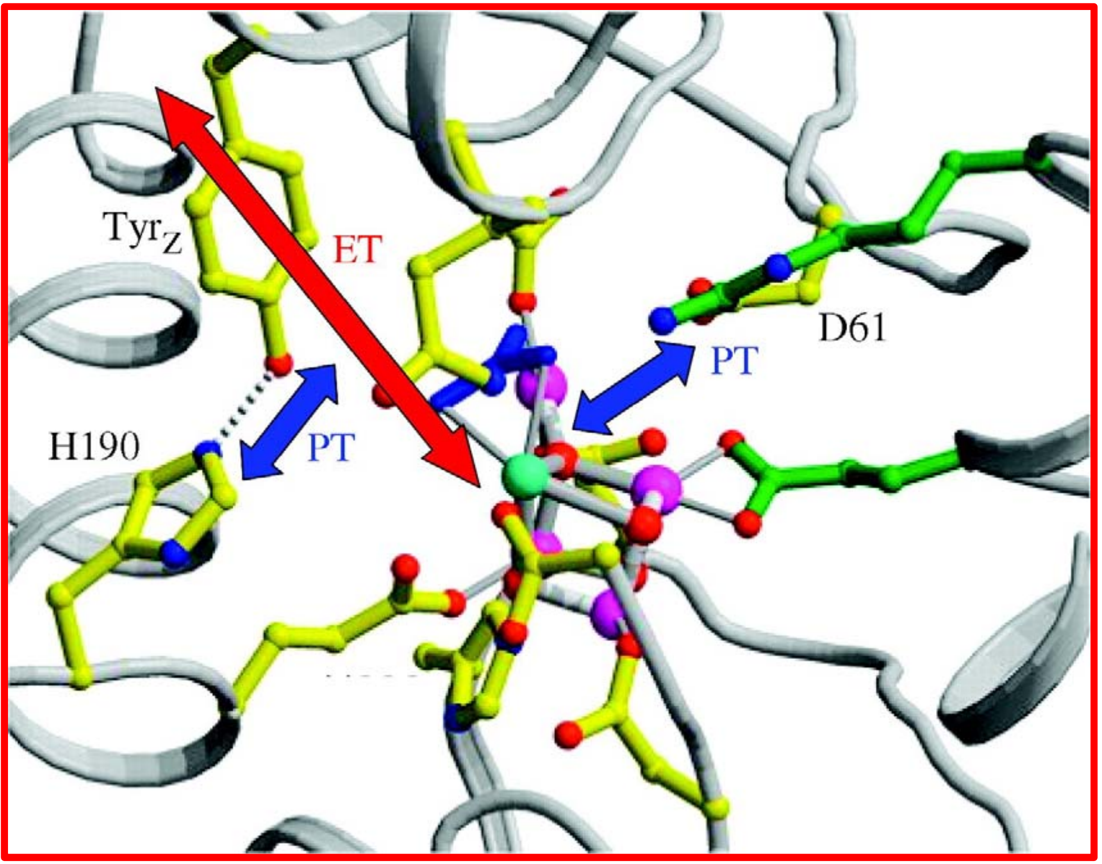
OEC in Photosystem II: Mn_3CaO_4-Mn

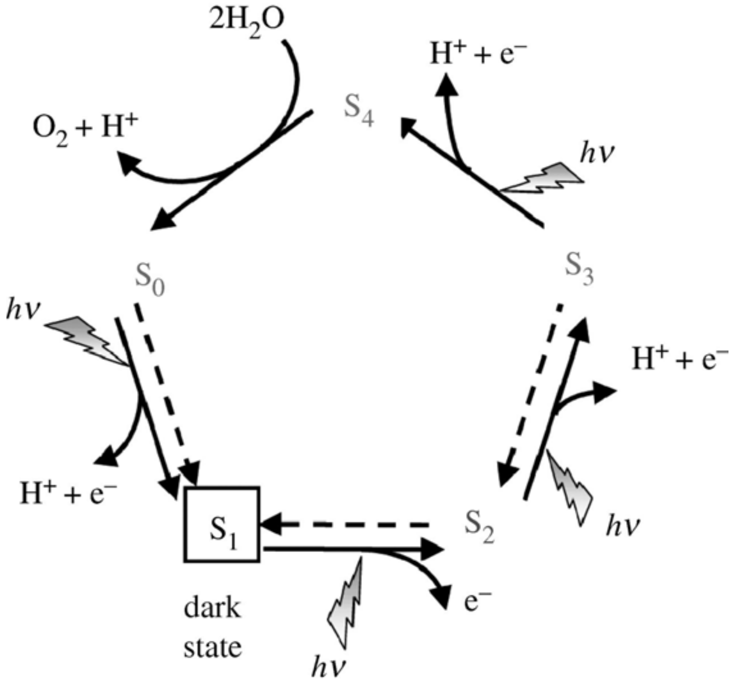


Oxygen evolving complex in PSII



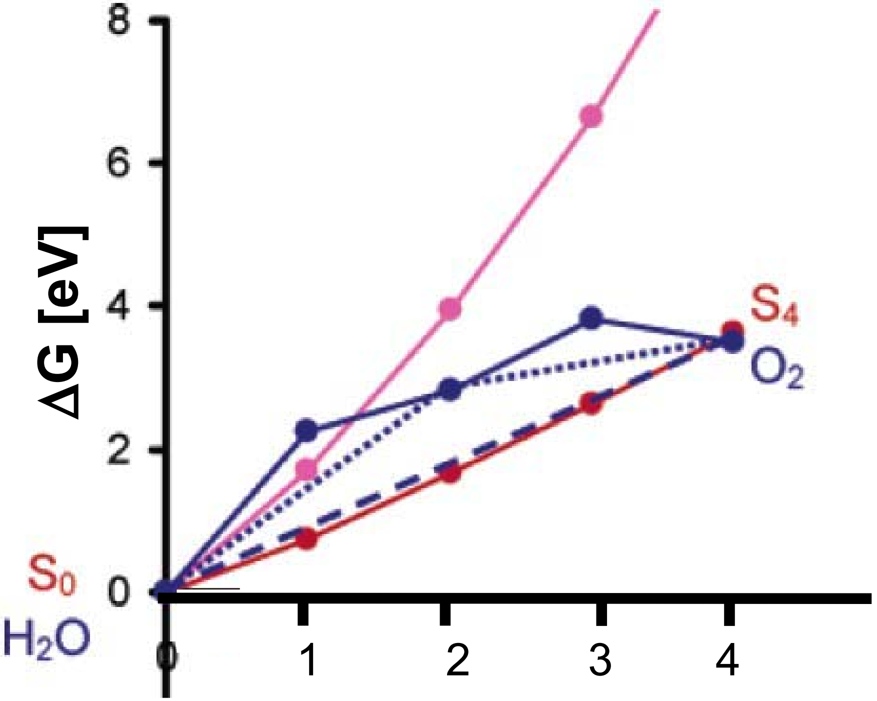
4 e's are involved: The catalyst must be able to undergo multiple oxidations

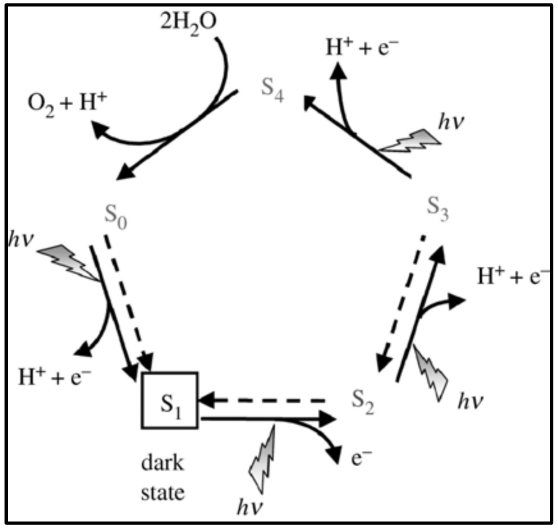




$2H_2O \rightarrow O_2 + 4H^+ + 4e^-$

Oxygen evolving complex in PSII





1-e : $H_2O \rightarrow OH^\bullet + H^+ + e^-$ $(\Delta G^0 = 2.31\ V)$

2-e : $2H_2O \rightarrow H_2O_2 + 2H^+ + 2e^-$ $(\Delta G^0 = 1.78\ V)$

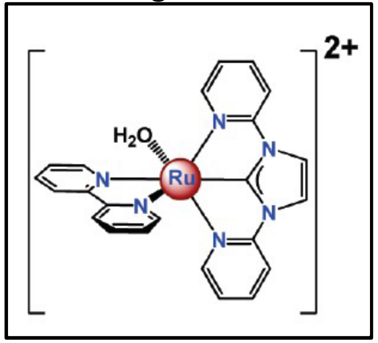
4-e : $2H_2O \rightarrow O_2 + 4H^+ + 4e^-$ $(\Delta G^0 = 1.23\ V)$

Figure from: JP McEvoy and GW Brudvige, Chemical Reviews **106**, 4455 (2006)

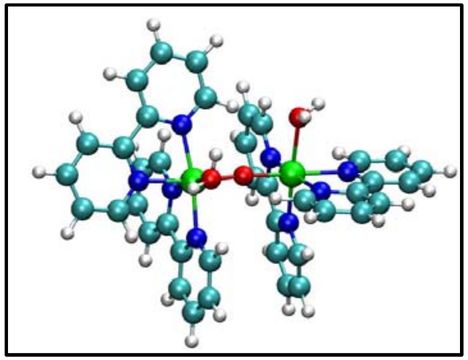
Artificial Catalysts for OER

Homogeneous catalysts for OER

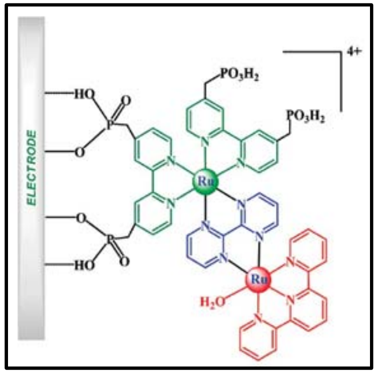
single-site



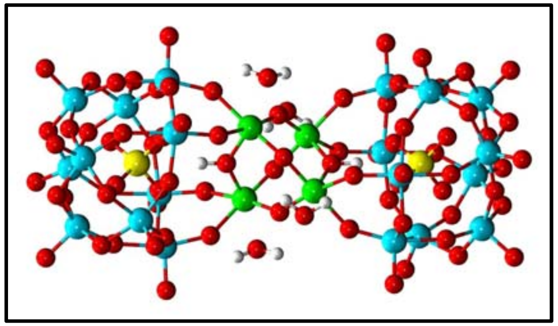
multi-sites



anchored on electrodes

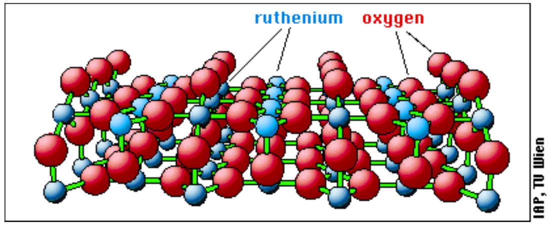


Ru-, Co-POM

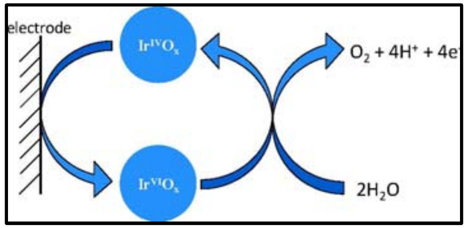


Heterogeneous catalysts for OER

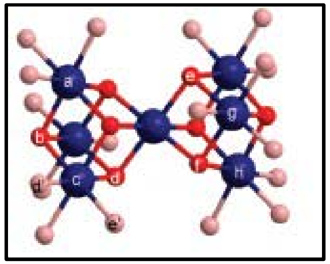
RuO_2, IrO_2 surfaces



IrO_2 nanoparticles



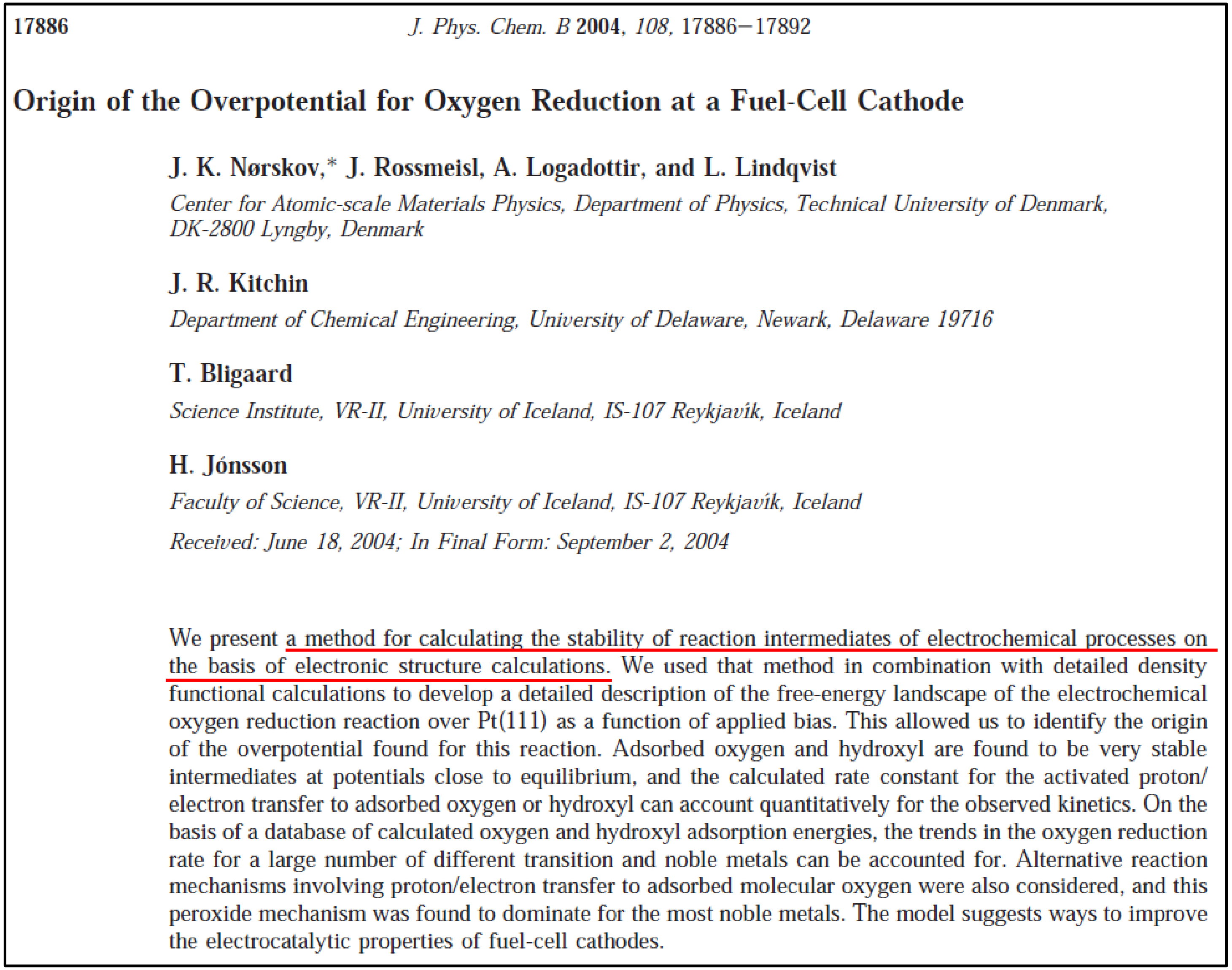
Co-Pi amorphous



Artificial Catalysts for OER

- Mechanism of water oxidation?
- What determines the efficiency of a catalyst ?

Nørskov's approach: Computational NHE



17886 J. Phys. Chem. B **2004**, 108, 17886−17892

Origin of the Overpotential for Oxygen Reduction at a Fuel-Cell Cathode

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We present a method for calculating the stability of reaction intermediates of electrochemical processes on the basis of electronic structure calculations. We used that method in combination with detailed density functional calculations to develop a detailed description of the free-energy landscape of the electrochemical oxygen reduction reaction over Pt(111) as a function of applied bias. This allowed us to identify the origin of the overpotential found for this reaction. Adsorbed oxygen and hydroxyl are found to be very stable intermediates at potentials close to equilibrium, and the calculated rate constant for the activated proton/electron transfer to adsorbed oxygen or hydroxyl can account quantitatively for the observed kinetics. On the basis of a database of calculated oxygen and hydroxyl adsorption energies, the trends in the oxygen reduction rate for a large number of different transition and noble metals can be accounted for. Alternative reaction mechanisms involving proton/electron transfer to adsorbed molecular oxygen were also considered, and this peroxide mechanism was found to dominate for the most noble metals. The model suggests ways to improve the electrocatalytic properties of fuel-cell cathodes.

Nørskov's approach: Computational NHE

Zero bias: At V=0 relative to the NHE we have:

$E^0_{NHE} = \Delta G^0_{NHE} = 0 \quad \Rightarrow \quad 2H^+(aq) + 2\,e^- \leftrightarrow H_2\,(g)$

$\Rightarrow \; G^0(H^+ + e^-) = G^0(1/2\;H_2)$

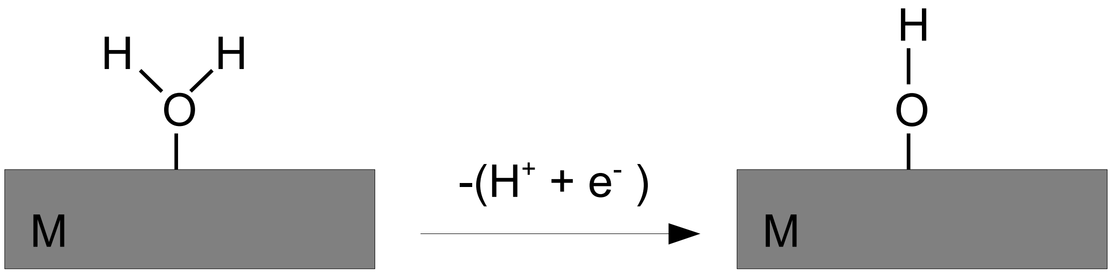
Therefore, using NHE as reference, we can compute the chemical potential of the $(H^+ + e^-)$ pair from the chemical potential of gas phase H_2

We do need to estimate $\mu(H^+) + \mu(e^-)$ separately

Nørskov's approach: Computational NHE

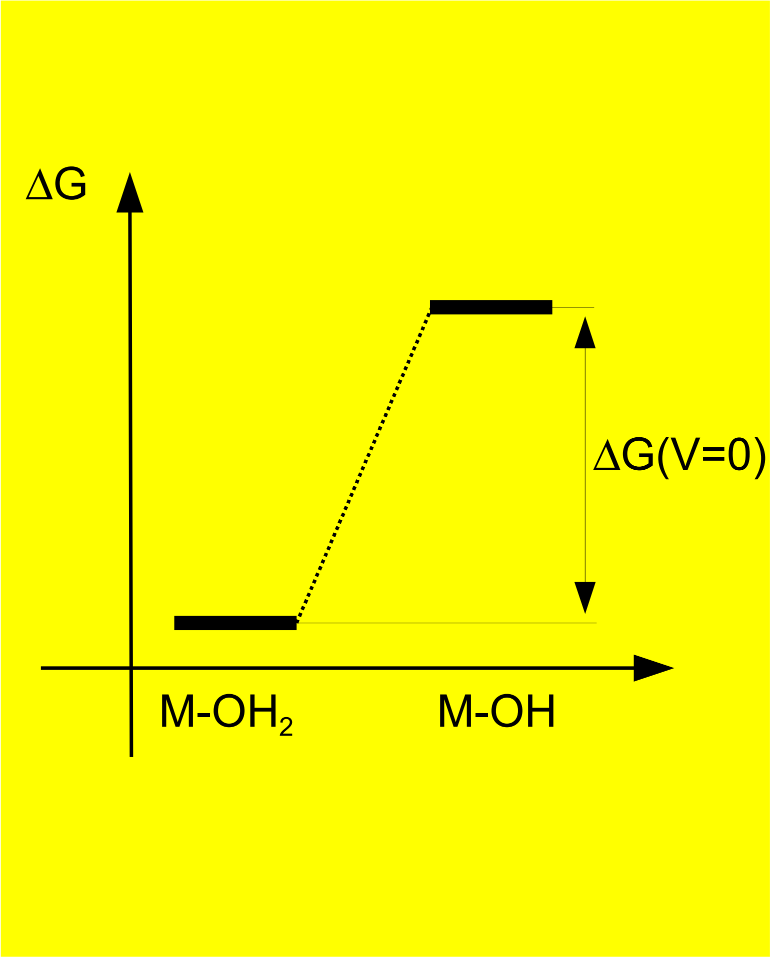
Example: Suppose we want to compute the free energy change ΔG w.r.t. NHE at V=0 for the following half cell reaction:

$M\text{-}OH_2 \rightarrow M\text{-}OH + H^+ + e^-$



G(M-OH$_2$)

G(M-OH)



$$\Delta G = G(M\text{-}OH) + \underbrace{\mu(H^+) + \mu(e^-)} - G(M\text{-}OH_2)$$

$$= G(M\text{-}OH_2) + 1/2\mu(H_2) - G(M\text{-}OH)$$

$$E^0 = -\Delta G^0/F$$

Nørskov's approach: Computational NHE

***Finite V*:**

V=0 $\mu(H^+) + \mu(e^-) = 1/2\mu(H_2)$

$V \neq 0$ $\mu(e^-) \rightarrow \mu(e^-) - eV$

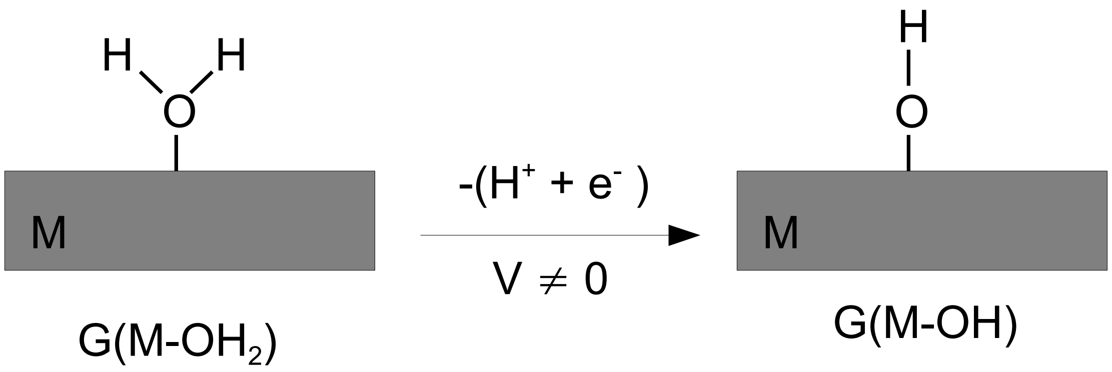
$\mu(H^+) + \mu(e^-) = 1/2\mu(H_2) - eV$

All other effects of the bias V are neglected in this approach

Nørskov's approach: Computational NHE

Example: $V \neq 0$

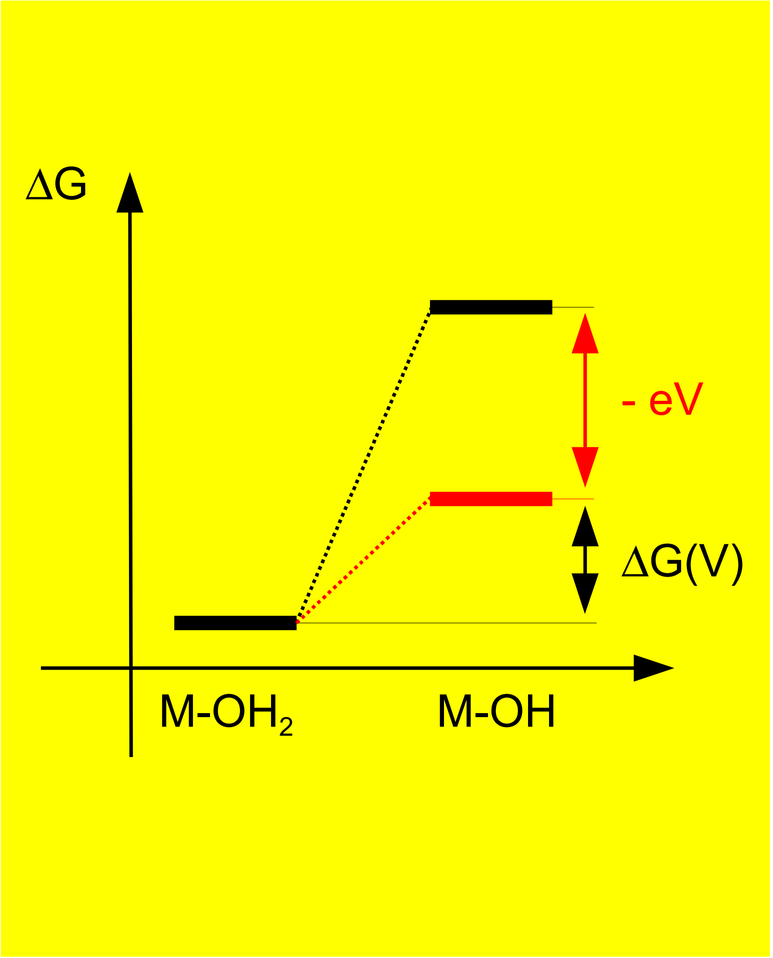
$M\text{-}OH_2 \rightarrow M\text{-}OH + H^+ + e^-$



$$\Delta G(V) = G(M\text{-}OH) + \underbrace{\mu(H^+) + \mu(e^-)} - G(M\text{-}OH_2)$$

$$= G(M\text{-}OH_2) + 1/2\mu(H_2) - eV - G(M\text{-}OH)$$

$$= \Delta G(V{=}0) - eV$$



The relative energies of the intermediates depend linearly on the bias V

Nørskov's approach: Computational NHE

Finite pH:

pH=0 $\mu(H^+) + \mu(e^-) = 1/2\mu(H_2)$

pH ≠ 0 $\mu(H^+) \rightarrow \mu(H^+) - 2.303\ kT \times pH$

$\mu(H^+) + \mu(e^-) = 1/2\mu(H_2) - 2.303\ kT \times pH$

Nørskov's approach: Computational NHE

Free energies: the free energy changes at V=0 and pH=0 are computed according to:

$\Delta G \simeq \Delta E + \Delta ZPE - T\Delta S$

Where:

- ΔE is the reaction energy (*DFT calculation*)
- ΔZPE is the change in zero-point-energy (*normal mode analysis*)
- ΔS is the change in entropy (*from thermochemical tables*)

Solvent: the effect of one monolayer of water has been included (O* interacts negligibly with water while OH* makes hydrogen bonds)

Double layer: the field in the double layer (~1V/3Å) couples weakly to the dipole moments of the adsorbed species (~0.05 eÅ), giving rise to effects of the order of 0.01 eV

Nørskov's approach: Computational NHE

Limits: *only (H^+ + e^-) pairs (PCET). No ET nor PT steps*

Limits: no dynamical (configurational entropy) effects due to the solvent rearrangement upon the formation of new intermediates are neglected. This is probably a good approximation for (H^+ + e^-) steps, since the overall charge of the system is constant.

Limits: thermodynamics only. No kinetics.

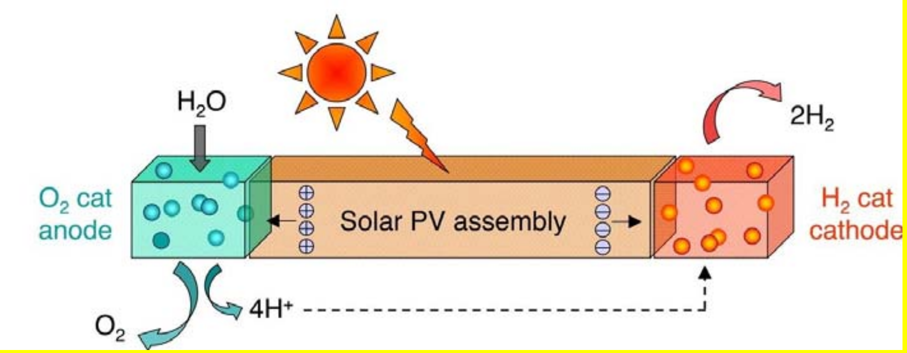
OER and ORR

Electrolysis

$2H_2O \rightarrow O_2 + 2H_2$ $\Delta G^0 = 4.92$ eV

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

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

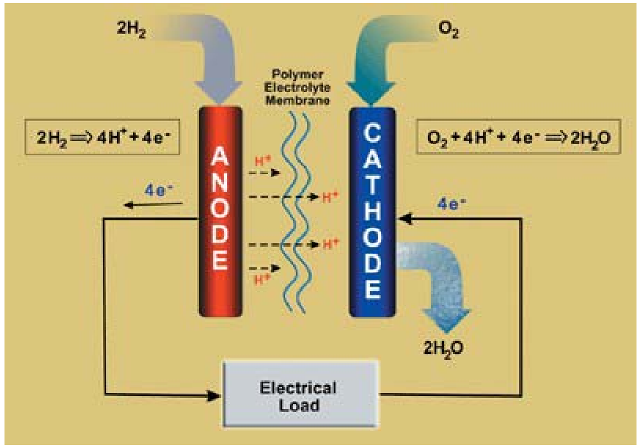


PEM Fuel cells

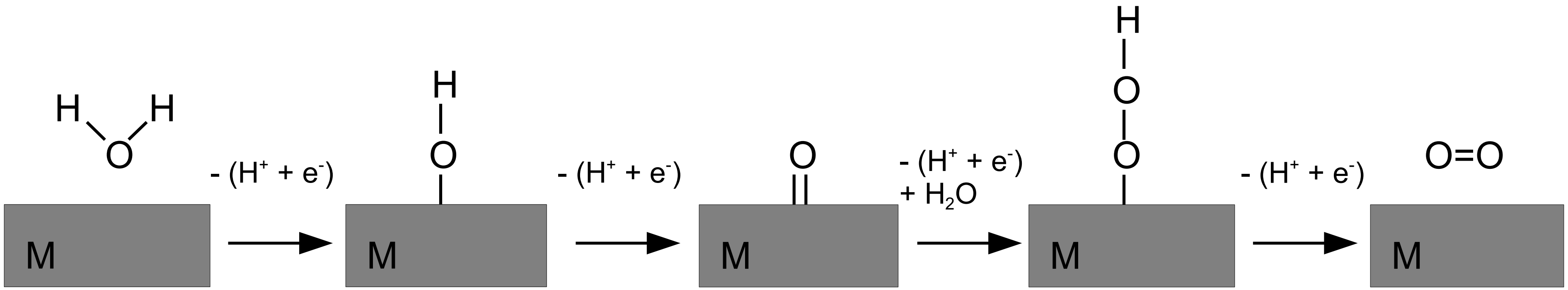
$O_2 + 2H_2 \rightarrow 2H_2O$ $\Delta G^0 = -4.92$ eV

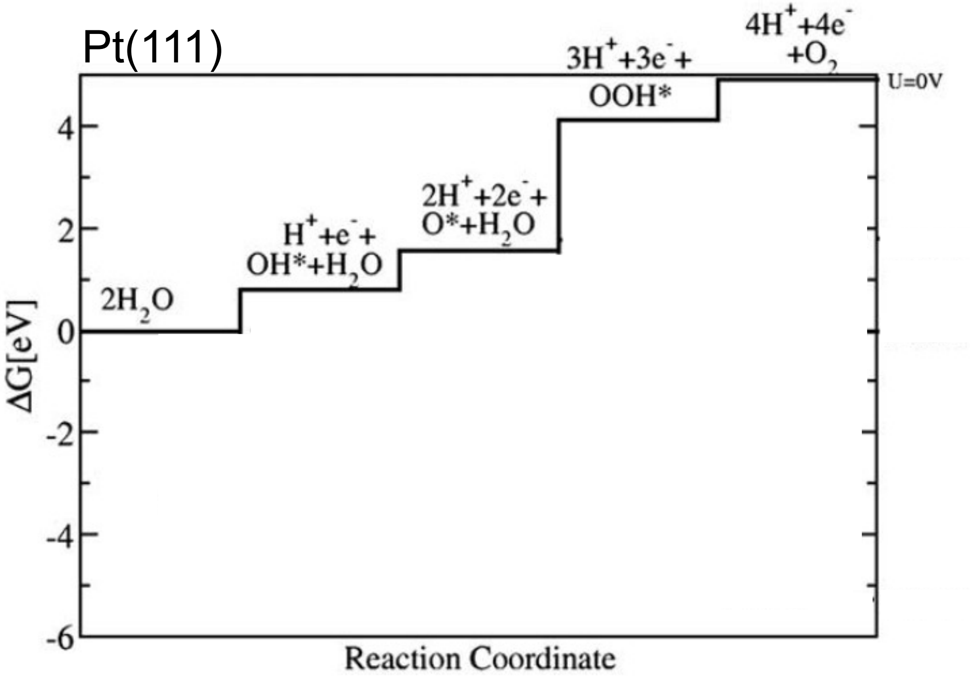
ORR: $O_2 + 4H^+ + 4e^- \rightarrow 2H_2O$

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



Water oxidation on metal surfaces





Investigated mechanism (OER)

$H_2O + * \rightarrow OH^* + (H^+ + e^-)$

$OH^* \rightarrow O^* + (H^+ + e^-)$

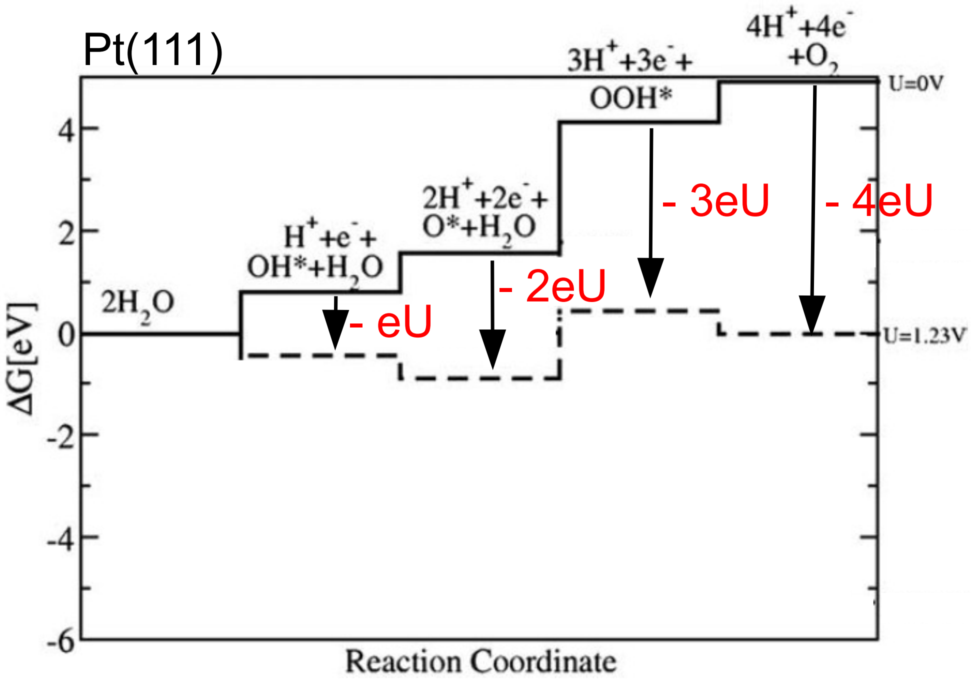
$O^* + H_2O \rightarrow OOH^* + (H^+ + e^-)$

$OOH^* \rightarrow O_2 + (H^+ + e^-)$

Figures from: Rossmeisl *et al.* Phys. Chem **319**, 178-184 (2005)

Water oxidation on metal surfaces

$$2H_2O \rightarrow O_2 + 4H^+ + 4e^- \qquad \Delta G^0 = 4.92\ \text{V}$$

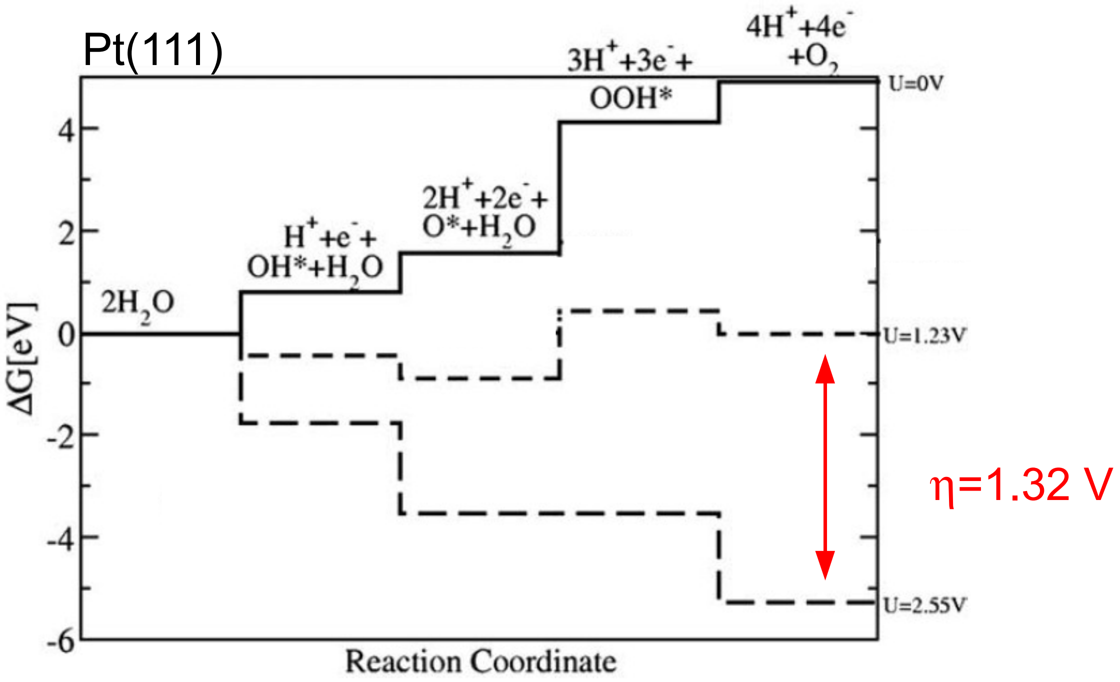


- U = 1.23 V is not sufficient to oxidize water on Pt(111): OOH* is too weakly bound compared to O*

Figures from: Rossmeisl *et al.* Phys. Chem **319**, 178-184 (2005)

Water oxidation on metal surfaces

$$\boxed{2H_2O \rightarrow O_2 + 4H^+ + 4e^- \qquad \Delta G^0 = 4.92\ \mathrm{V}}$$



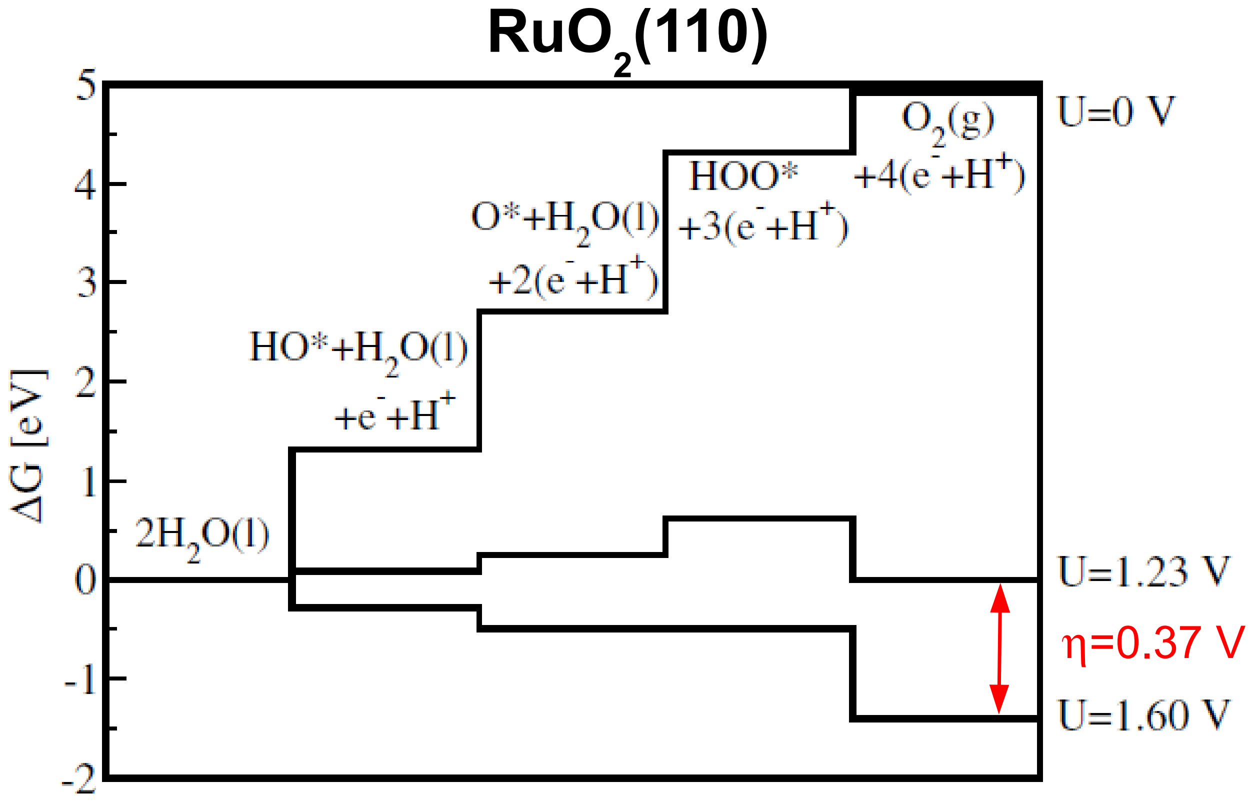
- U = 1.23 V is not sufficient to oxidize water on Pt(111): OOH* is too weakly bound compared to O*

- At U =2.55 V all steps are downhill in energy

- The overpotential of Pt(111) is 2.55-1.23 = 1.32 V

- The **ideal catalyst has 4 identical steps**, each with ΔG=1.23 eV (1.23×4=4.92 eV)

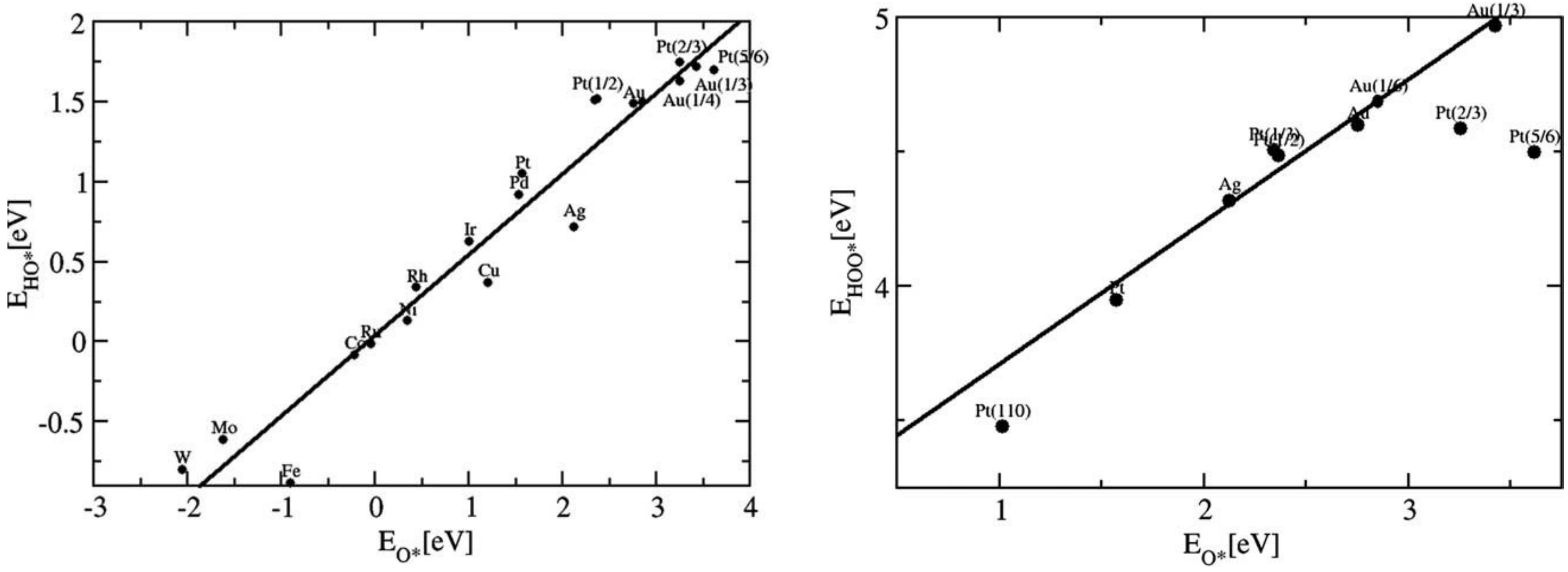
Water oxidation on oxide surfaces



- Also in this case the overpotential-determining step is $O^* + H_2O \rightarrow OOH^* + (H^+ + e^-)$
- The overpotential, however, is considerably lower than Pt(111)

Figures from: Rossmeisl *et al.* J. Electr. Chem **607**, 83-89 (2007)

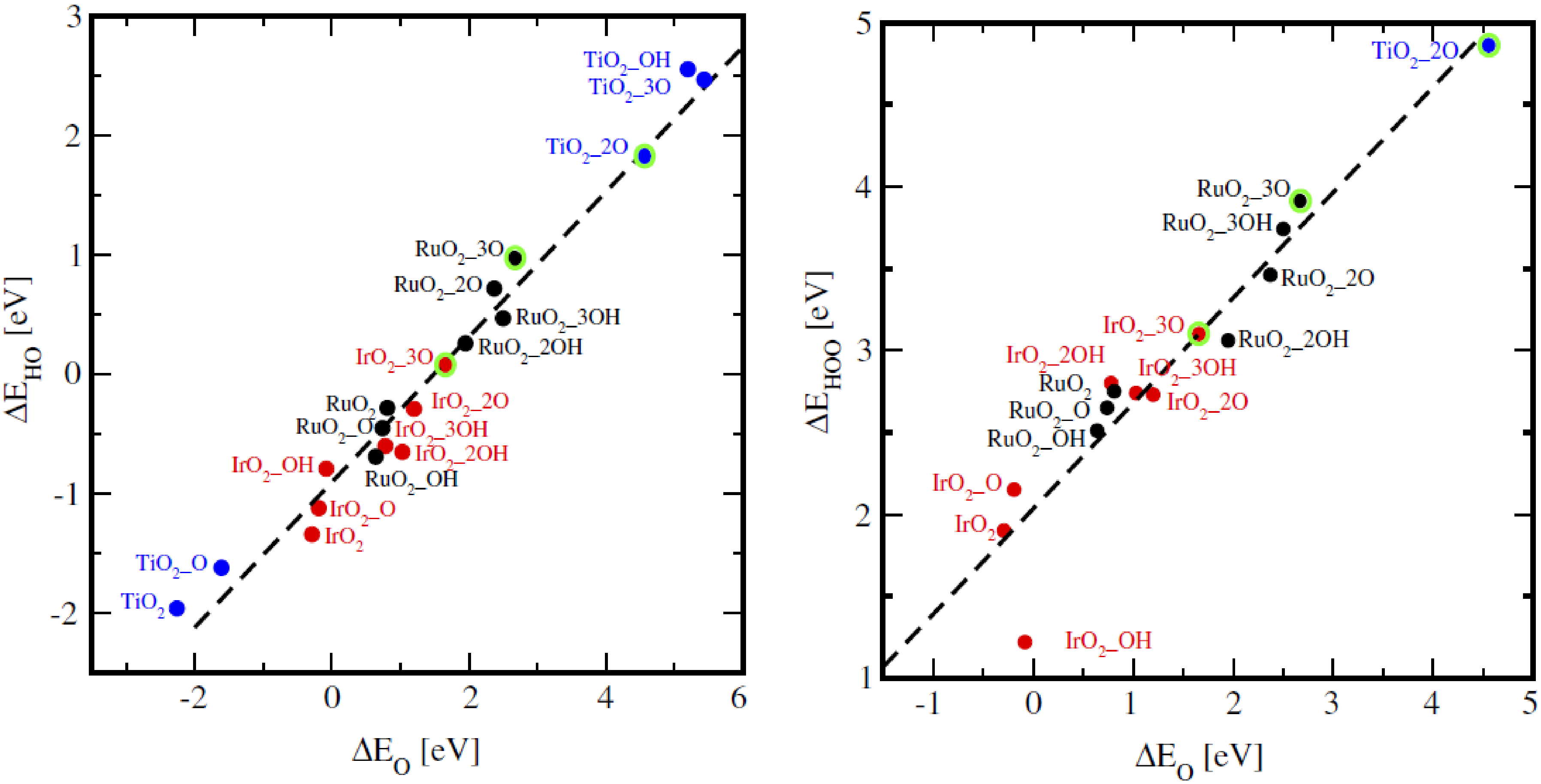
Water oxidation on metal surfaces



E_{O*}, E_{OH*} and E_{OOH*} are approximately linearly related

Figures from: Rossmeisl *et al.* Phys. Chem **319**, 178-184 (2005)

Water oxidation on oxide surfaces

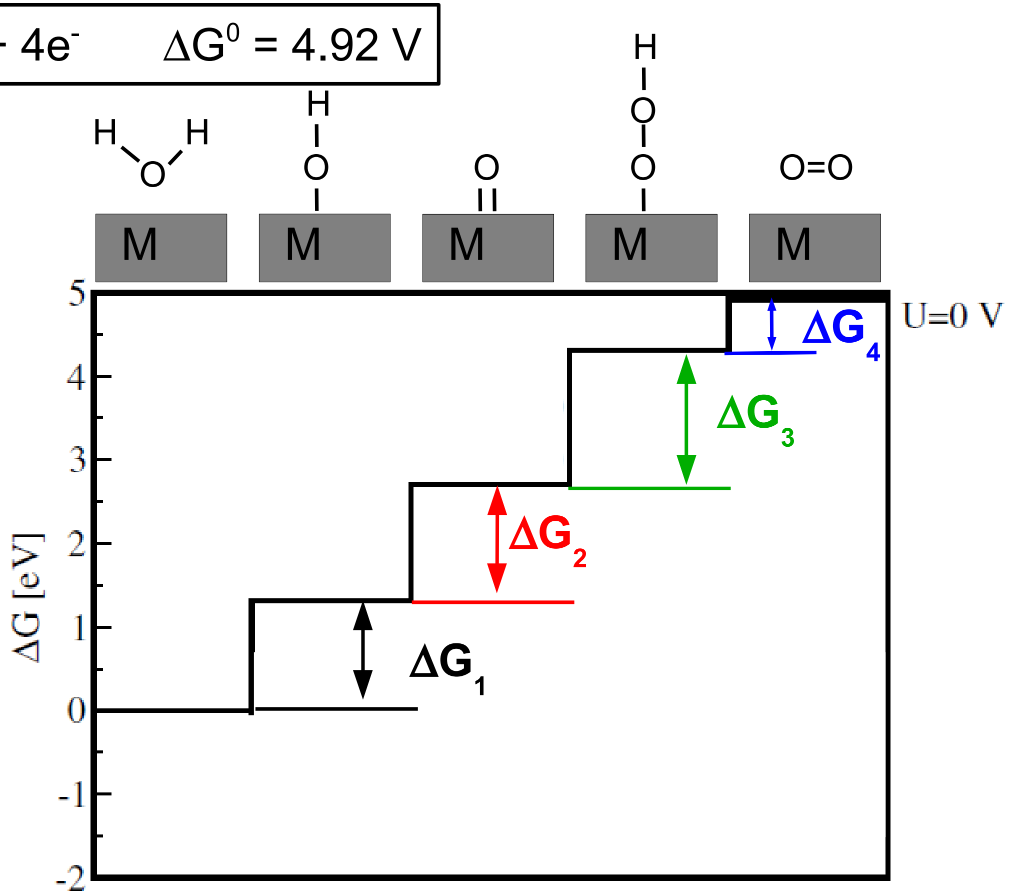


- Also in this case E_{O^*}, E_{OH^*} and E_{OOH^*} are approximately linearly related
- $\Delta E_O = 0$ eV is defined by the equilibrium: $H_2O \leftrightarrow O^* + H_2$

Figures from: Rossmeisl *et al.* J. Electr. Chem **607**, 83-89 (2007)

Water oxidation on oxide surfaces

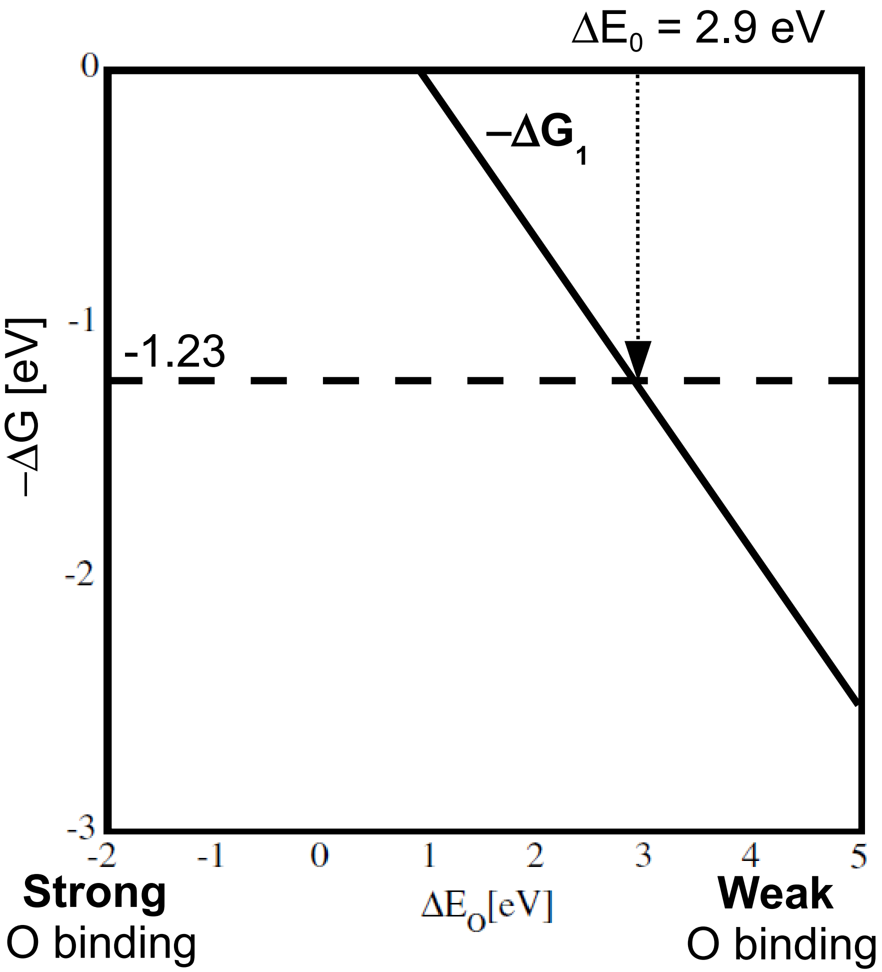
$2H_2O \rightarrow O_2 + 4H^+ + 4e^-$ $\Delta G^0 = 4.92$ V

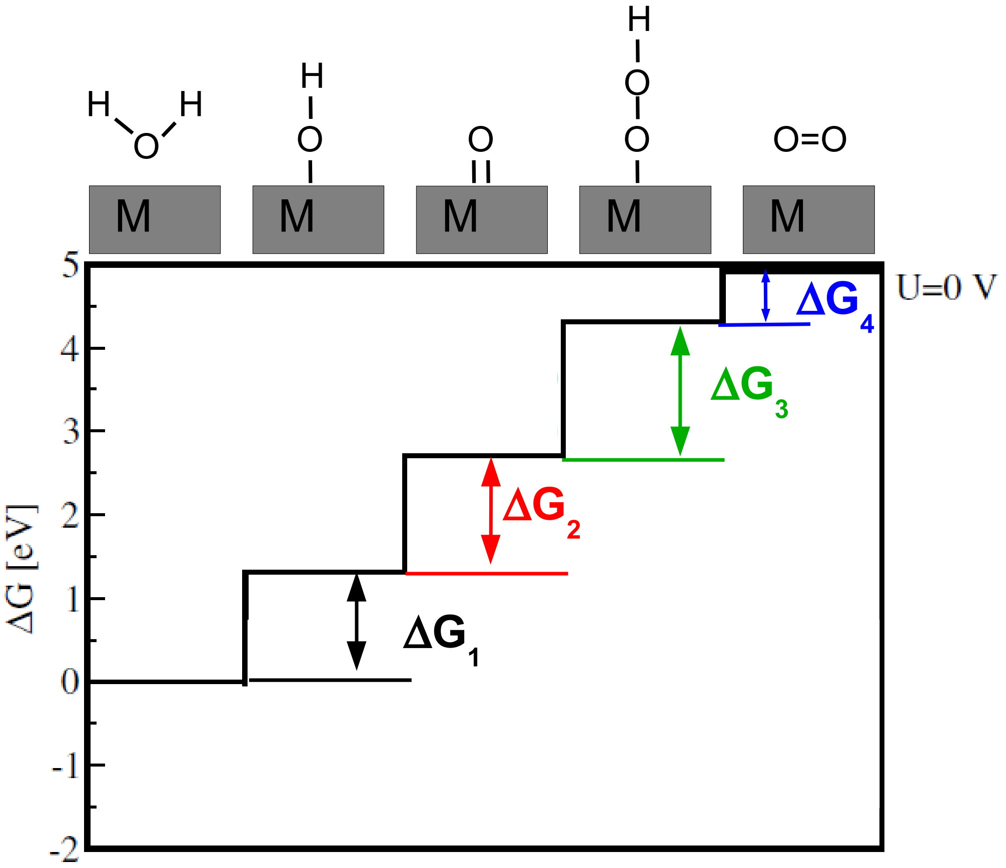


The height of each step $\Delta G_{1\text{-}4}$ is (approximately) a linear function of ΔE_0 (which is a material-dependent property)

Figures from: Rossmeisl *et al.* Phys. Chem **319**, 178-184 (2005)

Water oxidation on oxide surfaces

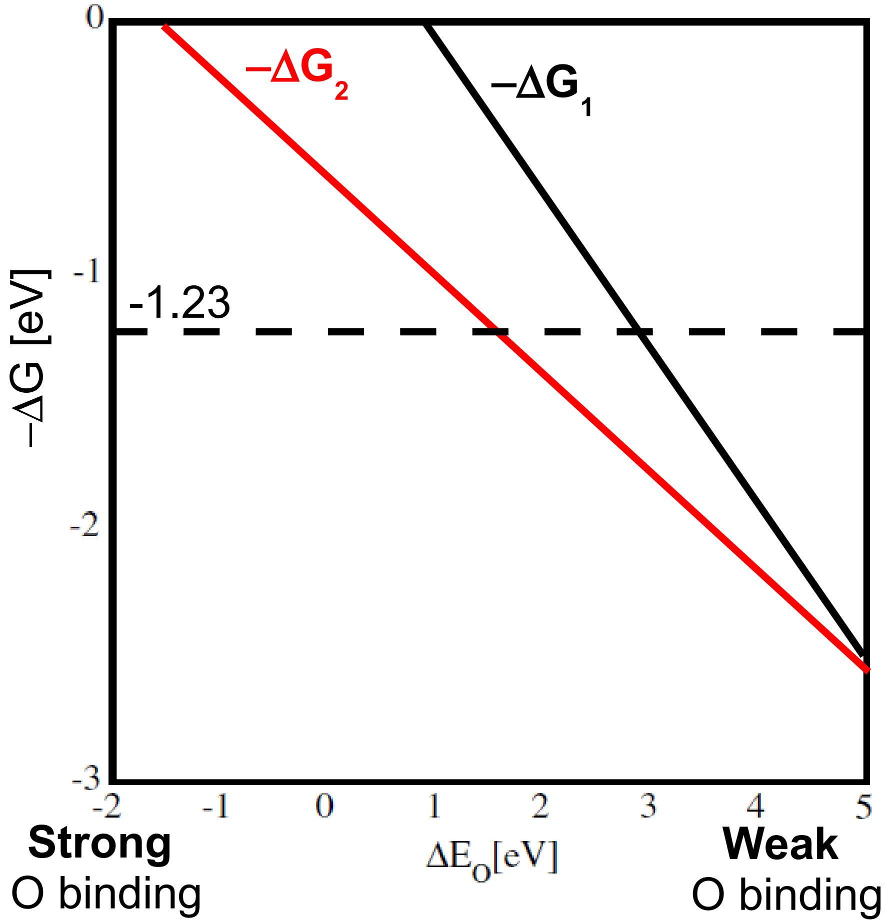


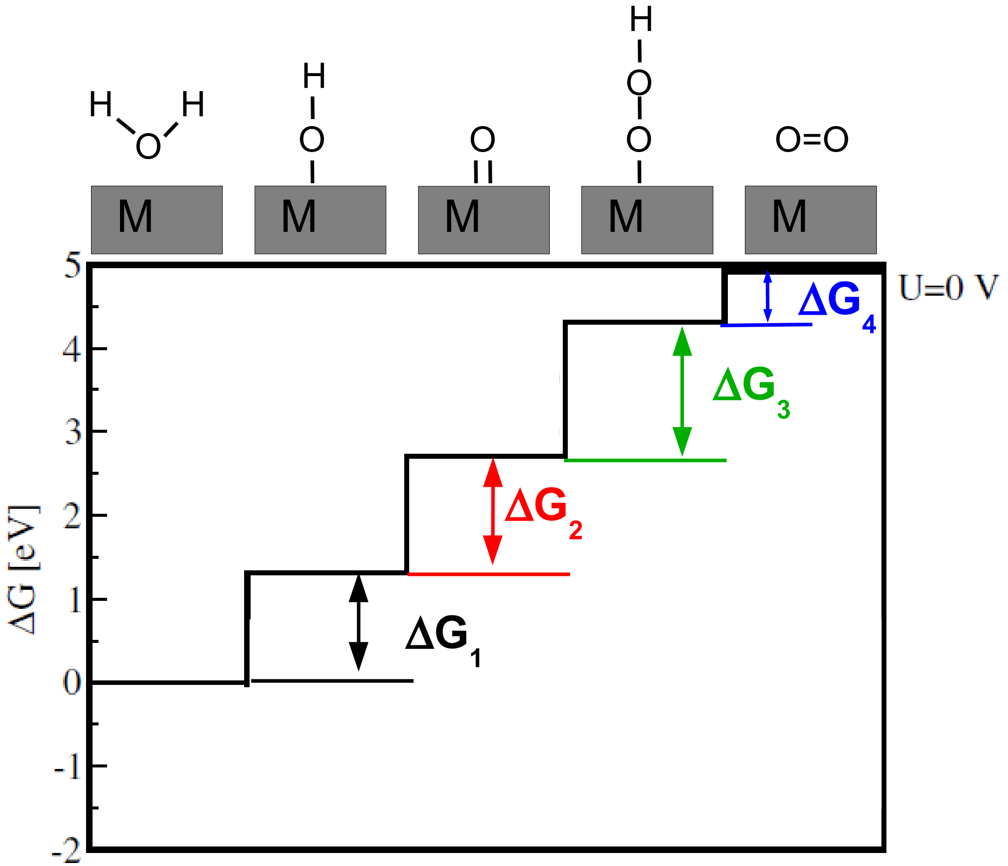


ΔG_1: The “ideal” catalyst should have $\Delta E_0 = 2.9$ eV

Figures from: Rossmeisl *et al.* J. Electr. Chem **607**, 83-89 (2007)

Water oxidation on oxide surfaces

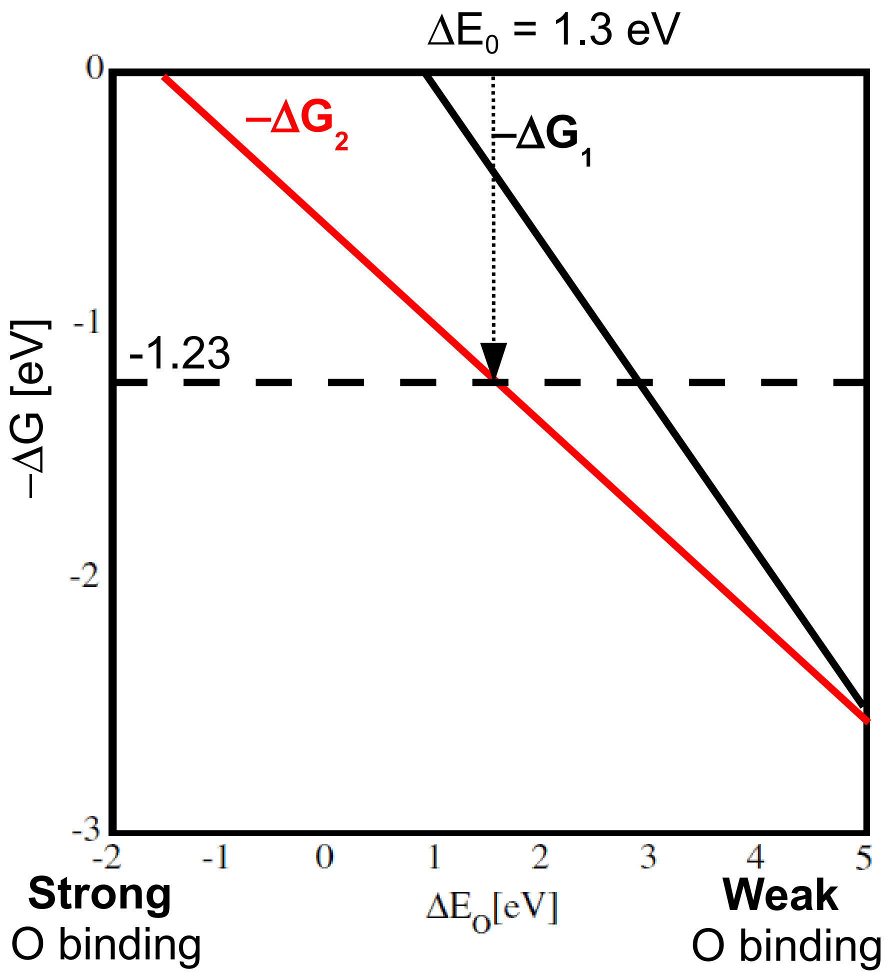


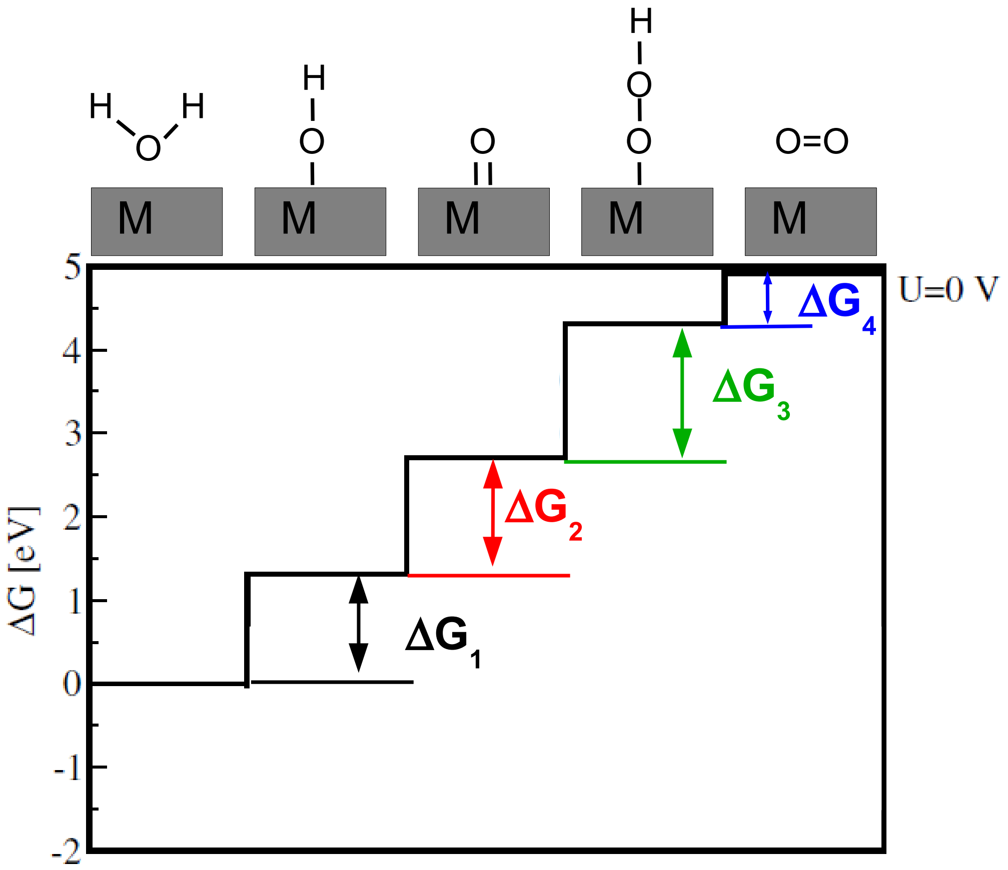


ΔG_1: The “ideal” catalyst should have ΔE_0 = 2.9 eV

Figures from: Rossmeisl *et al.* J. Electr. Chem **607**, 83-89 (2007)

Water oxidation on oxide surfaces



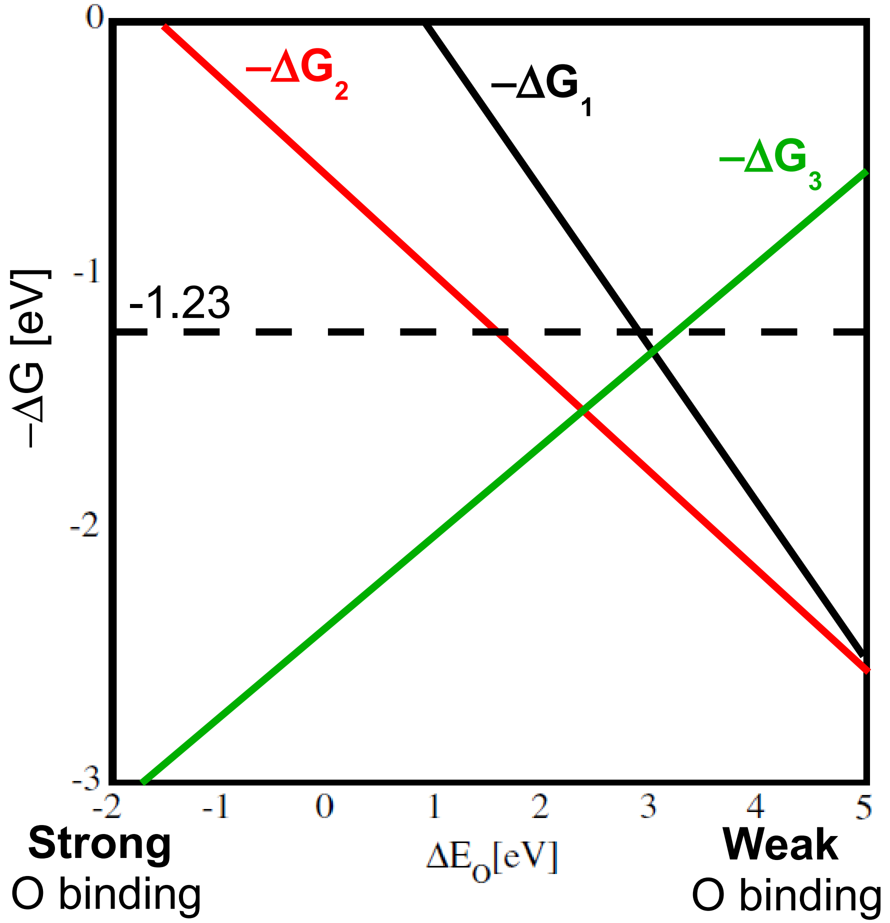


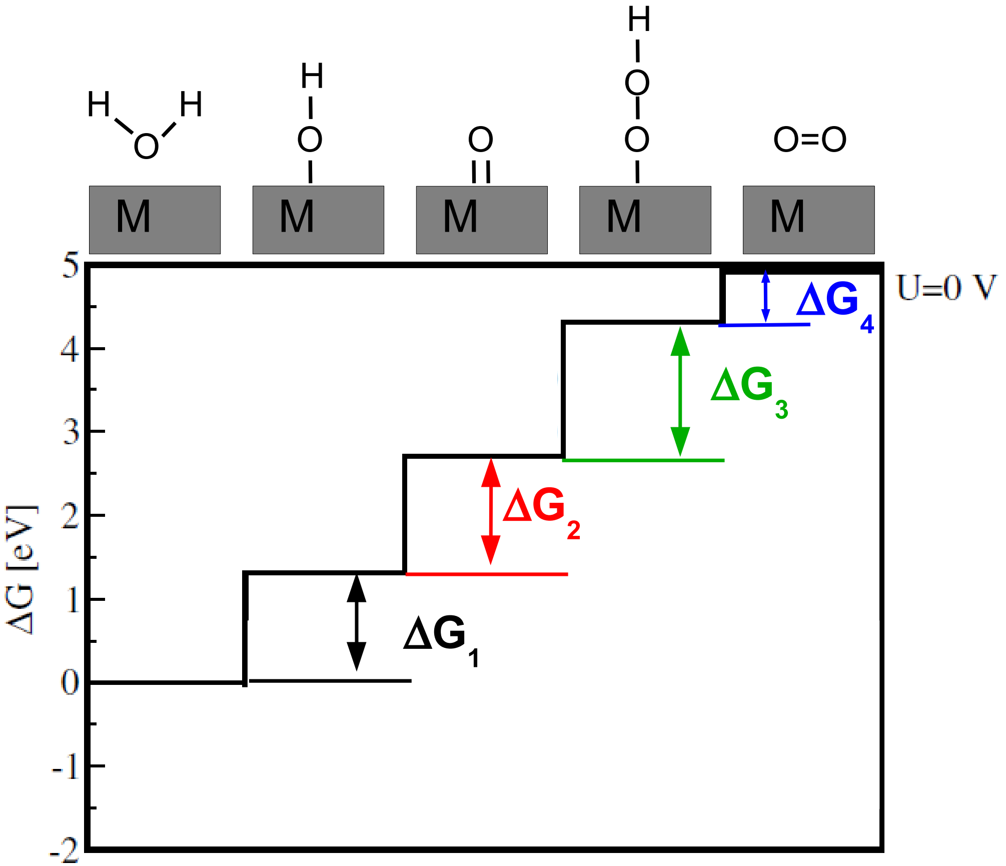
ΔG_1: The “ideal” catalyst should have ΔE_0 = 2.9 eV

ΔG_2: The “ideal” catalyst should have ΔE_0 = 1.3 eV

Figures from: Rossmeisl *et al.* J. Electr. Chem **607**, 83-89 (2007)

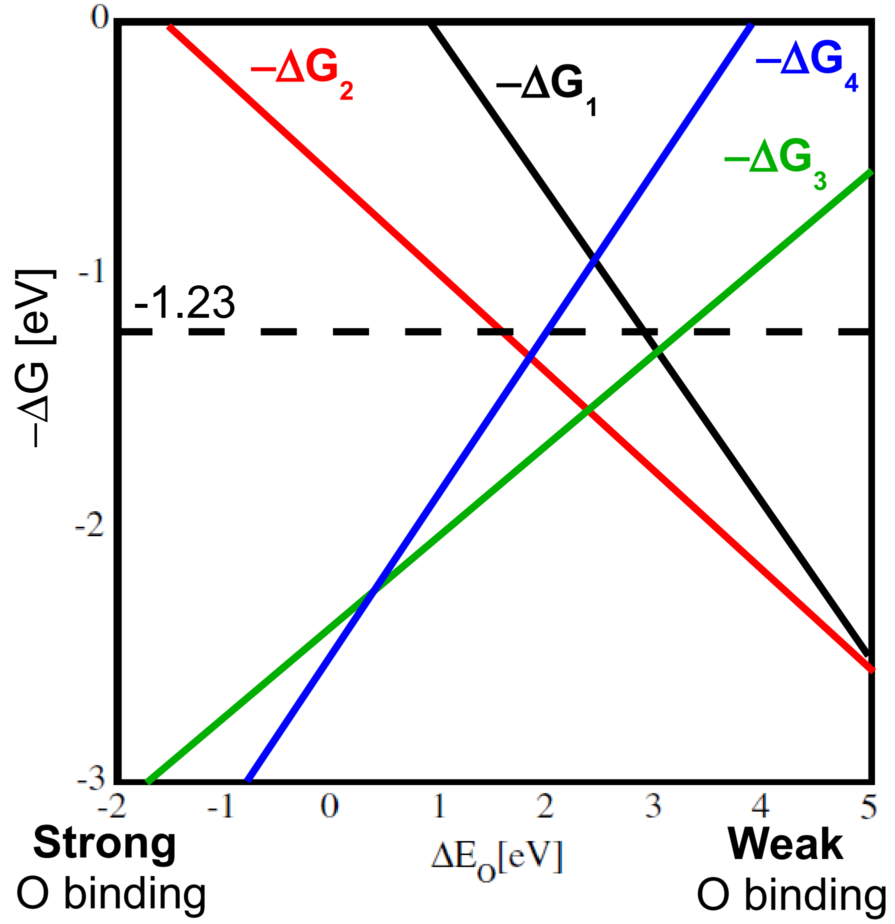
Water oxidation on oxide surfaces

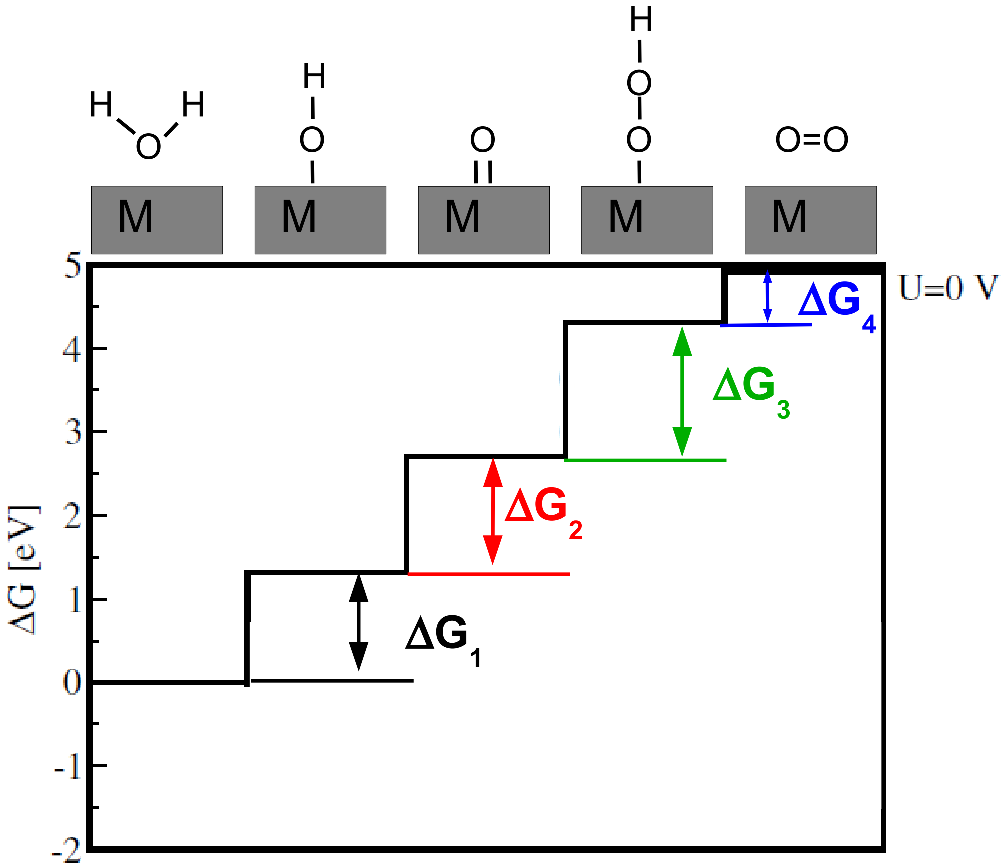




Figures from: Rossmeisl *et al.* J. Electr. Chem **607**, 83-89 (2007)

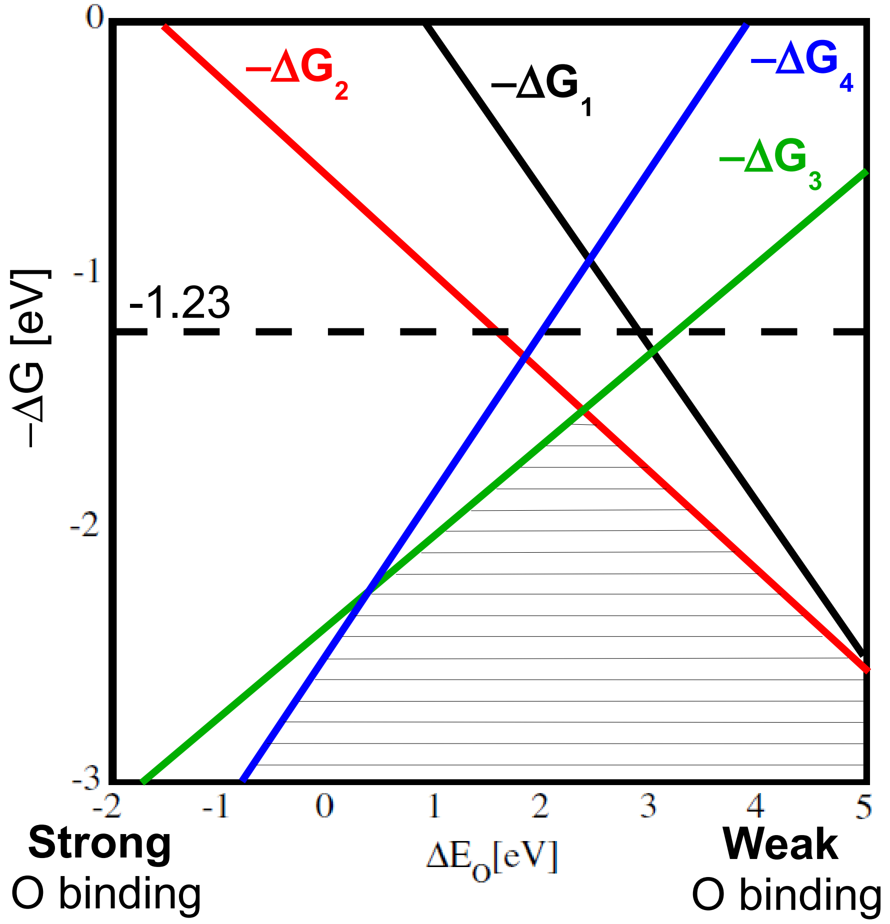
Water oxidation on oxide surfaces

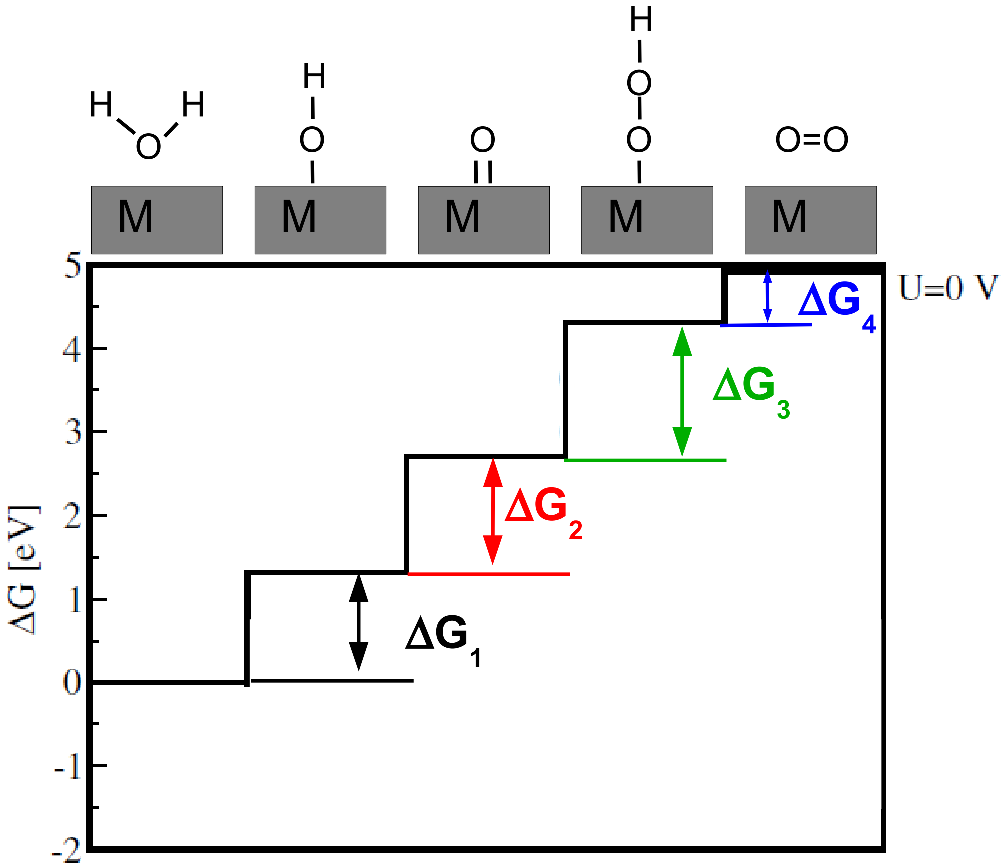




Figures from: Rossmeisl *et al.* J. Electr. Chem **607**, 83-89 (2007)

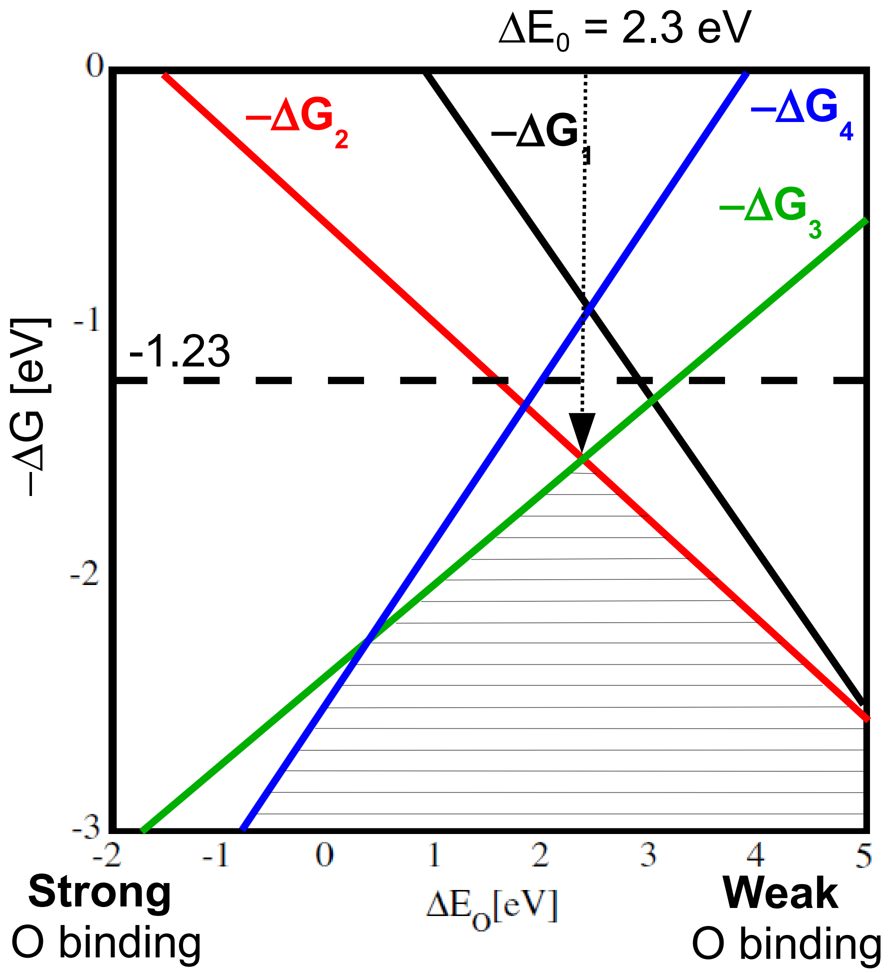
Water oxidation on oxide surfaces

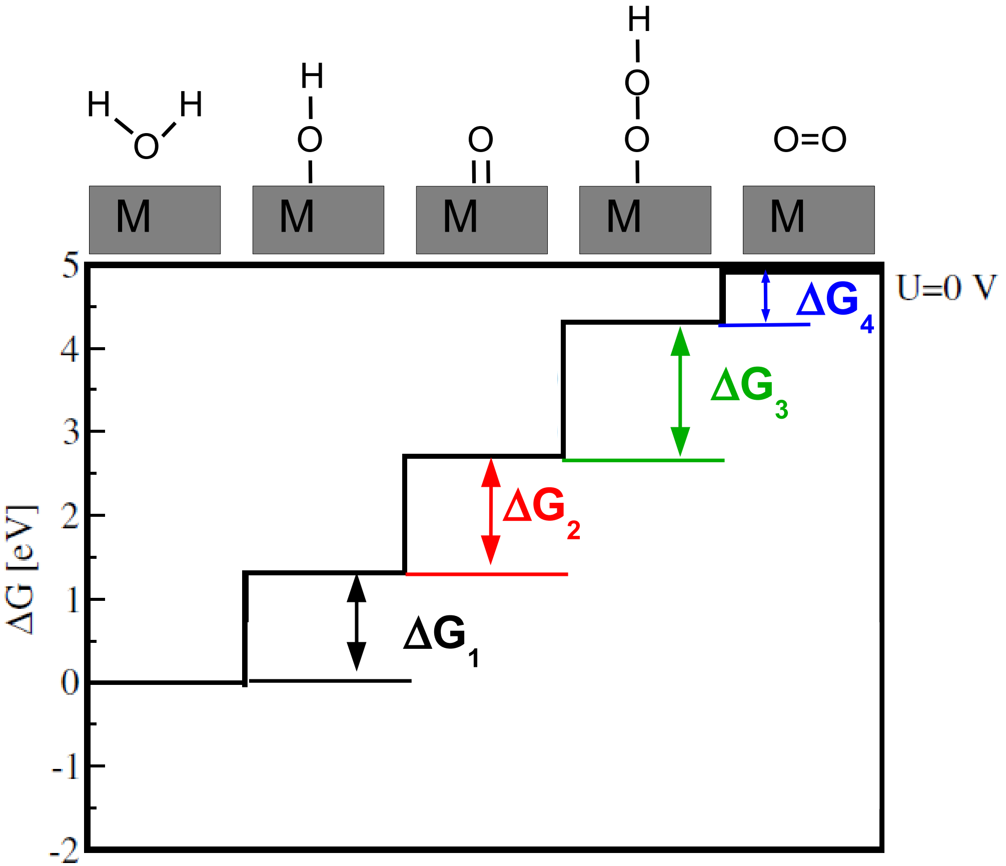




Figures from: Rossmeisl *et al.* J. Electr. Chem **607**, 83-89 (2007)

Water oxidation on oxide surfaces

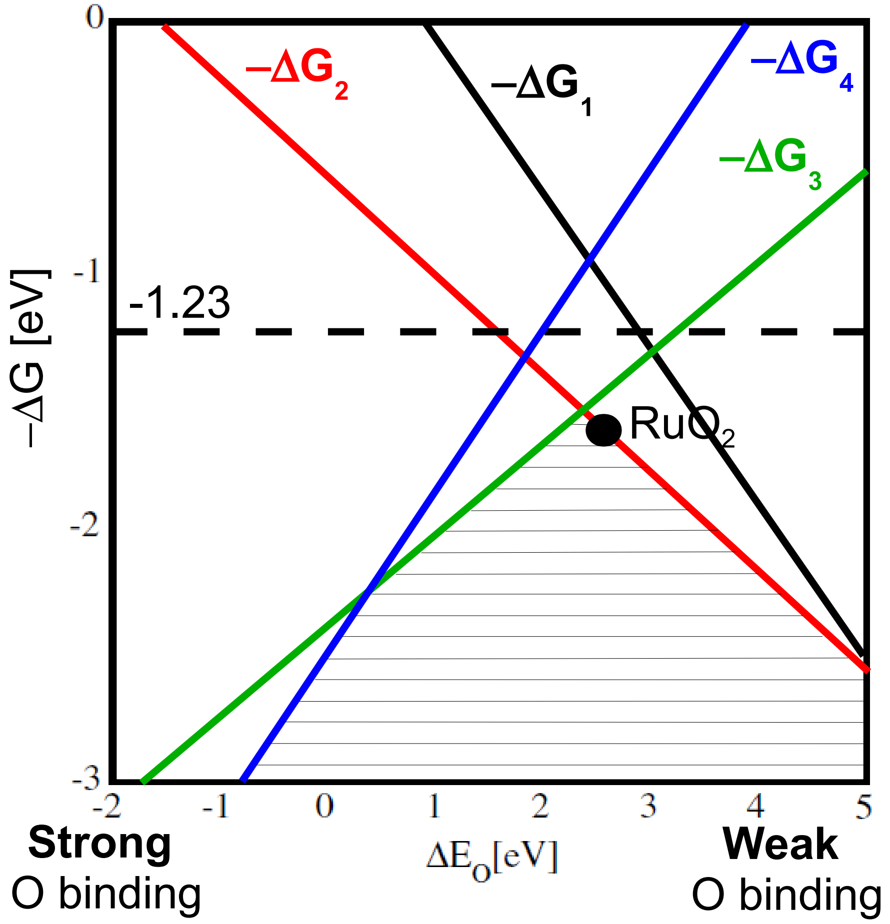


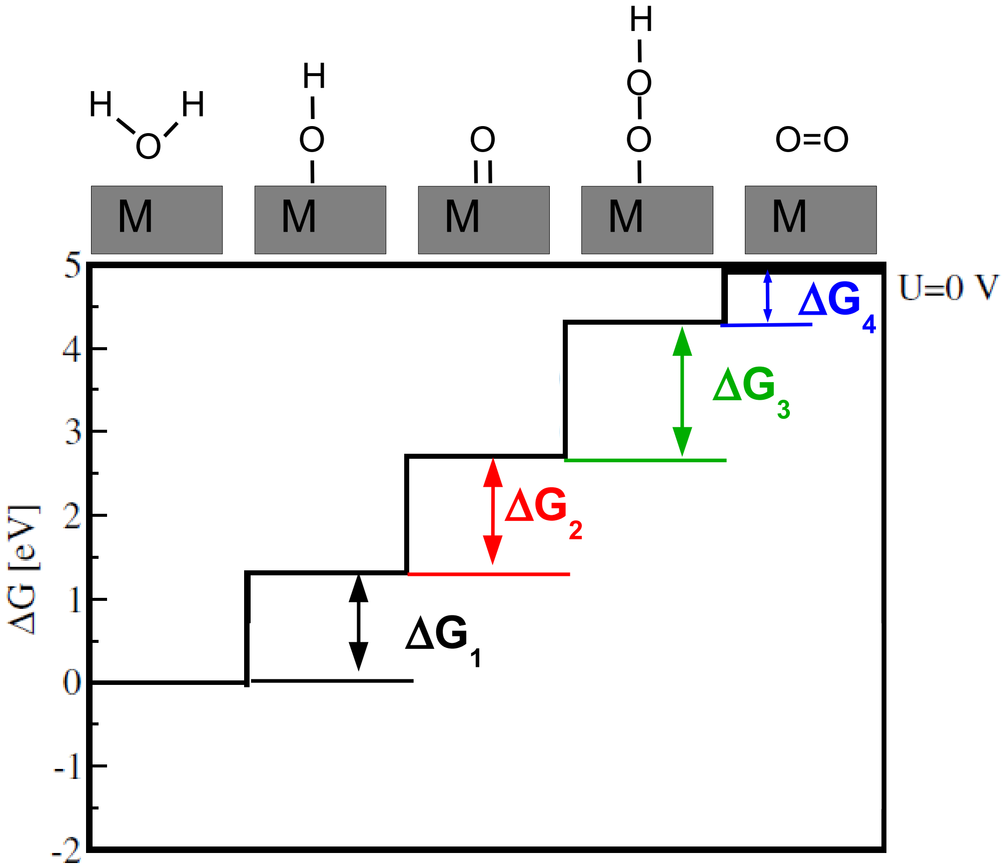


The “best” catalyst should have ΔE_0 = 2.3 eV

Figures from: Rossmeisl *et al.* J. Electr. Chem **607**, 83-89 (2007)

Water oxidation on oxide surfaces

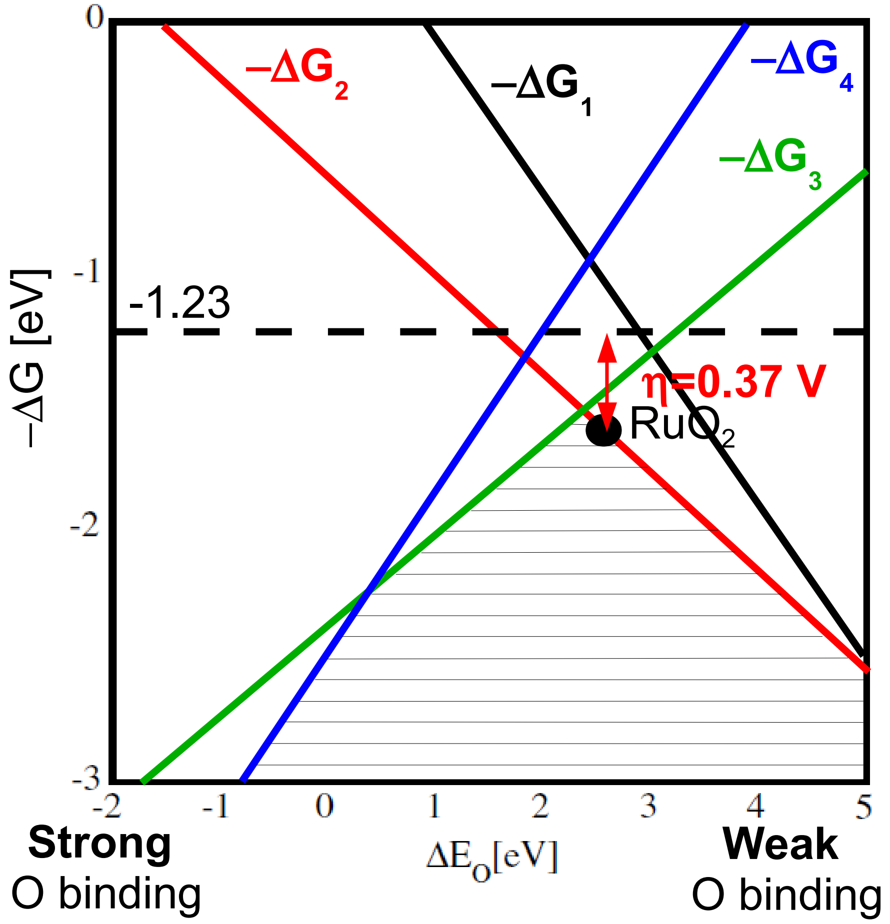


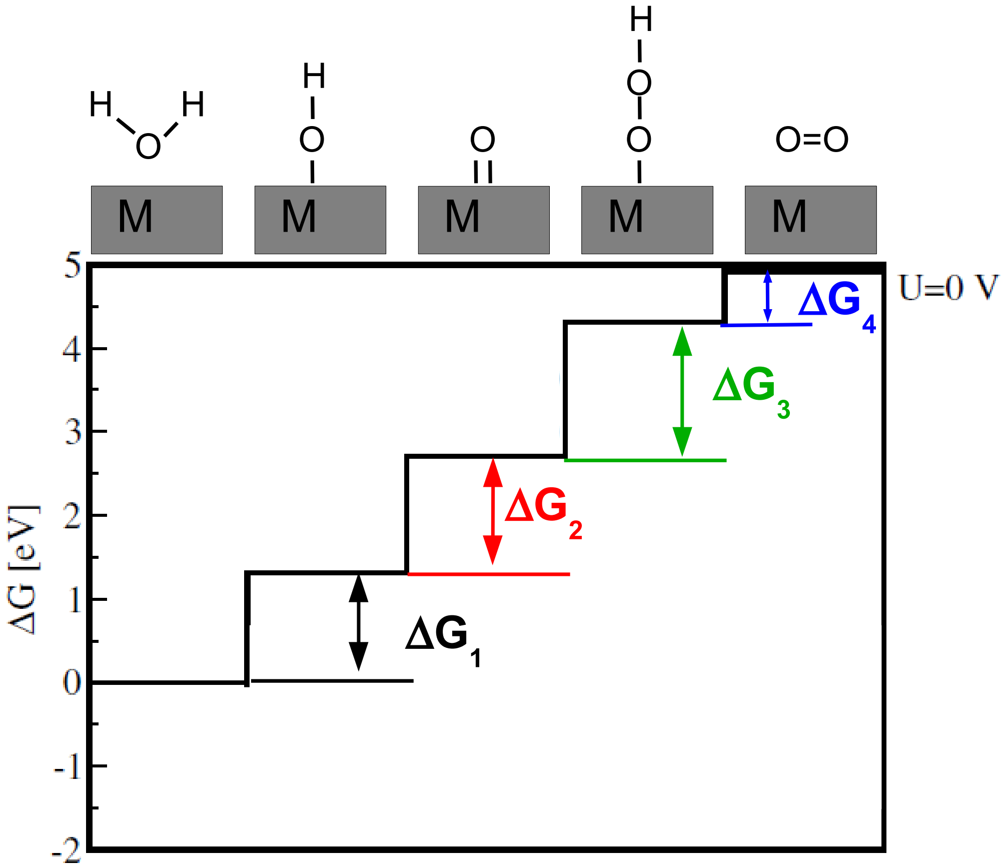


RuO_2 sits very near the top of the volcano
There's not much room for improvement.

Figures from: Rossmeisl *et al.* J. Electr. Chem **607**, 83-89 (2007)

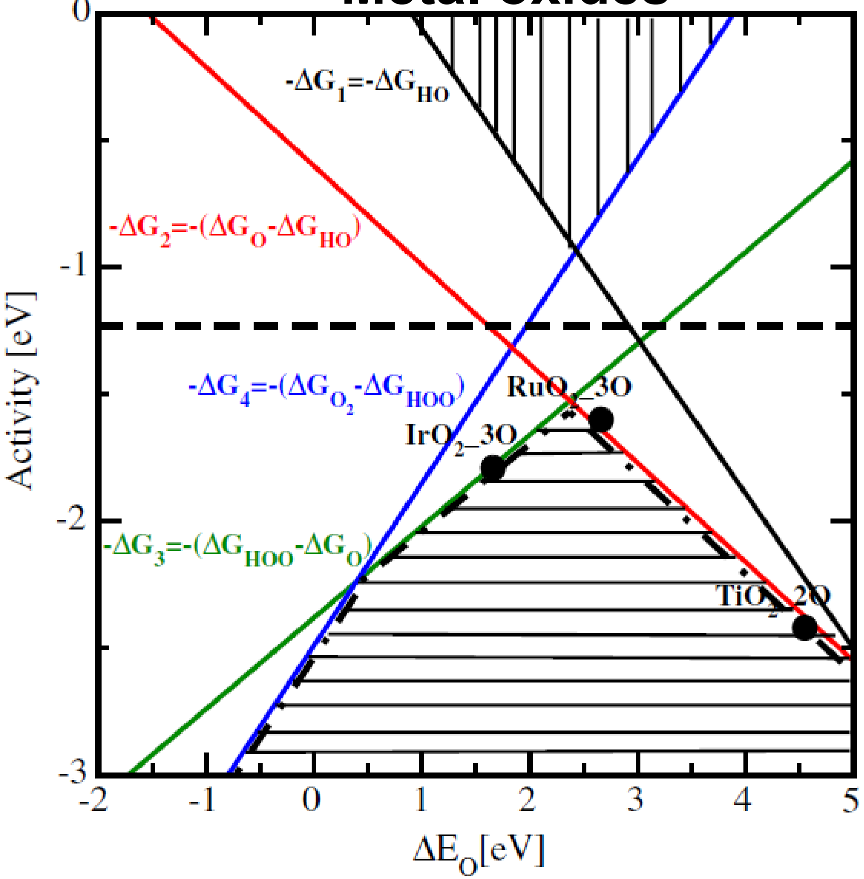
Water oxidation on oxide surfaces

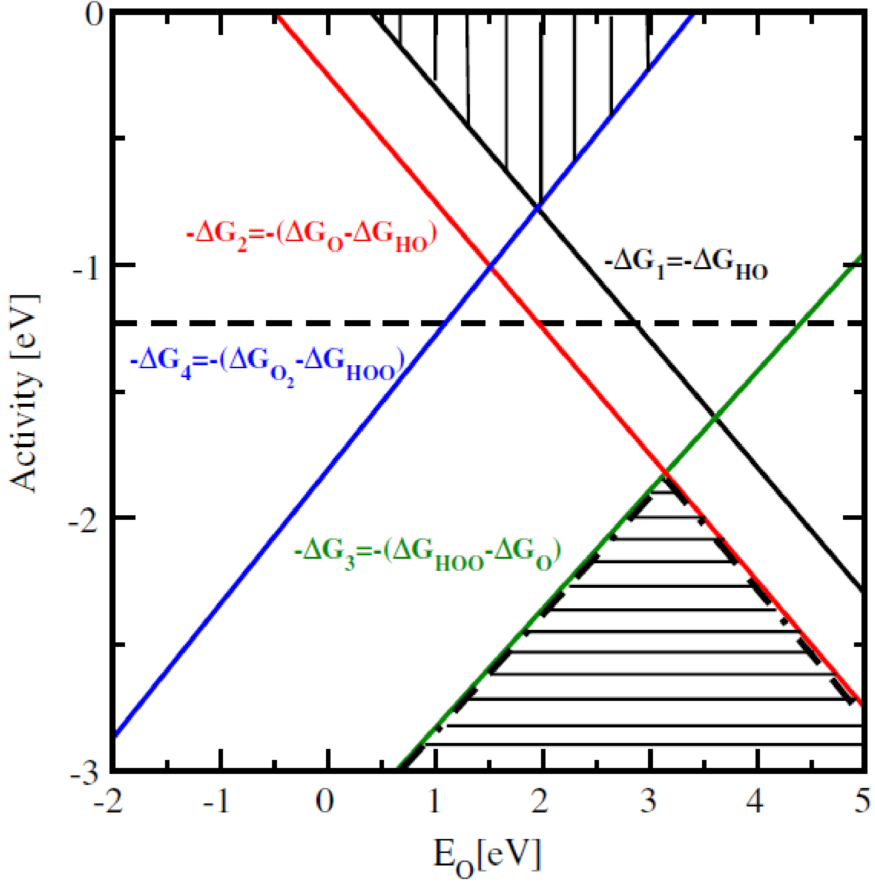




Figures from: Rossmeisl *et al.* J. Electr. Chem **607**, 83-89 (2007)

Water oxidation on oxide surfaces

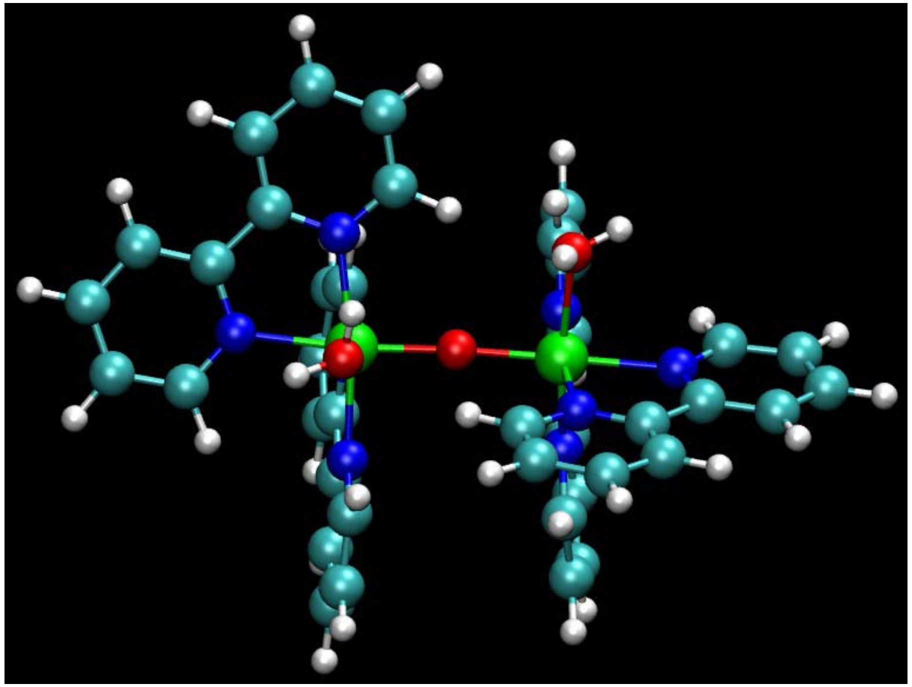

Metal oxides


Metals

- Using the linear relationships of the the binding energies of the intermediates vs. O*, the activity of different catalysts for OER and ORR can be established
- The “activity” is defined as the overpotential.
- RuO_2 and Pt sit very near the top of the volcanoes. There's not much room for improvement.

Figures from: Rossmeisl *et al.* J. Electr. Chem **607**, 83-89 (2007)

Molecular catalysts for OER: “blue dimer”



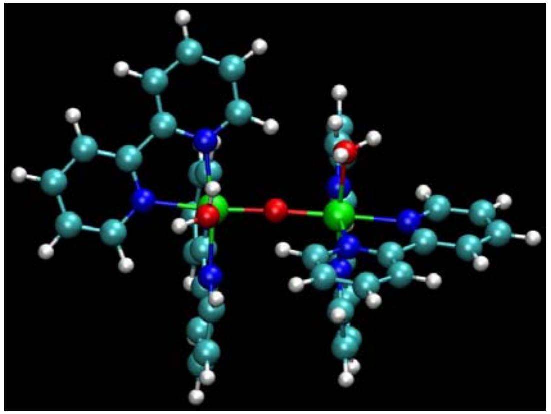
“**Blue dimer**”
Gersten *et al.* JACS **104**, 4029-4030 (1982)

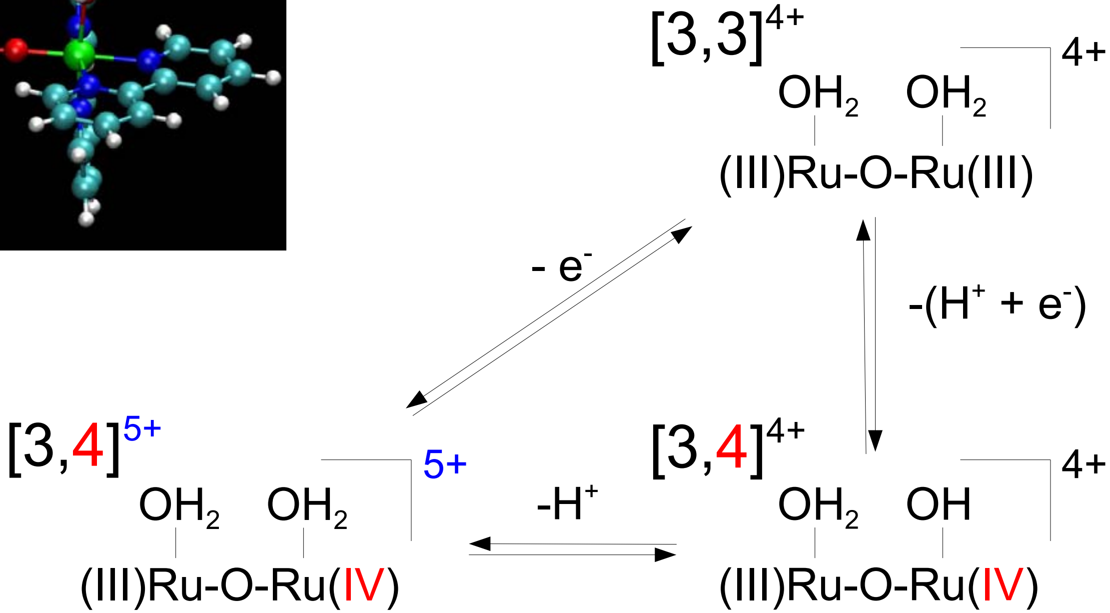
- Well characterized molecular catalyst

- Ru(III)-H_2O / Ru(V)=O cycle, followed by nucleophilic attack

- Small TN (13) due to deactivation of organic ligands

Molecular catalysts for OER: “blue dimer”





$[3,3]^{4+}$

$$\left[\begin{array}{c} \mathrm{OH_2}\quad\mathrm{OH_2} \\ |\qquad\quad | \\ \mathrm{(III)Ru\text{-}O\text{-}Ru(III)} \end{array}\right]^{4+}$$

- e^-

$-(H^+ + e^-)$

$[3,4]^{5+}$

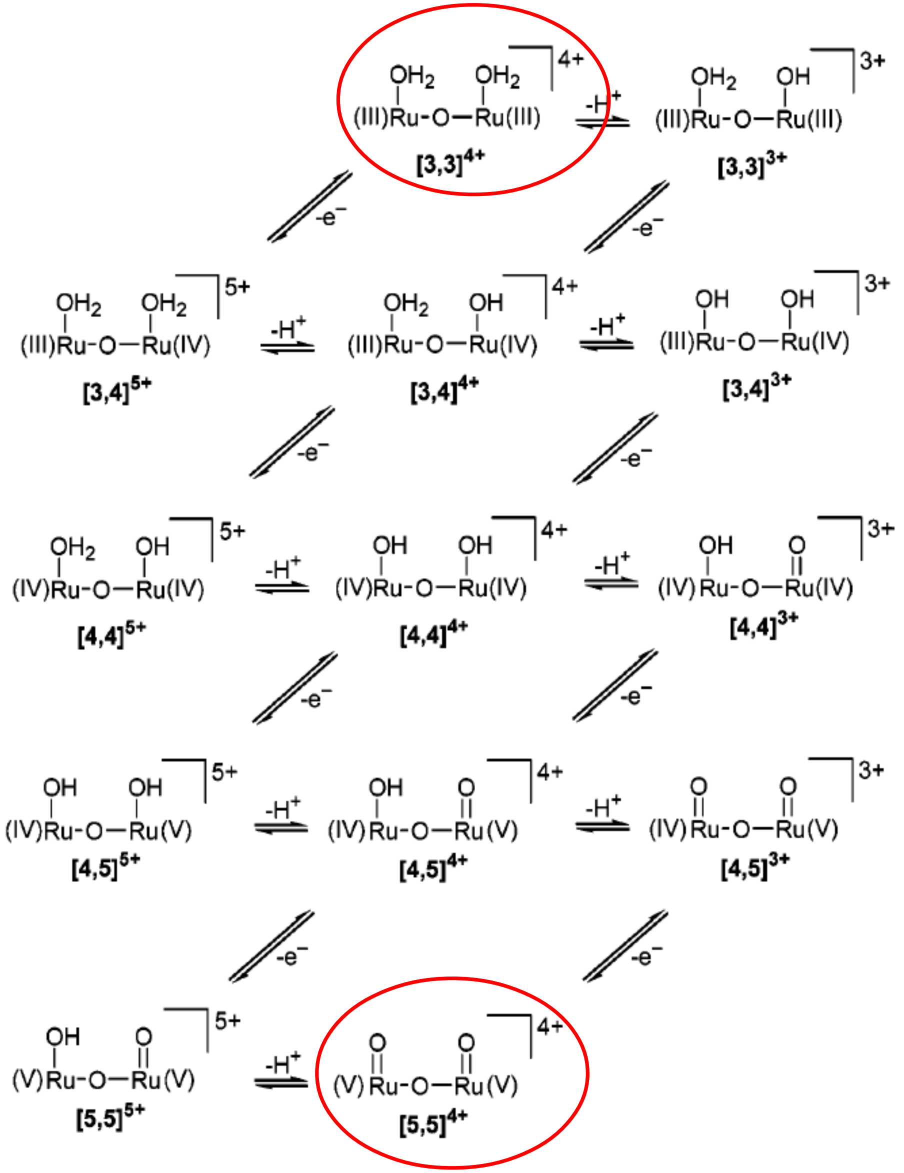
$$\left[\begin{array}{c} \mathrm{OH_2}\quad\mathrm{OH_2} \\ |\qquad\quad | \\ \mathrm{(III)Ru\text{-}O\text{-}Ru(IV)} \end{array}\right]^{5+}$$

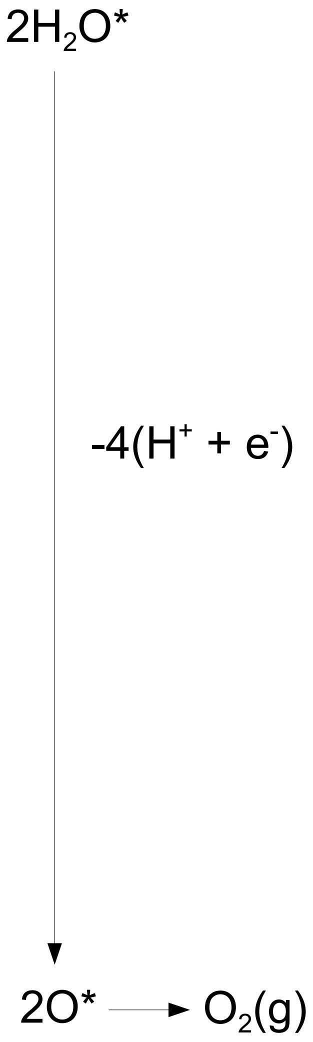
$-H^+$

$[3,4]^{4+}$

$$\left[\begin{array}{c} \mathrm{OH_2}\quad\mathrm{OH} \\ |\qquad\quad | \\ \mathrm{(III)Ru\text{-}O\text{-}Ru(IV)} \end{array}\right]^{4+}$$

Molecular catalysts for OER: “blue dimer”





$2H_2O^*$

$-4(H^+ + e^-)$

$2O^* \rightarrow O_2(g)$

OER: $2H_2O \rightarrow O_2(g) + 4(H^+ + e^-)$

Figures from: Yang and Baik, JACS **106**, 13222 (2004)

"Quantum chemistry" approach for OER

ET reactions: $[A]^n + e^- \rightarrow [A]^{n-1}$

$\Delta G(sol) = \Delta G(g) + \Delta G^{solv}$ *using a continuum solvation model (SCRF, PCM, ...)*
$\Delta G(g) = \Delta H(g) - T\Delta S(g)$ *from normal mode analysis*
$\Delta H(g) = \Delta H^{SCF} + \Delta ZPE(g) + \Delta H^T$ *from normal mode analysis*

$\Delta G(sol) = -FE^0$

- E^0 needs to be referenced to some standard electrode (NHE)
- The absolute potential of the standard hydrogen electrode is difficult to determine precisely: $\phi = 4.43\ V - 4.85\ V$

PT reactions: $[AH]^n \rightarrow [A]^{n-1} + H^+(sol)$

In this case we need the free energy of a proton in solution:

$G(H^+) = H^g(H^+) - TS + 3/2RT + G^{solv}(H^+)$

In this approach the chemical potentials $\mu(H^+) + \mu(e^-)$ need to be estimated separately, and each of them is determined only approximately.

from: Baik *et al.* J. Phys. Chem A **106**, 7407-7412 (2002)

Tuesday, 18 October 2011 (Room:Leonardo da Vinci Building Main Lecture Hall)

18 October 2011

08:30 - 09:30	**Christopher CRAMER** / *Dept. of Chemistry & Supercomputer Inst., Univ. Minnesota, Minneapolis, U.S.A.* **Practicalities of molecular computational modeling relevant to renewable energy technologies**
09:30 - 10:30	**Robert SCHLOGL** / *Dept. of Inorganic Chemistry, FHI der MPG, Berlin, Germany* **Material challenges in electro catalysis**
10:30 - 11:00	--- Coffee break ---
11:00 - 12:00	**Sossina M. HAILE** / *Steele Laboratories, Materials Science, Pasadena, CA, U.S.A.* **Advancing electrocatalysis in intermediate temperature fuel cells**
12:00 - 14:00	--- Lunch break ---
14:00 - 15:00	**Michiel SPRIK** / *Dept. of Chemistry, Univ. Cambridge, U.K.* **The thermochemistry of oxidative dehydrogenation of a water molecule at a TiO2/water interface**
15:00 - 16:00	**Nicola MARZARI** / *Dept. of Materials, University of Oxford, U.K.* **What can I do for first-principles simulations?**
16:00 - 16:30	--- Coffee break ---
16:30 - 17:30	**Alexander SOUDACKOV** / *Dept. of Chemistry, The Pennsylvania State Univ., University Park, PA, U.S.A.* **Theoretical modeling of proton-coupled electron transfer reactions in energy related materials**
17:30 - 18:30	**CONTRIBUTED TALKS**

Summary

- Splitting water into O_2 and H_2 to store (solar) energy involves electrochemical processes

- The anodic reaction (water oxidation) is a complex 4-electron reaction that require suitable (efficient, stable, cheap) catalysts

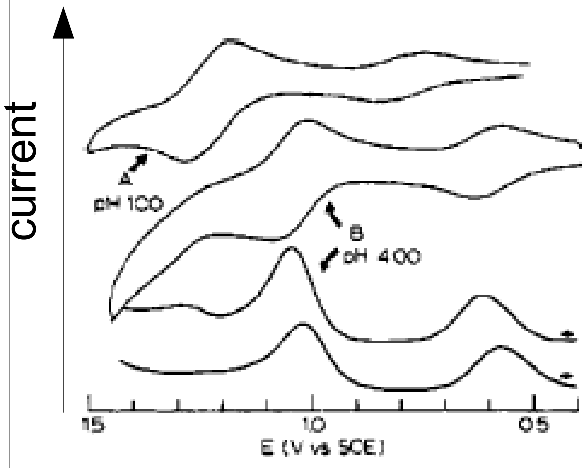
- The overpotential is determined by the most endergonic electrochemical step (highest ΔG)

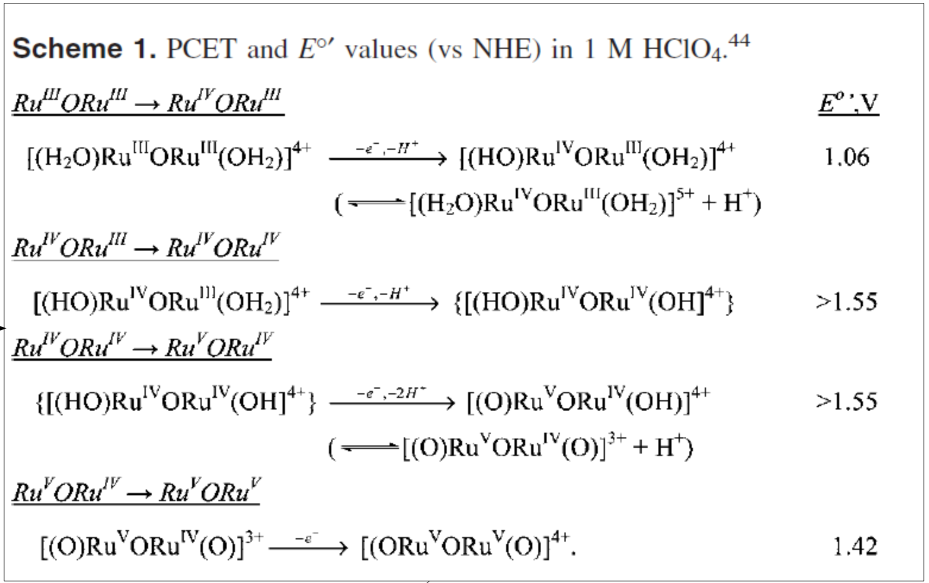
- If electrons and protons are removed at the same time (PCET) the approach proposed by Nørskov *et al.* is particularly convenient

- For a vast class of metals and metal oxides there exist linear relationships between the energies of the intermediates: ΔE_O is a good descriptor, optimal catalysts can be identified

Molecular catalysts for OER: “blue dimer”

Cyclic voltammetry

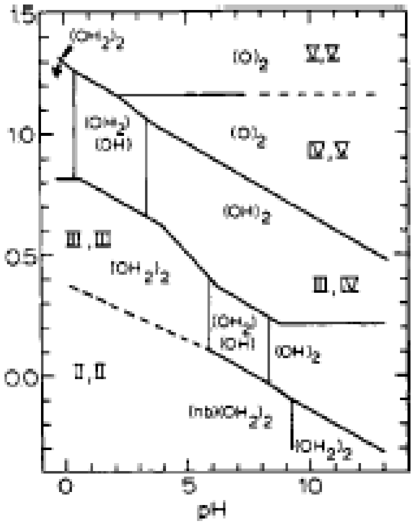




Scheme 1. PCET and $E^{\circ\prime}$ values (vs NHE) in 1 M $HClO_4$.[44]

$\underline{Ru^{III}ORu^{III} \rightarrow Ru^{IV}ORu^{III}}$	$\underline{E^{o}{}^{\prime}, V}$
$[(H_2O)Ru^{III}ORu^{III}(OH_2)]^{4+} \xrightarrow{-e^-, -H^+} [(HO)Ru^{IV}ORu^{III}(OH_2)]^{4+}$ $(\rightleftharpoons [(H_2O)Ru^{IV}ORu^{III}(OH_2)]^{5+} + H^+)$	1.06
$\underline{Ru^{IV}ORu^{III} \rightarrow Ru^{IV}ORu^{IV}}$	
$[(HO)Ru^{IV}ORu^{III}(OH_2)]^{4+} \xrightarrow{-e^-, -H^+} \{[(HO)Ru^{IV}ORu^{IV}(OH]^{4+}\}$	>1.55
$\underline{Ru^{IV}ORu^{IV} \rightarrow Ru^{V}ORu^{IV}}$	
$\{[(HO)Ru^{IV}ORu^{IV}(OH]^{4+}\} \xrightarrow{-e^-, -2H^+} [(O)Ru^{V}ORu^{IV}(OH)]^{4+}$ $(\rightleftharpoons [(O)Ru^{V}ORu^{IV}(O)]^{3+} + H^+)$	>1.55
$\underline{Ru^{V}ORu^{IV} \rightarrow Ru^{V}ORu^{V}}$	
$[(O)Ru^{V}ORu^{IV}(O)]^{3+} \xrightarrow{-e^-} [(ORu^{V}ORu^{V}(O)]^{4+}.$	1.42

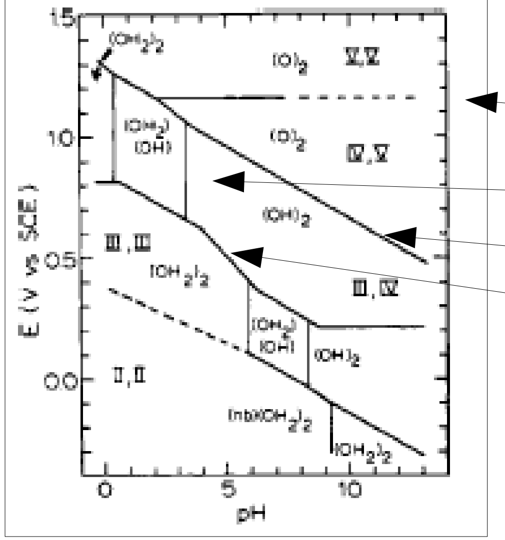
Pourbaix diagram



Figures from: Liu *et al.* Inorg. Chem. **47**, 1727 (2008)

Molecular catalysts for OER: “blue dimer”

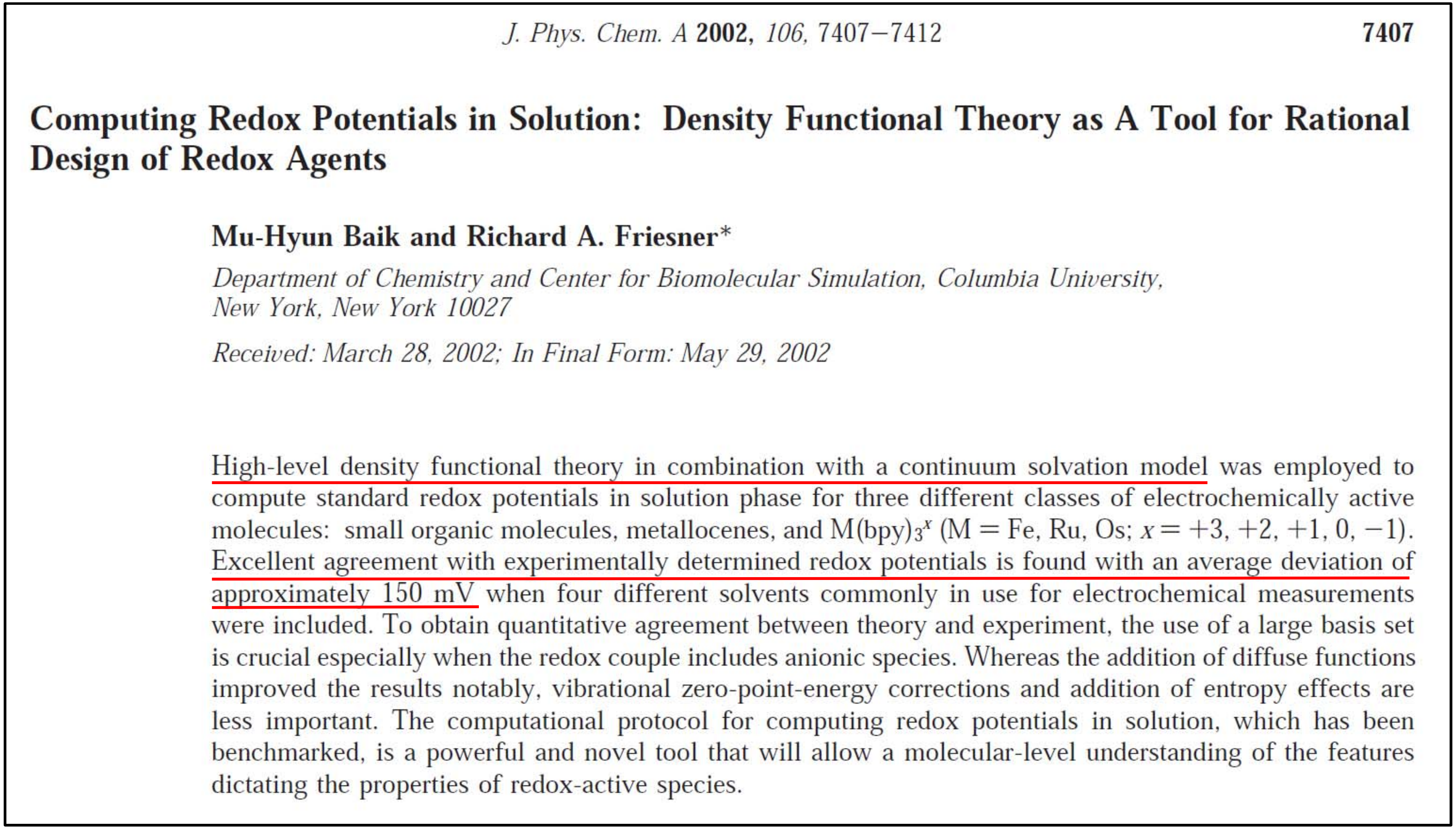
Pourbaix diagram



Slope [meV/pH]	Event
0	e^-
∞	H^+
59	$H^+ + e^-$
2×59	$2H^+ + e^-$

Figures from: Liu *et al.* Inorg. Chem. **47**, 1727 (2008)

“Quantum chemistry” approach for OER



J. Phys. Chem. A **2002,** *106,* 7407−7412 **7407**

Computing Redox Potentials in Solution: Density Functional Theory as A Tool for Rational Design of Redox Agents

Mu-Hyun Baik and Richard A. Friesner*

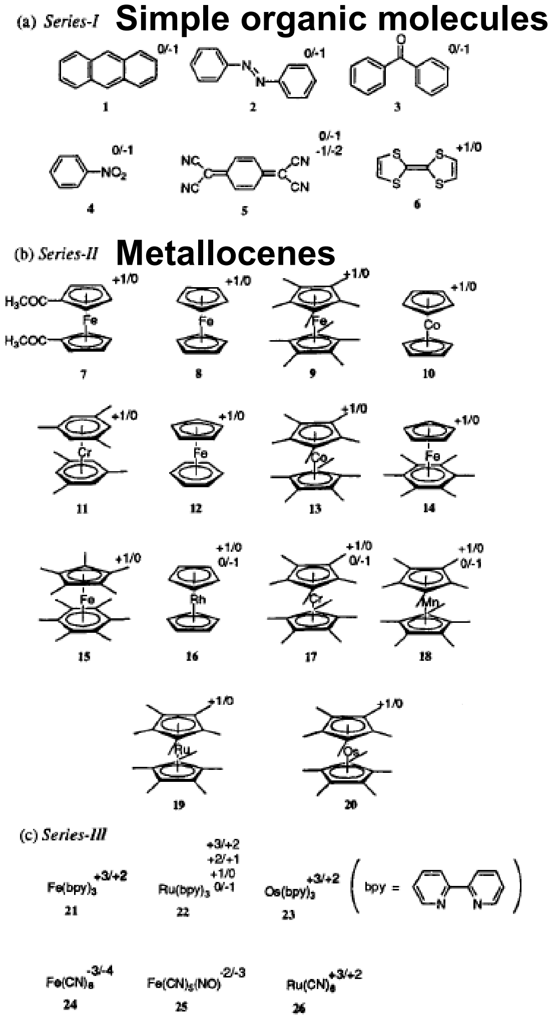
Department of Chemistry and Center for Biomolecular Simulation, Columbia University,
New York, New York 10027

Received: March 28, 2002; In Final Form: May 29, 2002

High-level density functional theory in combination with a continuum solvation model was employed to compute standard redox potentials in solution phase for three different classes of electrochemically active molecules: small organic molecules, metallocenes, and $M(bpy)_3^x$ ($M = Fe, Ru, Os$; $x = +3, +2, +1, 0, -1$). Excellent agreement with experimentally determined redox potentials is found with an average deviation of approximately 150 mV when four different solvents commonly in use for electrochemical measurements were included. To obtain quantitative agreement between theory and experiment, the use of a large basis set is crucial especially when the redox couple includes anionic species. Whereas the addition of diffuse functions improved the results notably, vibrational zero-point-energy corrections and addition of entropy effects are less important. The computational protocol for computing redox potentials in solution, which has been benchmarked, is a powerful and novel tool that will allow a molecular-level understanding of the features dictating the properties of redox-active species.

“Quantum chemistry” approach for OER

SCHEME 1: Redox Active Systems Considered in This Study^a



M(bpy)$_3$ and ML$_6$

- B3LYP functional

- Basis set(s):
(a) 6-31G** and LACV3P** for TM
(b) cc-pVTZ(-f)++ and LACV3P**++ for TM

- SCRF continuum model for the solvents, using gas-phase geometries

- Different solvents (water, acetonitrile, dimethylformamide, dichloromethane)

Figures from: Baik *et al.* J. Phys. Chem A **106**, 7407-7412 (2002)

“Quantum chemistry” approach for OER

6-31G** and LACV3P**

MAE = 0.425 V

MAE = 0.307 V

MAE = 0.563 V

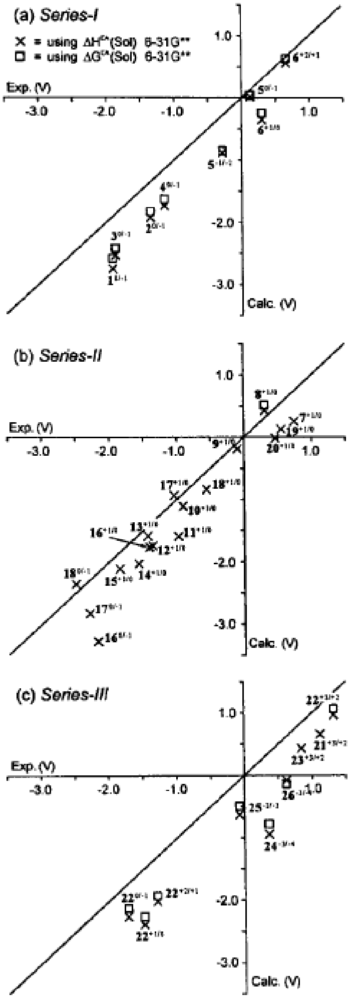
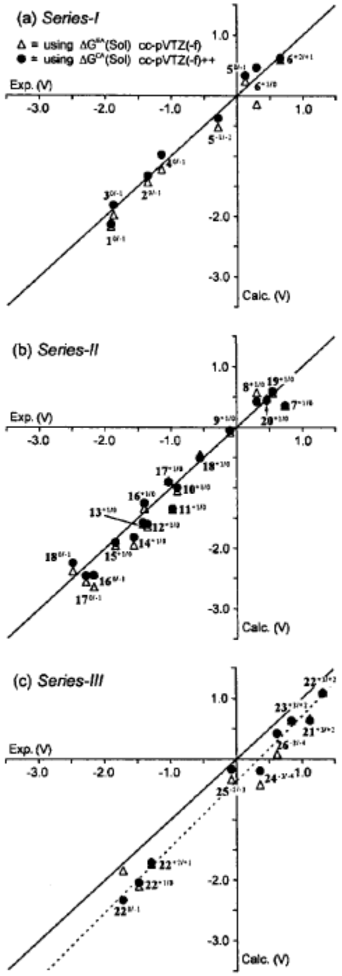


Figure 1. Correlation diagram of the experimental vs calculated redox potentials on the B3LYP/6-31G** level of theory with and without ZPE/entropy corrections.

cc-pVTZ(-f)++ and LACV3P**++



MAE = 0.120 V

MAE = 0.165 V

MAE = 0.372 V

Figure 2. Correlation diagram of the experimental vs calculated redox potentials on the B3LYP/cc-pVTZ(-f) and B3LYP/cc-pVTZ(-f)++ levels of theory (ZPE/entropy-corrected).

Molecular catalysts for OER: “blue dimer”

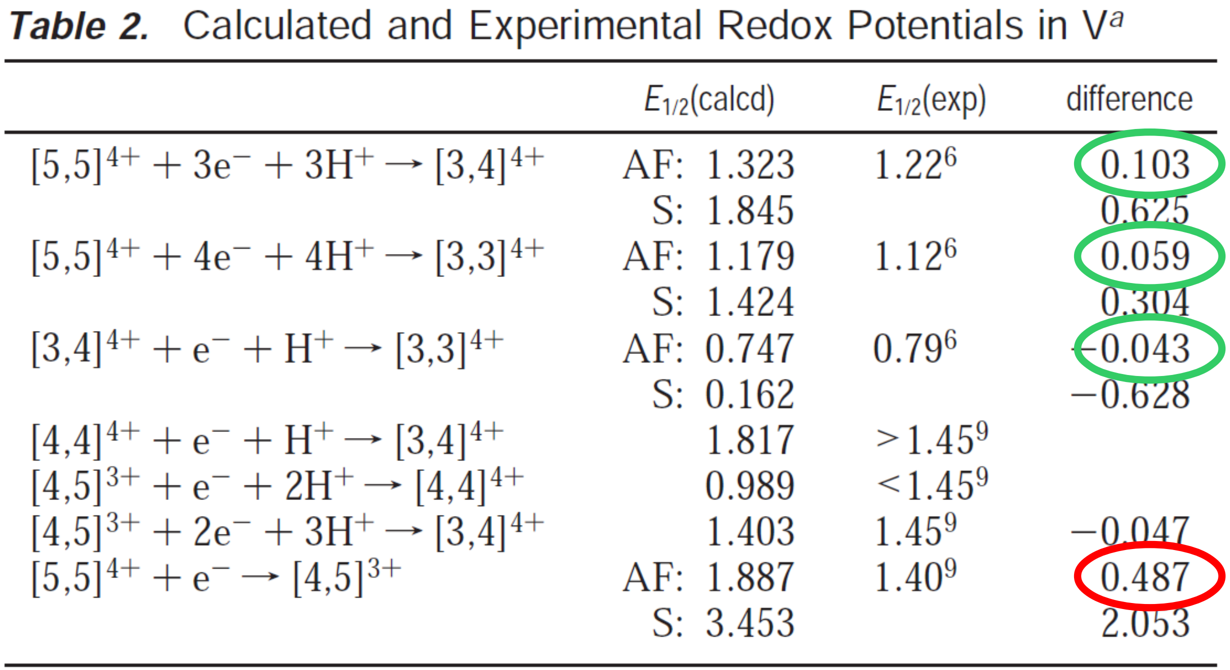
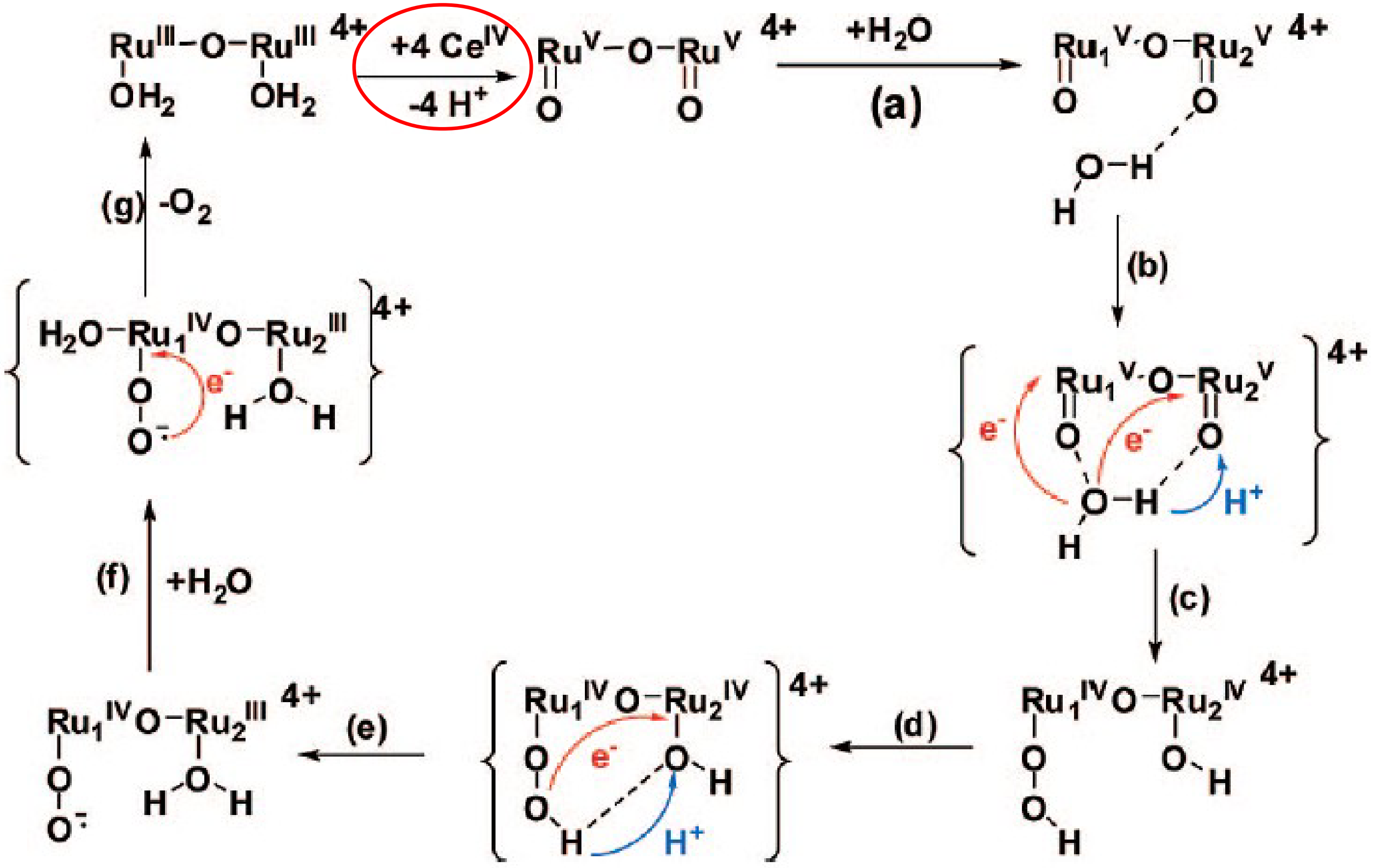


Table 2. Calculated and Experimental Redox Potentials in V[a]

	$E_{1/2}$(calcd)	$E_{1/2}$(exp)	difference		
$[5,5]^{4+} + 3e^- + 3H^+ \rightarrow [3,4]^{4+}$	AF: 1.323	1.22[6]	0.103	PCET	✓
	S: 1.845		0.625		
$[5,5]^{4+} + 4e^- + 4H^+ \rightarrow [3,3]^{4+}$	AF: 1.179	1.12[6]	0.059	PCET	✓
	S: 1.424		0.304		
$[3,4]^{4+} + e^- + H^+ \rightarrow [3,3]^{4+}$	AF: 0.747	0.79[6]	−0.043	PCET	✓
	S: 0.162		−0.628		
$[4,4]^{4+} + e^- + H^+ \rightarrow [3,4]^{4+}$	1.817	>1.45[9]			
$[4,5]^{3+} + e^- + 2H^+ \rightarrow [4,4]^{4+}$	0.989	<1.45[9]			
$[4,5]^{3+} + 2e^- + 3H^+ \rightarrow [3,4]^{4+}$	1.403	1.45[9]	−0.047		
$[5,5]^{4+} + e^- \rightarrow [4,5]^{3+}$	AF: 1.887	1.40[9]	0.487	ET	✗
	S: 3.453		2.053		

Figures from: Yang and Baik, JACS **106**, 13222 (2004)

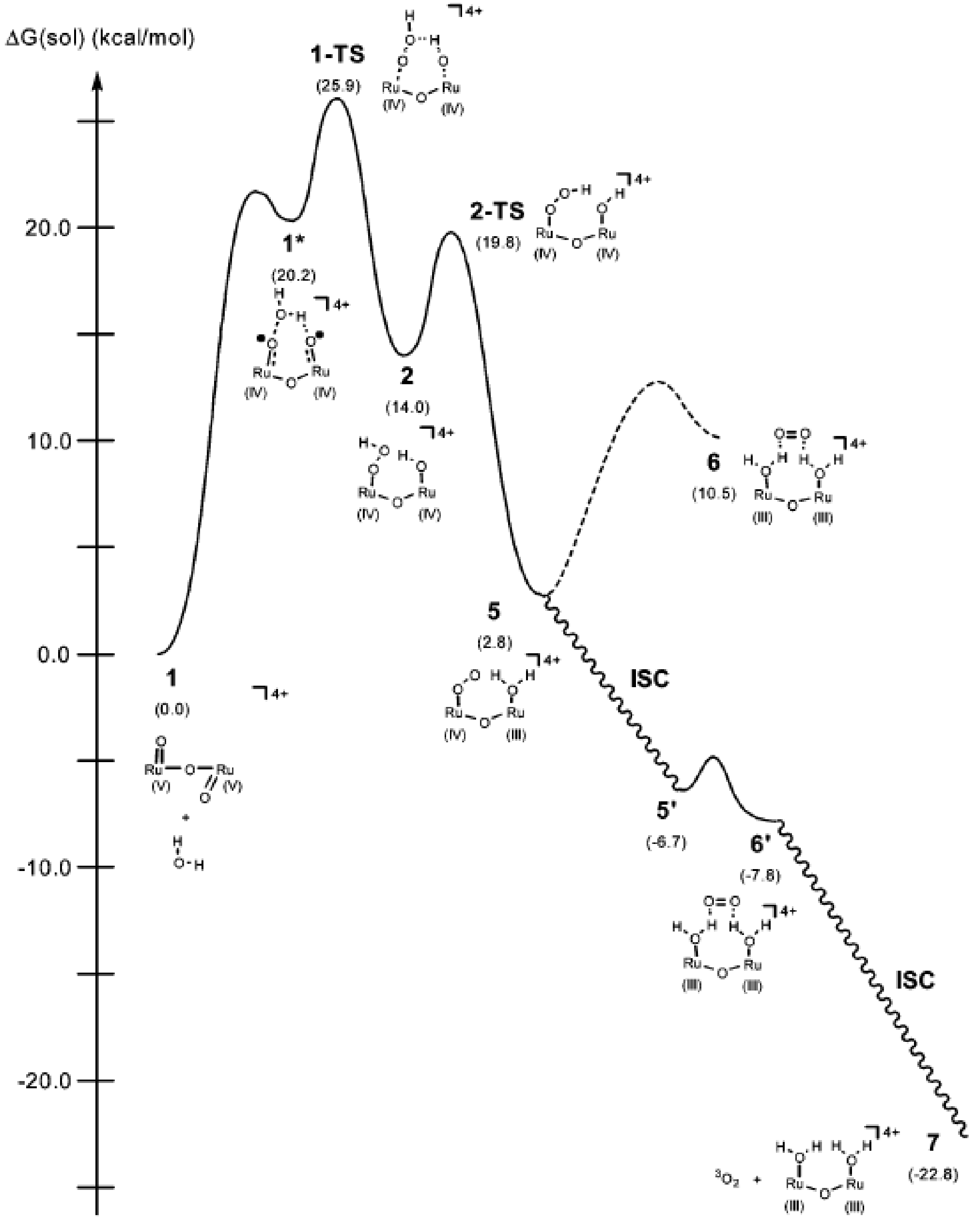
Molecular catalysts for OER: “blue dimer”



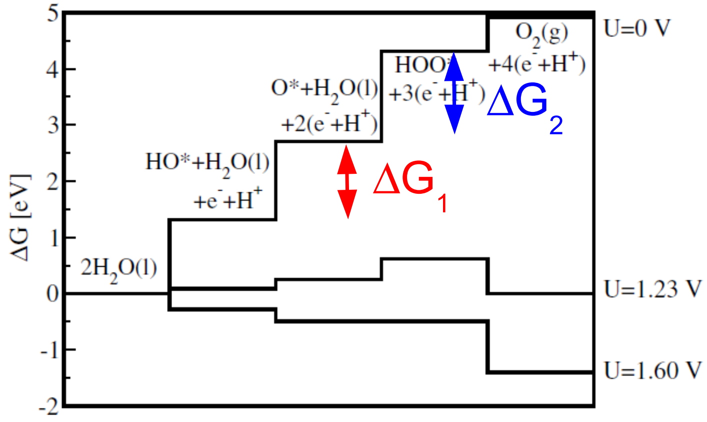
4 PCET

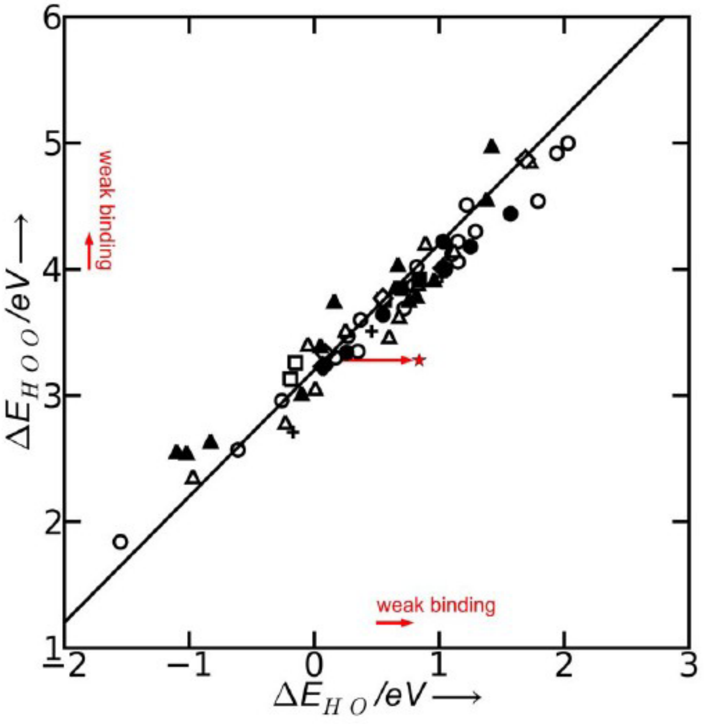
Figures from: Liu *et al.* Inorg. Chem. **47**, 1727 (2008)

Molecular catalysts for OER: “blue dimer”



Electrolysis of water on oxide surfaces





$\Delta G_1 = G(O^*) - G(OH^*) + 1/2\mu(H_2)$

$\Delta G_2 = G(OOH^*) - G(O^*) + 1/2\mu(H_2) - \mu(H_2O)$

Several linear relationships have been established:

- E_{OH^*} µ E_{O^*}
- E_{OOH^*} µ E_{O^*}
- E_{O^*} µ E_{OOH^*}

$\Delta G_1 + \Delta G_2 = 3.2$ eV ± 0.2 eV (68%)
± 0.4 eV (95%)

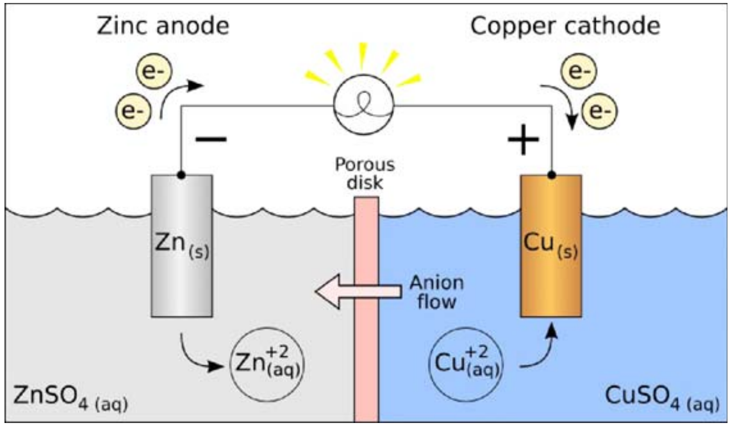
"Ideal" catalyst $\Delta G_1 = \Delta G_2 = 1.6$ eV ($\eta = 0.37$ eV)

RuO_2 is therefore as good a catalyst for OER as a metal oxide can be

Figures from: Man *et al.* ChemCatChem **3**, 1159-1165 (2011)

Electrochemistry: a quick overview

Galvanic cell



$Cu^{2+}(aq) + Zn(s) \rightarrow Cu(s) + Zn^{2+}(aq)$

Cathode (Red): $Cu^{2+}(aq) + 2e^- \rightarrow Cu(s)$

Anode (Ox): $Zn(s) \rightarrow Zn^{2+}(aq) + 2e^-$

Electromotive force (efm) E:

$-nFE = \Delta G$ $F=eN_A$ Faraday constant

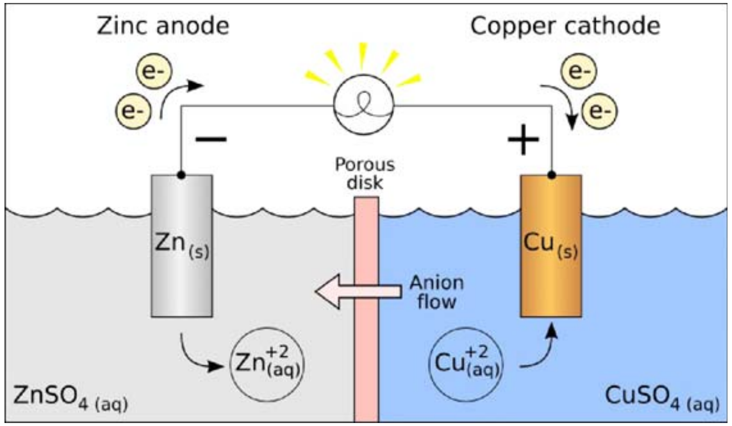
$\Delta G = \Delta G^0 + RT\ln(K)$ K: equilibrium constant

$E = -\Delta G^0/nF + (RT/nF)\ln(K)$

$E = E^0 + (RT/nF)\ln(K)$ **Nernst equation**

Electrochemistry: a quick overview

Galvanic cell



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Anode (Ox): $Zn(s) \rightarrow Zn^{2+}(aq) + 2e^-$

$E^0 = E^0_2 - E^0_1$

$E^0_{1,2}$ of a single electrode: not possible to measure

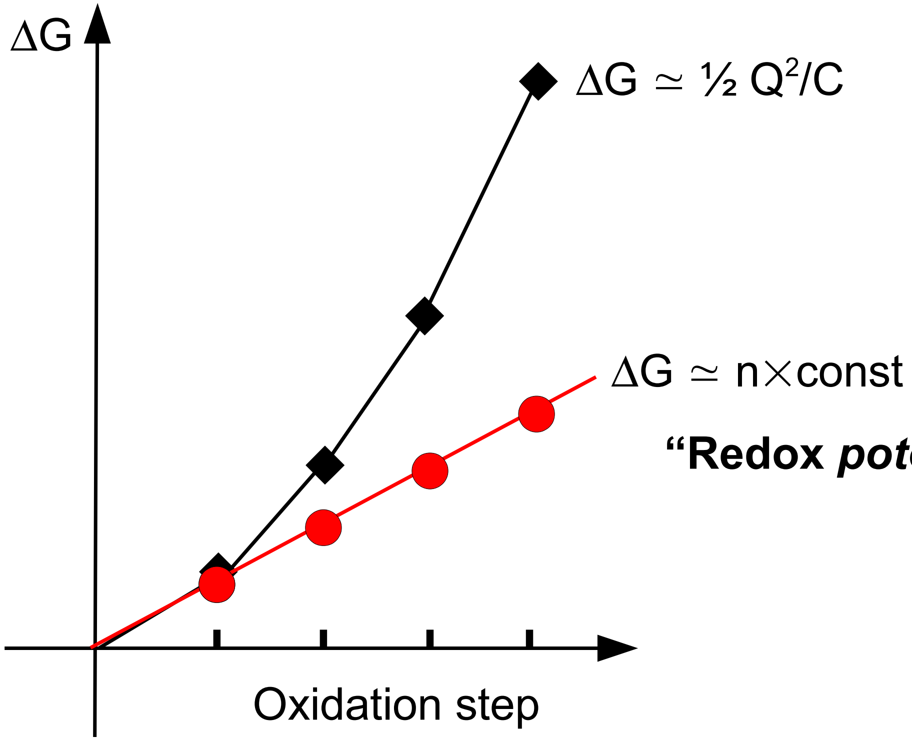
Reference electrode: NHE (SHE)

We define E^0_{NHE} of the NHE to be zero: $\mathbf{E^0_{NHE} = 0}$

PCET in water oxidation

ET: $$0 \xrightarrow{-e^-} +1 \xrightarrow{-e^-} +2 \xrightarrow{-e^-} +3 \xrightarrow{-e^-} +4$$

PCET: $$0 \xrightarrow{-(e^- + H^+)} 0 \xrightarrow{-(e^- + H^+)} 0 \xrightarrow{-(e^- + H^+)} 0 \xrightarrow{-(e^- + H^+)} 0$$



$$\boxed{-nFE^0 = \Delta G^0}$$

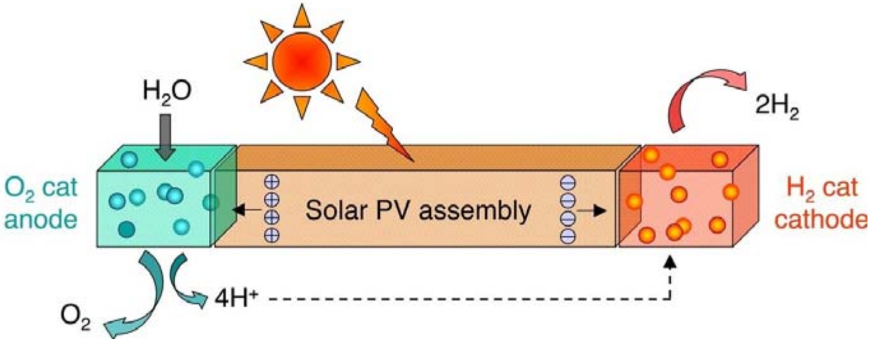
“Redox *potential leveling*”

OER and ORR

Electrolysis

$2H_2O \rightarrow O_2 + 2H_2$ $\Delta G^0 = 4.92$ eV

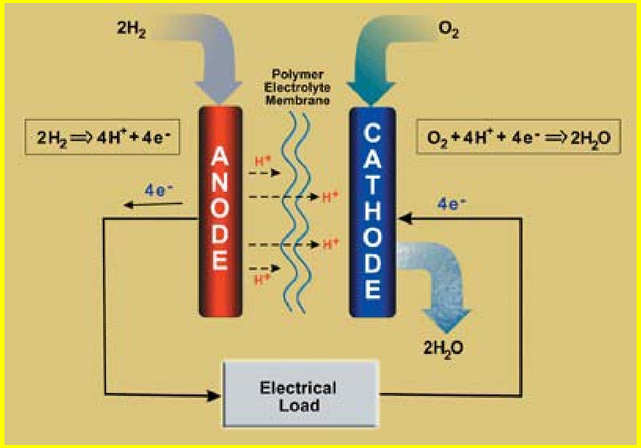
OER: $2H_2O \rightarrow O_2 + 4H^+ + 4e^-$
$2H^+ + 2e^- \rightarrow H_2$



PEM Fuel cells

$O_2 + 2H_2 \rightarrow 2H_2O$ $\Delta G^0 = -4.92$ eV

ORR: $O_2 + 4H^+ + 4e^- \rightarrow 2H_2O$
$H_2 \rightarrow 2H^+ + 2e^-$



Oxygen Reduction Reaction (ORR) in fuel cells

Cathode reaction (Red): $O_2 + 4(H^+ + e^-) \rightarrow 2H_2O$ **$E^0 = 1.23$ V**

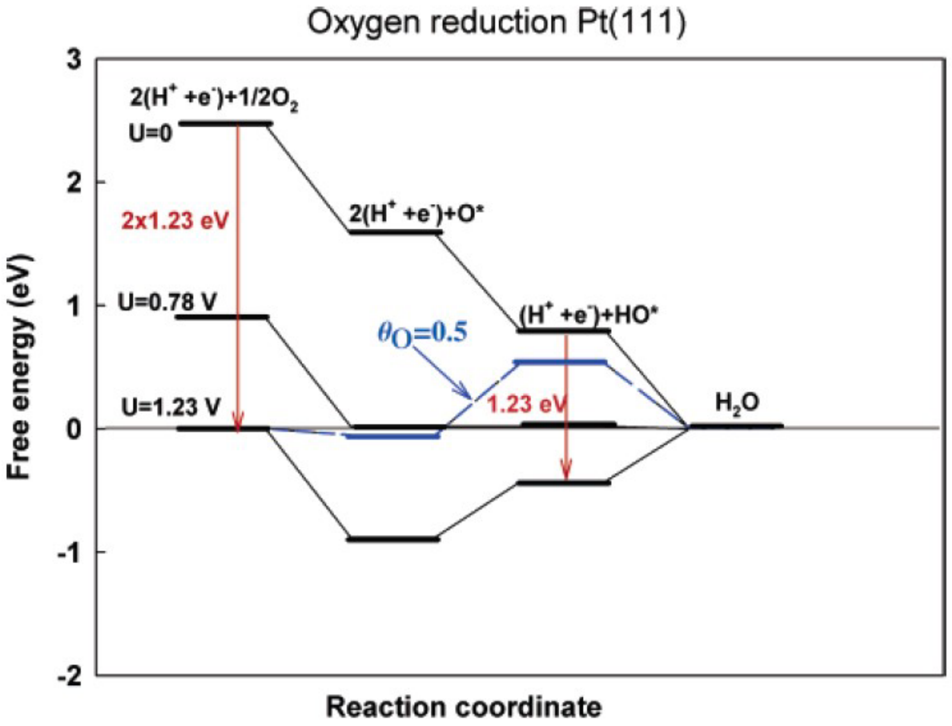
“Dissociative” mechanism

$$O_2 + * \rightarrow 2O*$$
$$O* + (H^+ + e^-) \rightarrow OH*$$
$$OH* + (H^+ + e^-) \rightarrow H_2O + *$$

“Associative” mechanism

$$O_2 + * \rightarrow O_2*$$
$$O_2* + (H^+ + e^-) \rightarrow OOH*$$
$$OOH* + (H^+ + e^-) \rightarrow H_2O + O*$$
$$O* + (H^+ + e^-) \rightarrow OH*$$
$$OH* + (H^+ + e^-) \rightarrow H_2O + *$$

Oxygen Reduction Reaction (ORR)



- Up to U = 0.78 V all steps are downhill

- At the theoretical potential U=1.23 V both ($H^+ + e^-$) steps are uphill.

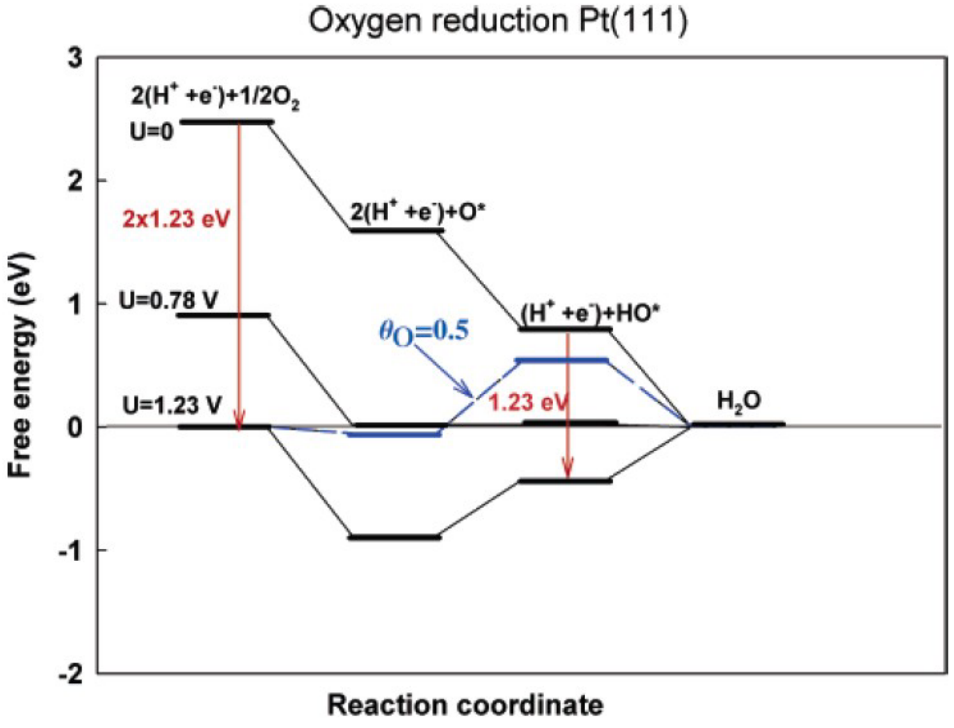
- Overpotential $\eta = 1.23 - 0.78 = 0.45$ V

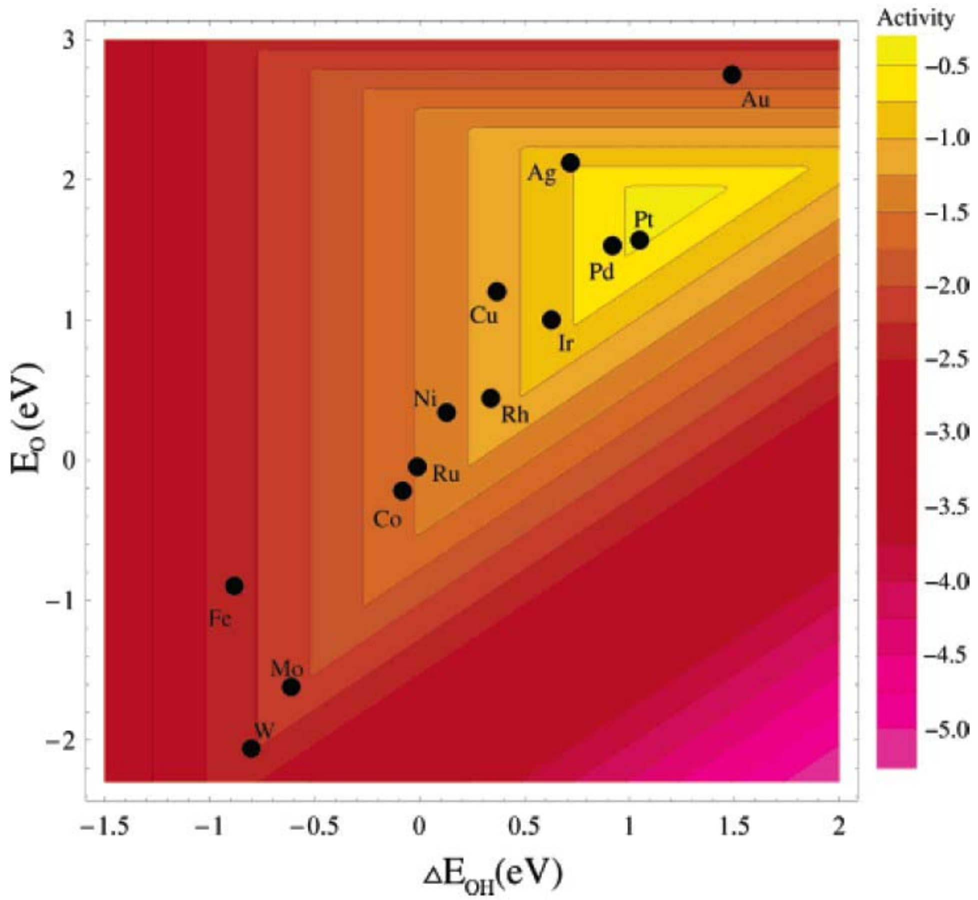
- Overpotential due to the stability of O* and OH* on Pt(111)

Ideal catalyst: $\Delta G_1(U=0) = \Delta G_2(U=0) = 1.23$ eV

Figures from: Norskov *et al.* J. Phys. Chem B **108**, 17886-17892 (2004)

Oxygen Reduction Reaction (ORR)

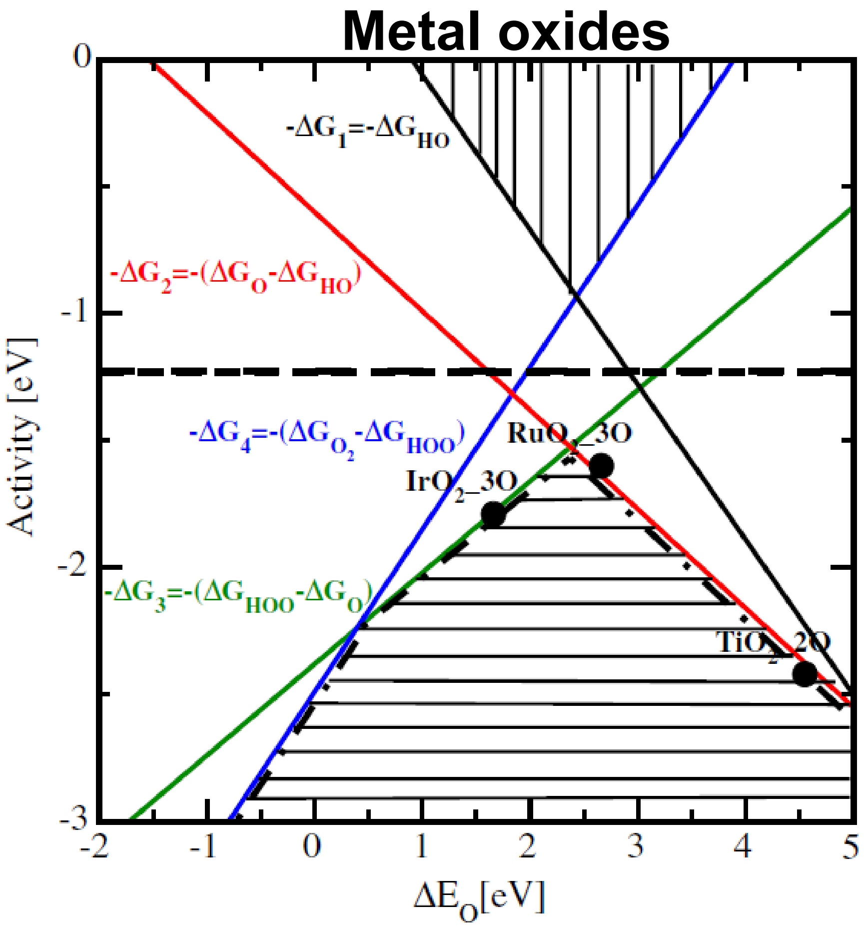


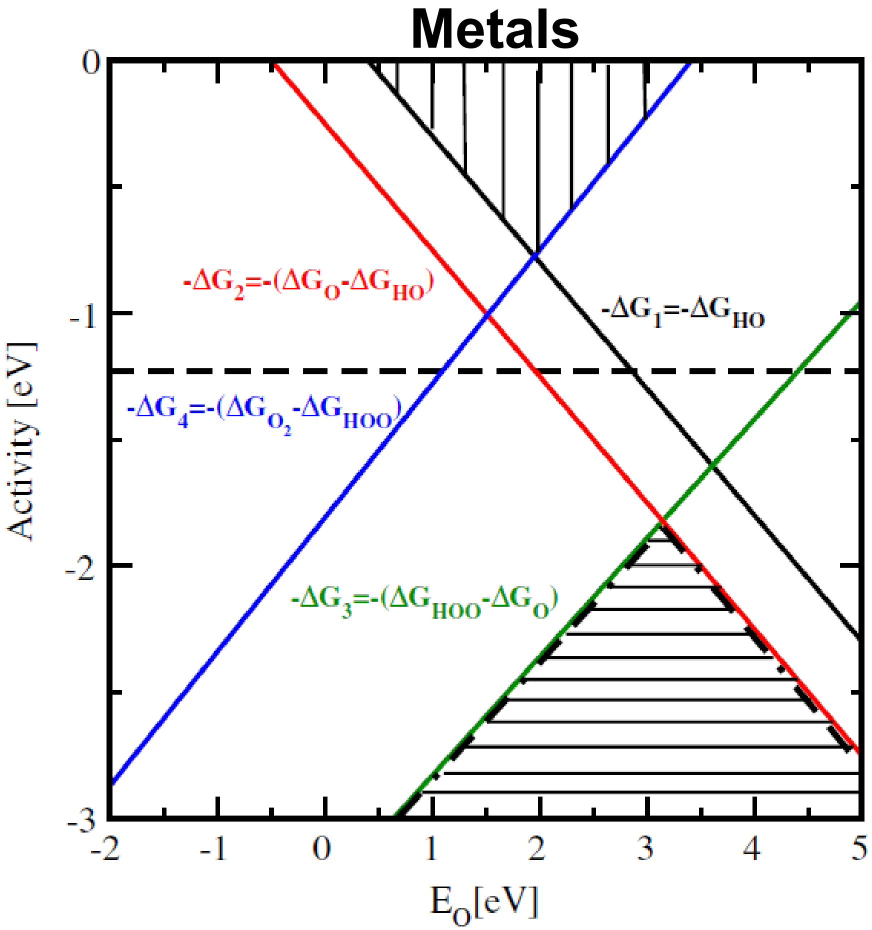


- Pt and Pd are at the top of the volcano
- E_b(OH*) and E_b(O*) are approximately linearly related

Figures from: Norskov *et al.* J. Phys. Chem B **108**, 17886-17892 (2004)

Electrolysis of water on oxide surfaces


Metal oxides


Metals

- Using the linear relationships of the the binding energies of the intermediates vs. O*, the activity of different catalysts for OER and ORR can be established
- The “activity” is defined as the overpotential.
- RuO_2 and Pt sit very near the top of the volcanoes. There's not much room for improvement.

Figures from: Rossmeisl *et al.* J. Electr. Chem **607**, 83-89 (2007)