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

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School on Numerical Methods for Materials Science Related to Renewable Energy Applications
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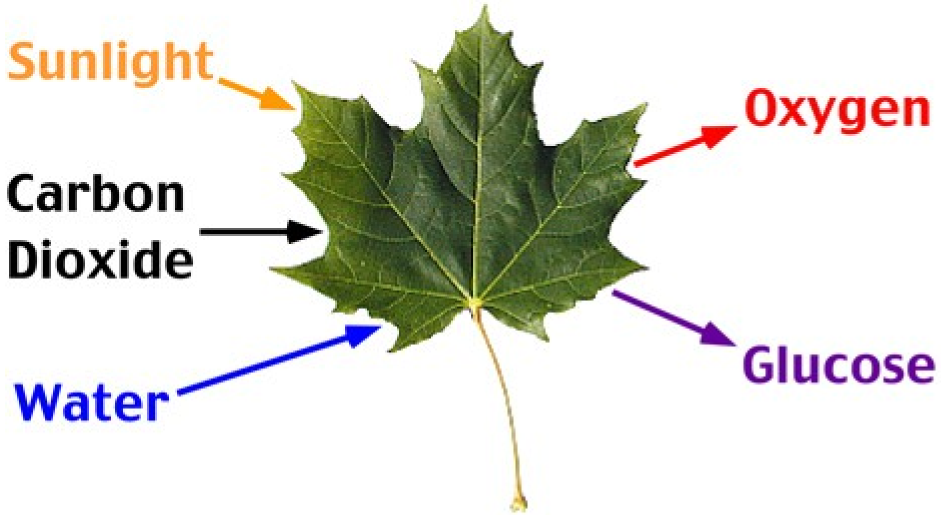
# Artificial photosynthesis: using light to make fuels



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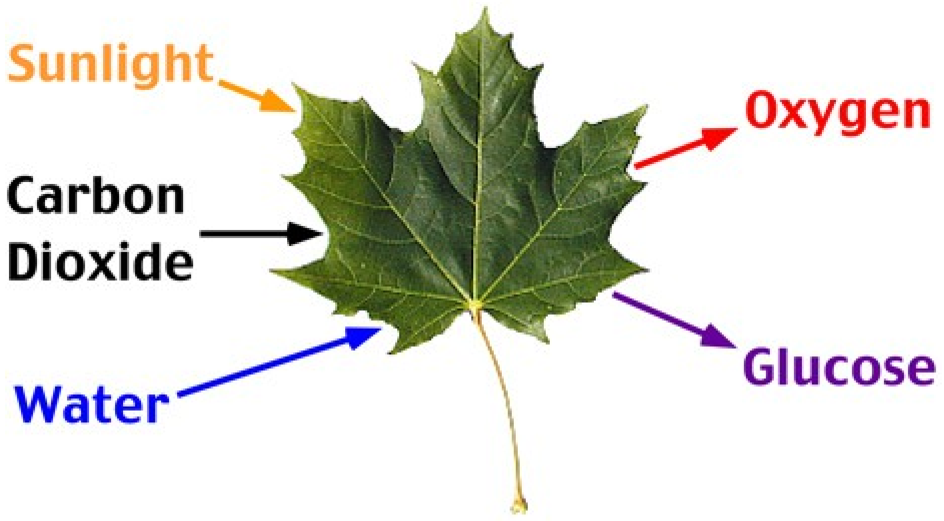


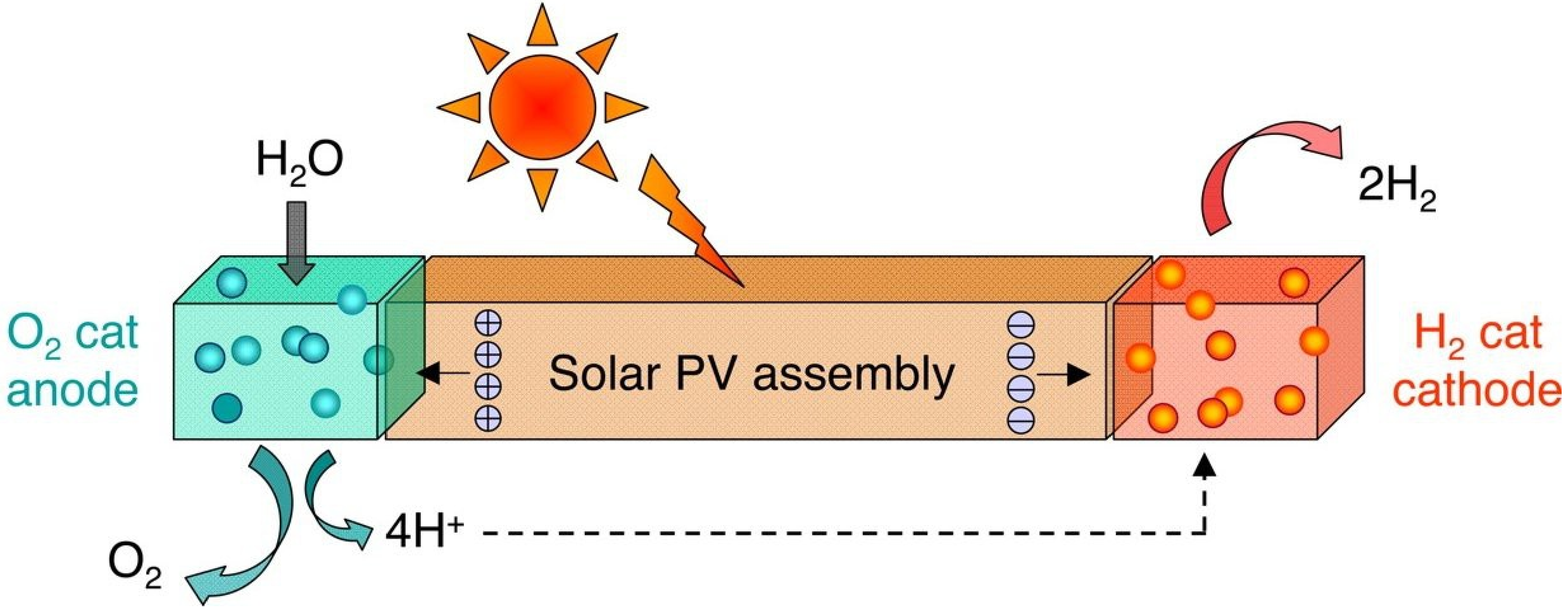
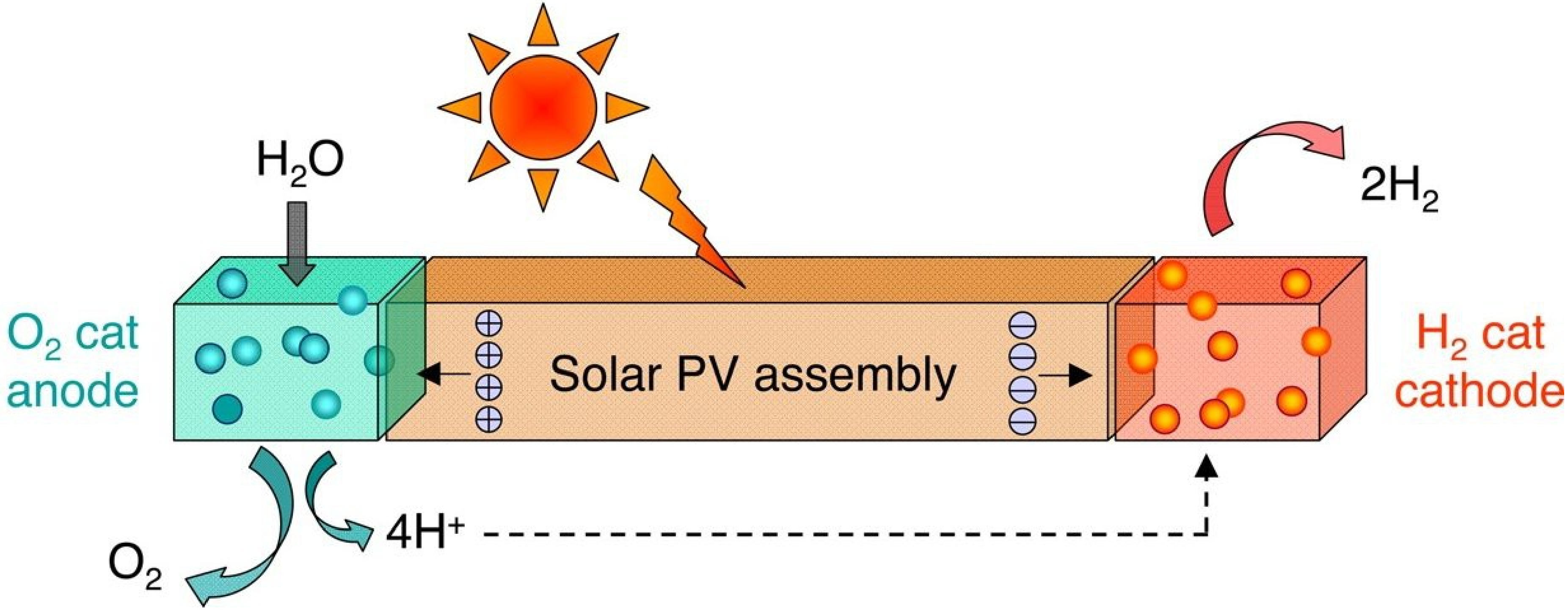


*Figure from:* Lewis and Nocera, PNAS **103**, 15729 (2006)

# Artificial photosynthesis: using light to make fuels



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

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

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

$\Delta$

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

# Outline

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

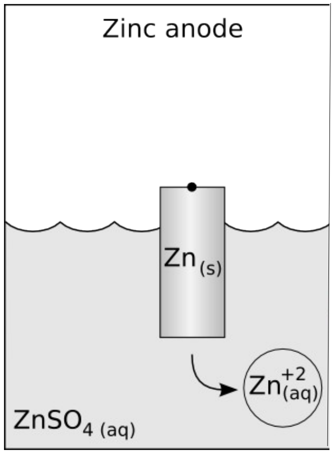
- Lessons from the oxygen evolving complex in PSII

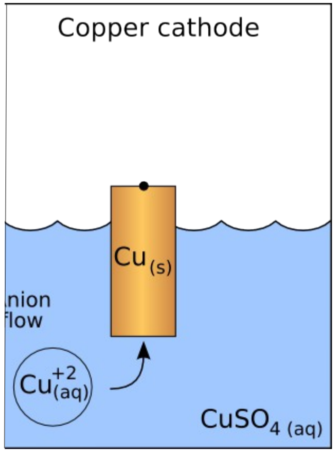
- Theoretical approaches for modeling electrochemical reactions:

    (a) Nørskov's approach

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

# Electrochemistry: a quick overview

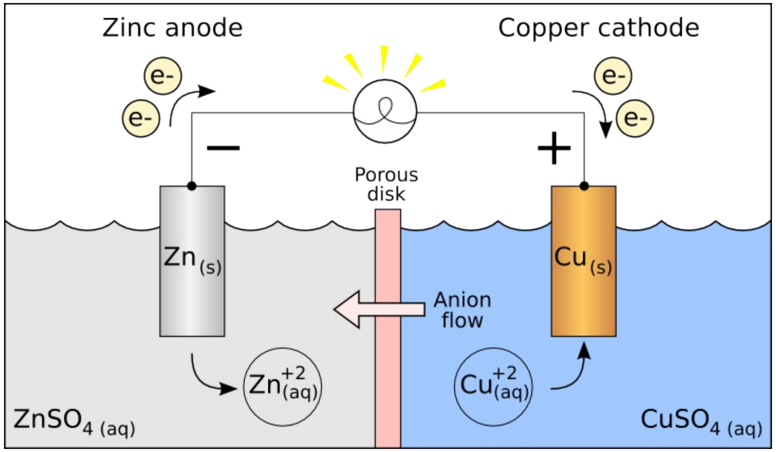




| | |
|---|---|
| Electrode1 | $Cu^{2+}(aq) + 2e^- \Leftrightarrow Cu(s)$ |
| Electrode2 | $Zn(s) \Leftrightarrow Zn^{2+}(aq) + 2e^-$ |

# Electrochemistry: a quick overview

Galvanic (electrochemical) cell



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

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

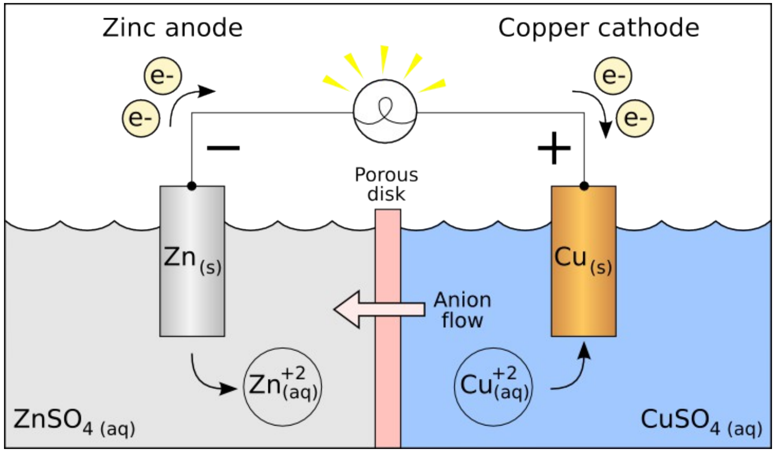
Anode (Ox): $Zn(s) \rightarrow Zn^{2+}(aq) + 2e^{-}$

Zn is oxidized
($e^{-}$ removed from Zn )

Cu is reduced
($e^{-}$ donated to Cu )

# Electrochemistry: a quick overview

Galvanic (electrochemical) cell



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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

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

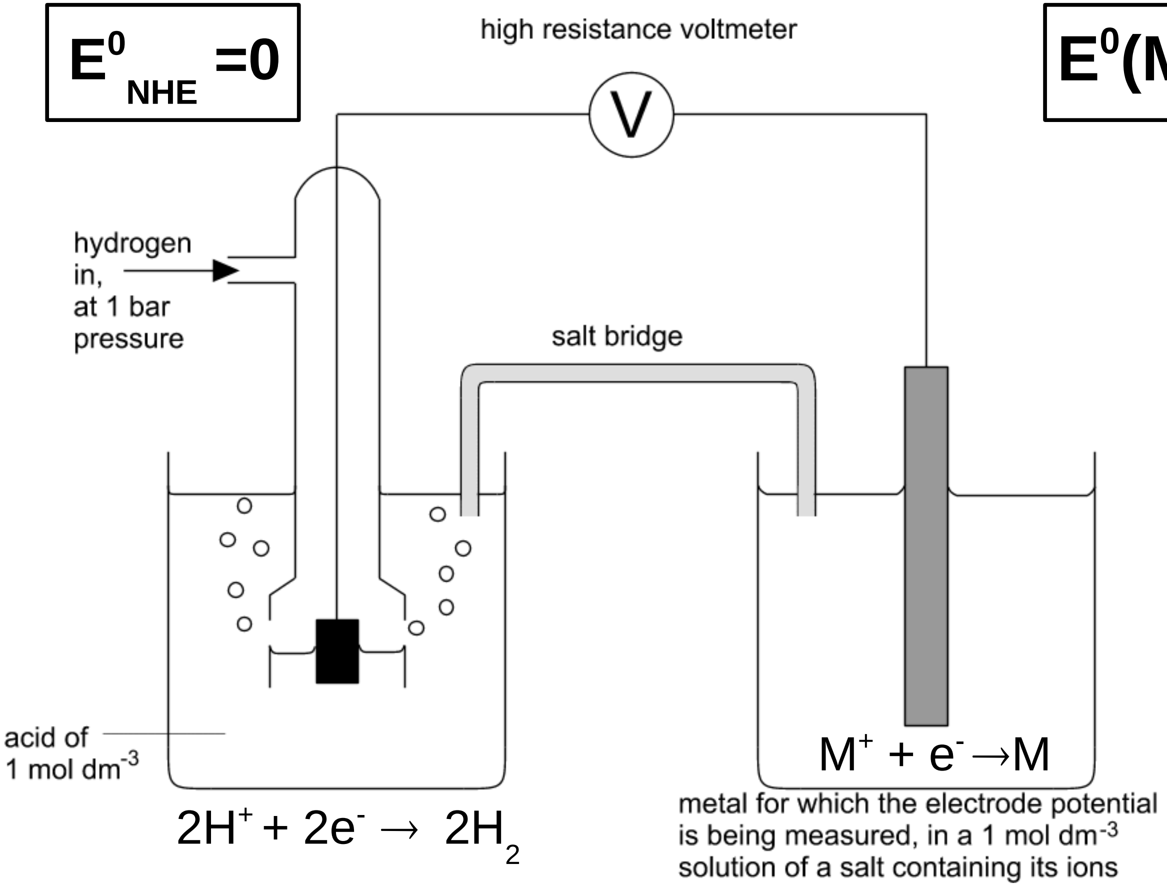
Higher $E^0$ : reduction

Lower $E^0$: oxidation

# Normal (Standard) Hydrogen Electrode (NHE)

$E^0_{NHE} = 0$

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



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

$M^+ + e^- \rightarrow M$

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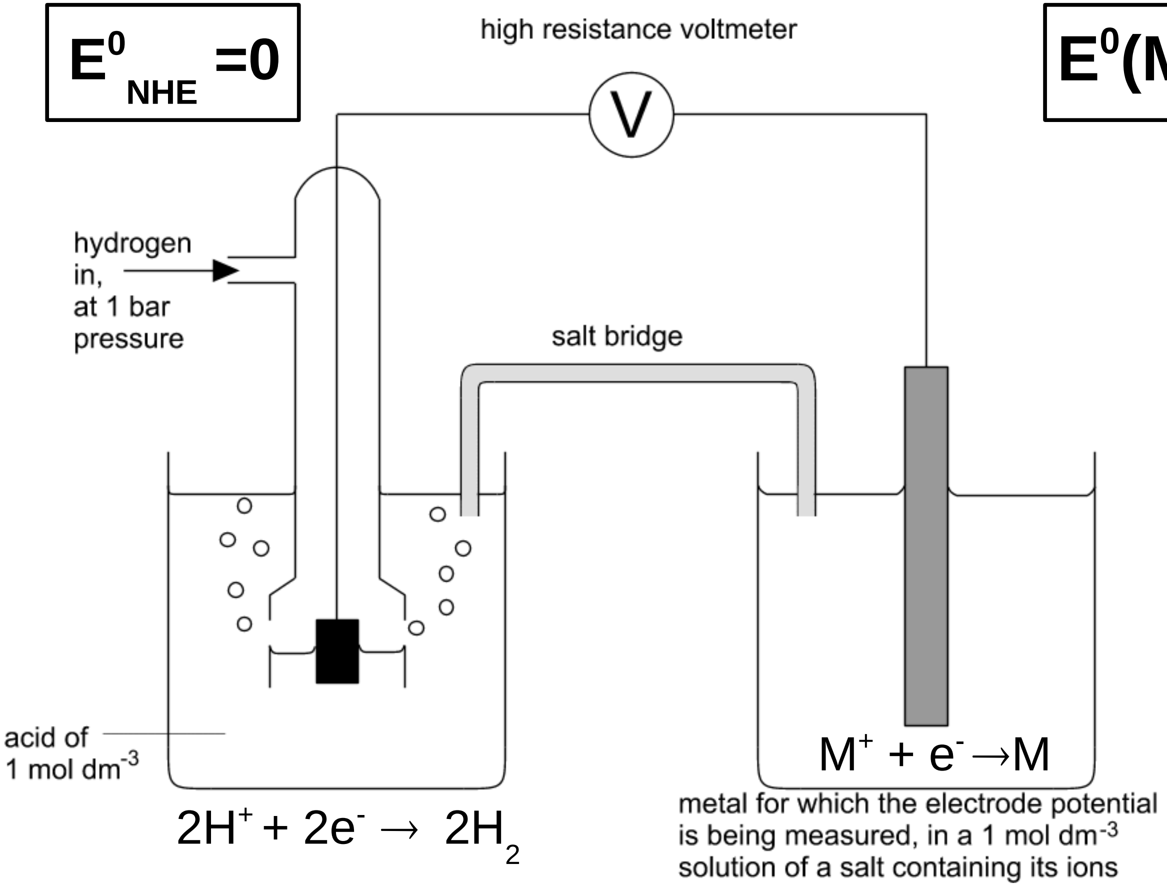

$$E^0_{NHE} = 0 \quad \Rightarrow \quad 2H^+ + 2e^- \leftrightarrow 2H_2 \quad \Rightarrow \quad G^0(H^+ + e^-) = \frac{1}{2} G^0(H_2)$$

# Electrochemistry: a quick overview

**ORR/OER**

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

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

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

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

# Electrochemistry: a quick overview

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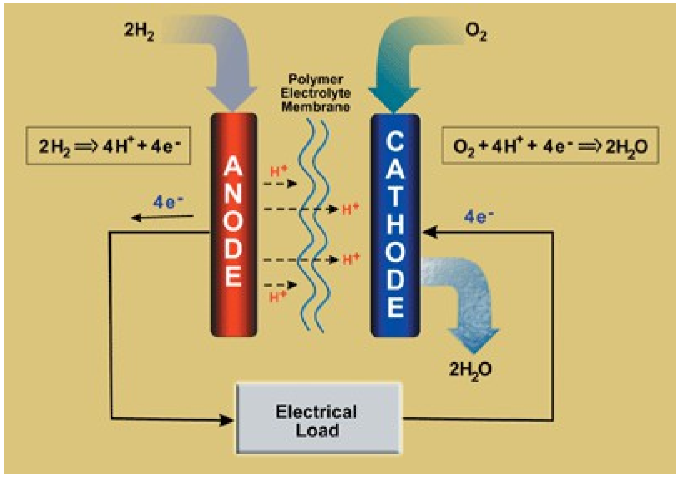
$H_2 \rightarrow 2H^+ + 2e^-$

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

$E^0 = 1.23$ V

## *PEM Fuel cells*



# Electrochemistry: a quick overview

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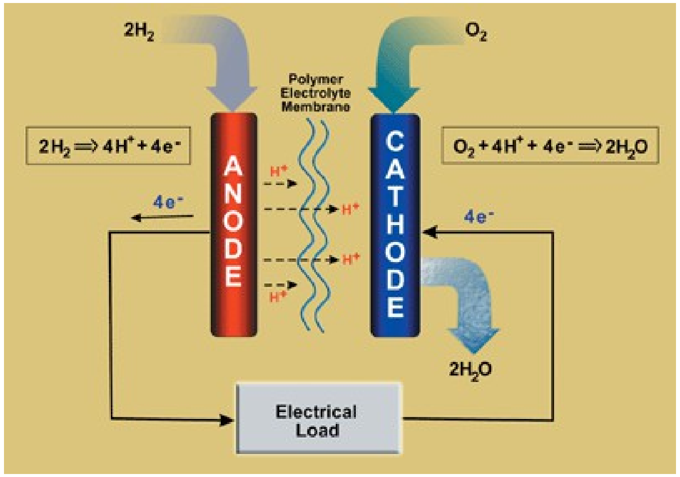

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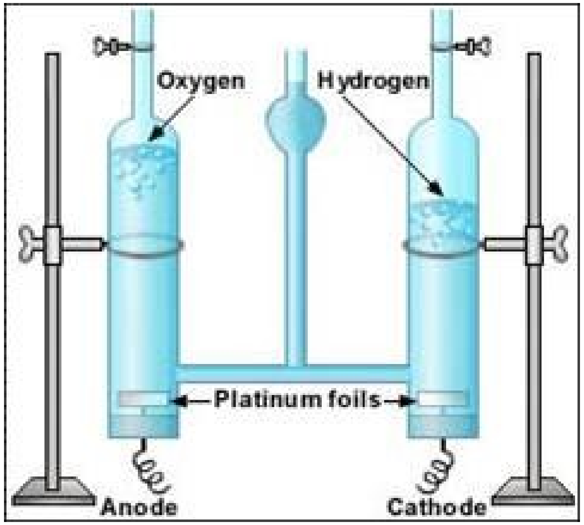
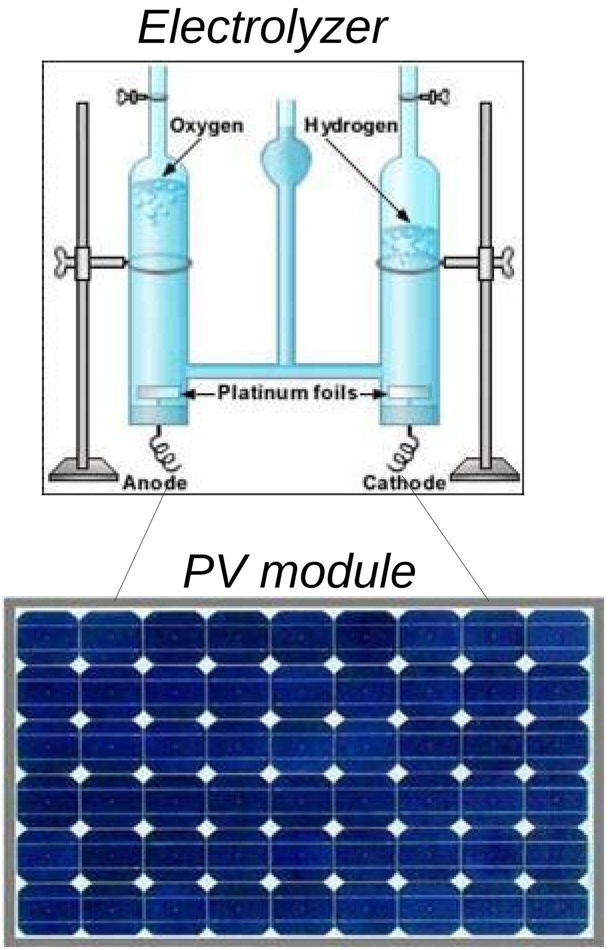
## *Electrolysis*



# Artificial photosynthesis: using light to make fuels

**Goal**: storing solar energy through water splitting



*Electrolyzer*

*PV module*

# Artificial photosynthesis: using light to make fuels

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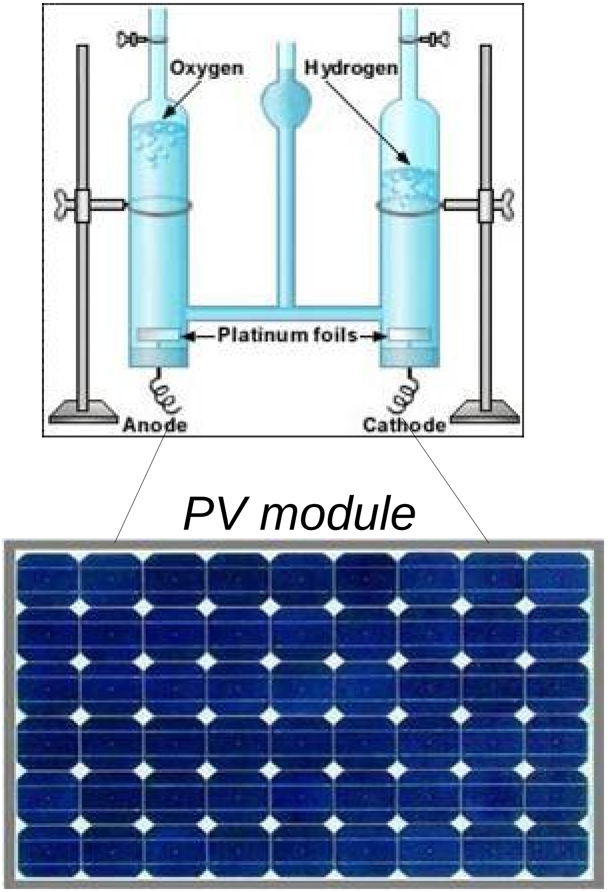
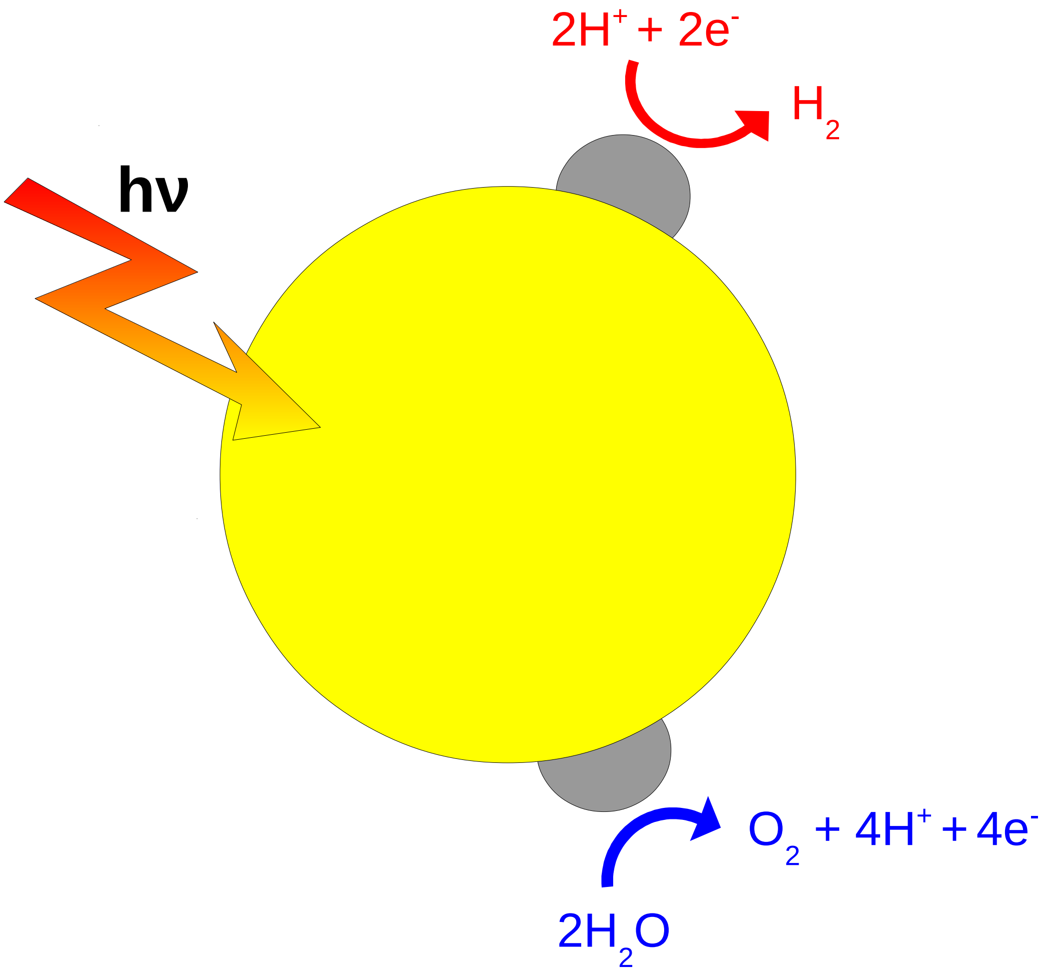
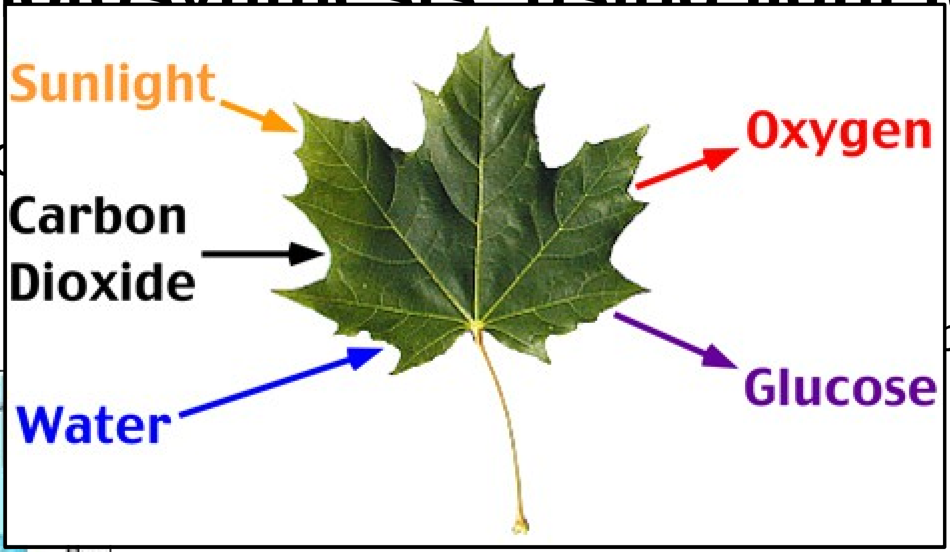


*Integrated photo-catalyst*



# Artificial photosynthesis: using light to make fuels

**Goal**: storing sc



*Electrolyzer*

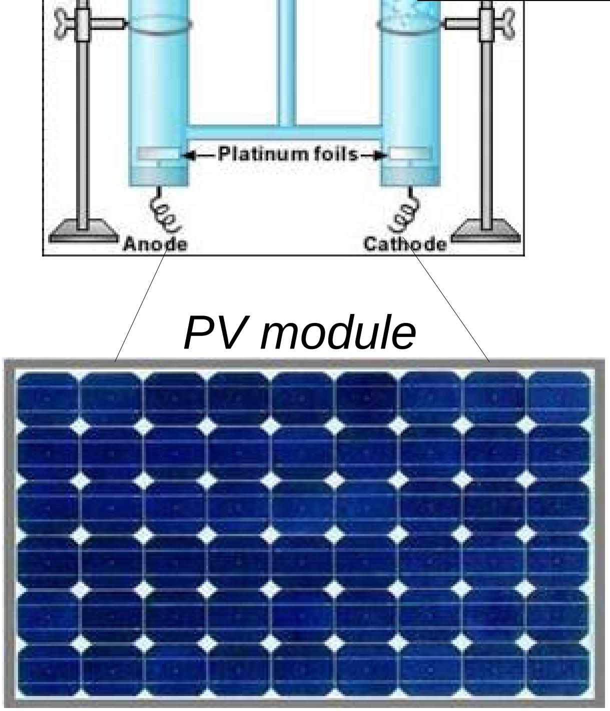
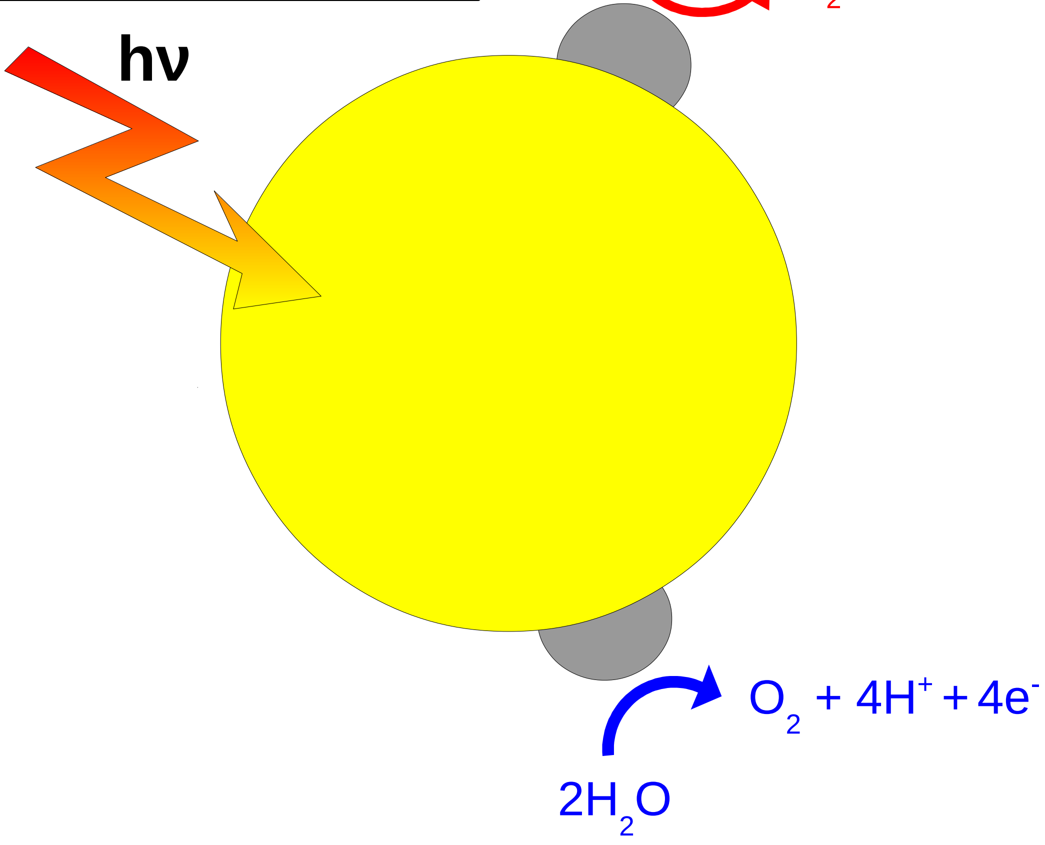


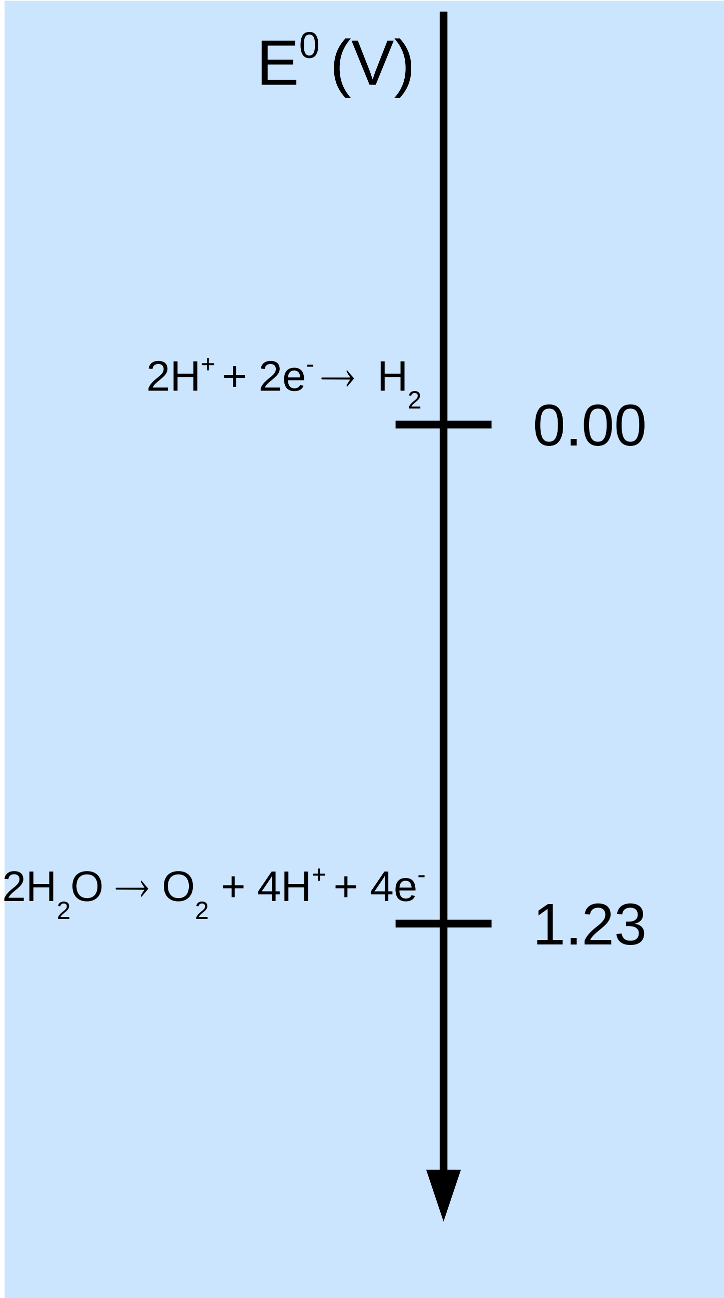
*photo-catalyst*



# 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

# Energy level alignment

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

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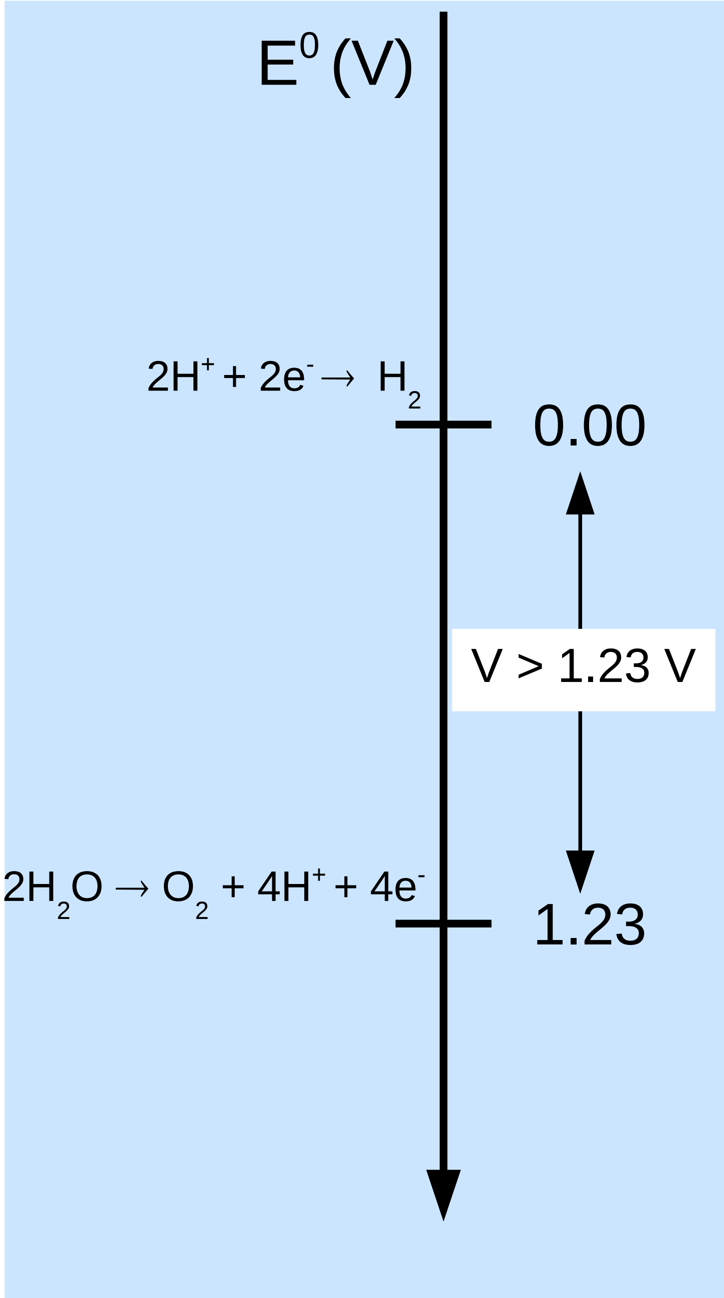

$E^0$ (V)

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

V > 1.23 V

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

# Energy level alignment

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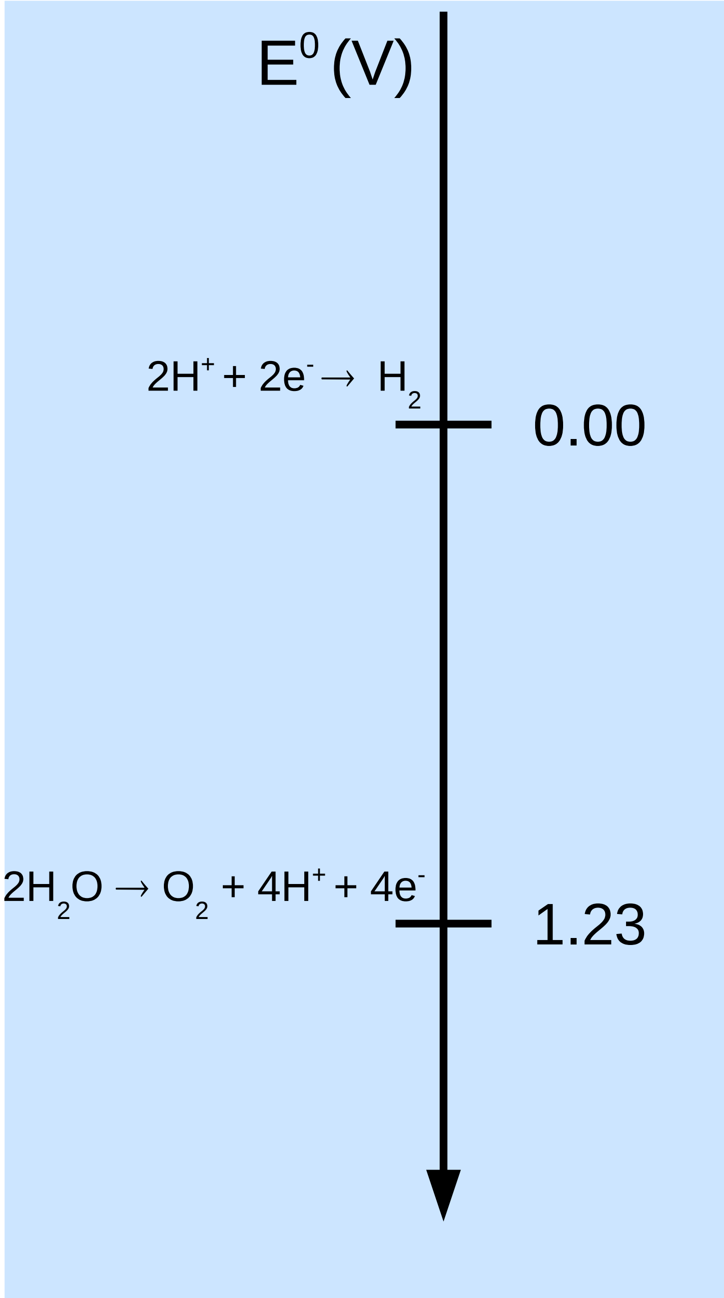

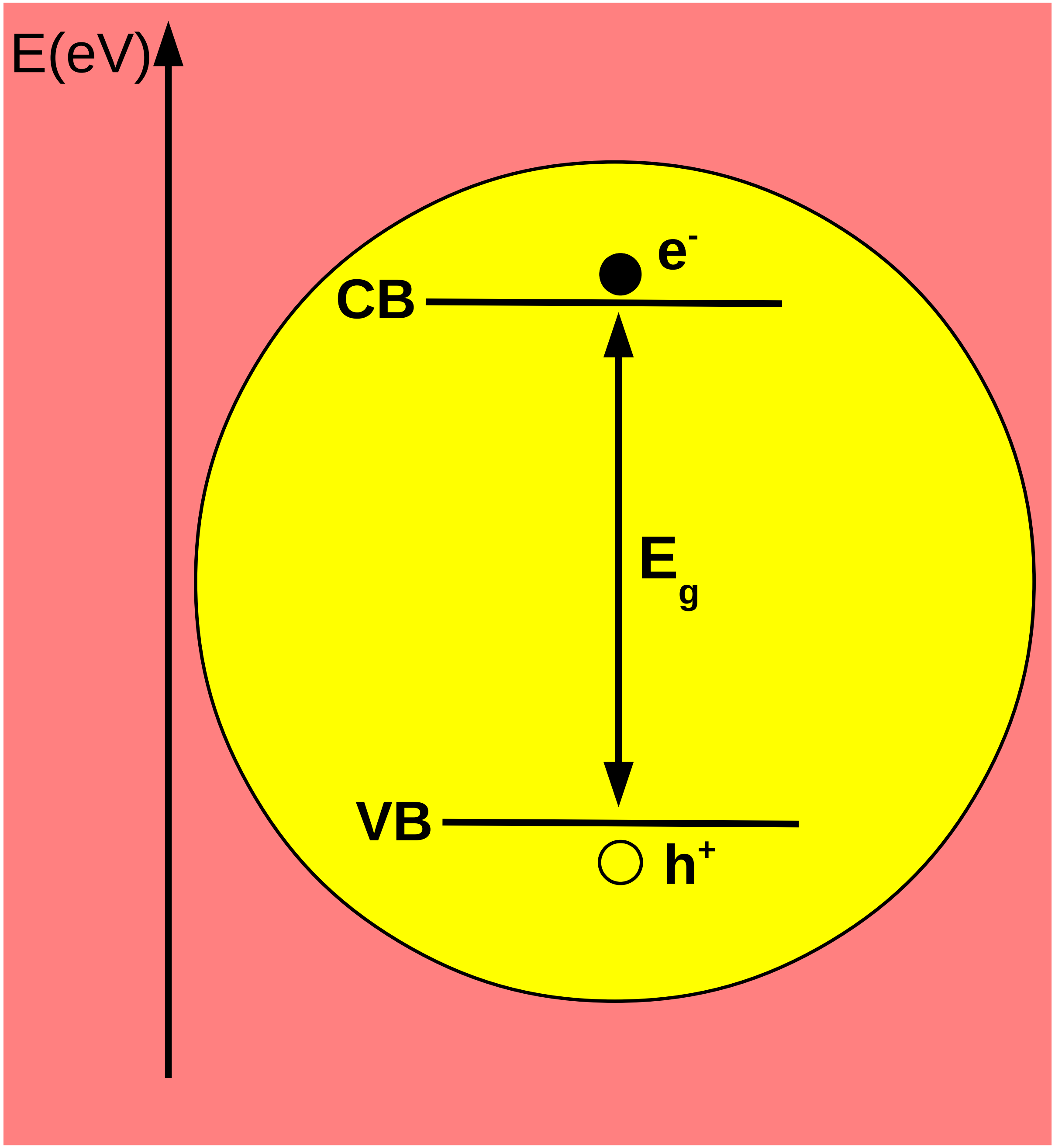

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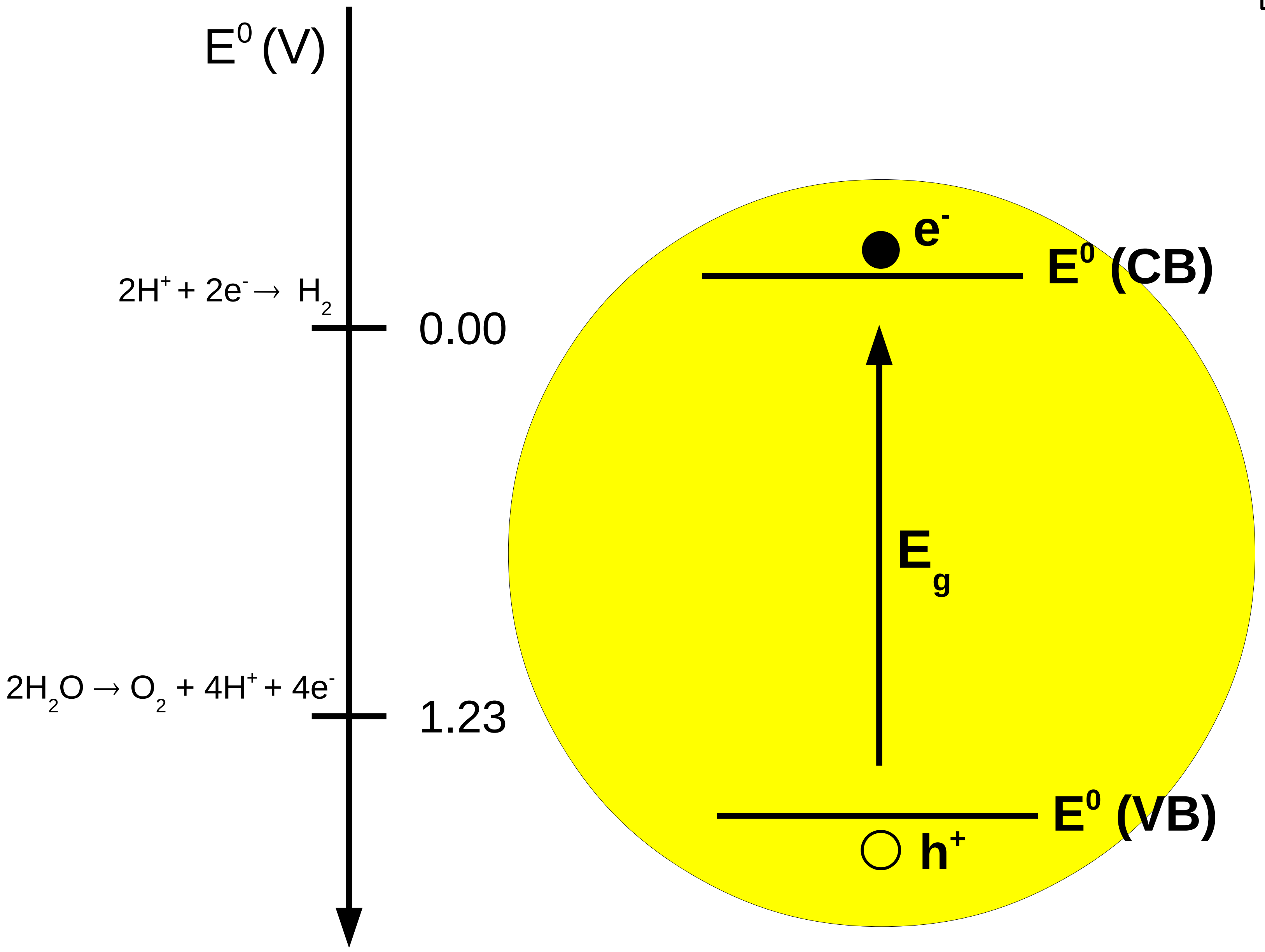


$E^0$ (V)

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

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

$e^-$

**$E^0$ (CB)**

**$E_g$**

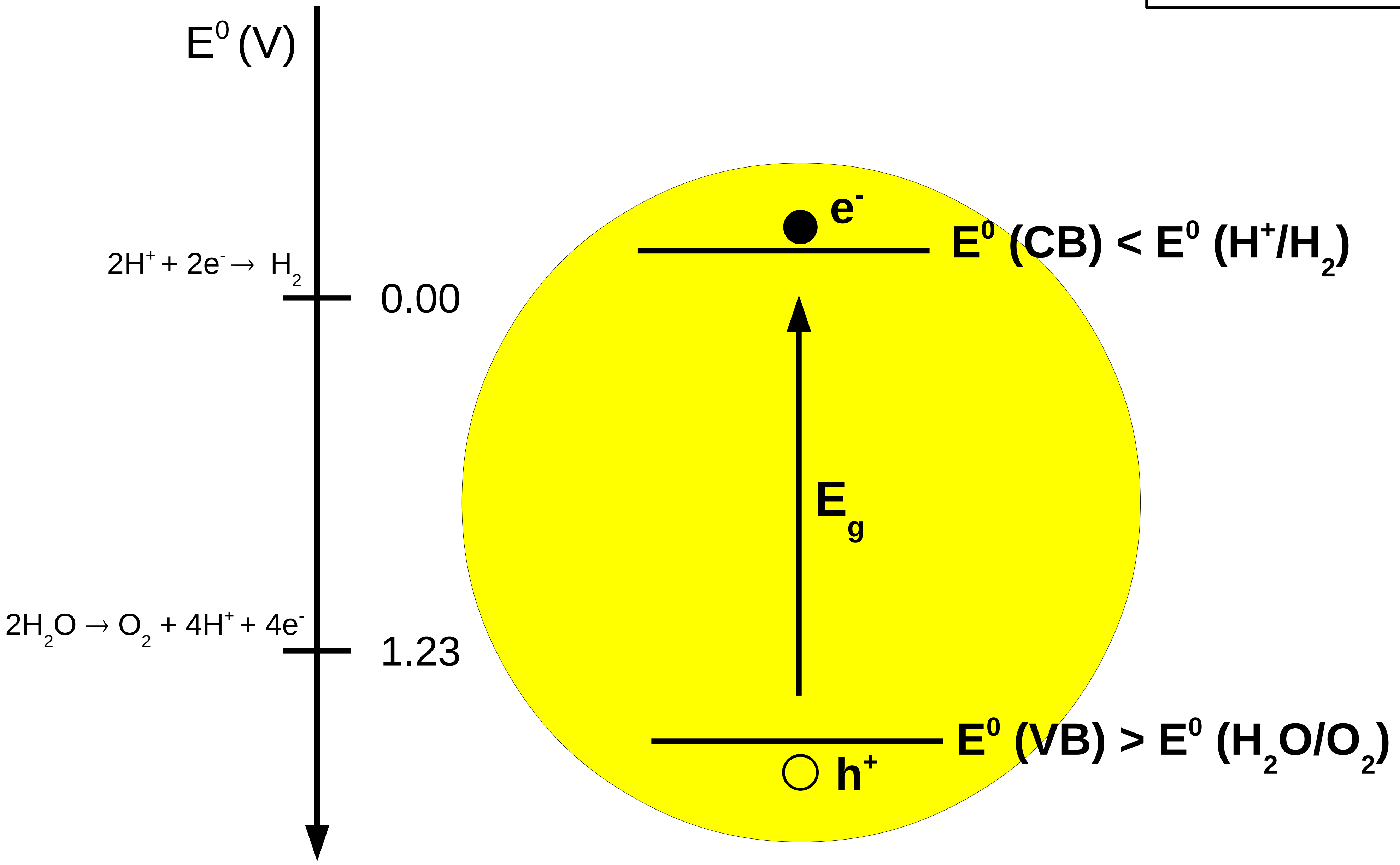
**$E^0$ (VB)**

$h^+$

# 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

**$e^-$**

**$E^0$ (CB) < $E^0$ ($H^+/H_2$)**

**$E_g$**

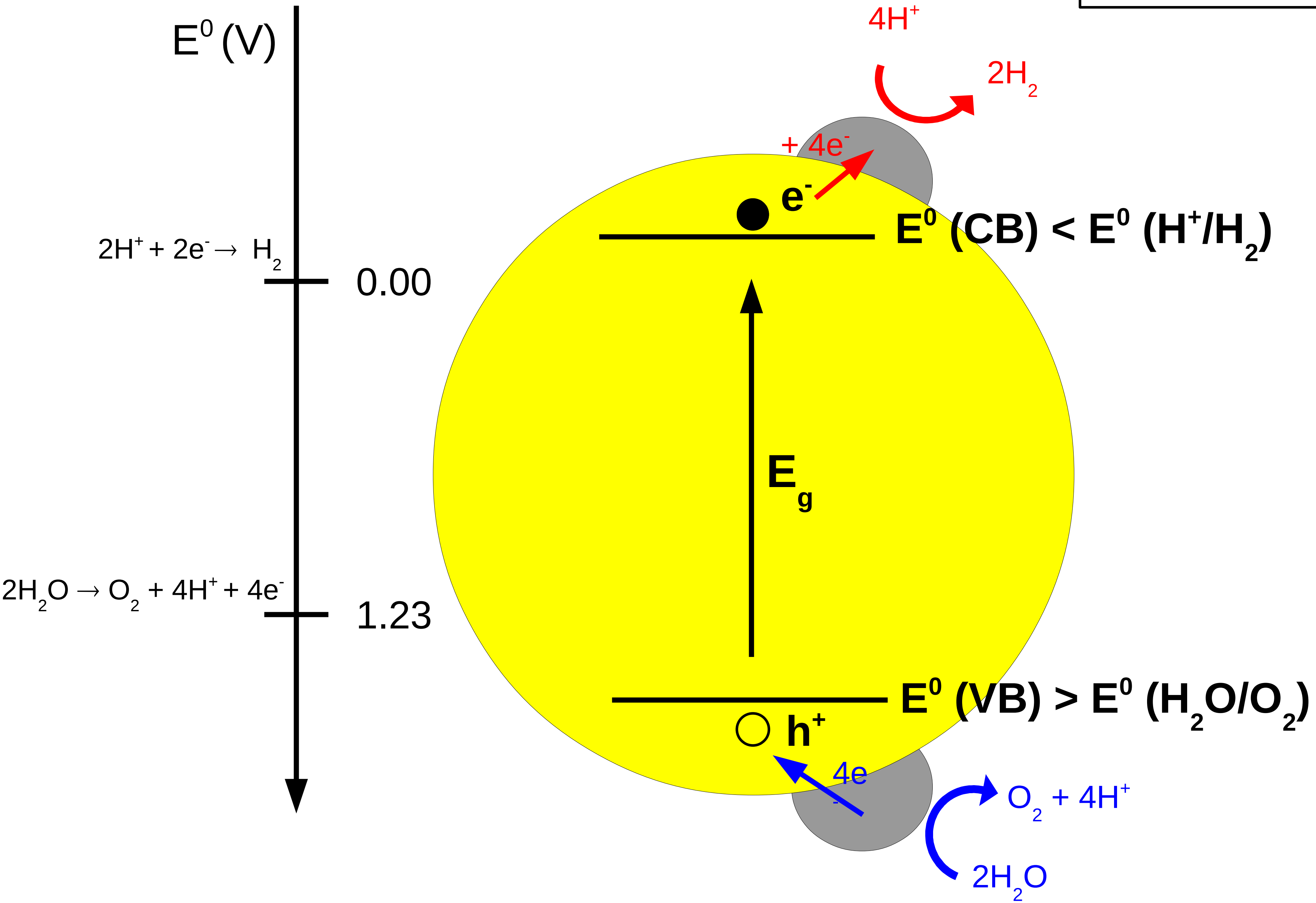
**$E^0$ (VB) > $E^0$ ($H_2O/O_2$)**

**$h^+$**

# Energy level alignment

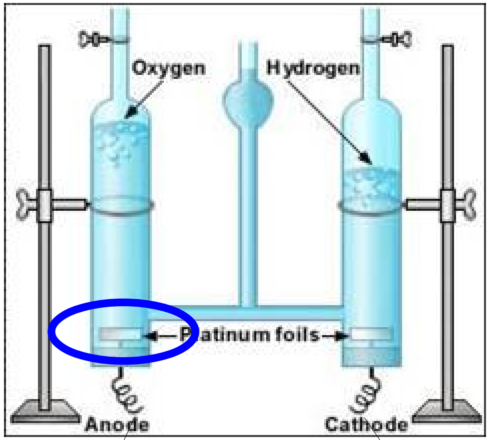
Higher $E^0$ : reduction
Lower $E^0$: oxidation

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

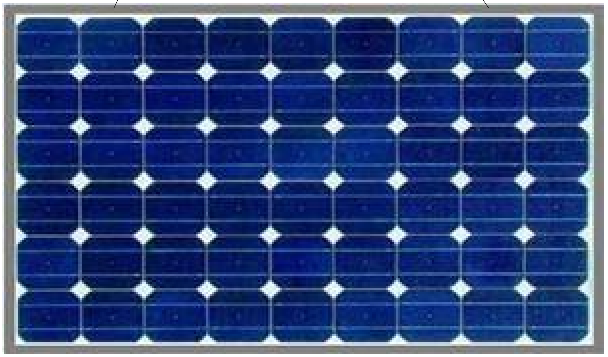


# Artificial photosynthesis: using light to make fuels

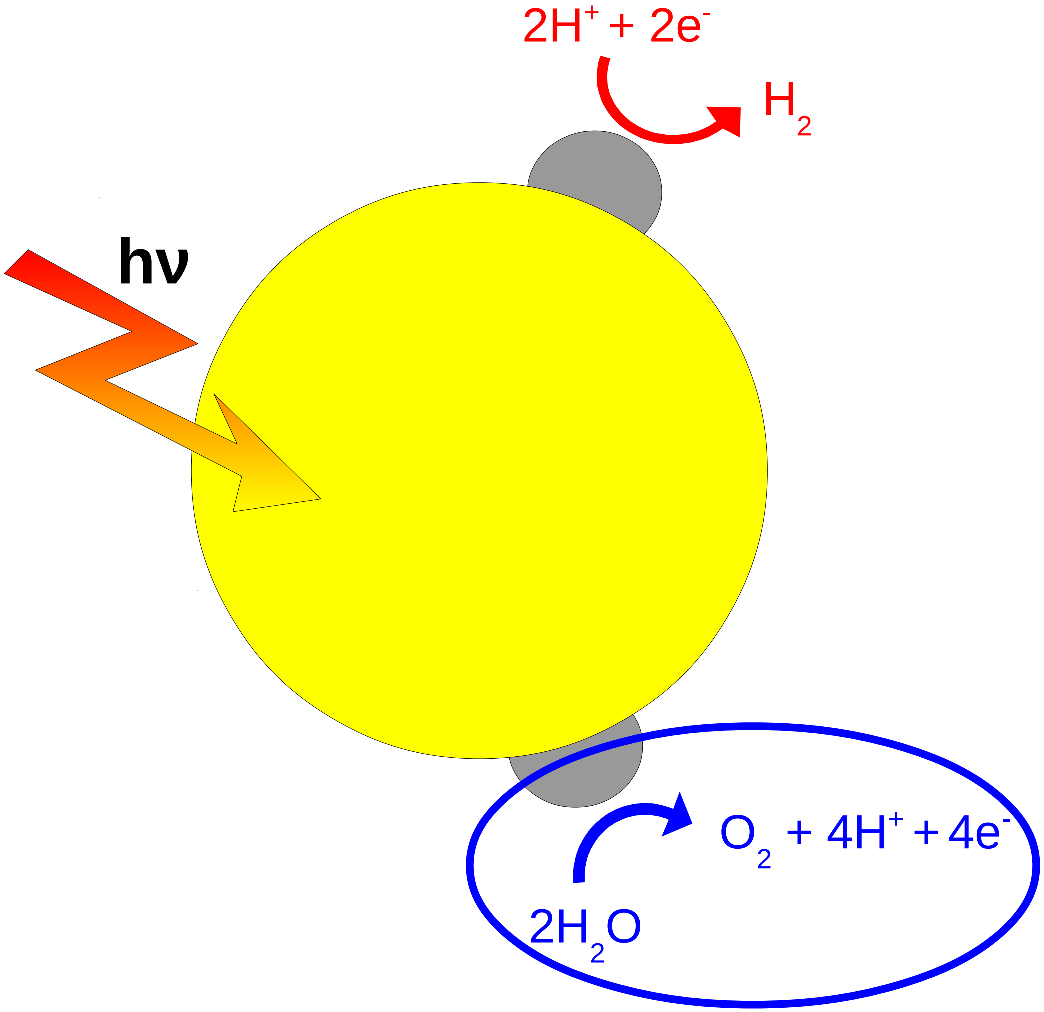
*Electrolyzer*



*PV module*



*Integrated photo-catalyst*



$2H^+ + 2e^-$ → $H_2$

$2H_2O$ → $O_2 + 4H^+ + 4e^-$

# 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

# Water oxidation: a 4 electron reaction

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

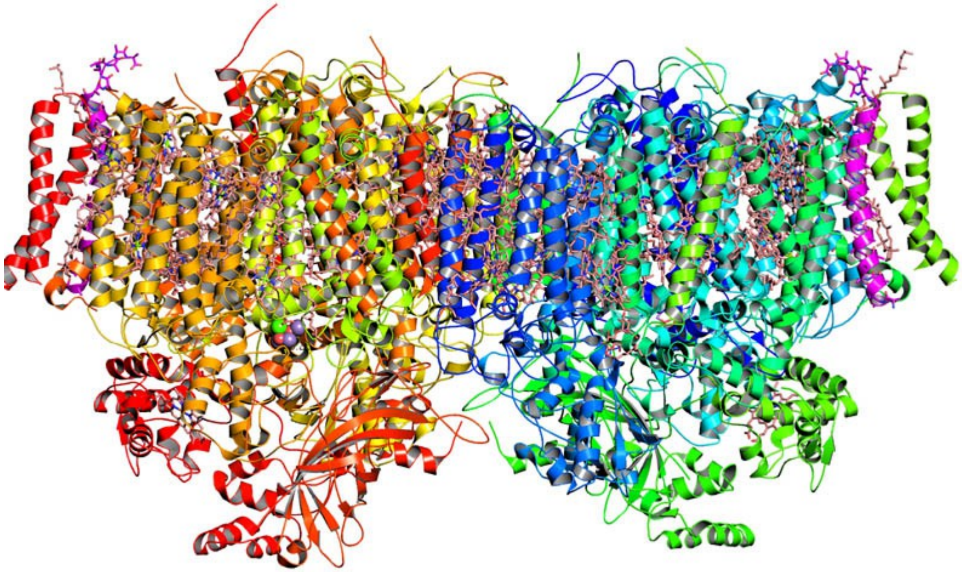
- Oxidizing water is thermodynamically demanding

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

1-electron mechanism: $H_2O \rightarrow OH^{\bullet} + H^+ + e^-$ $(\Delta G^0 = 2.31\ \text{V})$
2-electron mechanism: $2H_2O \rightarrow H_2O_2 + 2H^+ + 2e^-$ $(\Delta G^0 = 1.78\ \text{V})$
4-electron mechanism: $2H_2O \rightarrow O_2 + 4H^+ + 4e^-$ $(\Delta G^0 = 1.23\ \text{V})$

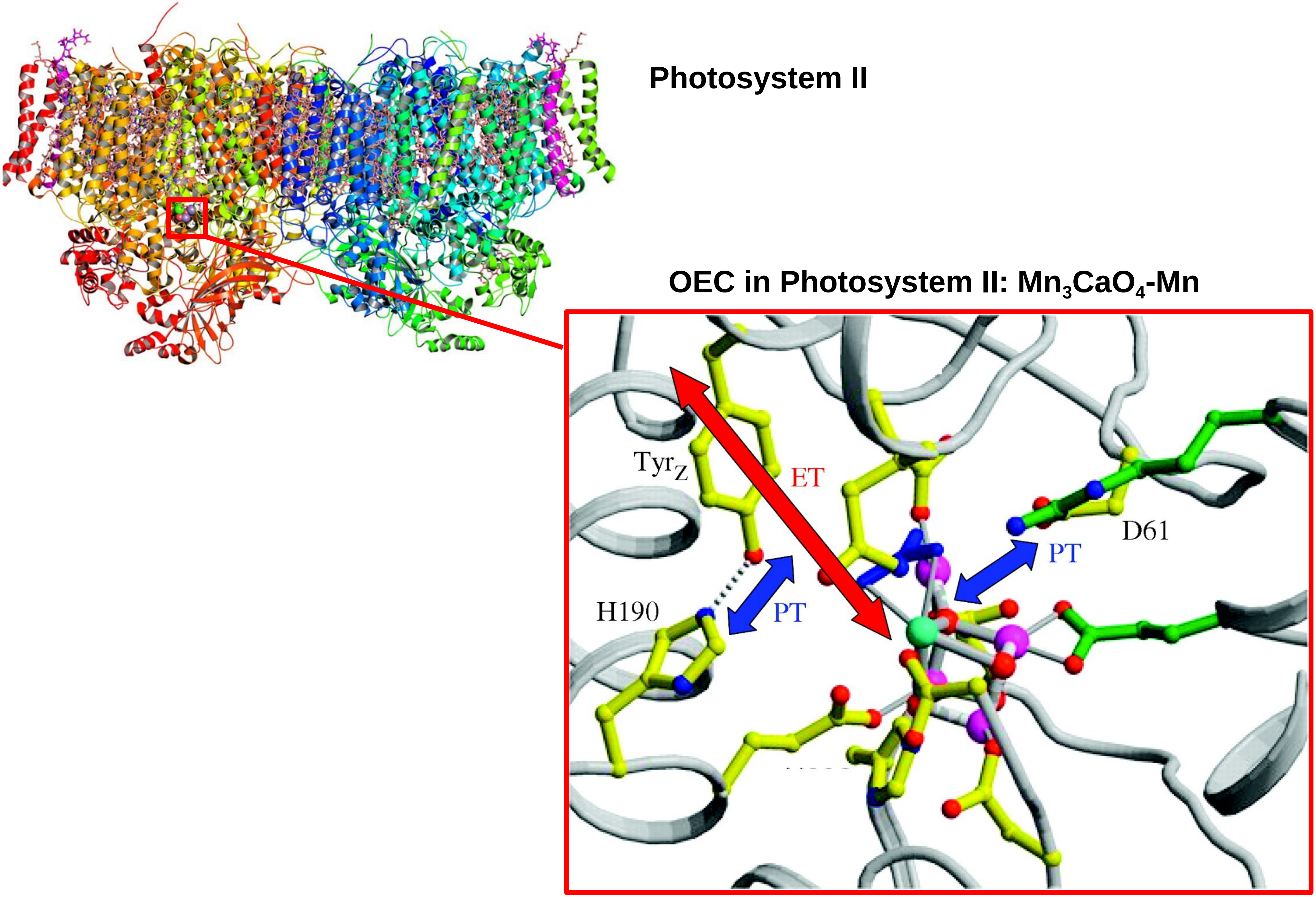
- We need **catalysts** that efficiently promote the 4-electron mechanism

# Oxygen evolving complex in PSII



Photosystem II

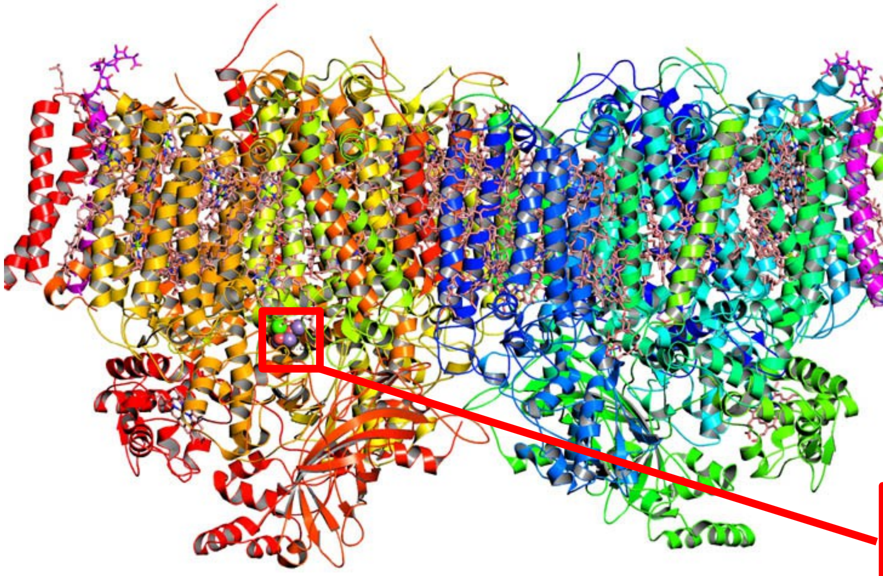
# Oxygen evolving complex in PSII



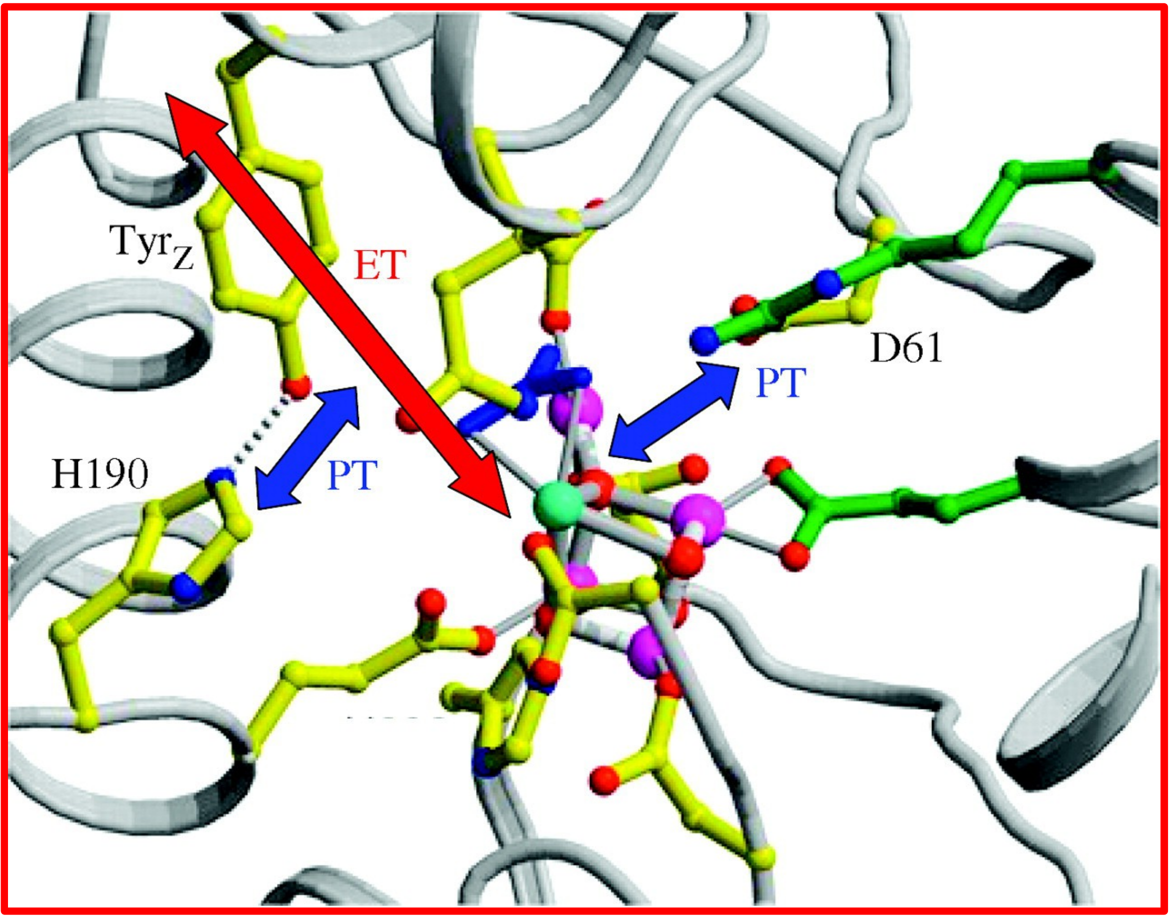
Photosystem II

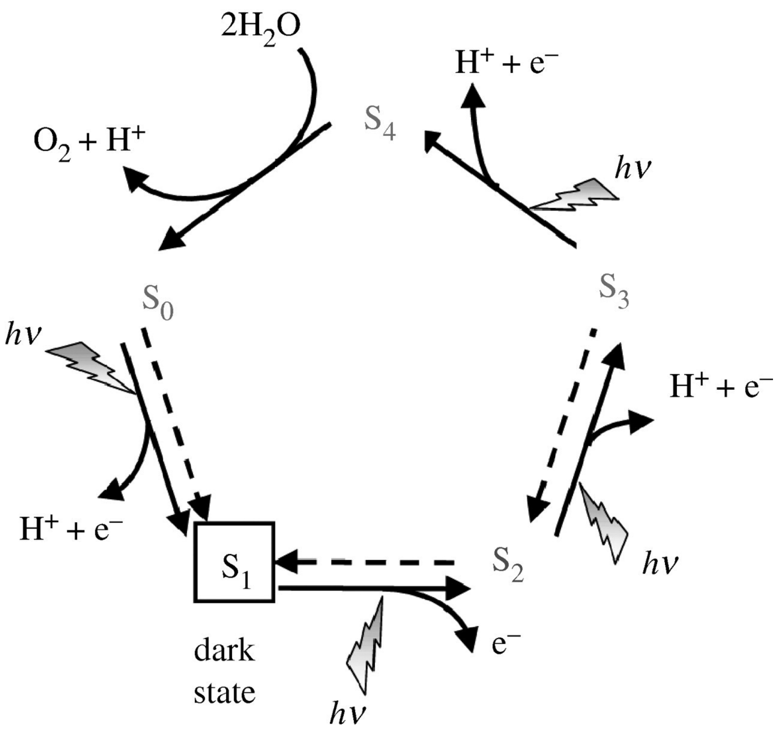
OEC in Photosystem II: $Mn_3CaO_4$-Mn

# Oxygen evolving complex in PSII



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



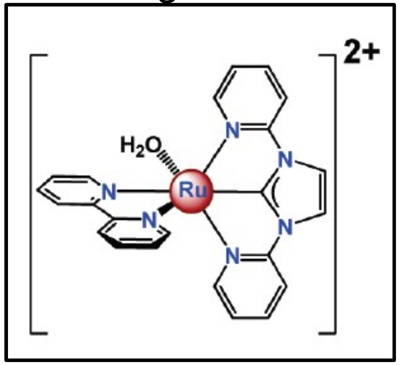


$$2H_2O \rightarrow O_2 + 4H^+ + 4e^-$$

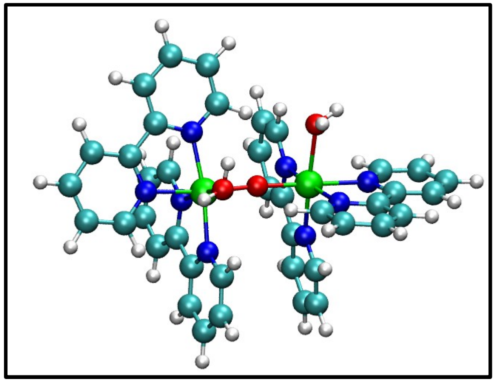
# Artificial Catalysts for OER

**Homogeneous catalysts for OER**

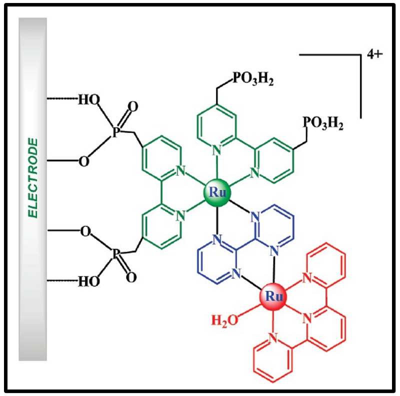
*single-site*



*multi-sites*



*anchored on electrodes*



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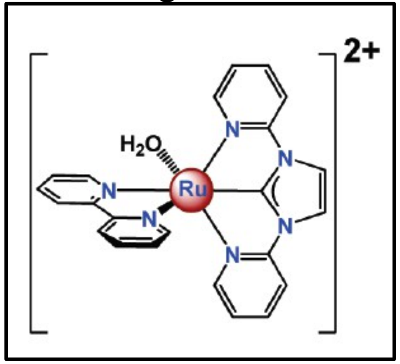
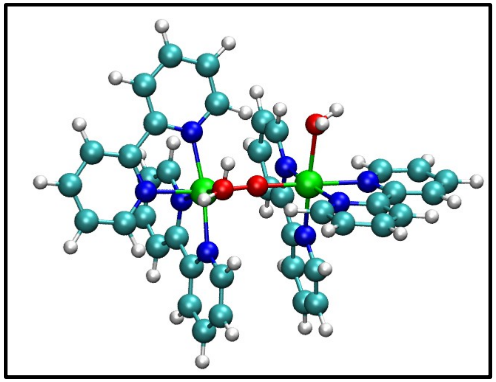


*multi-sites*



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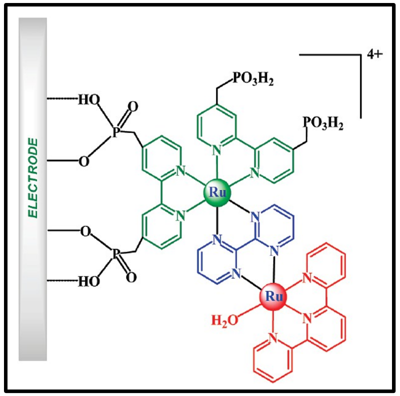
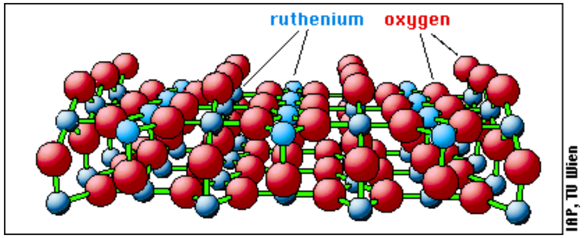
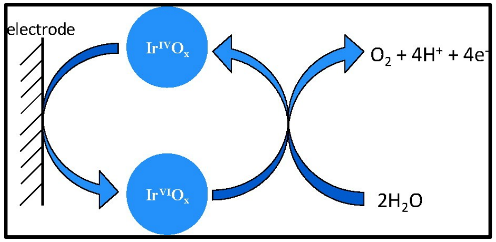


**Heterogeneous catalysts for OER**

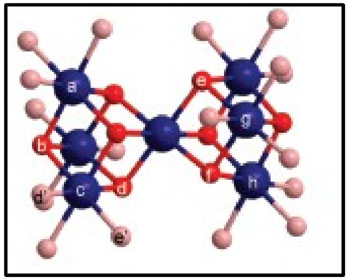
*$RuO_2$, $IrO_2$ surfaces*



*$IrO_2$ nanoparticles*



*Co-Pi amorphous*



# Artificial Catalysts for OER

**Homogeneous catalysts for OER**

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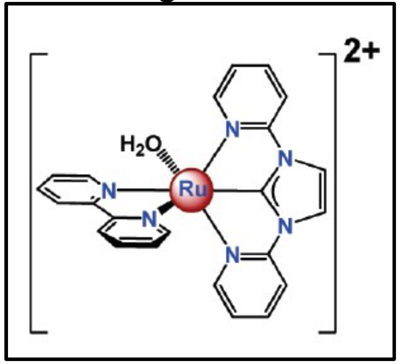

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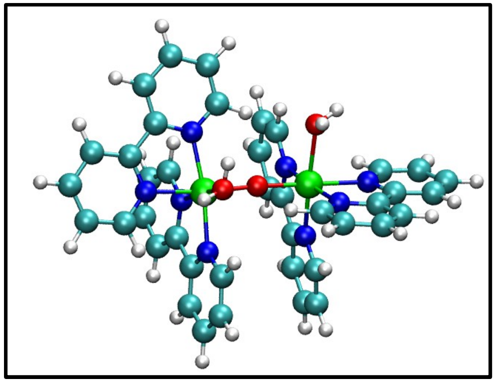
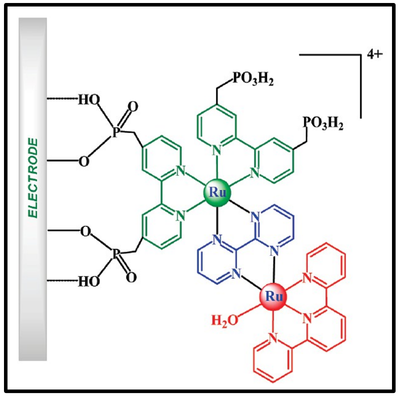
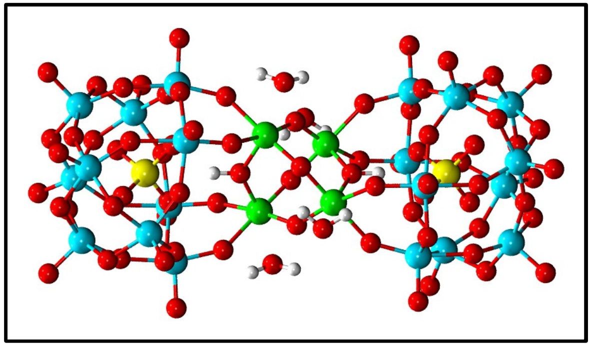


*anchored on electrodes*



*Ru-, Co-POM*



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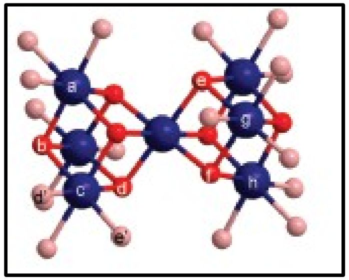
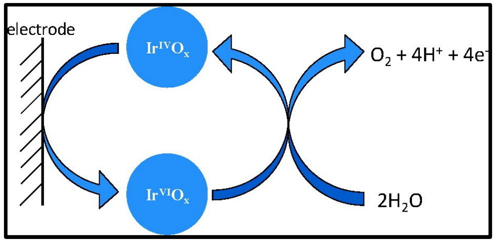
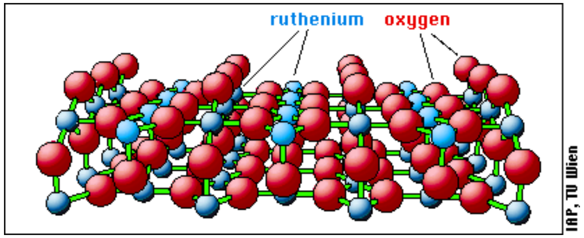


*$IrO_2$ nanoparticles*



*$RuO_2$, $IrO_2$ surfaces*

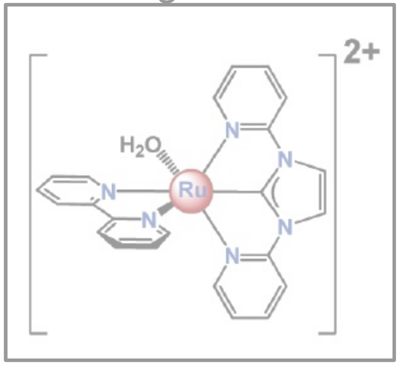


**Heterogeneous catalysts for OER**

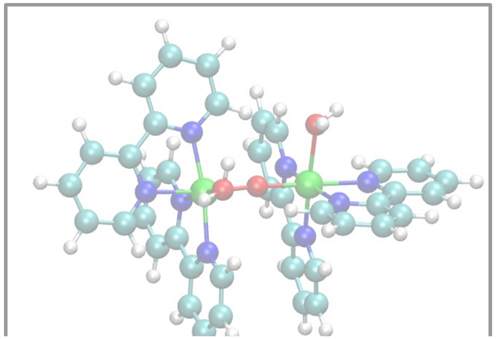
# Artificial Catalysts for OER

**Homogeneous catalysts for OER**

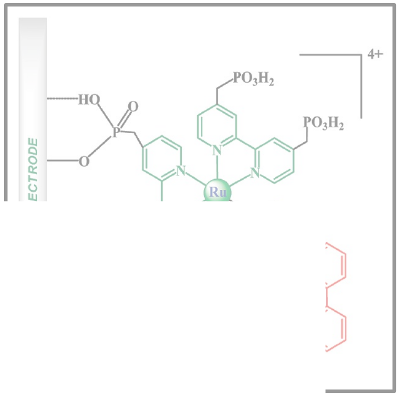
*single-site*



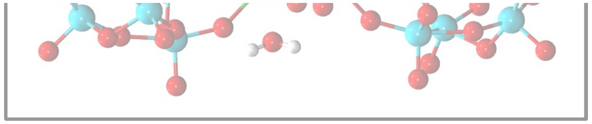
*multi-sites*



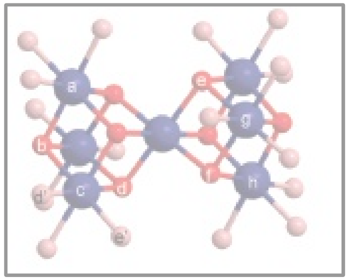
*anchored on electrodes*



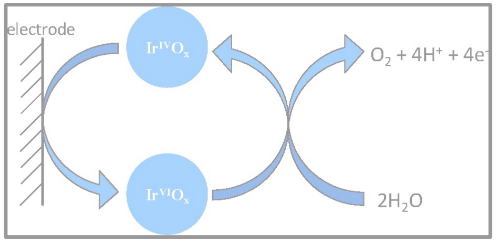
- **Mechanism of water oxidation?**
- **What determines the efficiency of a catalyst ?**



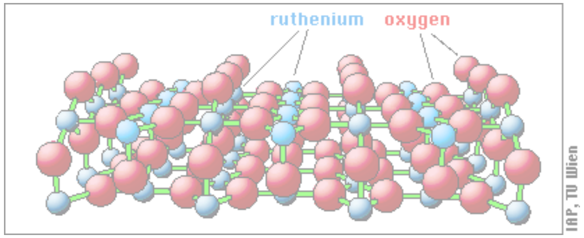
*Co-Pi amorphous*



*$IrO_2$ nanoparticles*

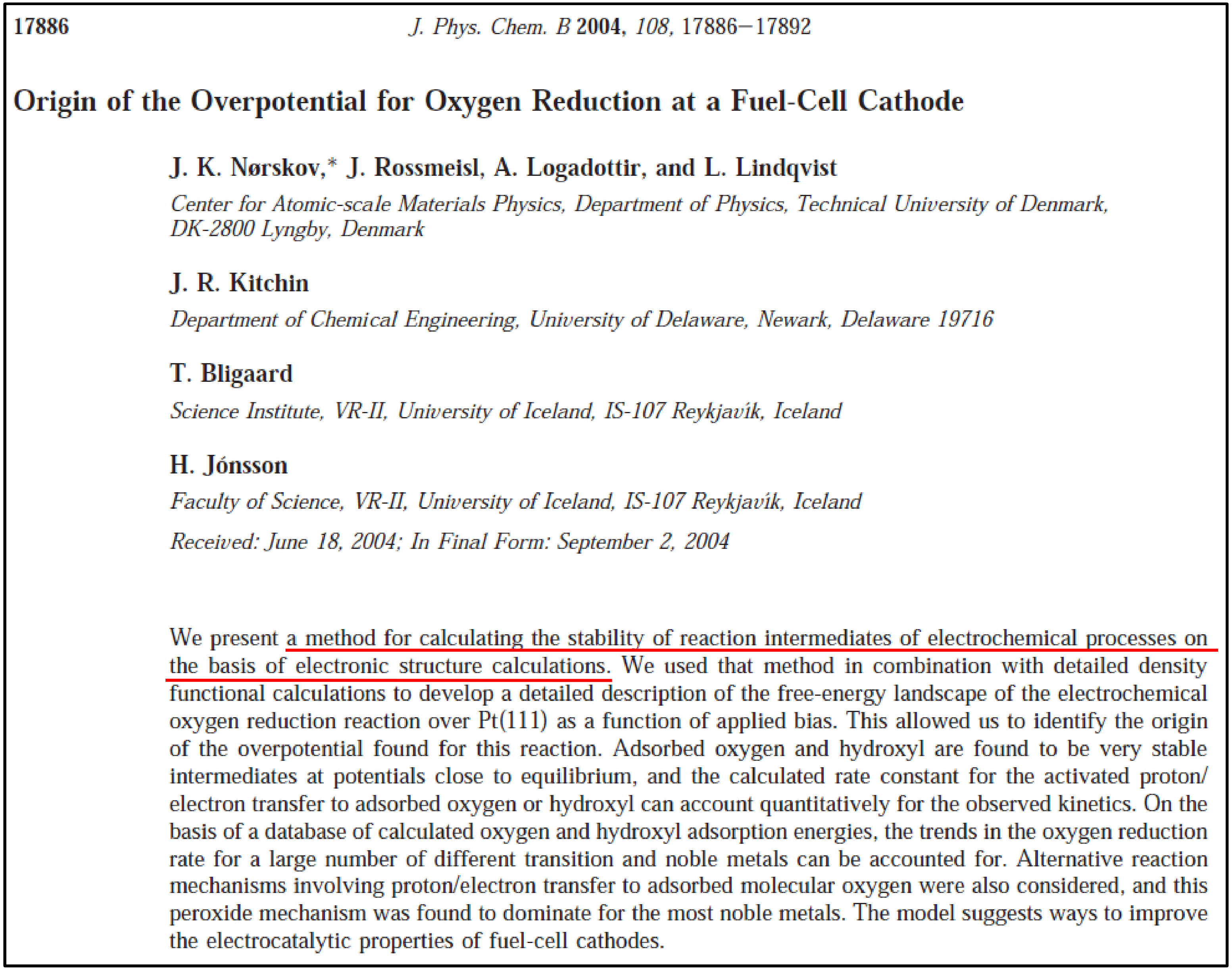


*$RuO_2$, $IrO_2$ surfaces*



**Heterogeneous catalysts for OER**

# 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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*Received: June 18, 2004; In Final Form: September 2, 2004*

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:

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

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

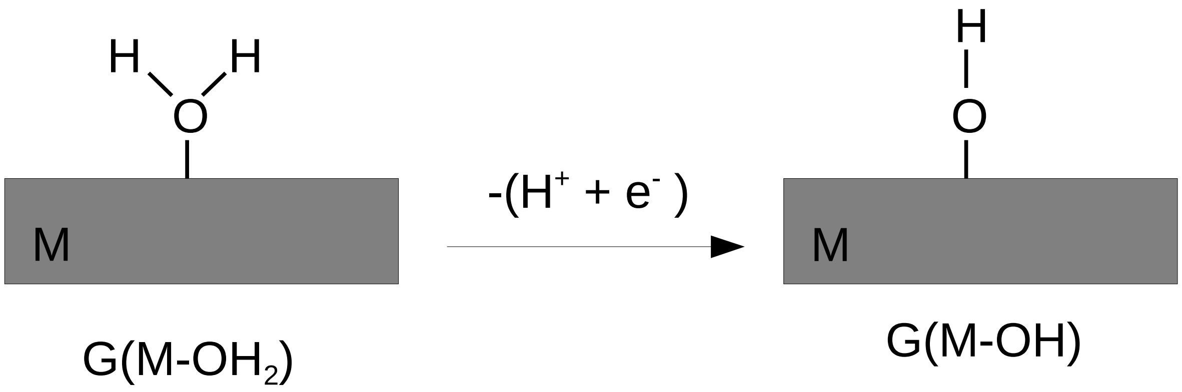
Therefore, using NHE as reference, we can compute the chemical potential of the $(H^+ + e^-)$ pair from the chemical potential of gas phase $H_2$

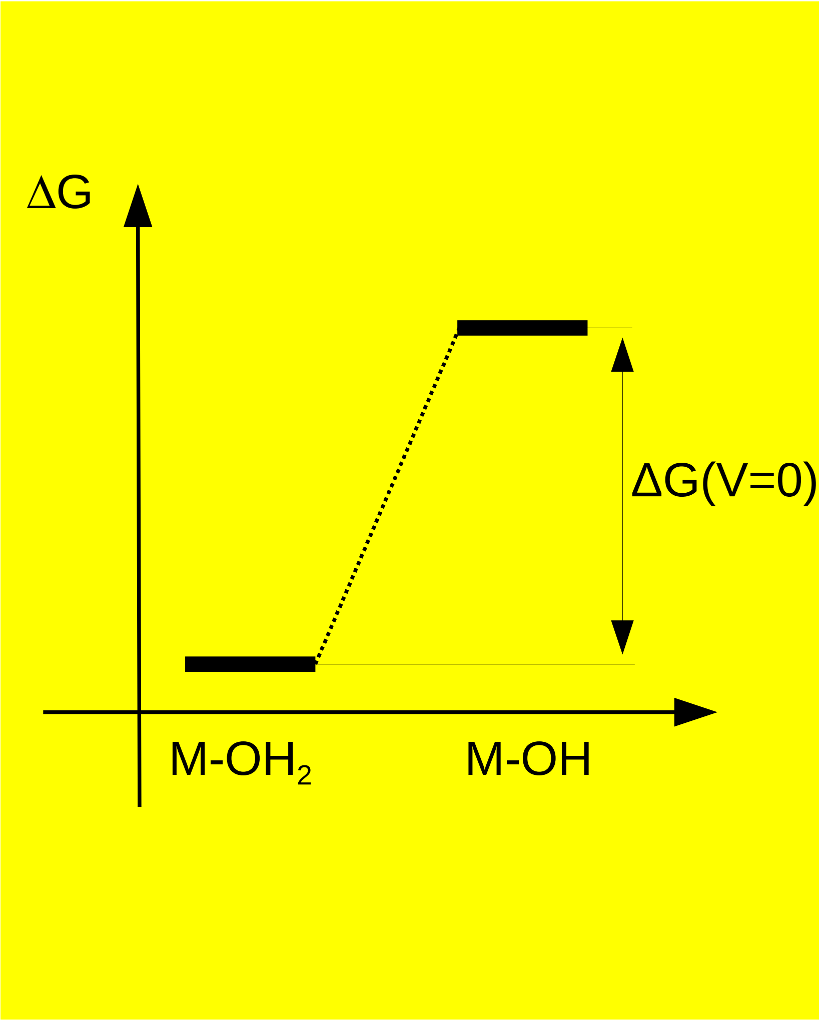
**We do need to estimate $\mu(H^+) + \mu(e^-)$ separately**

# 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:

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





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

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

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

# Nørskov's approach: Computational NHE

***Finite V***:

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

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

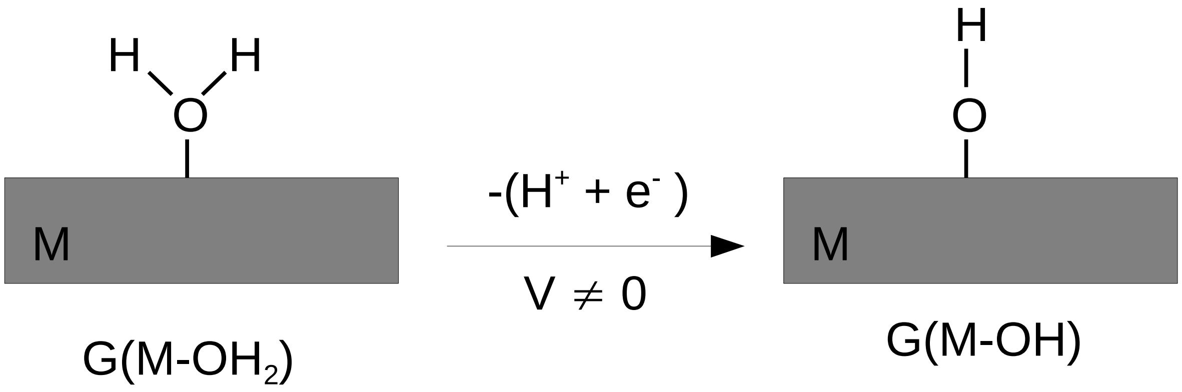
$\mu(H^+) + \mu(e^-) = 1/2\mu(H_2) - eV$

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

# Nørskov's approach: Computational NHE

***Example:*** $V \neq 0$

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



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

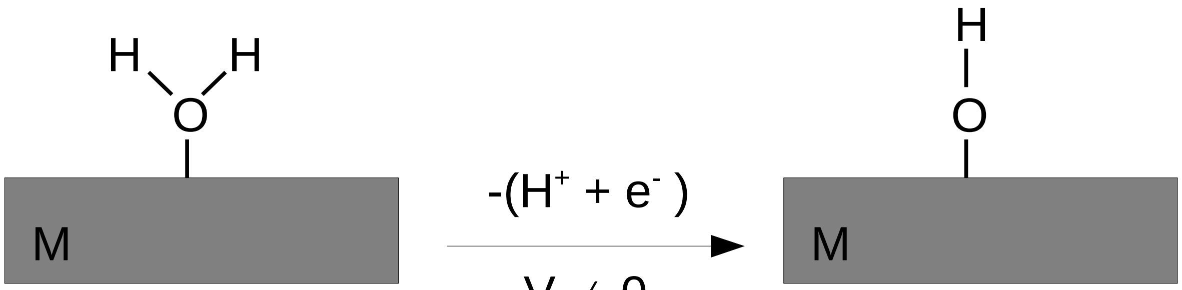
$$= G(M\text{-}OH_2) + 1/2\mu(H_2) - eV - G(M\text{-}OH)$$

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

# Nørskov's approach: Computational NHE

***Example:*** $V \neq 0$

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



$G(M\text{-}OH_2)$

$G(M\text{-}OH)$

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

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

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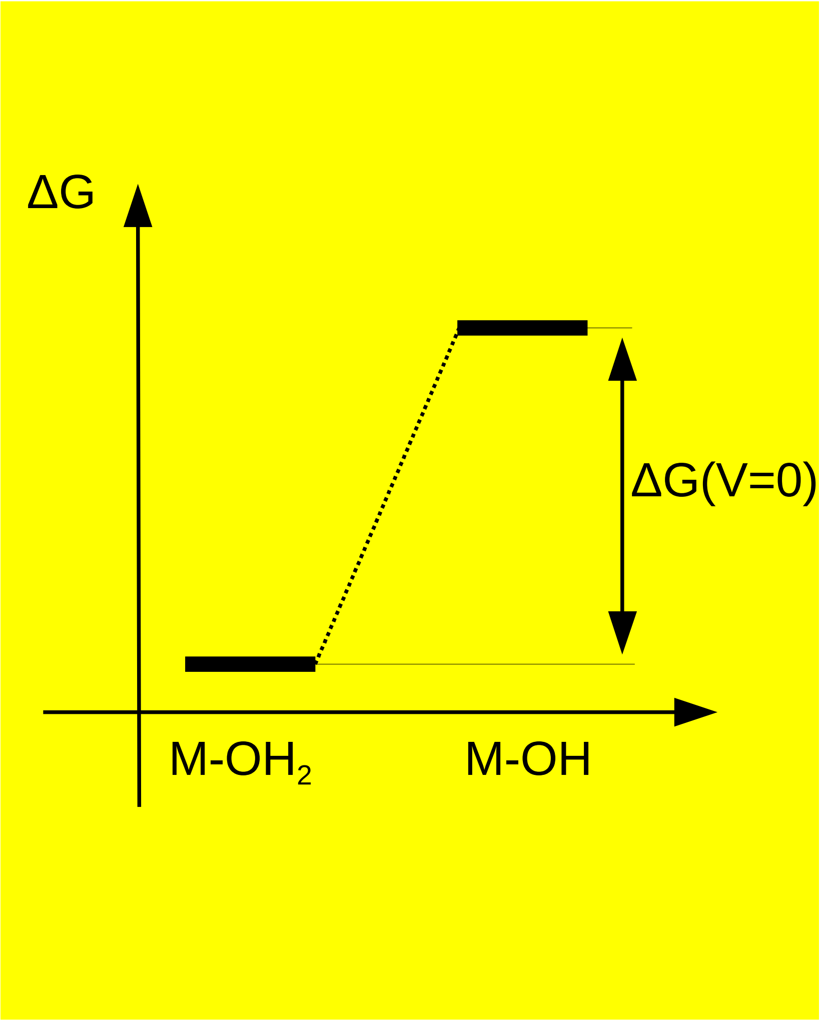
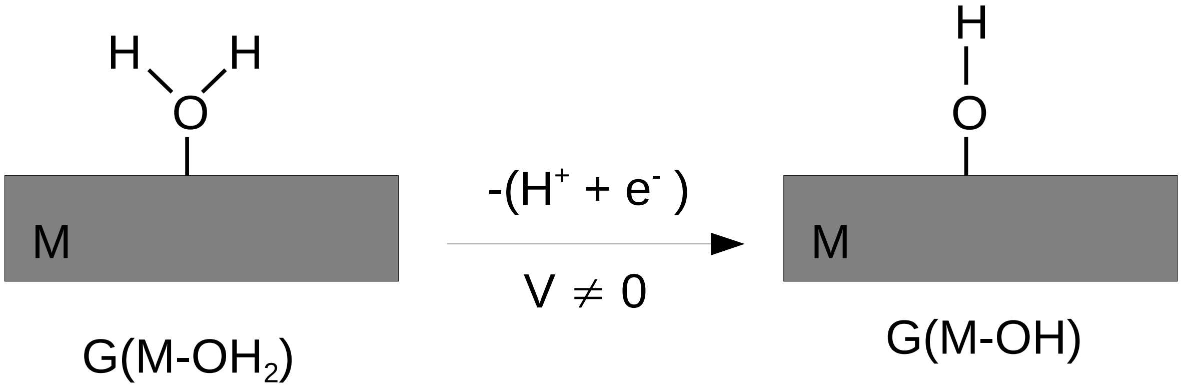


# Nørskov's approach: Computational NHE

***Example:*** $V \neq 0$

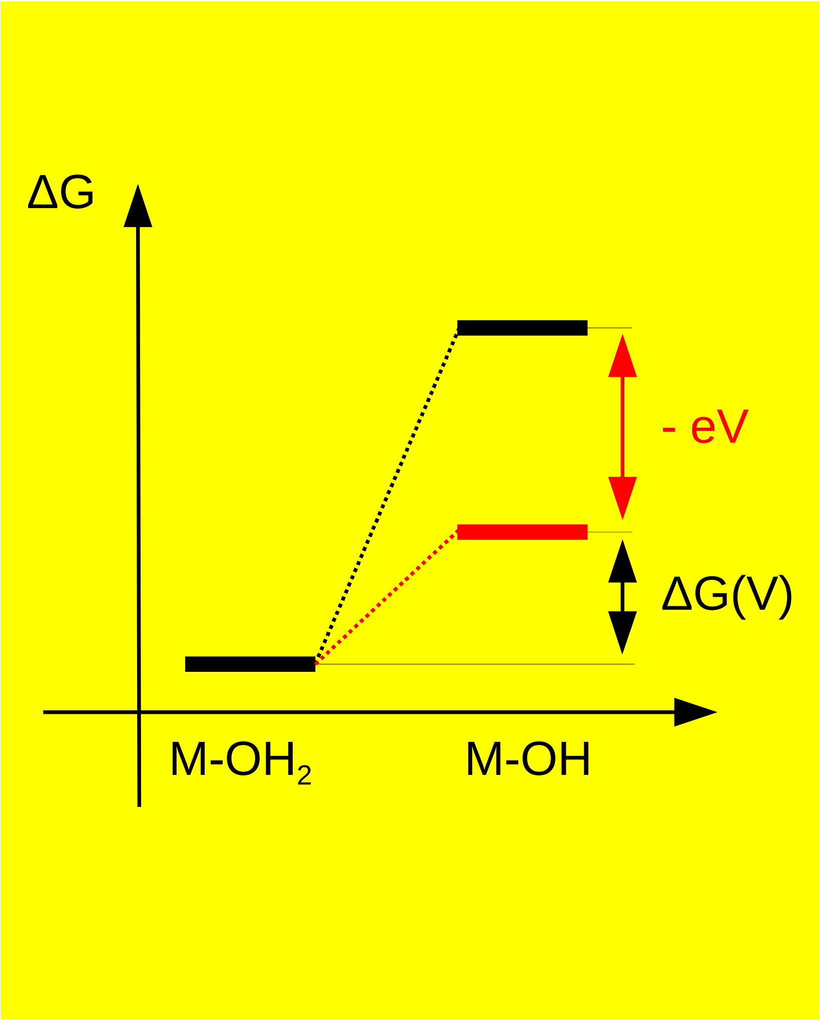
$M\text{-}OH_2 \rightarrow M\text{-}OH + H^+ + e^-$



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

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

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



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

# Nørskov's approach: Computational NHE

***Finite pH***:

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

$pH \neq 0$ $\mu(H^+) \rightarrow \mu(H^+) - 2.303\ k_BT \times pH$

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

# 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:

- $\Delta E$ is the reaction energy (*DFT calculation*)
- $\Delta ZPE$ is the change in zero-point-energy (*normal mode analysis*)
- $\Delta S$ is the change in entropy (*from thermochemical tables*)

***Solvent:*** the effect of a few layers of water have been studied (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

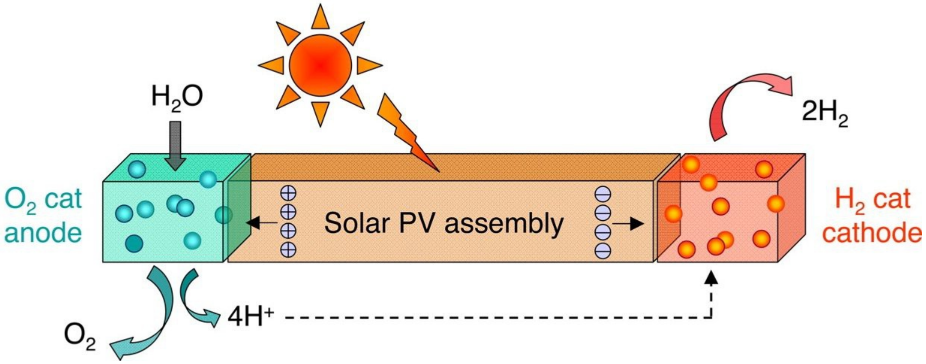
# Nørskov's approach: Computational NHE

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

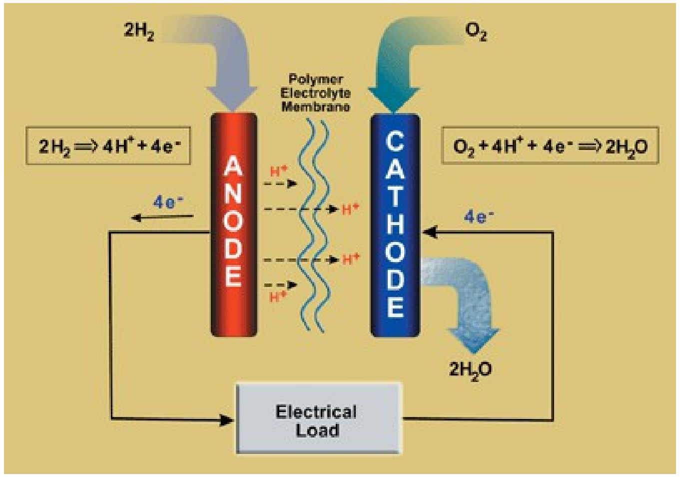
$2H^+ + 2e^- \rightarrow H_2$

## *PEM Fuel cells*

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

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

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



# OER and ORR

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

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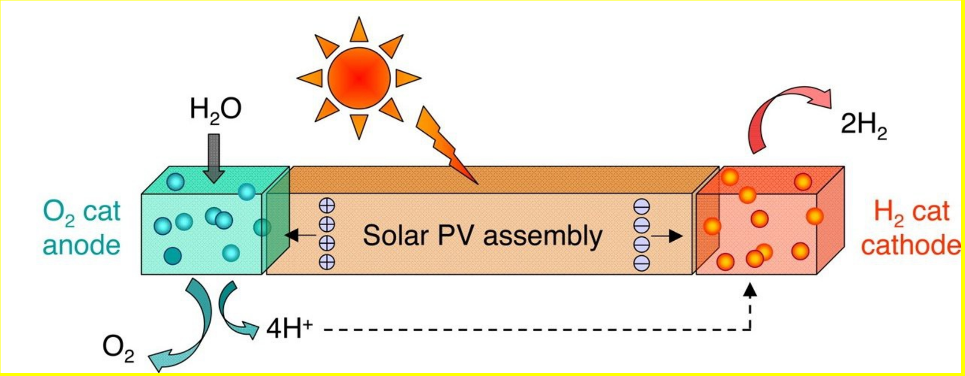

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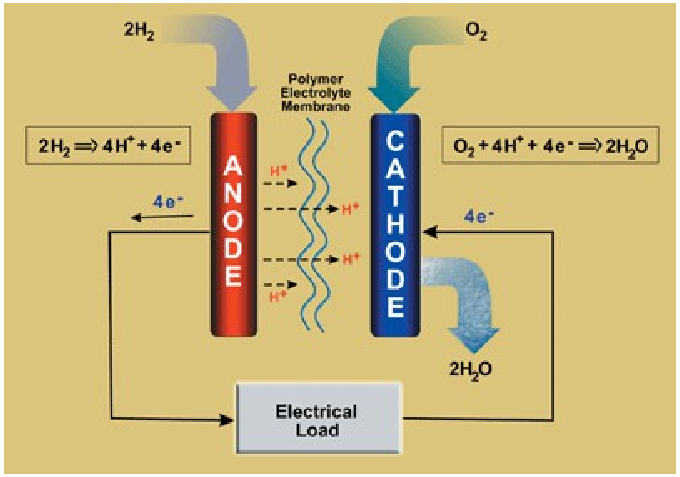
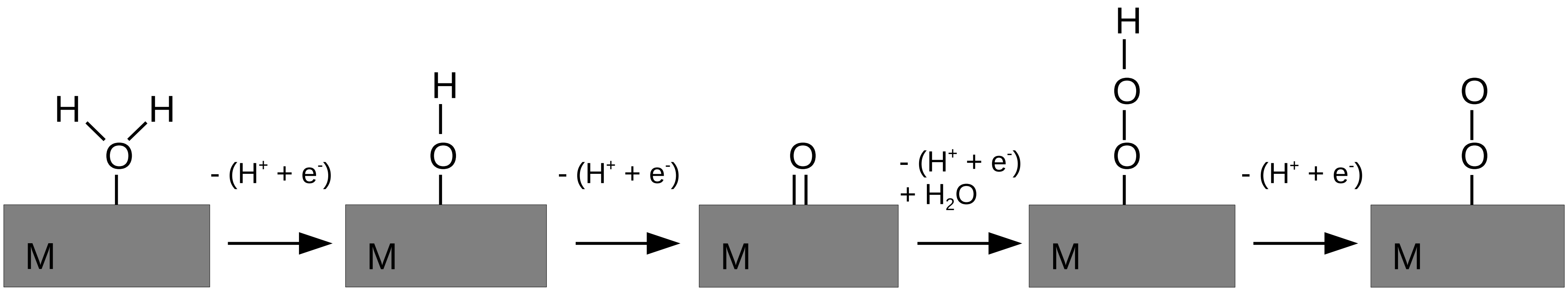


# Electrolysis of water on metal surfaces



*Investigated mechanism (OER)*

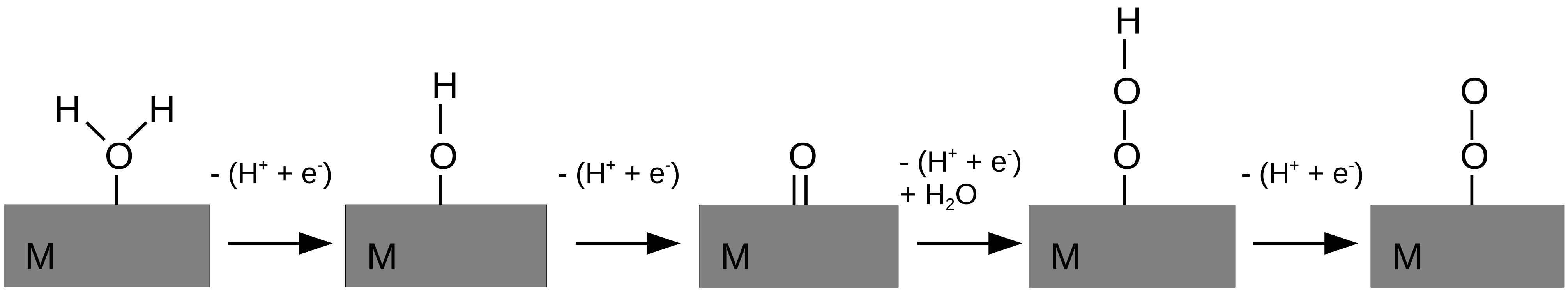
$H_2O + * \rightarrow OH^* + (H^+ + e^-)$

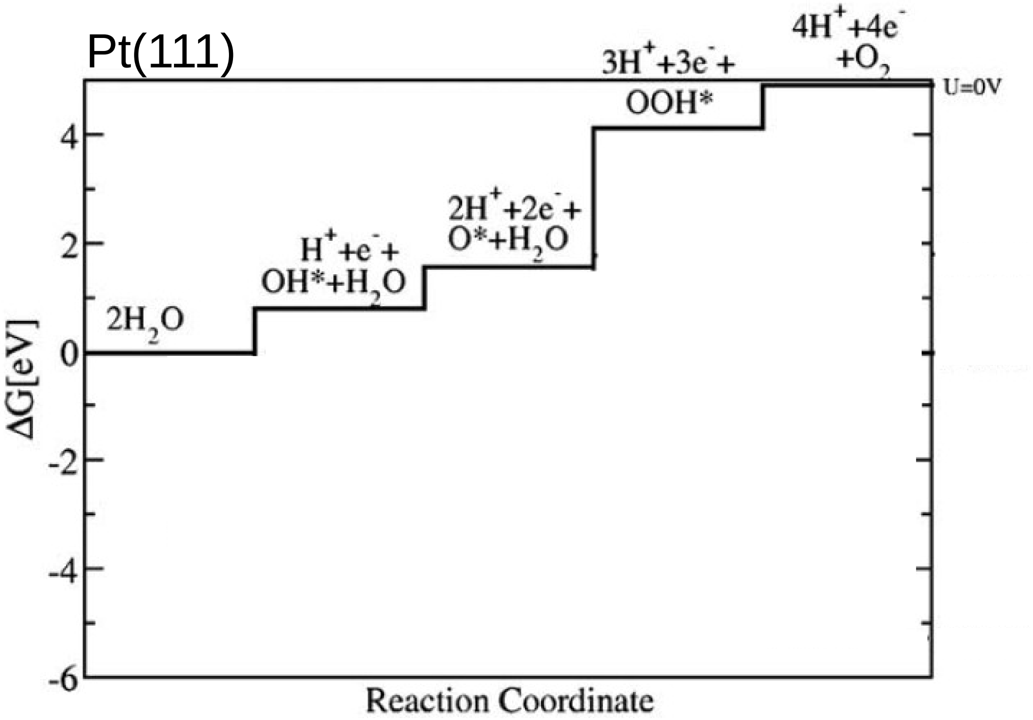
$OH^* \rightarrow O^* + (H^+ + e^-)$

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

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

# Electrolysis of water on metal surfaces




Pt(111)

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

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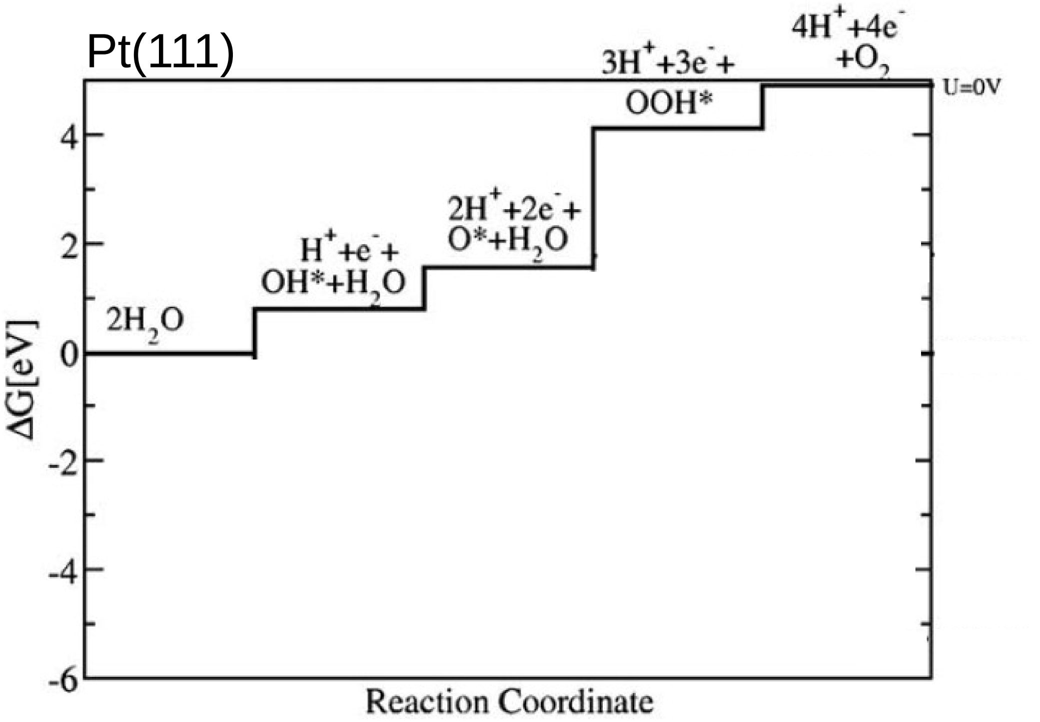
$O^* + H_2O \rightarrow OOH^* + (H^+ + e^-)$

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

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

# Electrolysis of water on metal surfaces

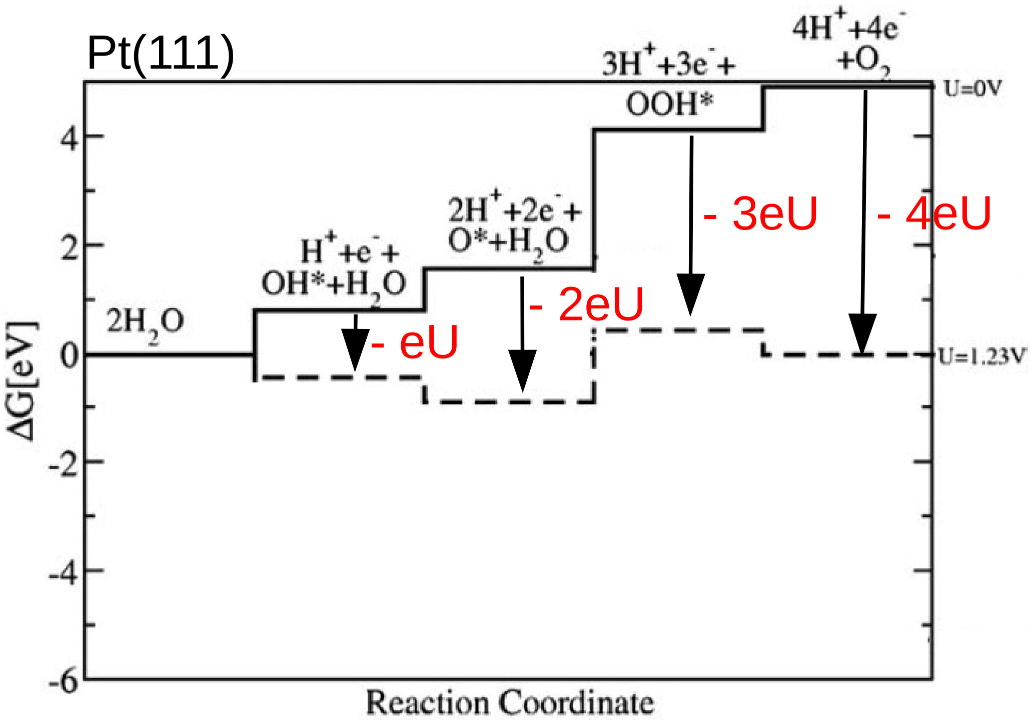
$2H_2O \rightarrow O_2 + 4H^+ + 4e^-$      $\Delta G^0 = 4.92$ V



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

# Electrolysis of water on metal surfaces

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



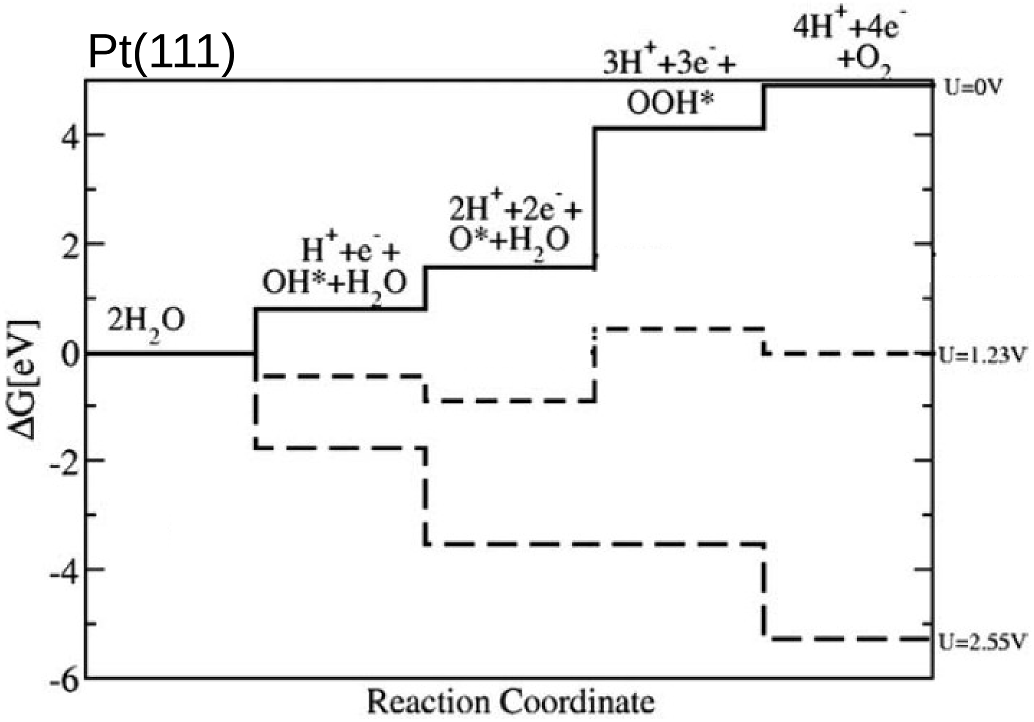
- U = 1.23 V is not sufficient to oxidize water on Pt(111): OOH* is too weakly bound compared to O*

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

# Electrolysis of water on metal surfaces

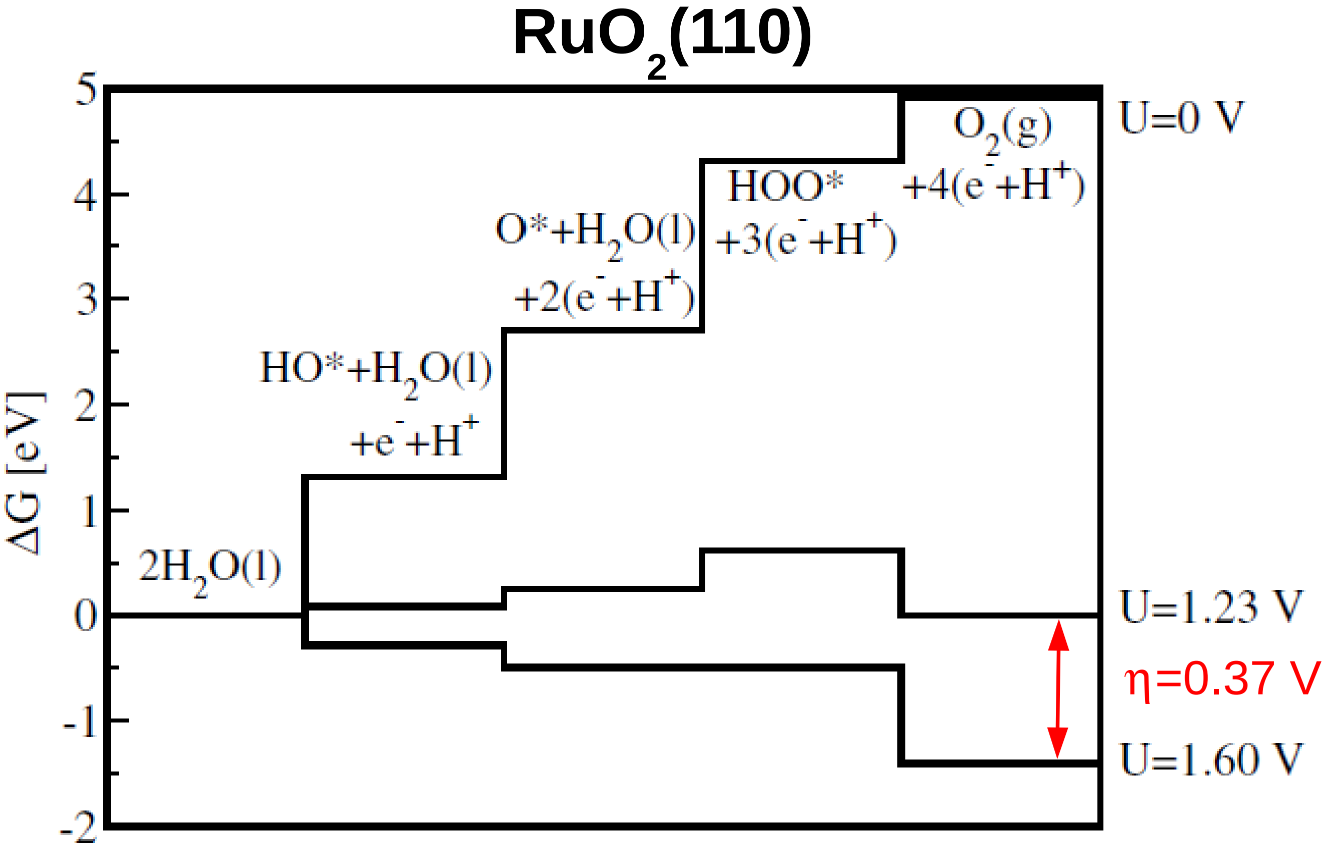
$2H_2O \rightarrow O_2 + 4H^+ + 4e^- \qquad \Delta G^0 = 4.92\ V$

Pt(111)



- 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 $\Delta G$=1.23 eV (1.23×4=4.92 eV)

# Electrolysis of water on oxide surfaces

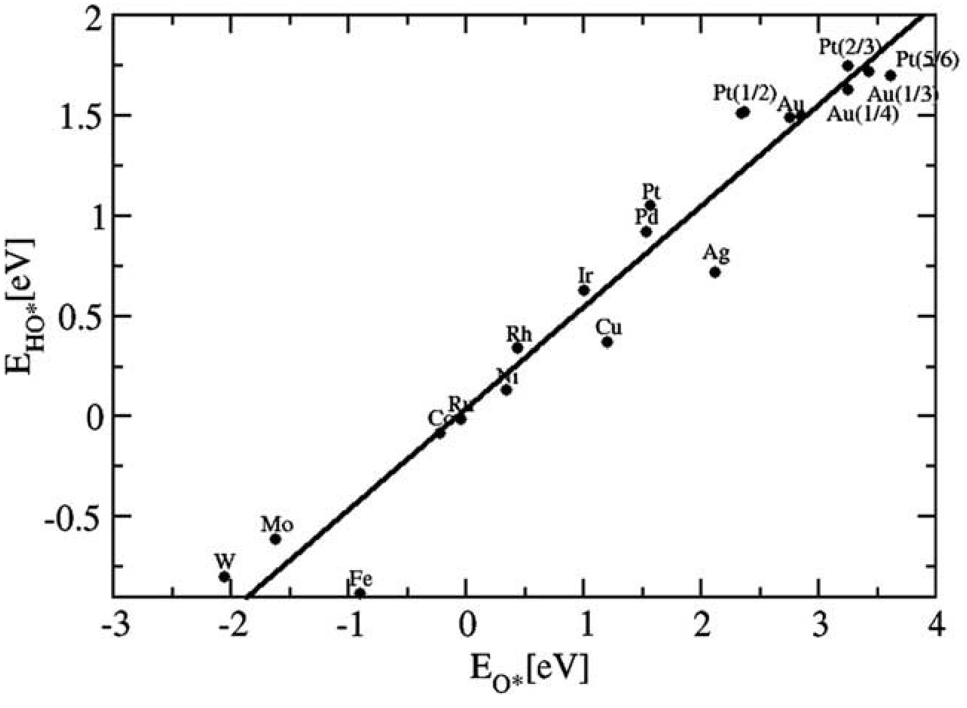


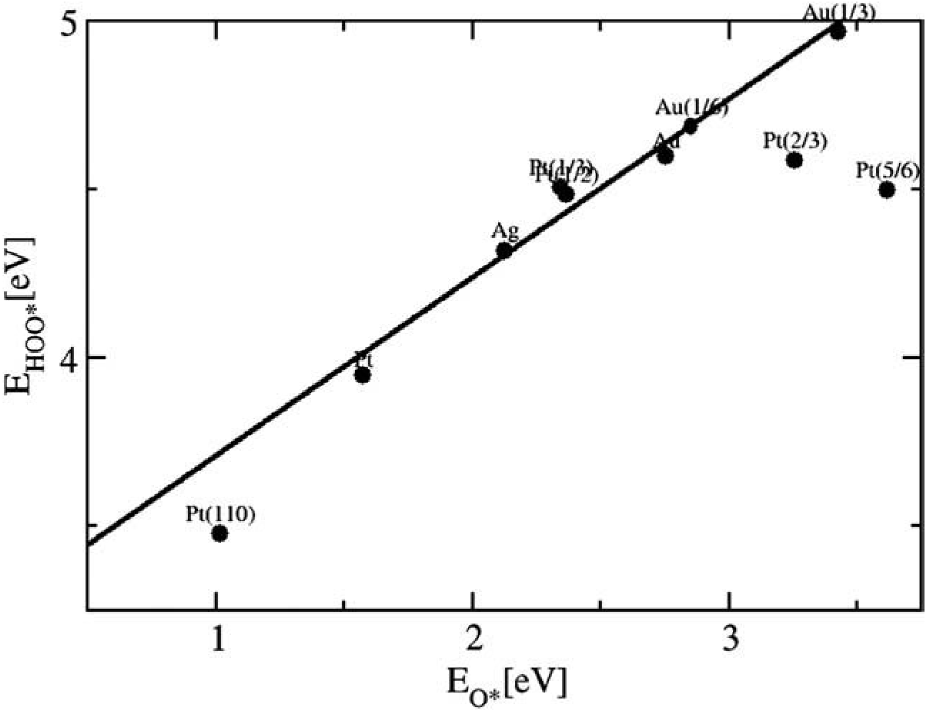
**$RuO_2(110)$**

- 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)

# Electrolysis of water on metal surfaces

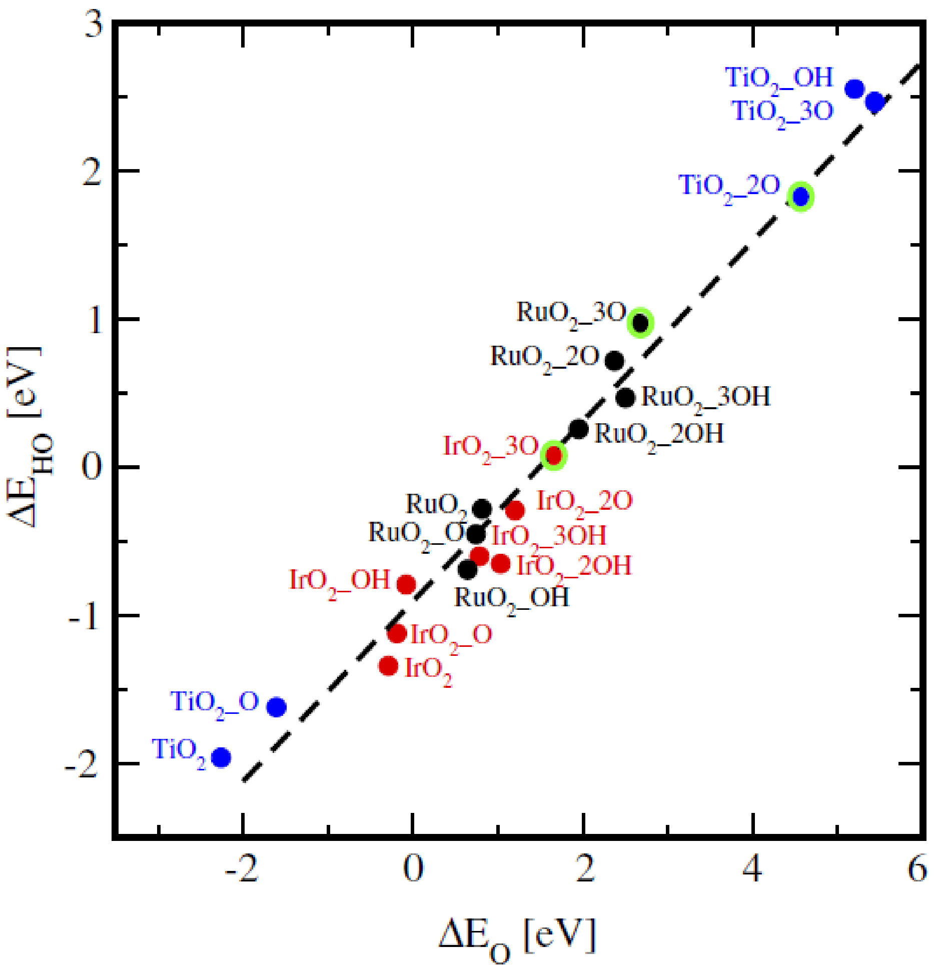


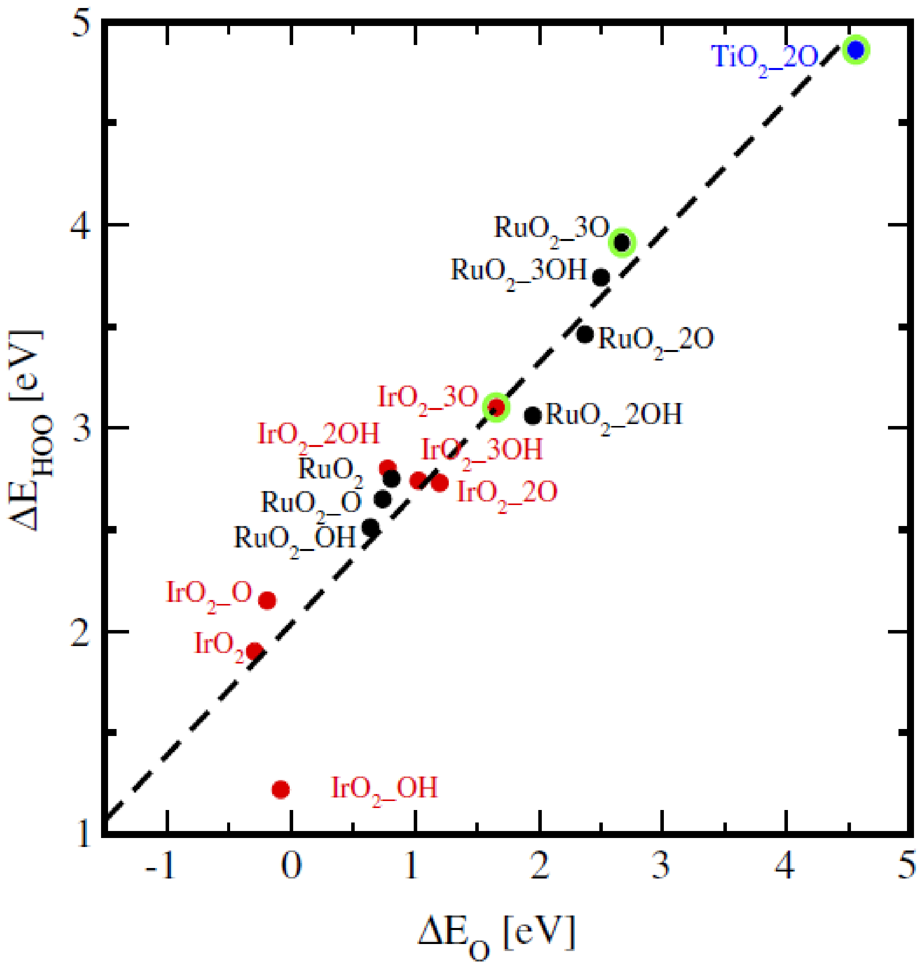


**$E_{O*}$, $E_{OH*}$ and $E_{OOH*}$ are approximately linearly related**

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

# Electrolysis of water on oxide surfaces





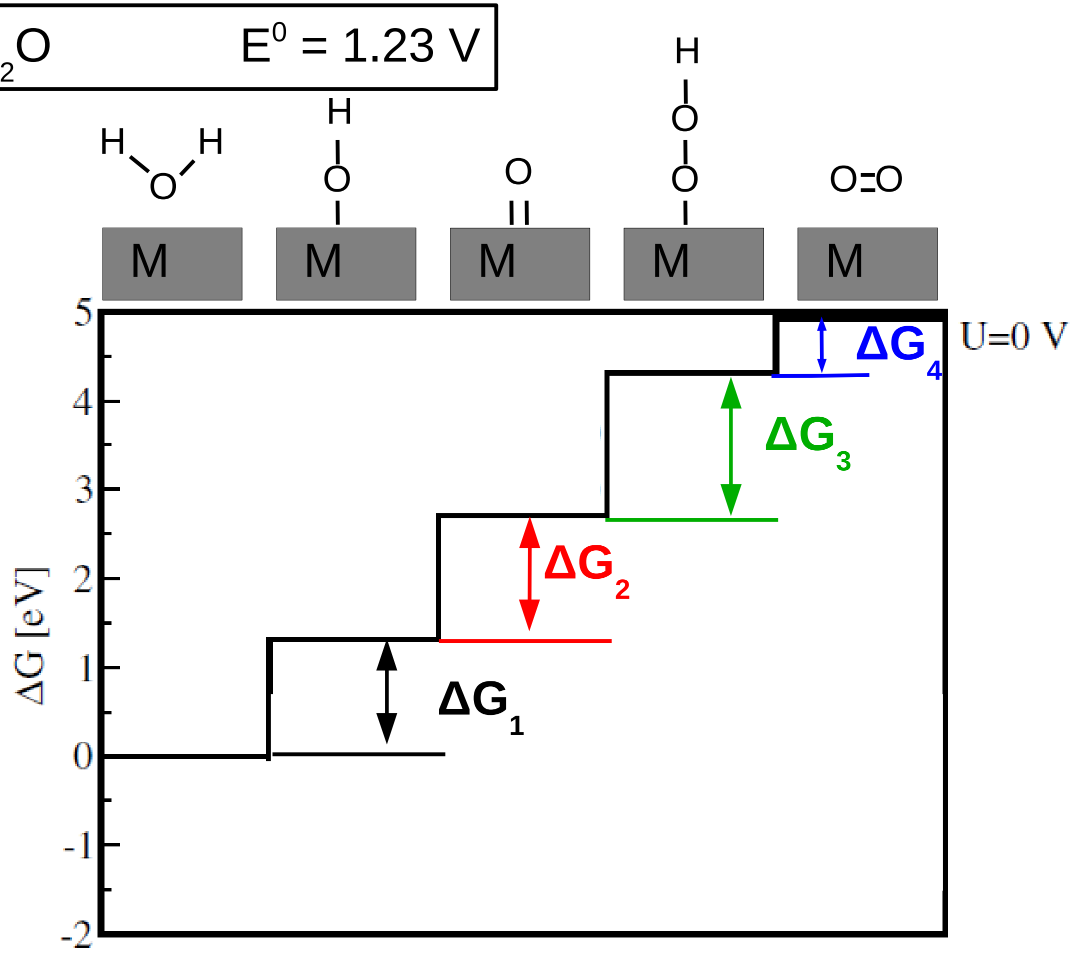
- Also in this case $E_{O*}$, $E_{OH*}$ and $E_{OOH*}$ are approximately linearly related

- $\Delta E_O = 0$ eV is defined by the equilibrium: $H_2O \leftrightarrow O^* + H_2$

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

# Electrolysis of water on oxide surfaces

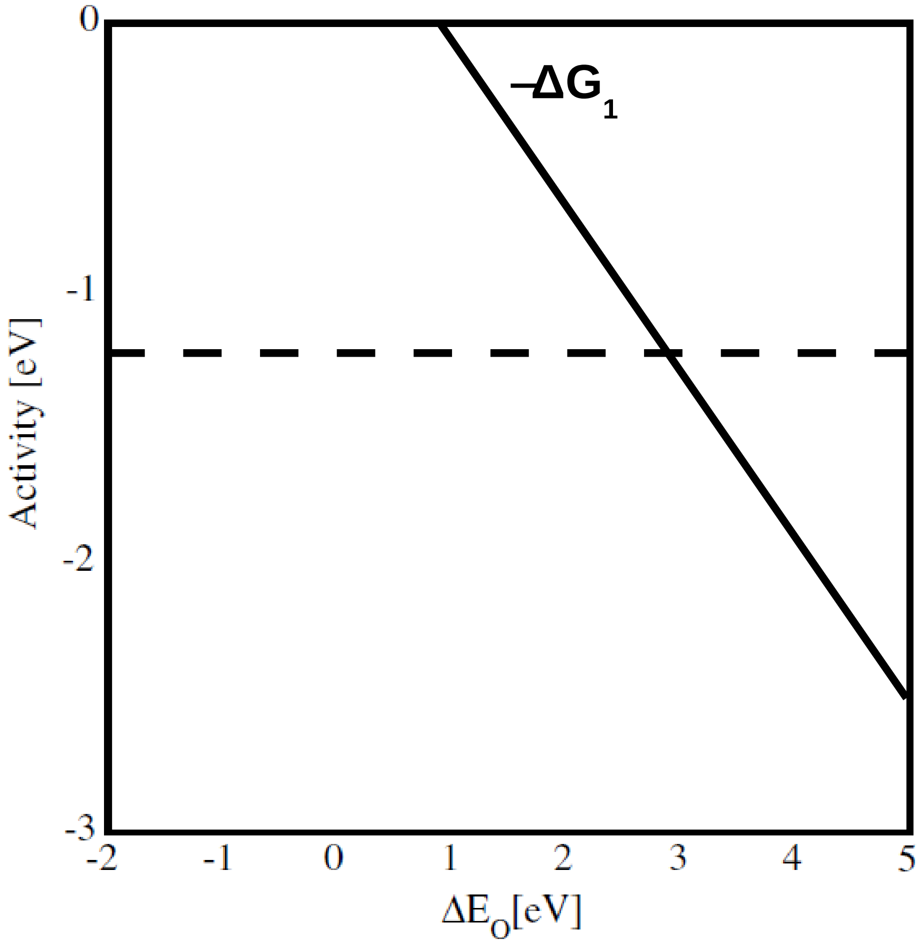
$O_2 + 4H^+ + 4e^- \rightarrow 2H_2O \qquad E^0 = 1.23\ \text{V}$

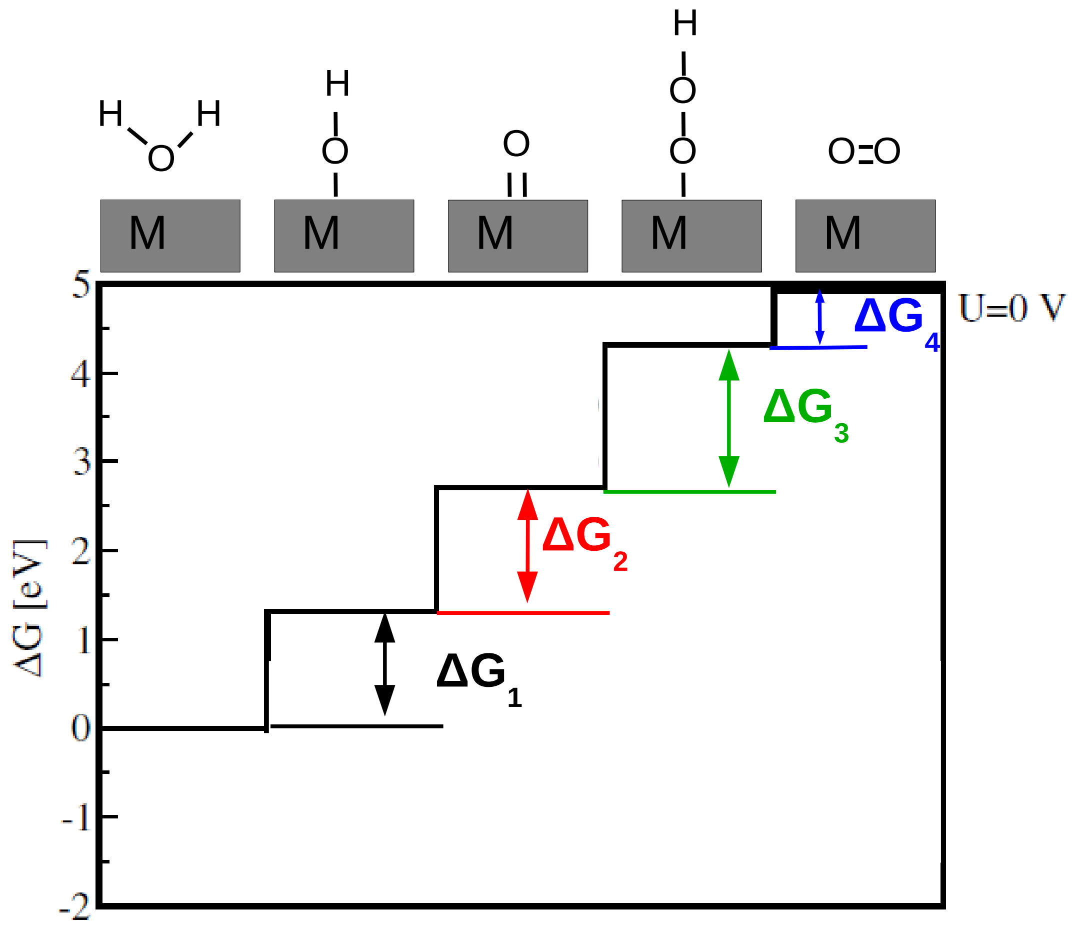


**The height of each step $\Delta G_{1\text{-}4}$ is (approximately ) a linear function of $\Delta E_0$ (which is a material-dependent property)**

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

# Electrolysis of water on oxide surfaces





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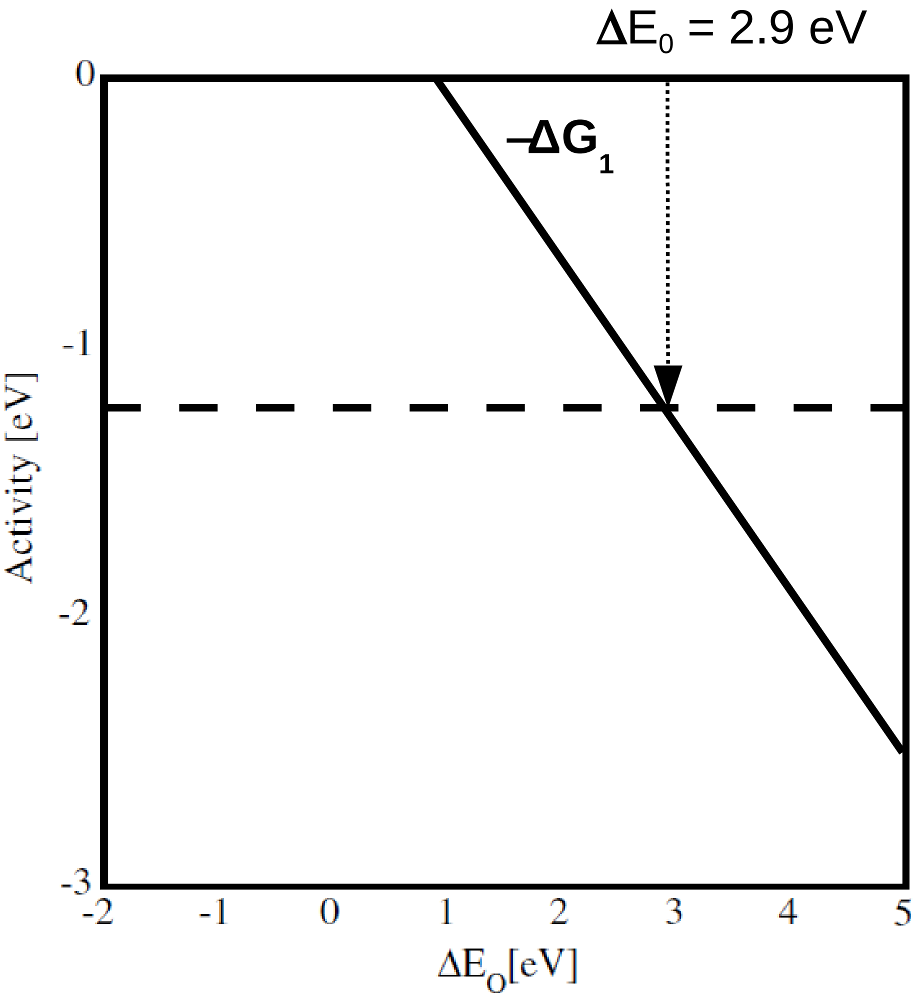
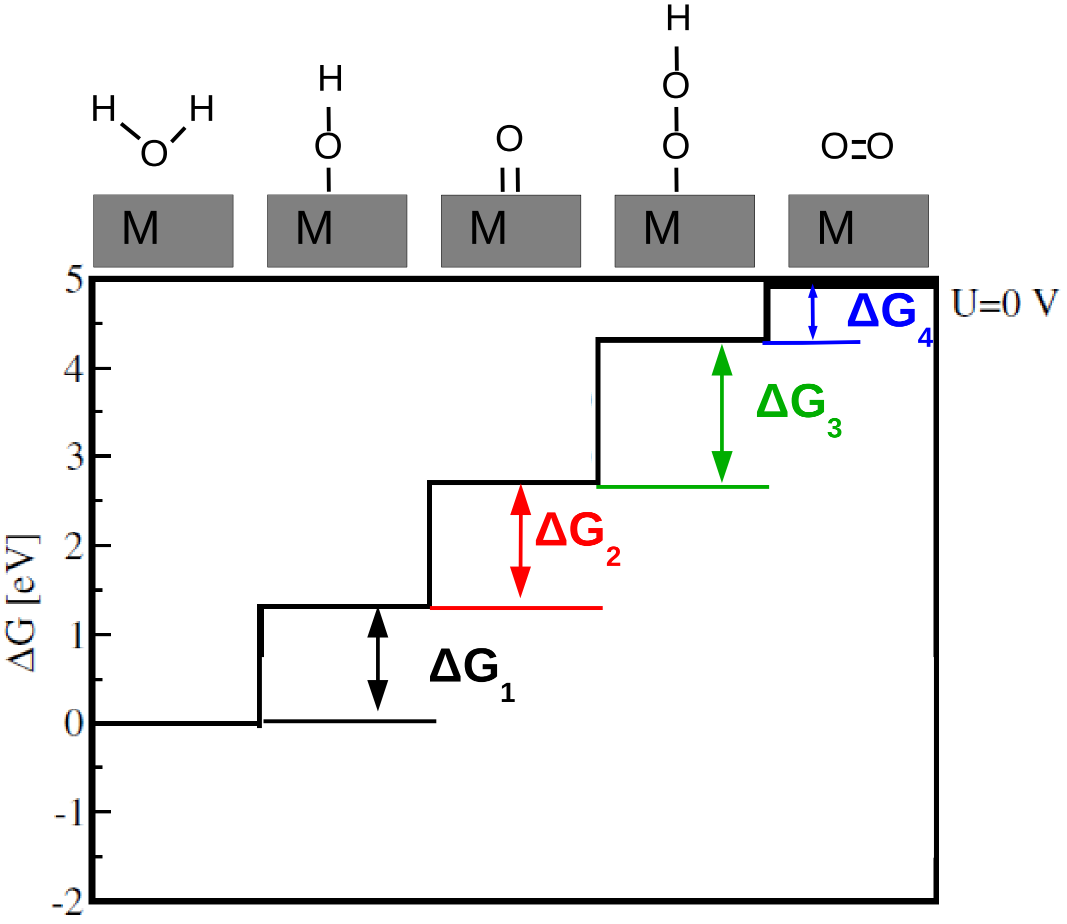
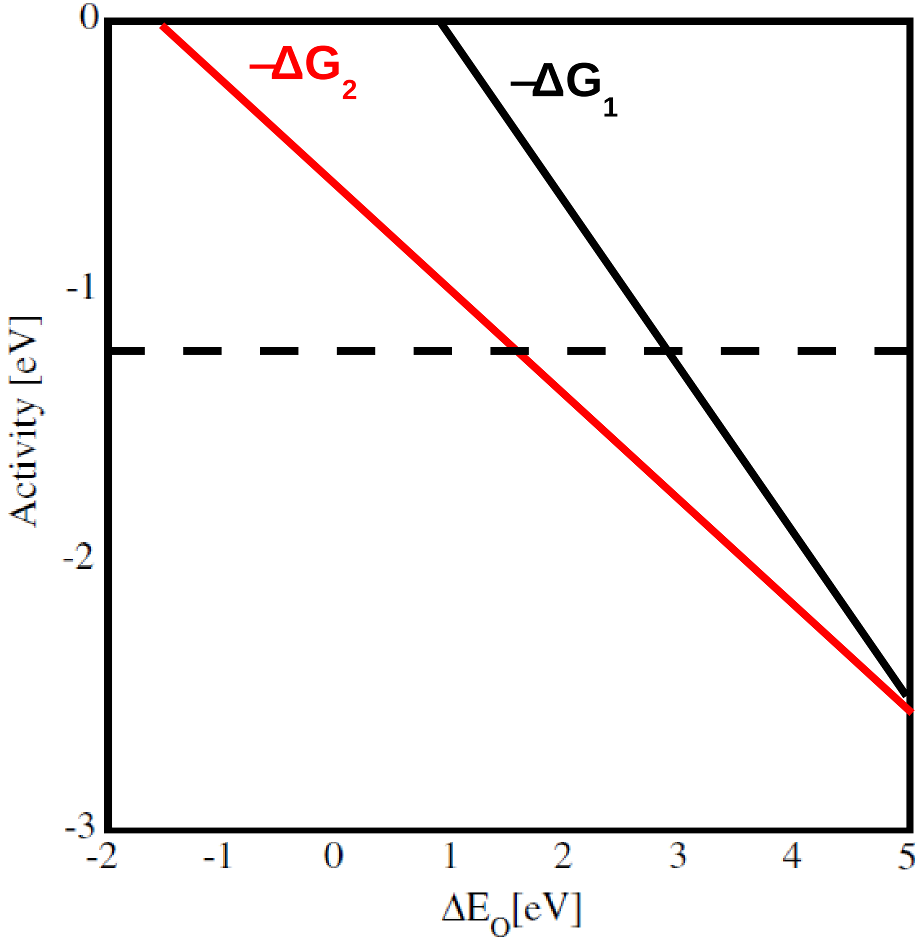


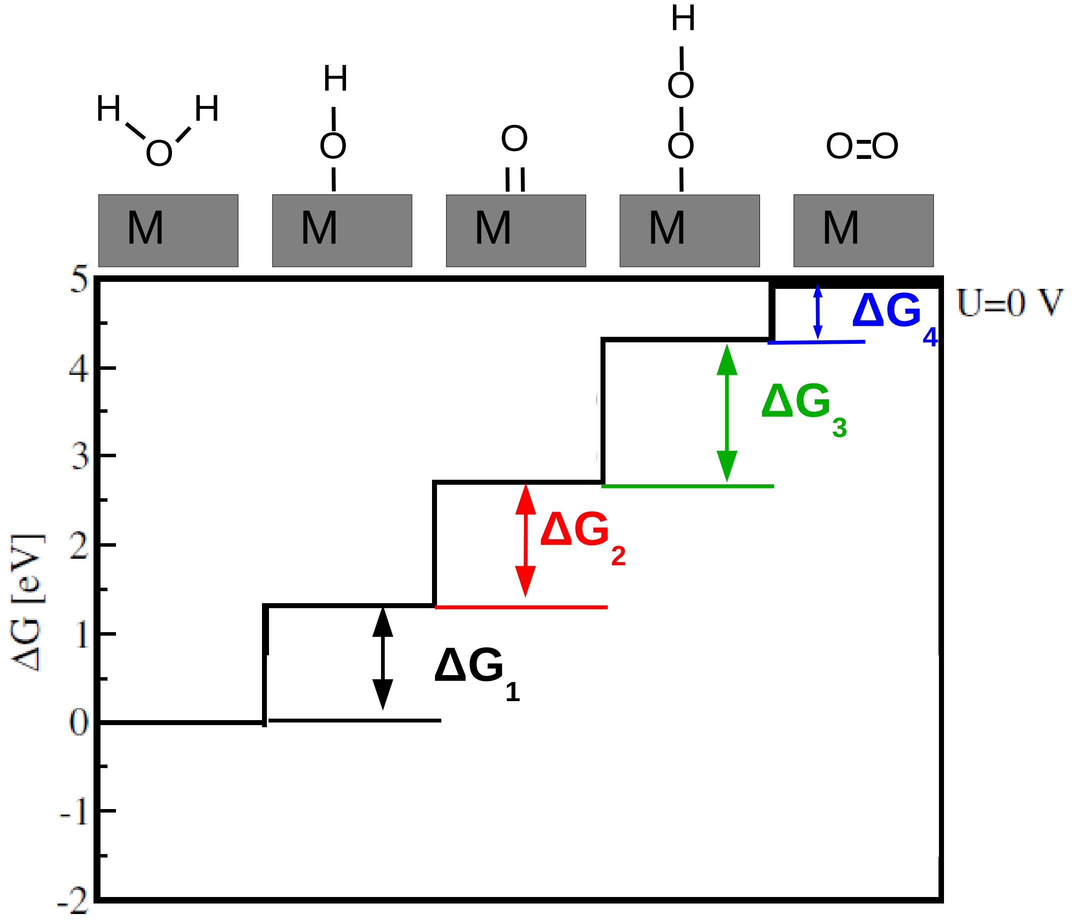


**$\Delta G_1$**: The “ideal” catalyst should have $\Delta E_0$ = 2.9 eV

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

# Electrolysis of water on oxide surfaces





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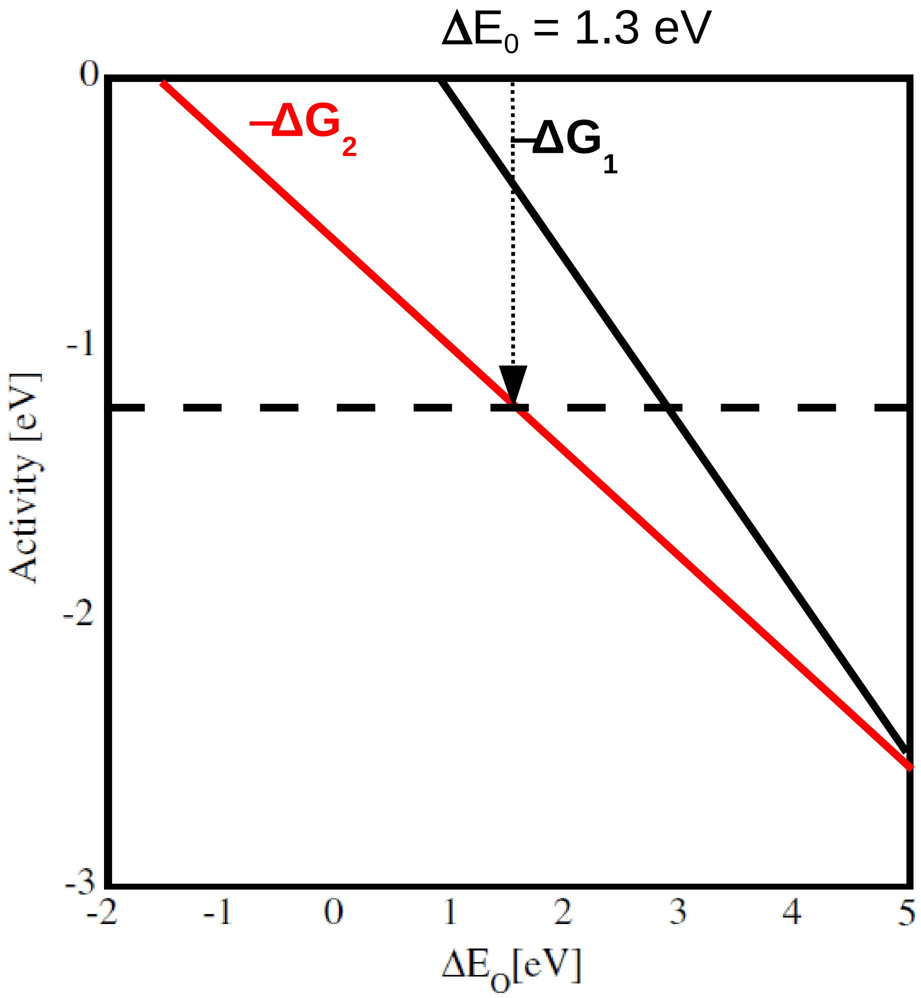
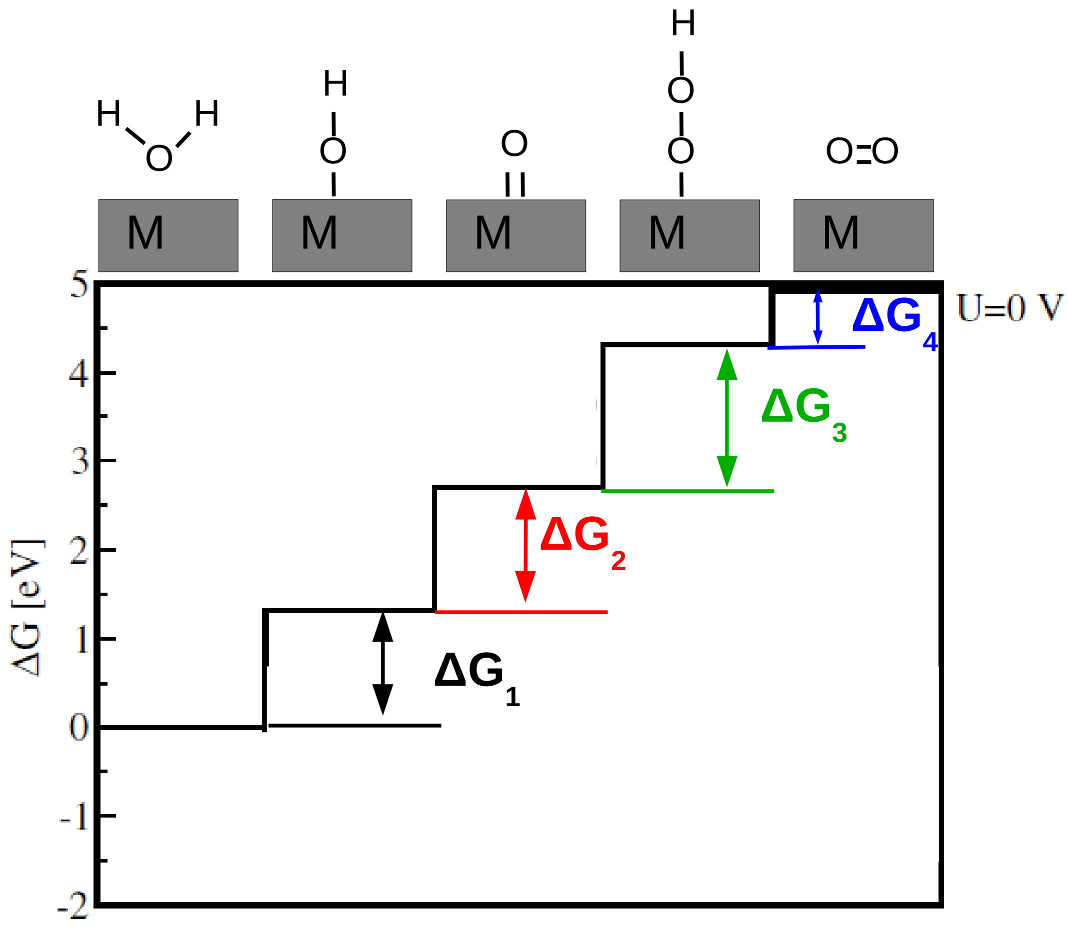


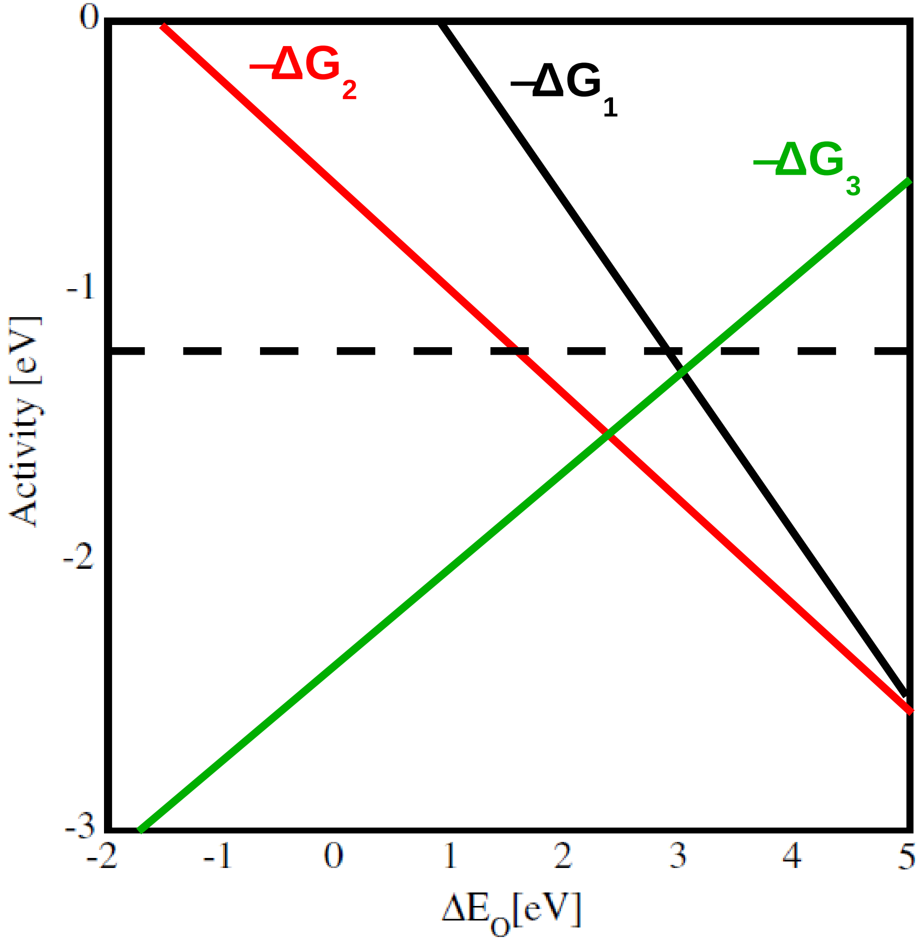


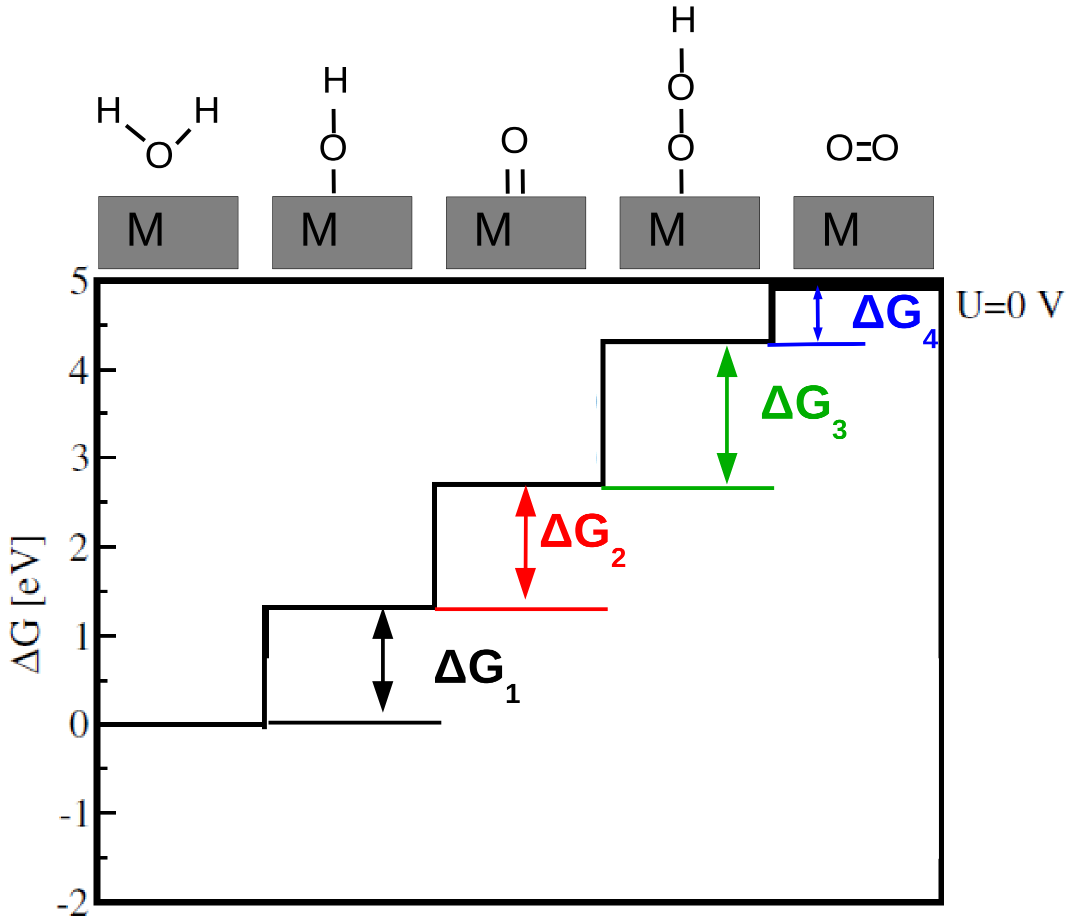
**$\Delta G_1$**: The "ideal" catalyst should have $\Delta E_0$ = 2.9 eV

**$\Delta G_2$**: The "ideal" catalyst should have $\Delta E_0$ = 1.3 eV

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

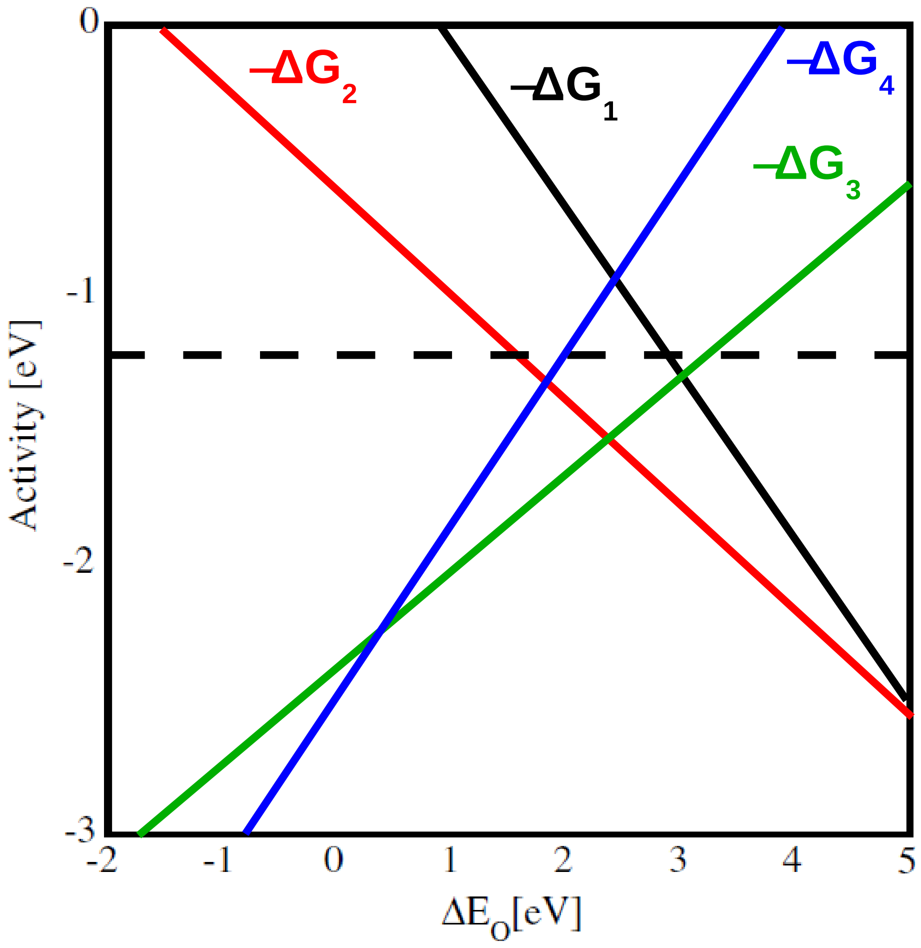
# Electrolysis of water on oxide surfaces

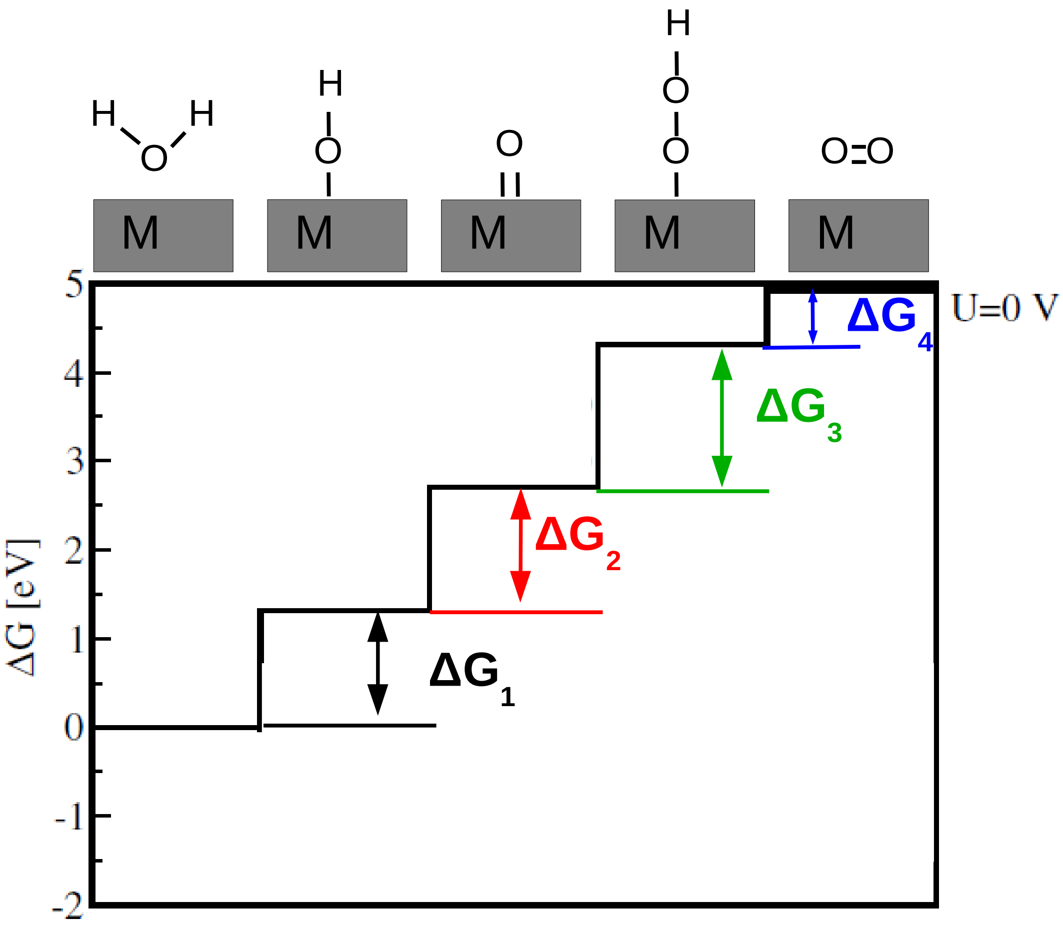




*Figures from:* Rossmeisl *et al.* J. Electr. Chem **607**, 83-89 (2007)

# Electrolysis of water on oxide surfaces





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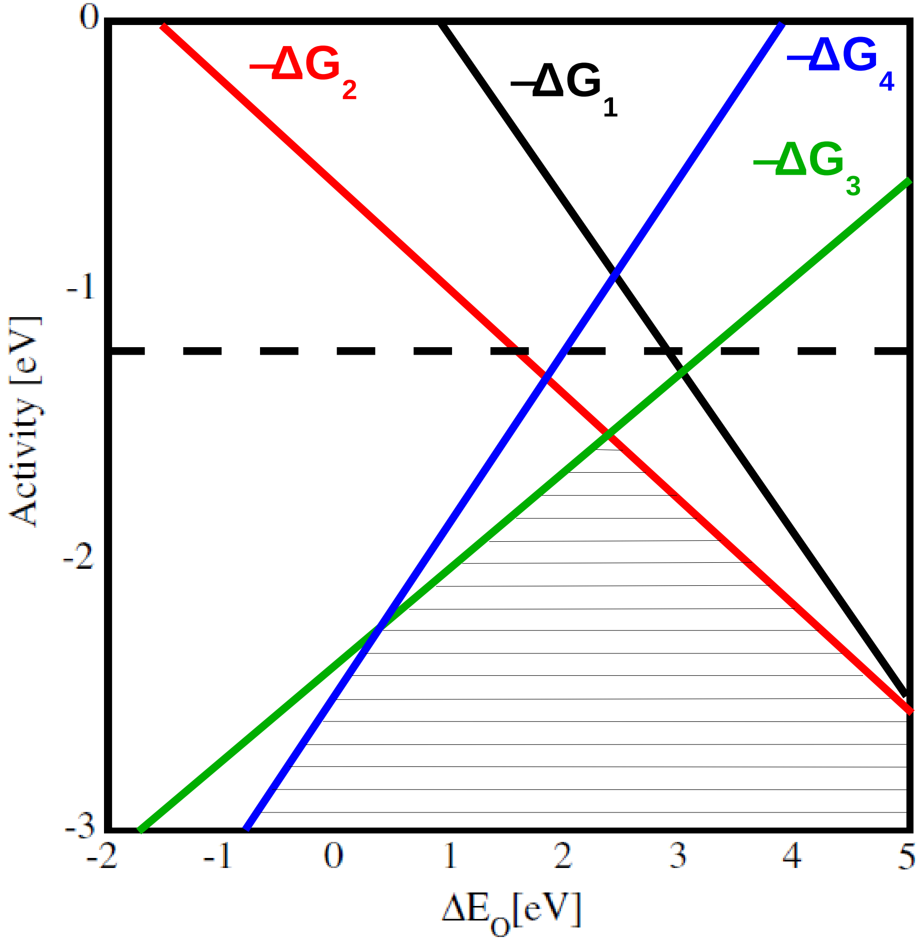
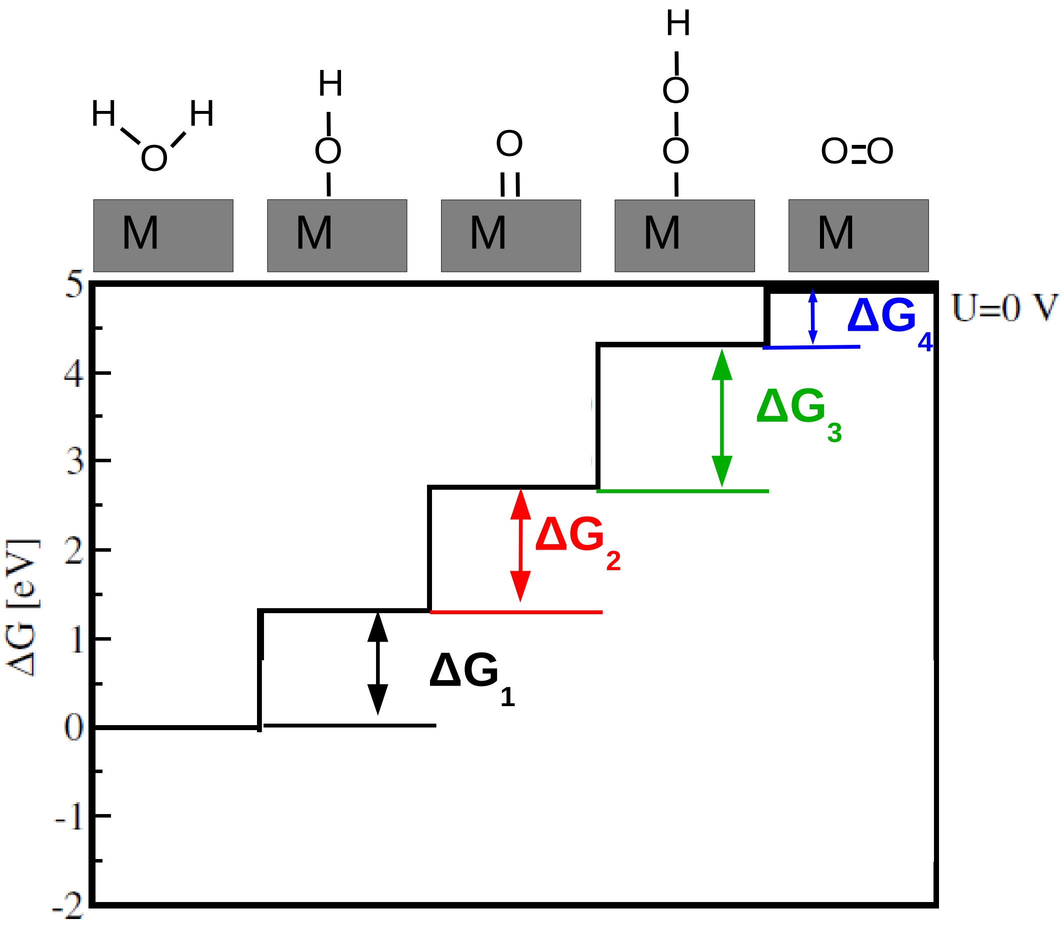
# Electrolysis of water on oxide surfaces





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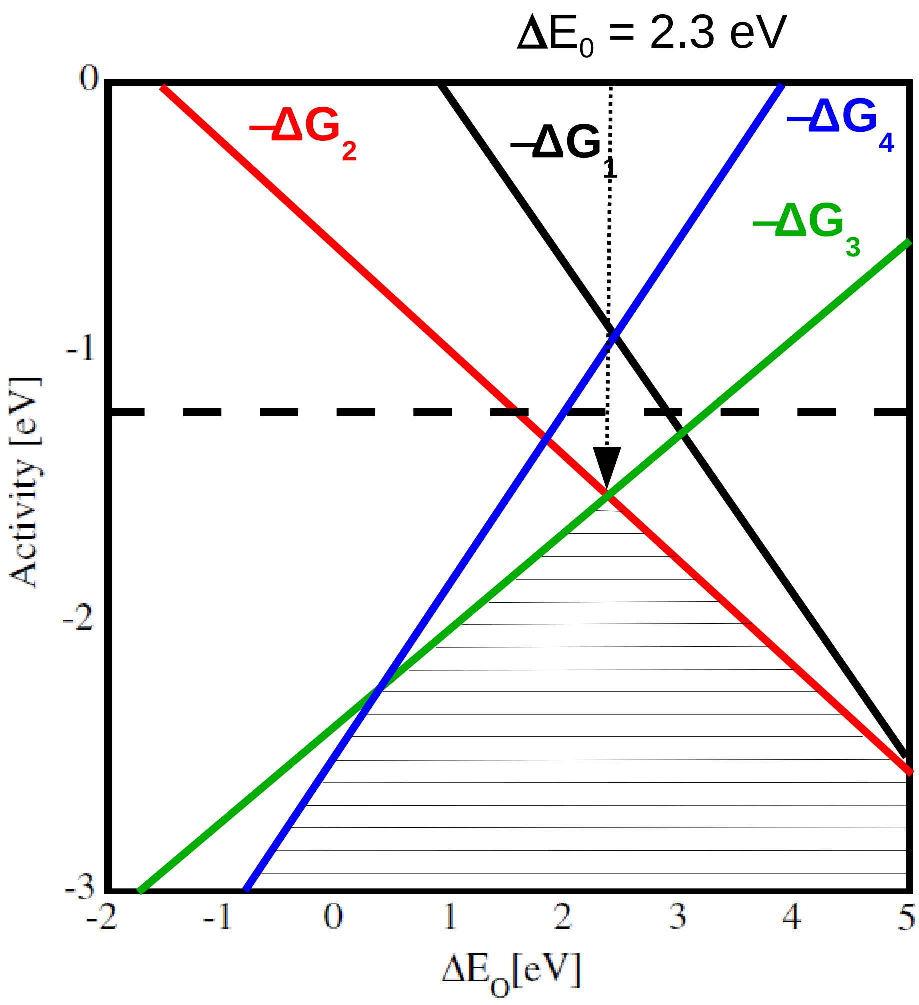
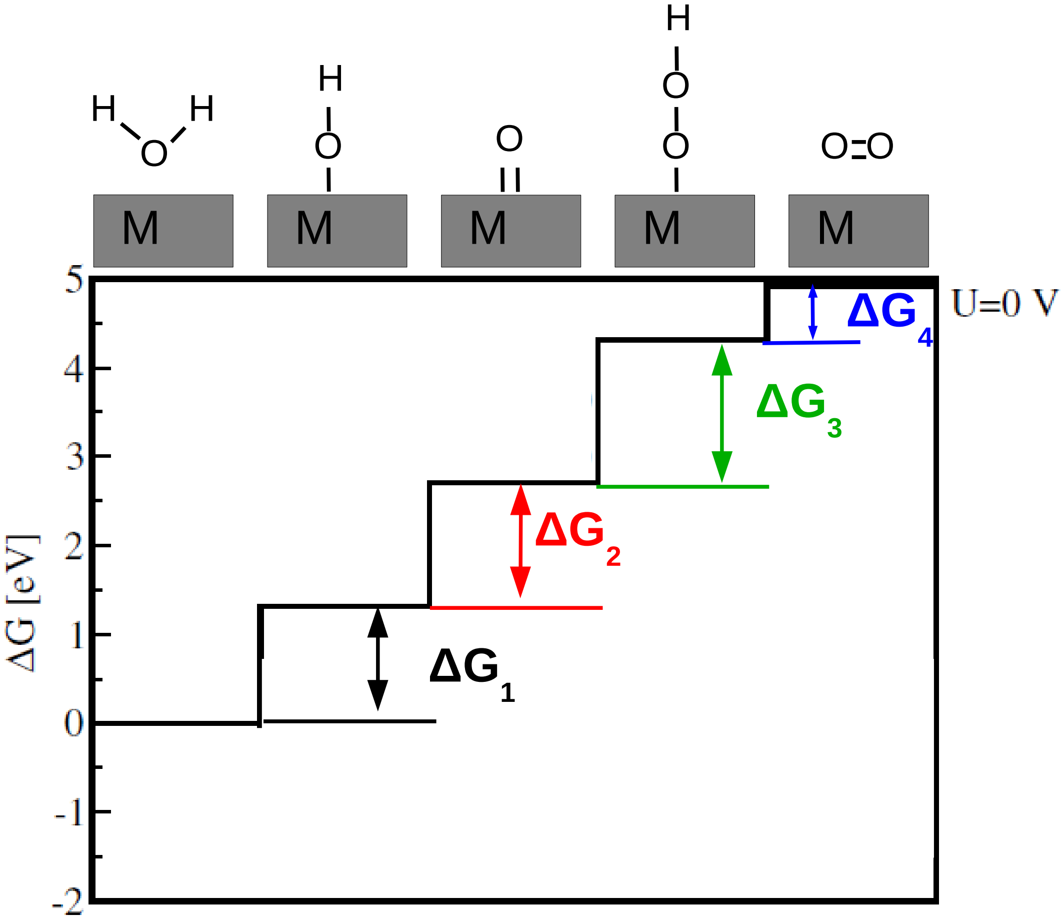
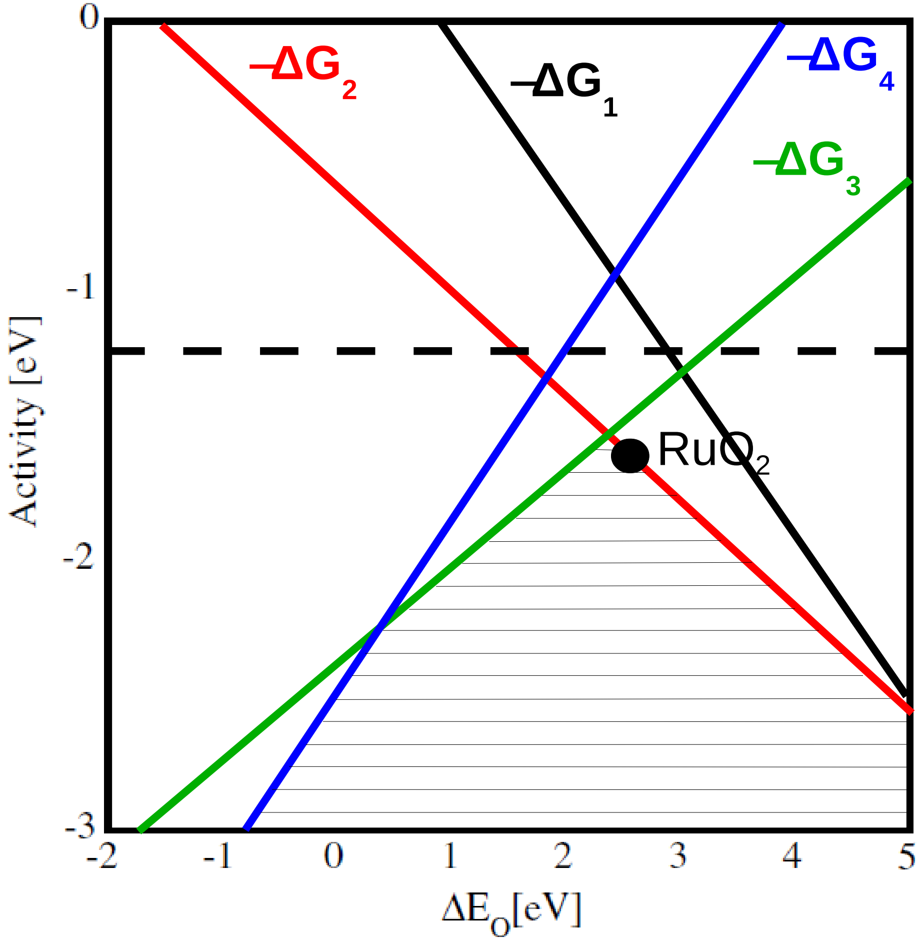


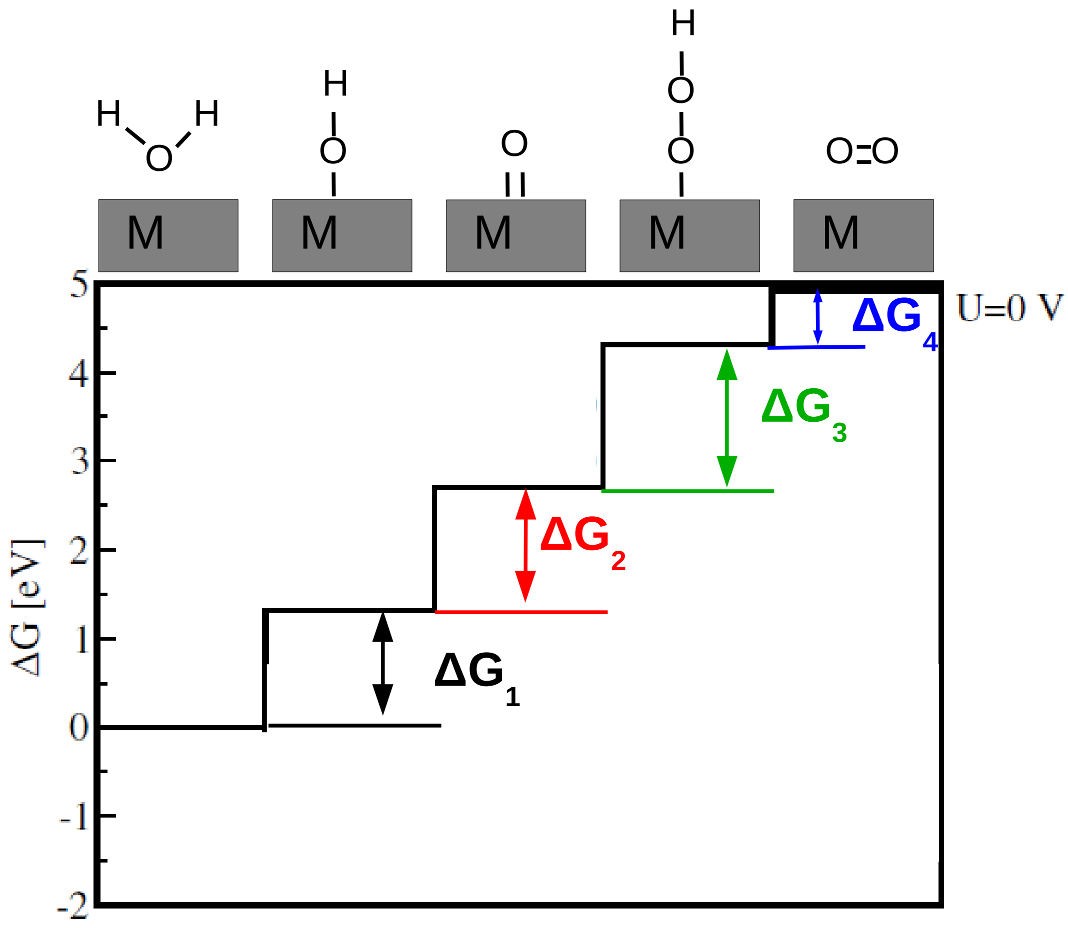


The “best” catalyst should have $\Delta E_0$ = 2.3 eV

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

# Electrolysis of water on oxide surfaces

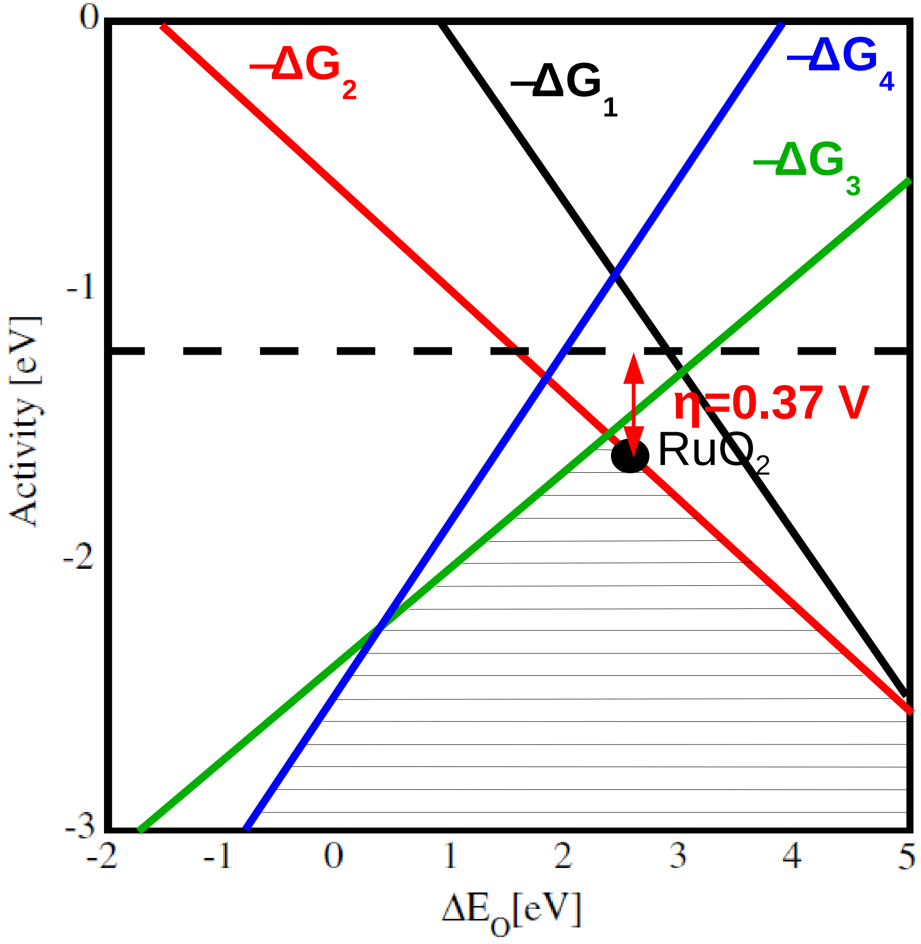


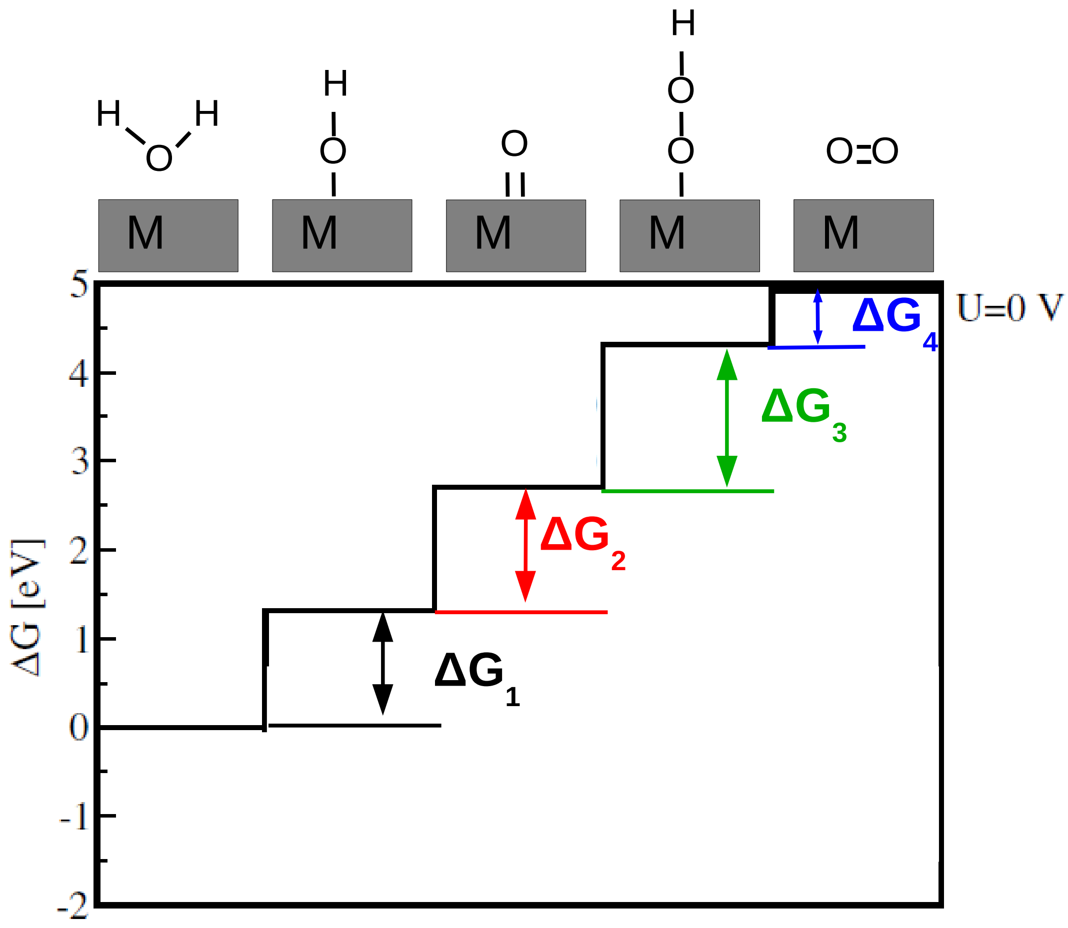


**$RuO_2$** sits very near the top of the volcano
There's not much room for improvement.

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

# Electrolysis of water on oxide surfaces





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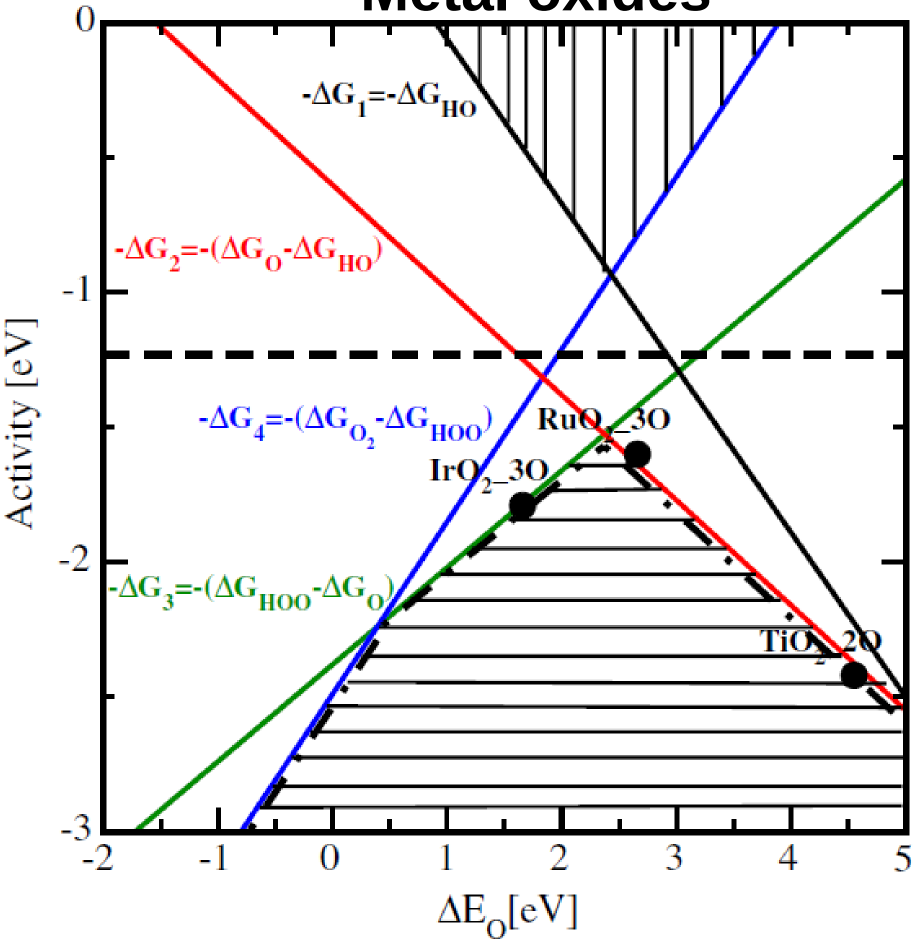
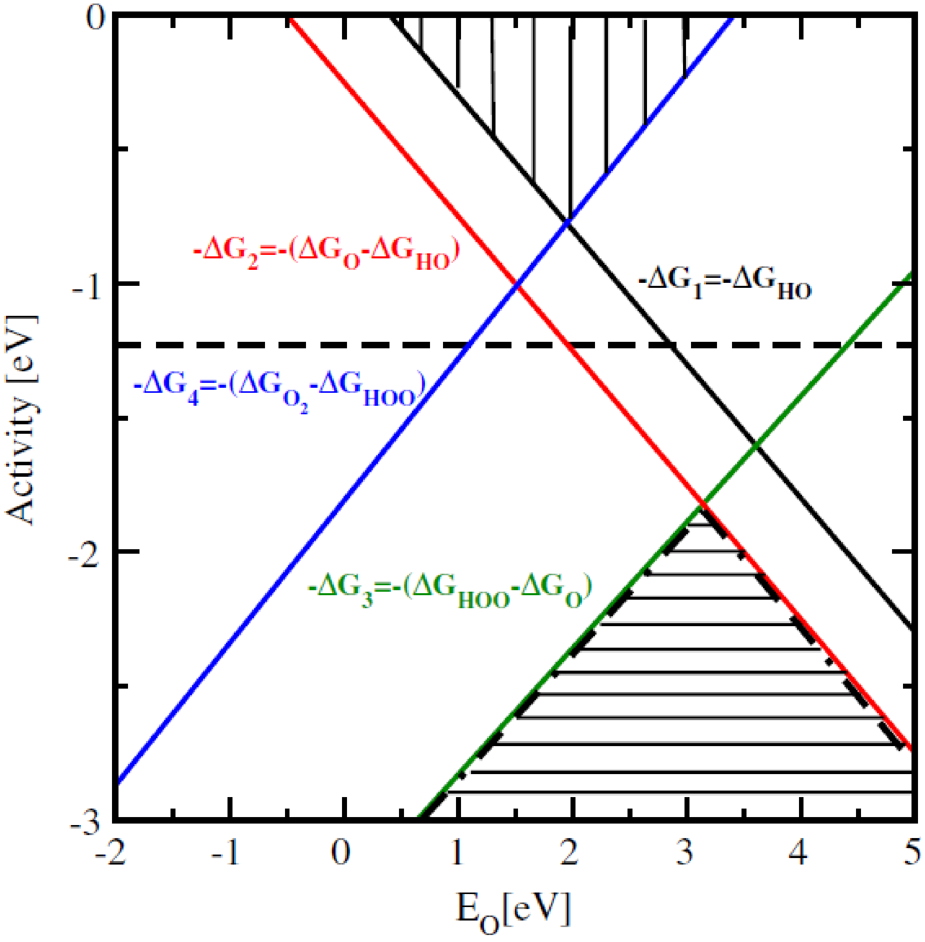
# Electrolysis of water on oxide surfaces

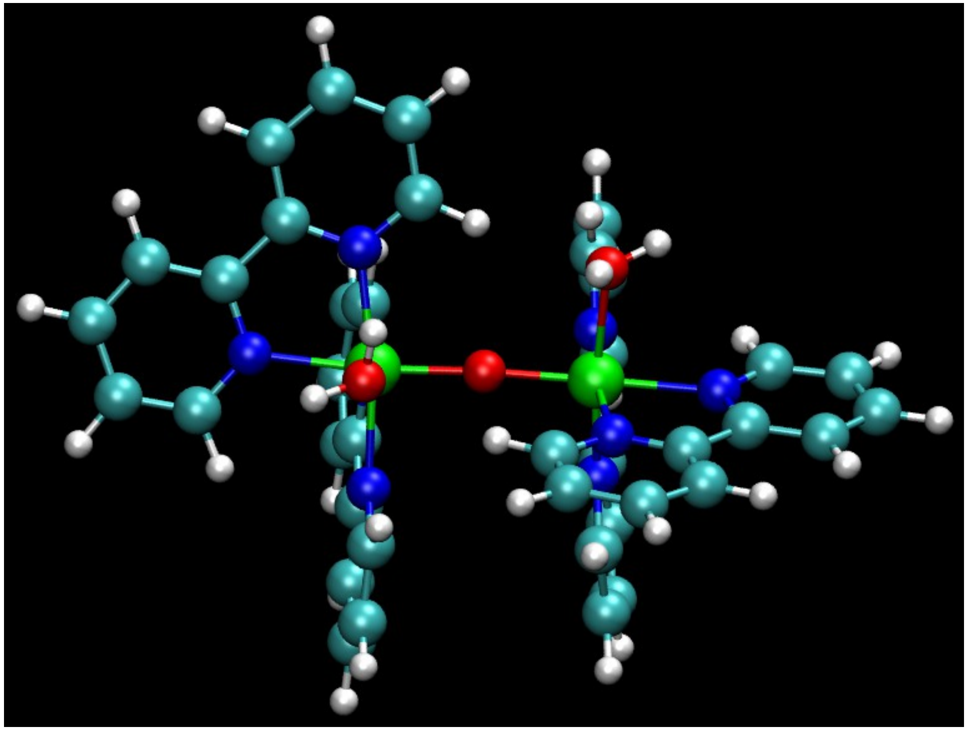

**Metal oxides**


**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)

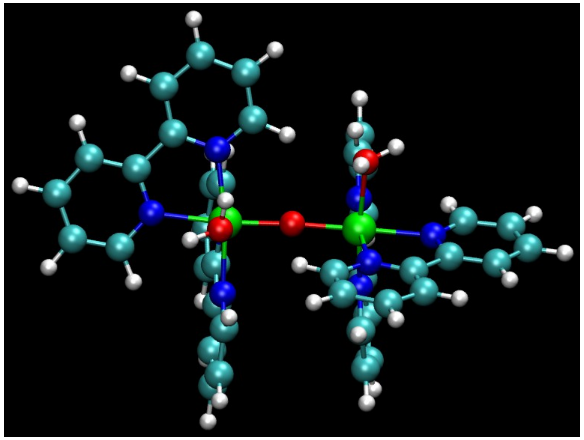
# Molecular catalysts for OER: “blue dimer”

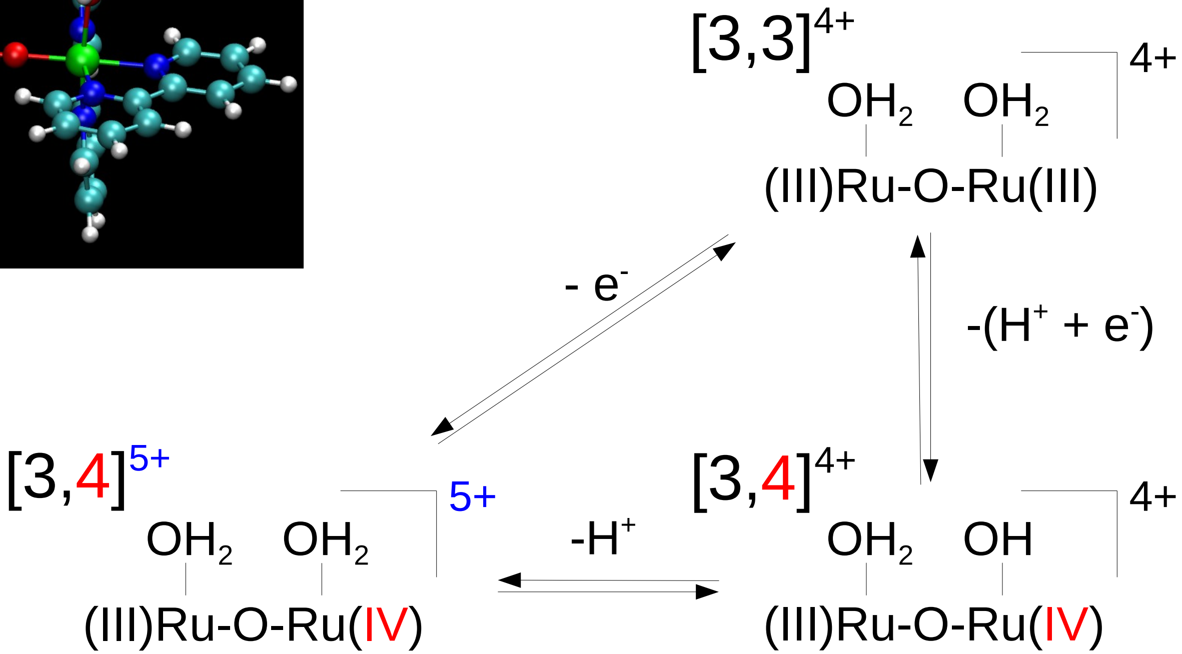


“**Blue dimer**”
Gersten *et al.* JACS **104**, 4029-4030 (1982)

- 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”





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

$OH_2$ $OH_2$ $4+$

(III)Ru-O-Ru(III)

$- e^-$

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

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

$OH_2$ $OH_2$ $5+$

(III)Ru-O-Ru(IV)

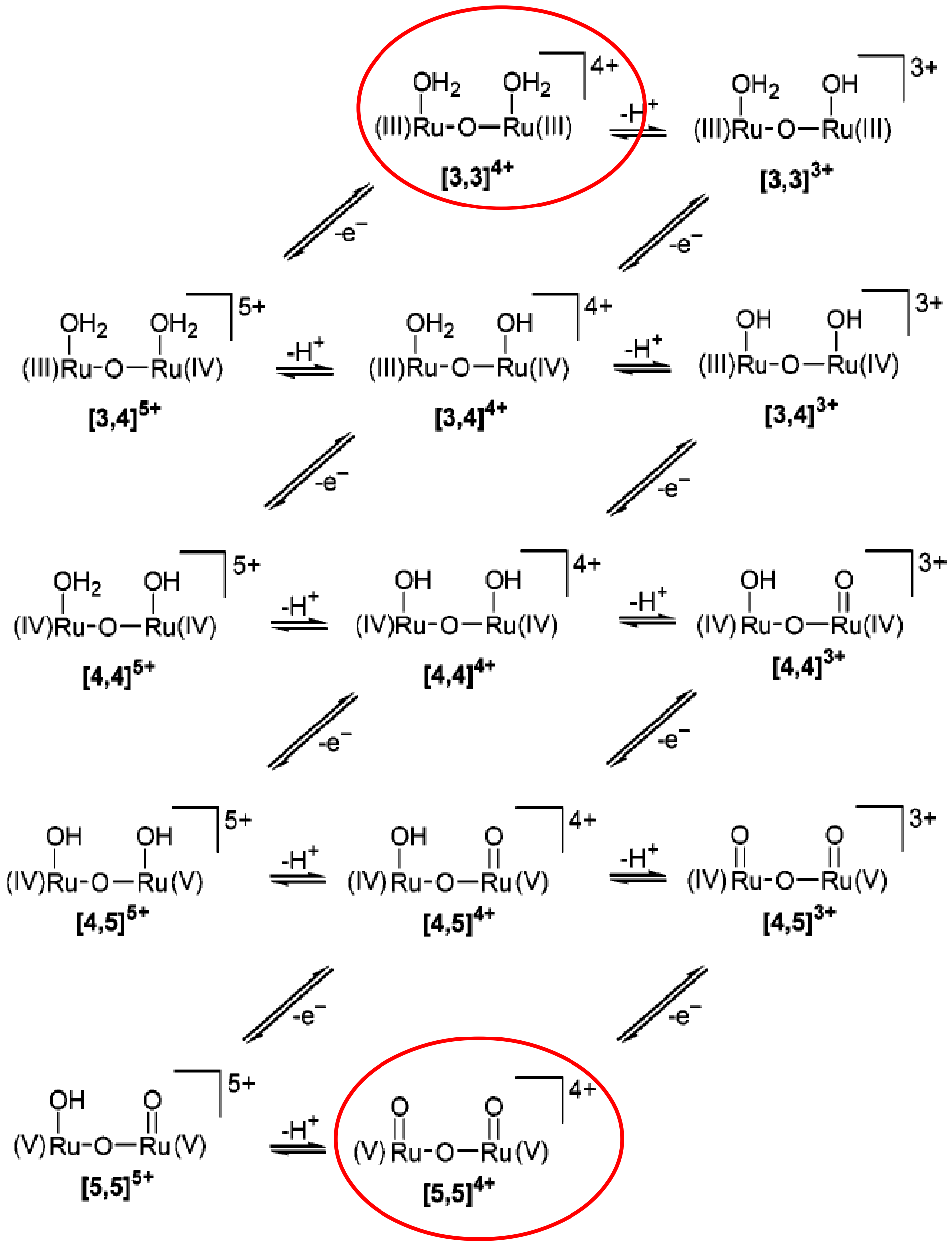
$-H^+$

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

$OH_2$ OH $4+$

(III)Ru-O-Ru(IV)

# 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: $\phi = 4.44$ 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)

# 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

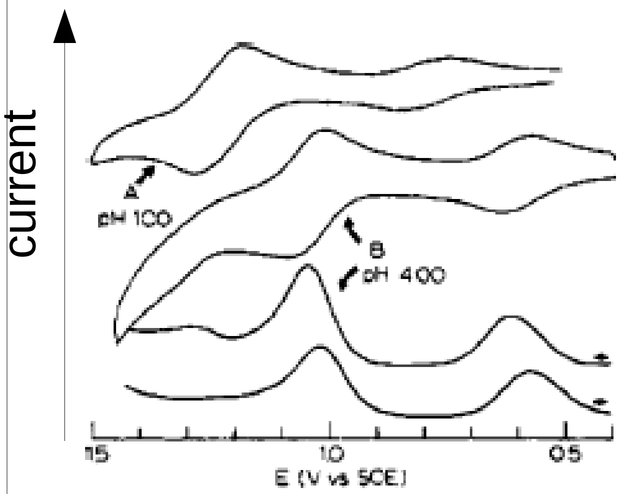
- The overpotential is determined by the most endergonic electrochemical step (highest $\Delta G$)

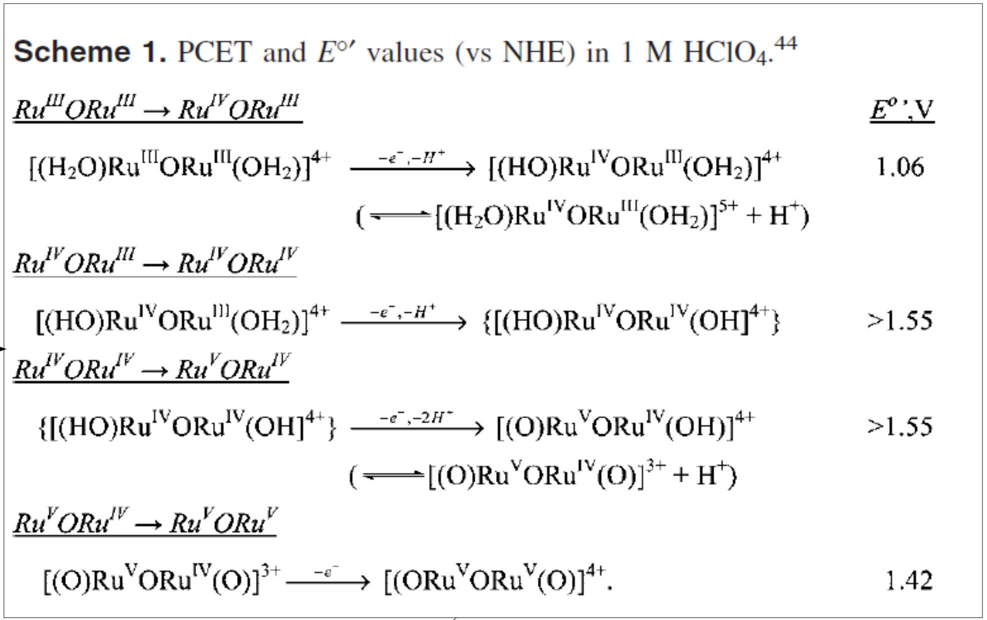
- If electrons and protons are removed at the same time (PCET) the approach proposed by Nørskov *et al.* is particularly covenient

- For a vast class of metals and metal oxides there exist linear relationships between the energies of the intermediates: $\Delta E_O$ 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]

$\underline{Ru^{III}ORu^{III} \rightarrow Ru^{IV}ORu^{III}}$ — $\underline{E^{o\prime};V}$

$[(H_2O)Ru^{III}ORu^{III}(OH_2)]^{4+} \xrightarrow{-e^-,-H^+} [(HO)Ru^{IV}ORu^{III}(OH_2)]^{4+}$ 1.06

$(\longleftarrow [(H_2O)Ru^{IV}ORu^{III}(OH_2)]^{5+} + H^+)$

$\underline{Ru^{IV}ORu^{III} \rightarrow Ru^{IV}ORu^{IV}}$

$[(HO)Ru^{IV}ORu^{III}(OH_2)]^{4+} \xrightarrow{-e^-,-H^+} \{[(HO)Ru^{IV}ORu^{IV}(OH]^{4+}\}$ >1.55

$\underline{Ru^{IV}ORu^{IV} \rightarrow Ru^{V}ORu^{IV}}$

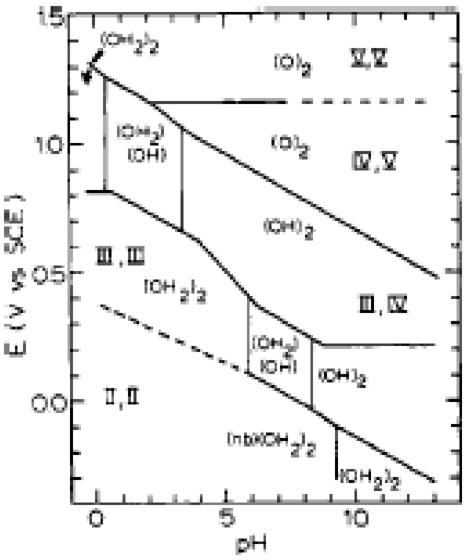
$\{[(HO)Ru^{IV}ORu^{IV}(OH]^{4+}\} \xrightarrow{-e^-,-2H^+} [(O)Ru^{V}ORu^{IV}(OH)]^{4+}$ >1.55

$(\longleftarrow [(O)Ru^{V}ORu^{IV}(O)]^{3+} + H^+)$

$\underline{Ru^{V}ORu^{IV} \rightarrow Ru^{V}ORu^{V}}$

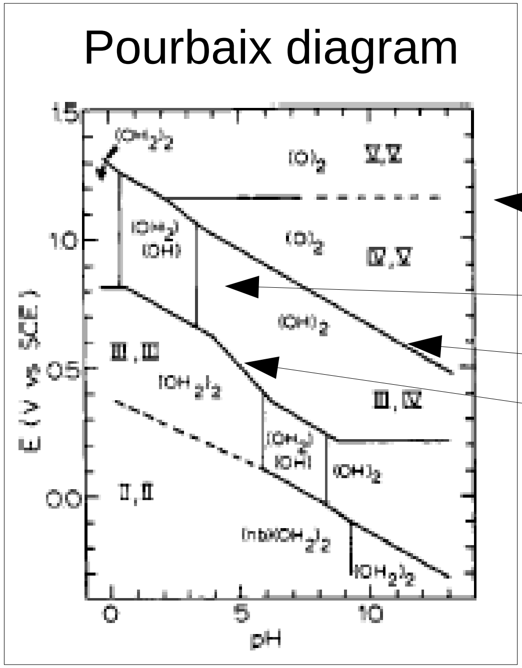
$[(O)Ru^{V}ORu^{IV}(O)]^{3+} \xrightarrow{-e^-} [(ORu^{V}ORu^{V}(O)]^{4+}.$ 1.42

Pourbaix diagram



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

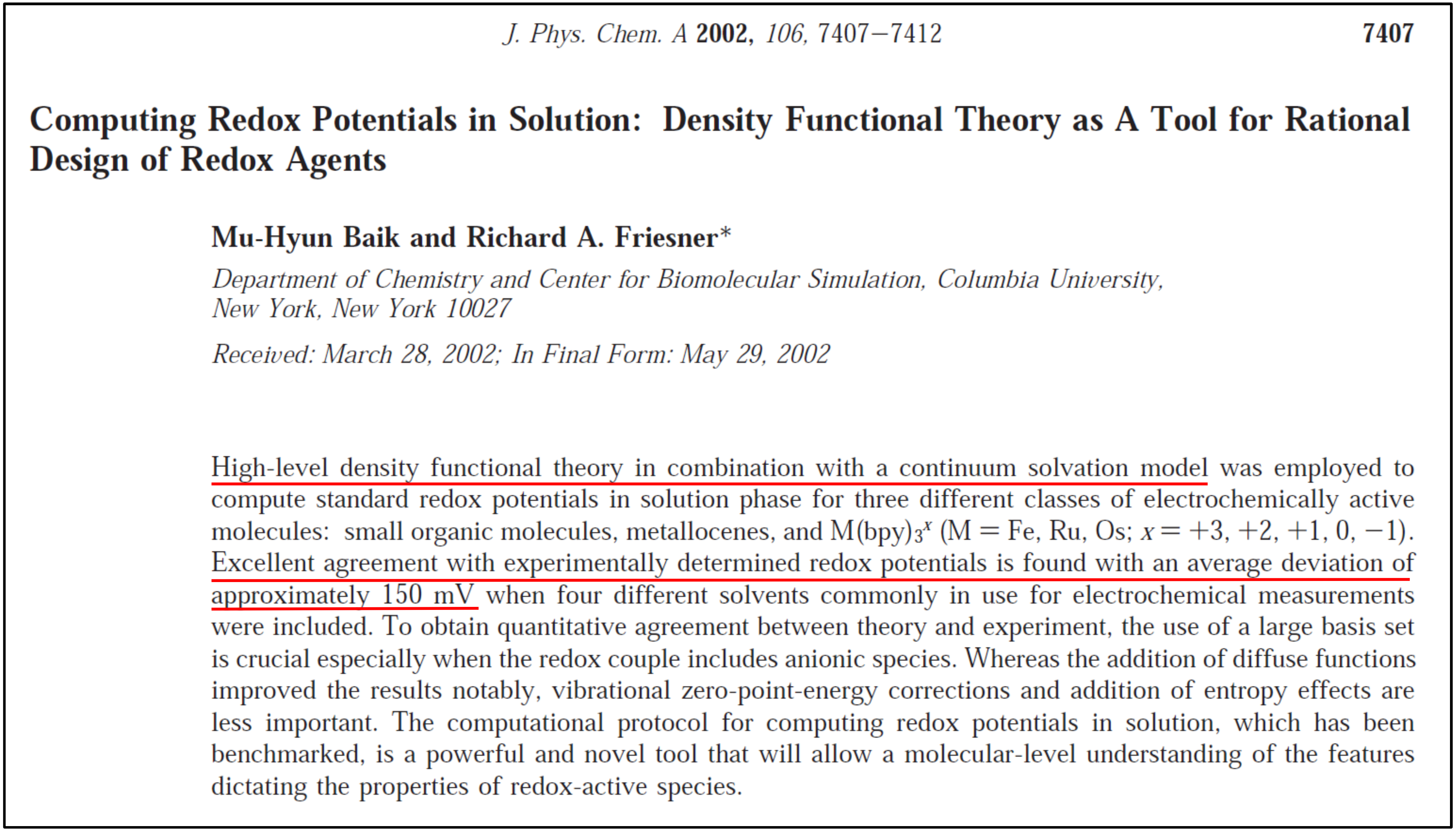
# Molecular catalysts for OER: “blue dimer”


Pourbaix diagram

| Slope [meV/pH] | Event |
|---|---|
| 0 | $e^-$ |
| ∞ | $H^+$ |
| 59 | $H^+ + e^-$ |
| $2\times59$ | $2H^+ + e^-$ |

*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***

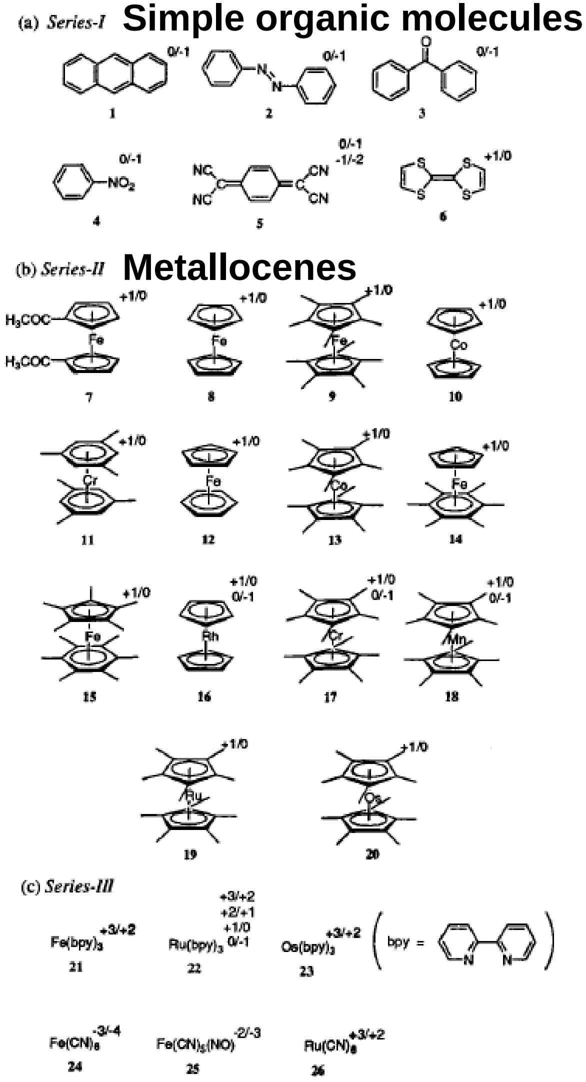
*Department of Chemistry and Center for Biomolecular Simulation, Columbia University,*
*New York, New York 10027*

*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

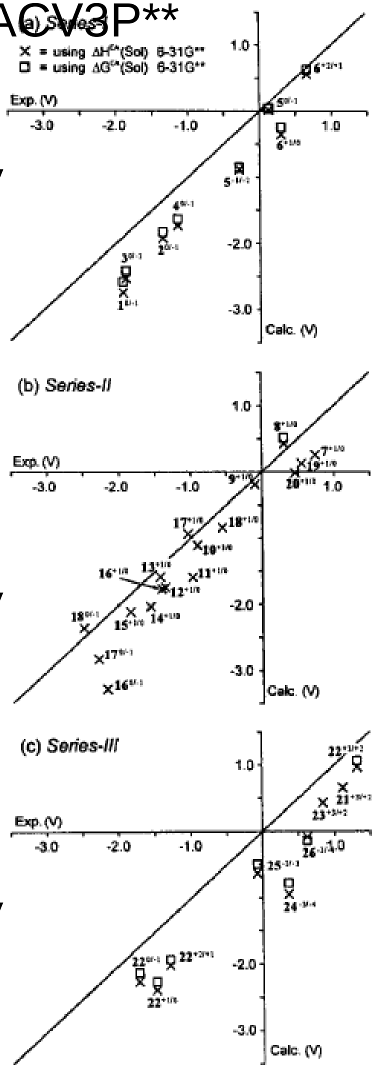


**Figure 1.** Correlation diagram of the experimental vs calculated redox potentials on the B3LYP/6-31G** level of theory with and without ZPE/entropy corrections.

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

MAE = 0.120 V

MAE = 0.165 V

MAE = 0.372 V

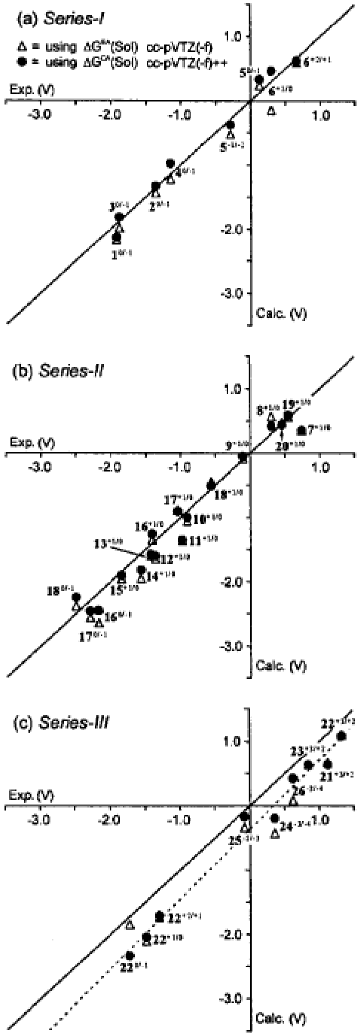


**Figure 2.** Correlation diagram of the experimental vs calculated redox potentials on the B3LYP/cc-pVTZ(-f) and B3LYP/cc-pVTZ(-f)++ levels of theory (ZPE/entropy-corrected).

# Molecular catalysts for OER: “blue dimer”

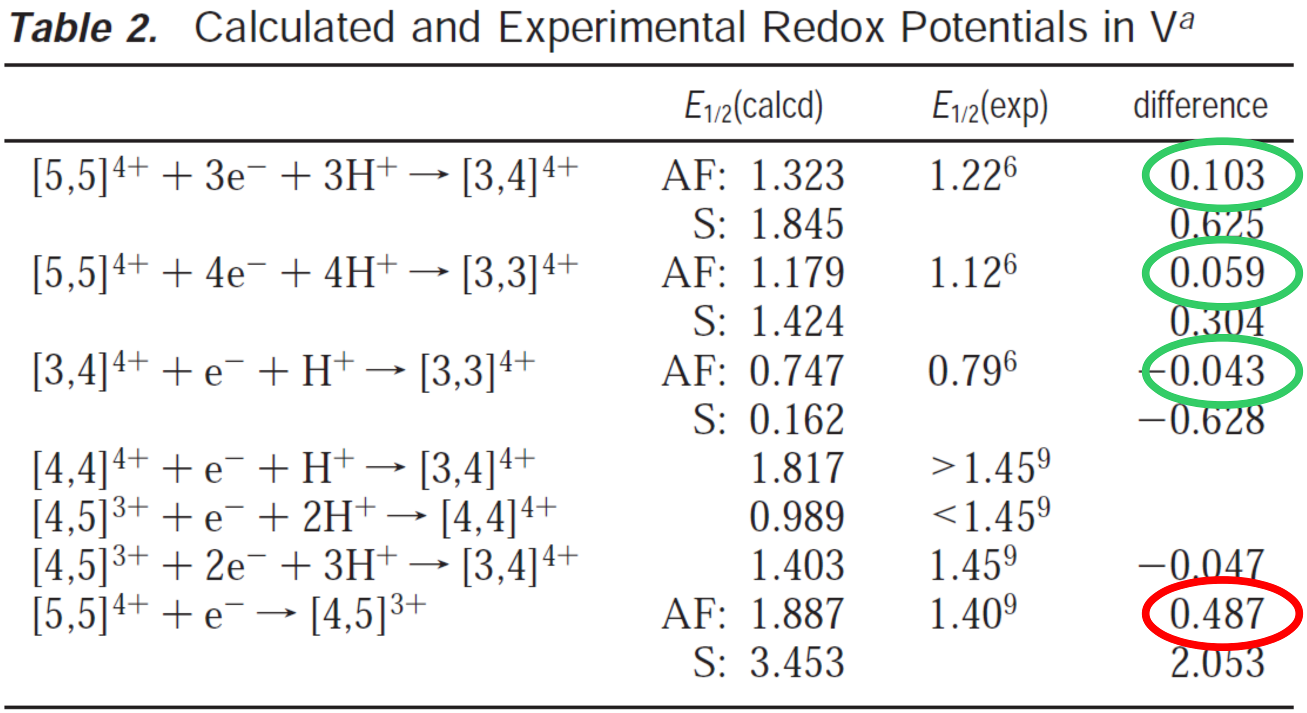
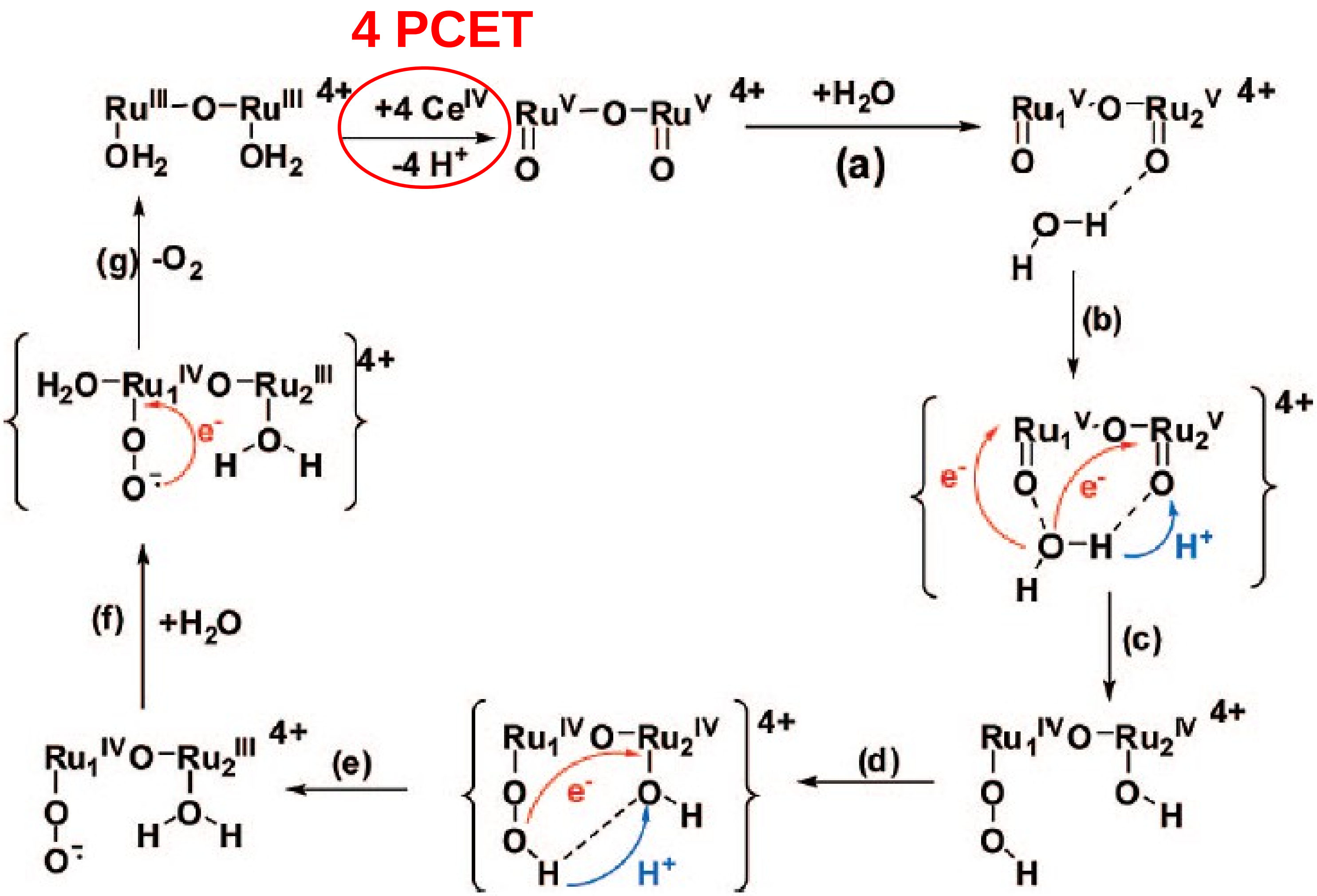


*Table 2.* Calculated and Experimental Redox Potentials in V[a]

| | $E_{1/2}$(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”



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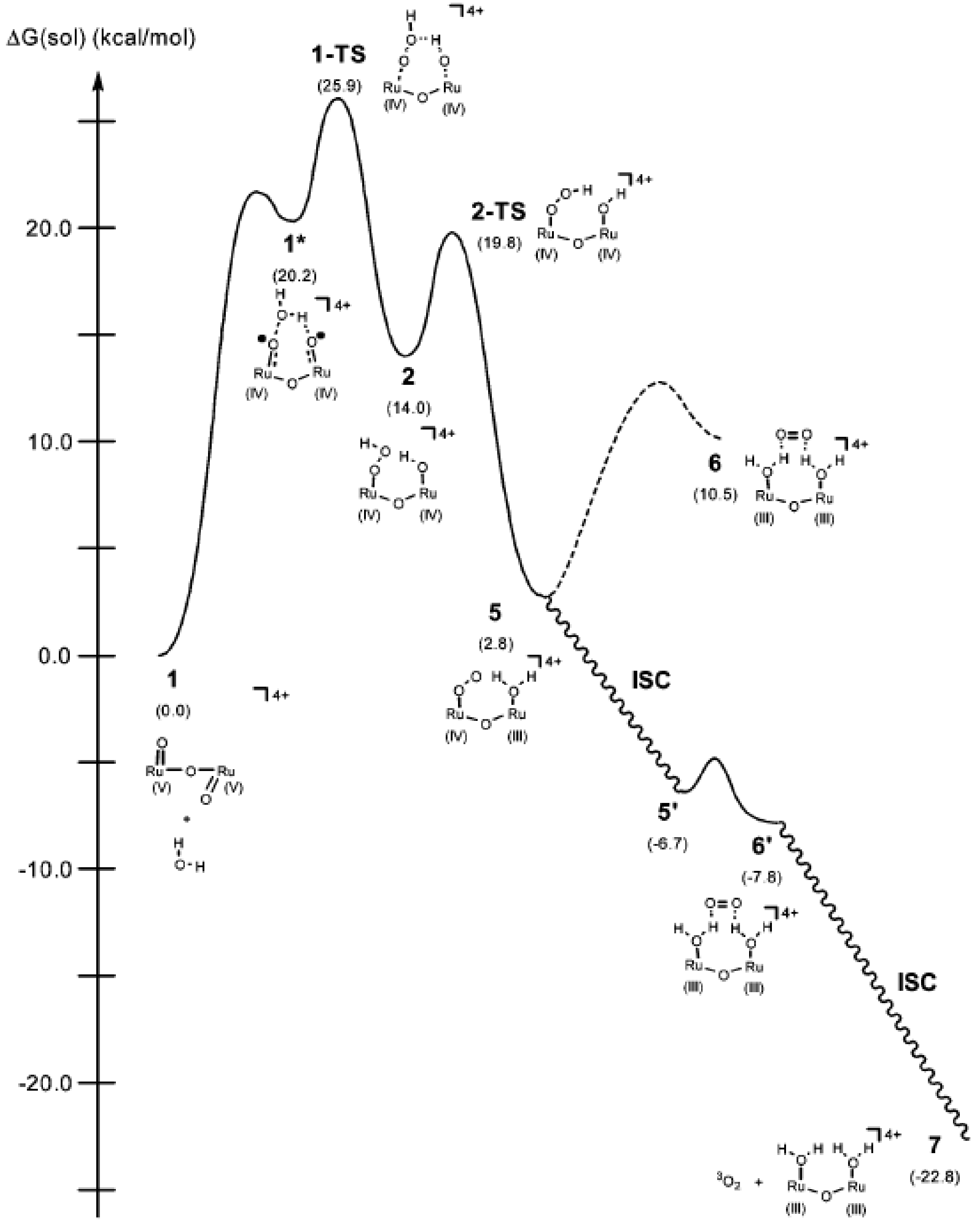
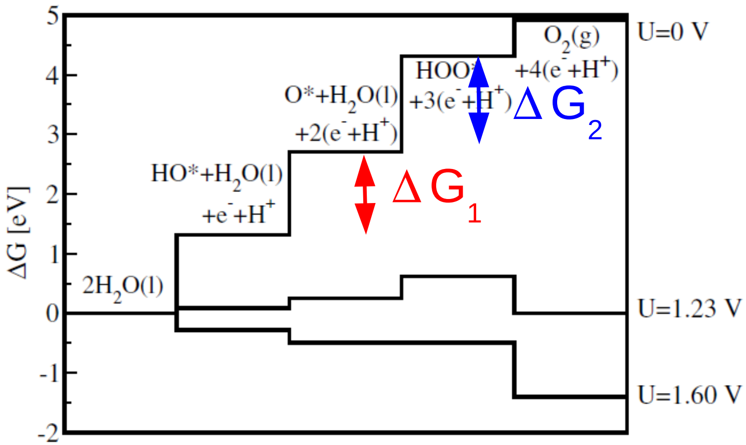
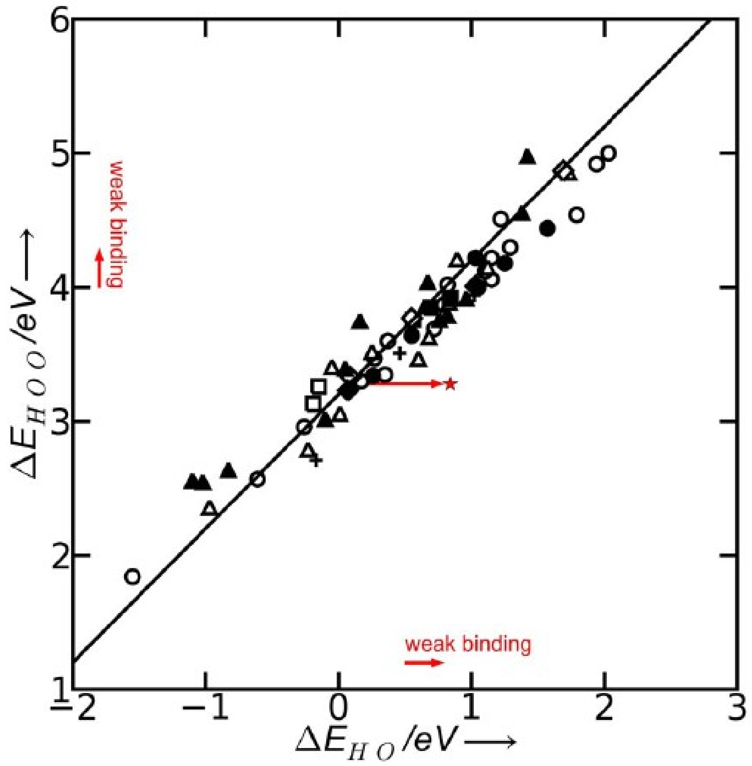


# Electrolysis of water on oxide surfaces



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

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



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

# Electrochemistry: a quick overview

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

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

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

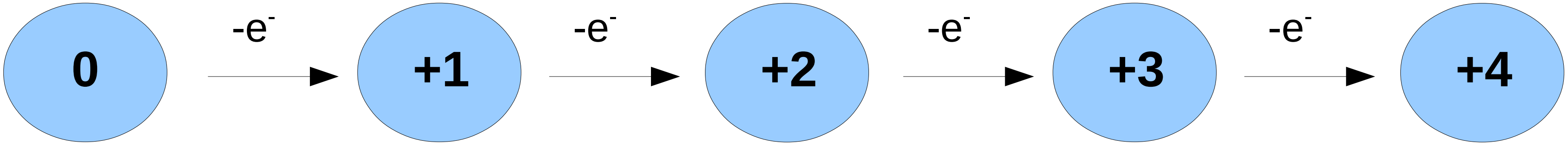
$E^0_{1,2}$ of a single electrode: not possible to measure

Reference electrode: NHE (SHE)

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

# PCET in water oxidation

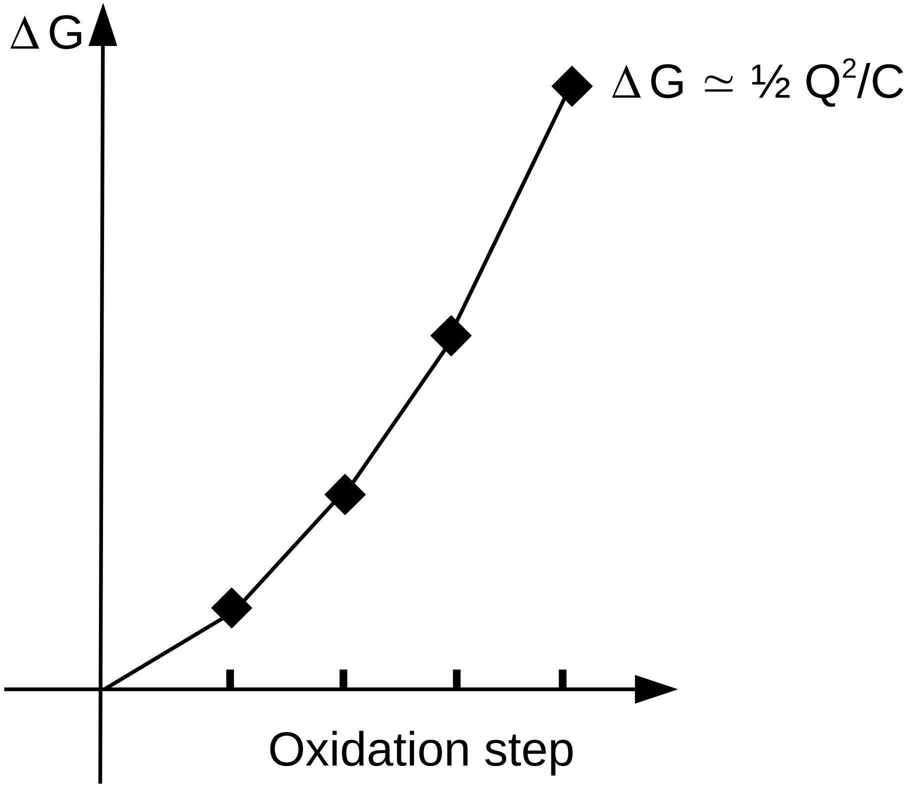
**ET:**



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

# PCET in water oxidation

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



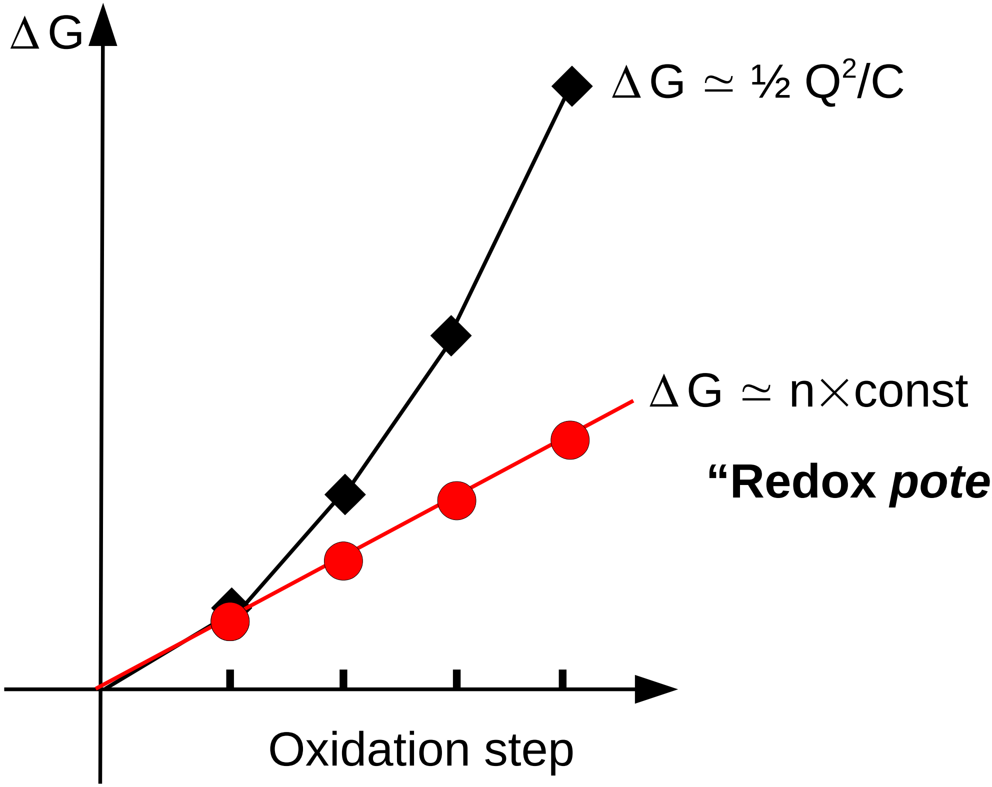
$\Delta G \simeq \frac{1}{2} Q^2/C$

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

# PCET in water oxidation

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

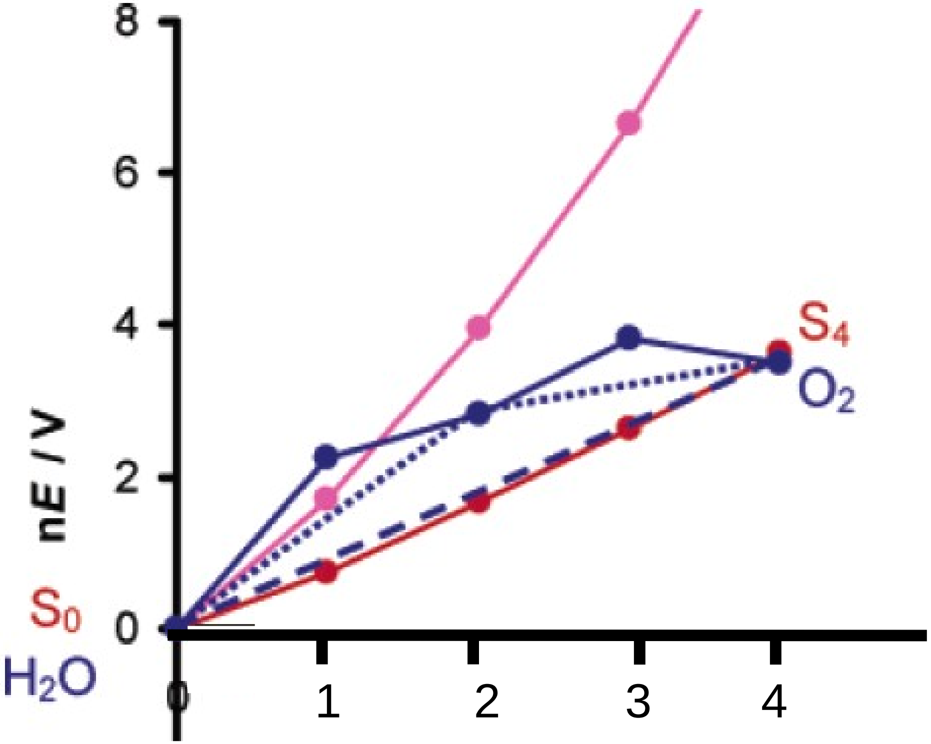
**PCET:** $$0 \xrightarrow{-(e^- + H^+)} 0 \xrightarrow{-(e^- + H^+)} 0 \xrightarrow{-(e^- + H^+)} 0 \xrightarrow{-(e^- + H^+)} 0$$



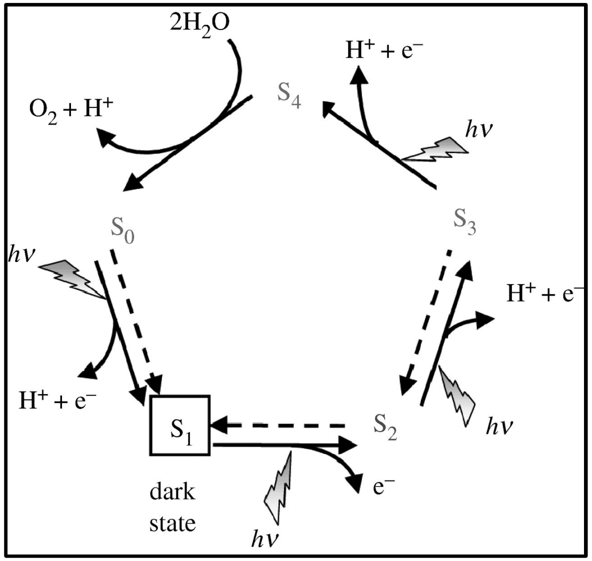
**“Redox *potential leveling*”**

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

# Oxygen evolving complex in PSII



- ▬ 1 e's mechanism
- ┈ 2 e's mechanism
- ╌ 4 e's mechanism
- ▬ OEC
- ▬ OEC (ET only)



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

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

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

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

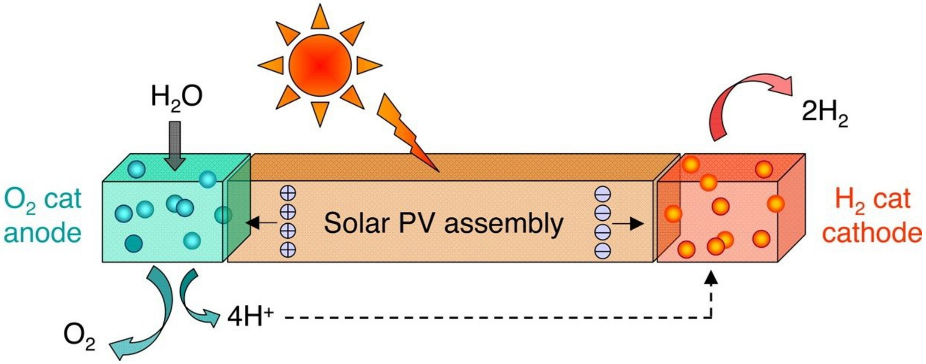
# OER and ORR

## *Electrolysis*

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

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

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

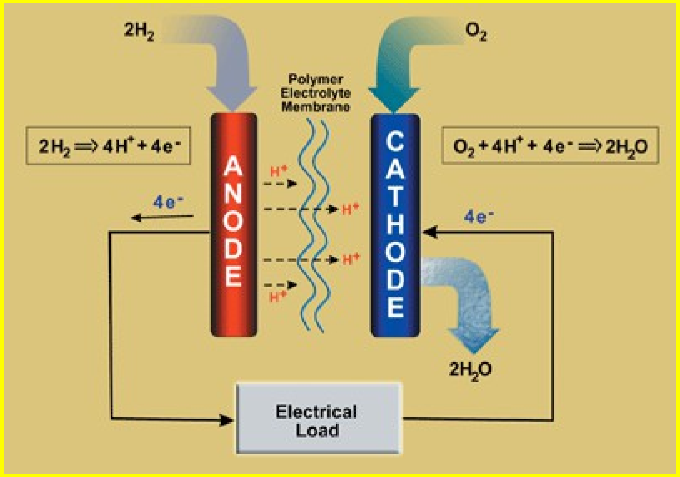


## *PEM Fuel cells*

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

$O_2 + * \rightarrow O_2*$

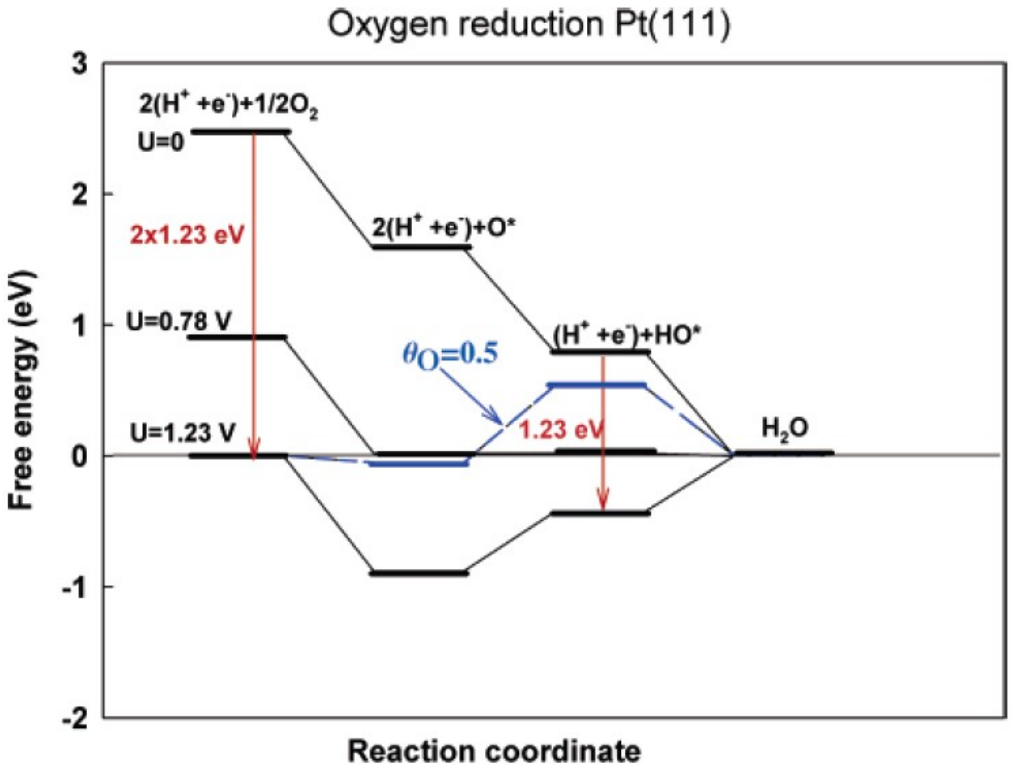
$O_2* + (H^+ + e^-) \rightarrow OOH*$

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

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

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

# Oxygen Reduction Reaction (ORR)

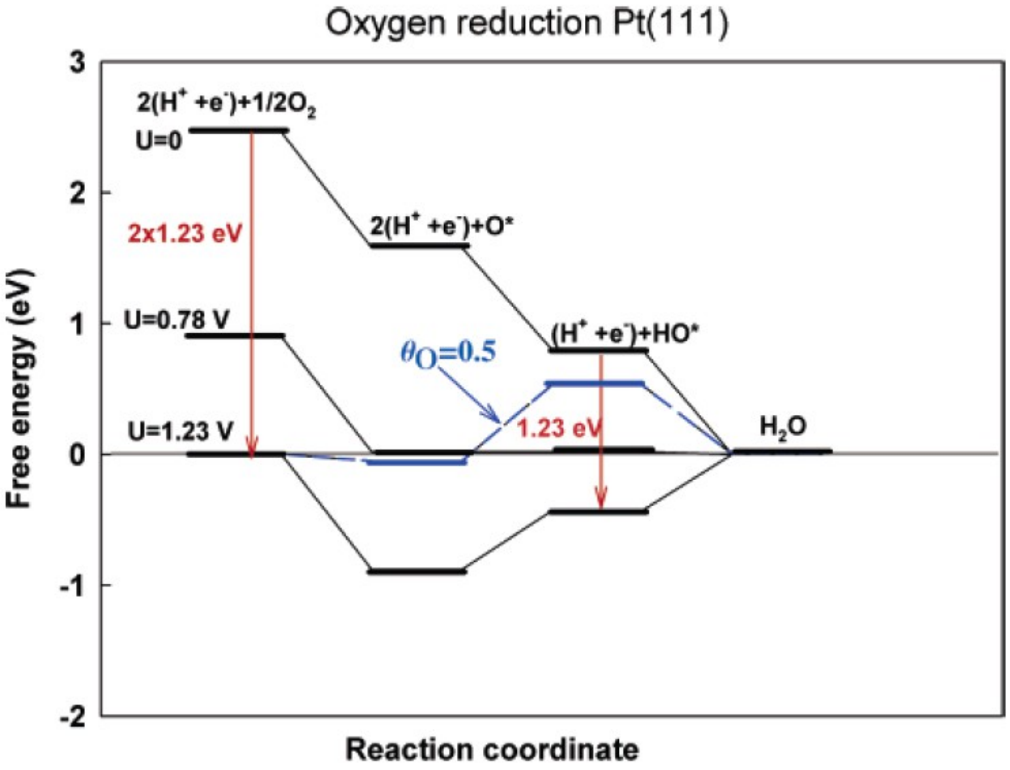


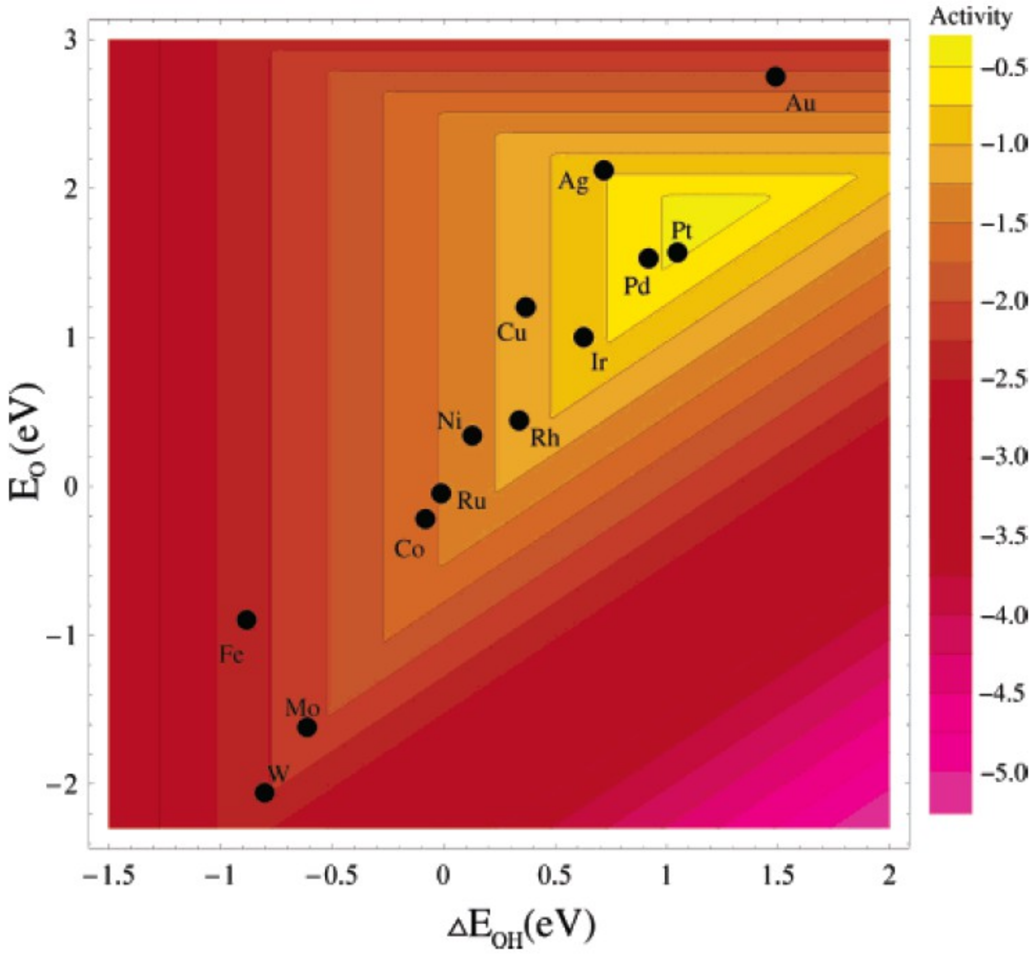
- Up to U = 0.78 V all steps are downhill
- At the theoretical potential U=1.23 V both ($H^+$ + $e^-$) steps are uphill.
- Overpotential $\eta$= 1.23-0.78 = 0.45 V
- Overpotential due to the stability of O* and OH* on Pt(111)

**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)

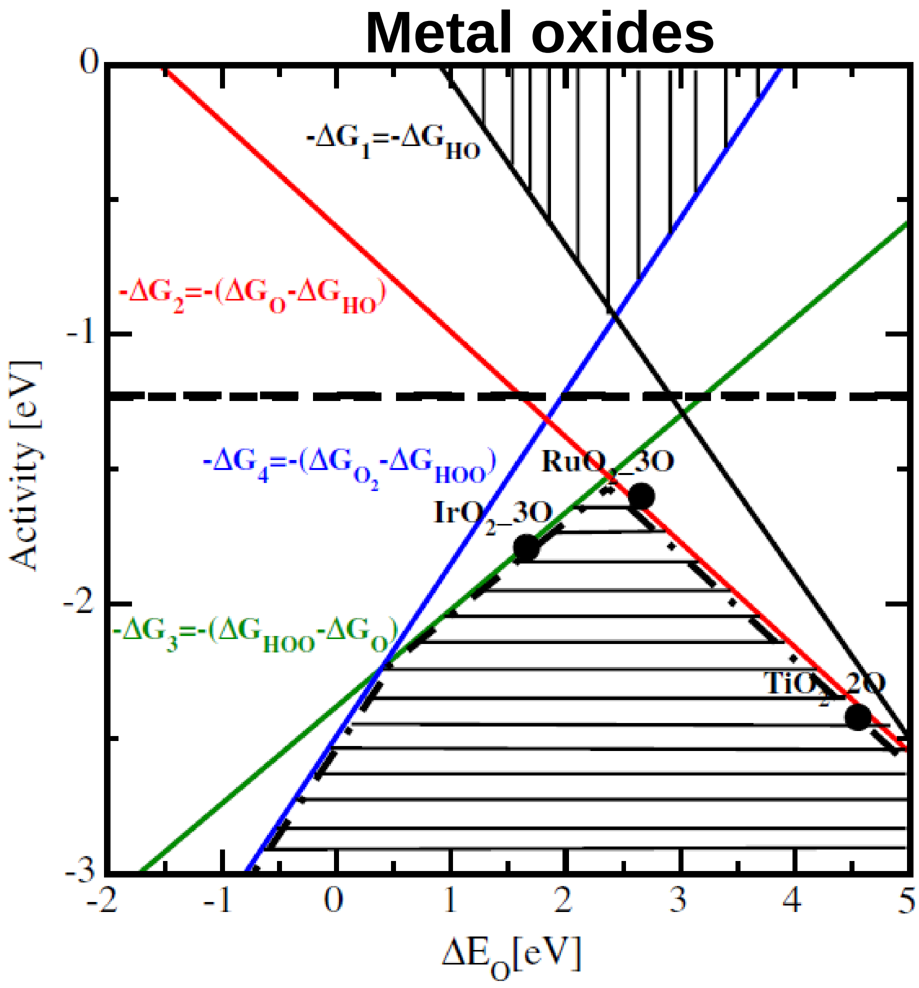


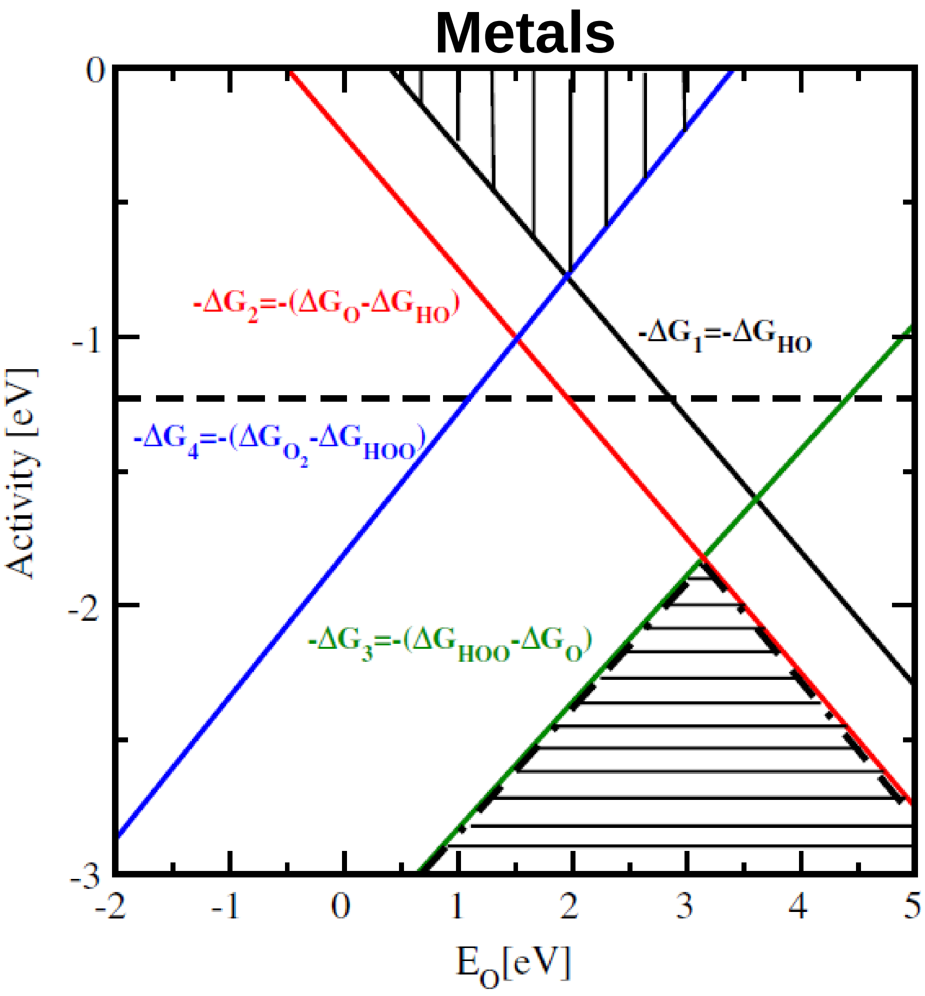


- Pt and Pd are at the top of the volcano
- $E_b(OH^*)$ and $E_b(O^*)$ are approximately linearly related

*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)