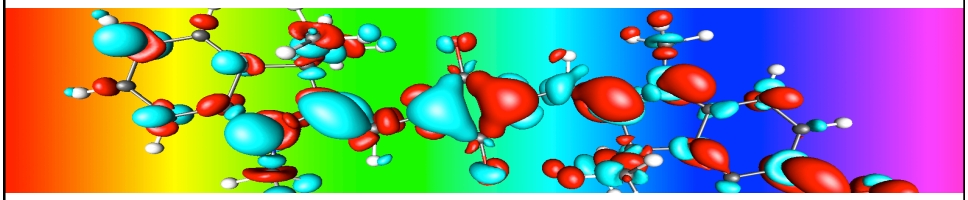
ICTP CARIBBEAN SCHOOL ON MATERIALS FOR CLEAN ENERGY
Cartagena, Colombia, May 30 – June 05, 2019

Water splitting on hematite surfaces: insights from density-functional theory



Ralph Gebauer

The Abdus Salam International Centre for Theoretical Physics

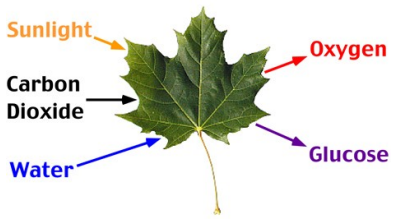
Tuesday, June 4th, 2019

Hydrogen production as key element for solar fuels

Solar fuels are

- chemical energy carriers
- like e.g. hydrogen, methane, or diesel fuel
- which are produced from sunlight
- through artificial photosynthesis or thermochemical reactions

Artificial photosynthesis: using light to make fuels



Solar fuels are a very timely topic:

From: R.F. Service, Science 349, 1158 (2015)

Solar fuels: which role in a renewable-energy landscape?

Providing a sustainable alternative to fossil fuels for mobility (road, air, etc.) is an important motivation

Filling up your car ...

energy content of diesel fuel: 43.2 MJ/kg
density: 0.745 kg/L
➔32.2 MJ/L

at the filling station:
50L in 2.5 min

energy “current”: 10.7 MJ/s = 10.7 MW

Artificial photosynthesis: using light to make fuels

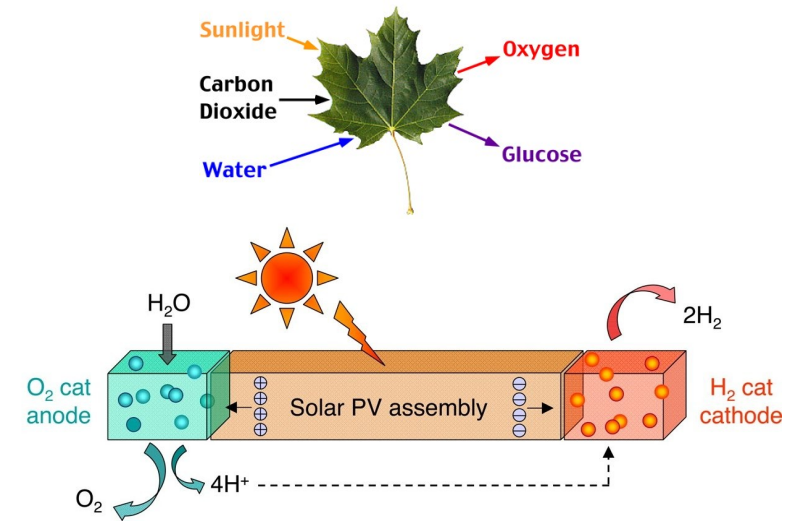
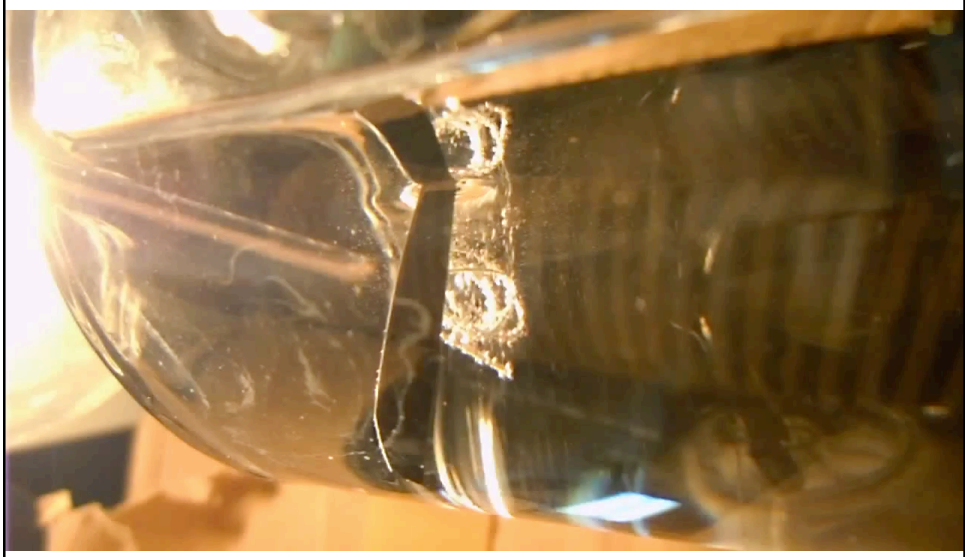
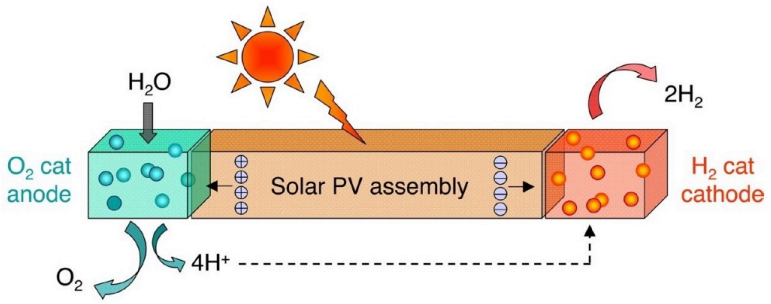


Figure from: Lewis and Nocera, PNAS **103**, 15729 (2006)



Artificial photosynthesis: using light to make fuels

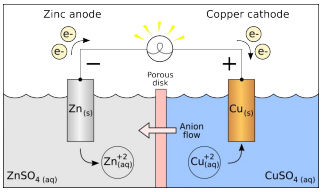


Overall reaction:	$2H_2O$	$\rightarrow O_2 + 2H_2$	(ΔG^0 = 4.92 eV, E^0 = -1.23 V)
Oxidation:	$2H_2O$	$\rightarrow O_2 + 4H^+ + 4e^-$	(E^0 = 1.23 V)
Reduction:	$2H^+ + 2e^-$	$\rightarrow H_2$	(E^0 = 0.00 V)

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

Electrochemistry: a quick overview

Galvanic cell



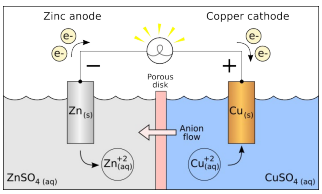
$Cu^{2+}(aq) + Zn(s) \rightarrow Cu(s) + Zn^{2+}(aq)$
Cathode (Red): $Cu^{2+}(aq) + 2e^- \rightarrow Cu(s)$
Anode (Ox): $Zn(s) \rightarrow Zn^{2+}(aq) + 2e^-$

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

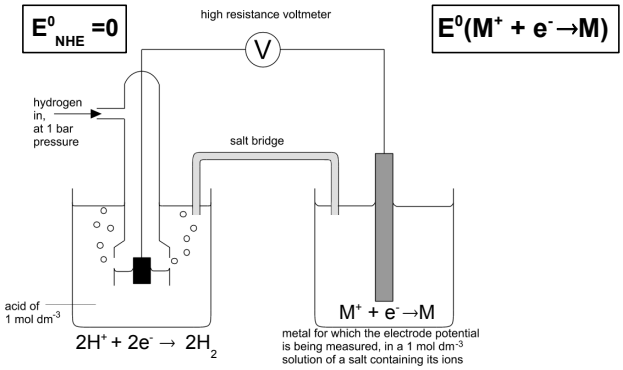
$E^0 = 0.34 - (-0.76) = 1.10$ V

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

Higher E^0 : reduction

Lower E^0: oxidation

Normal (Standard) Hydrogen Electrode (NHE)



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

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

Electrochemistry: a quick overview

ORR/OER

$O_2 + 4H^+ + 4e^- \rightarrow 2H_2O$	$E^0 = 1.23$ V
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Higher E^0 : reduction
Lower E^0: oxidation

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

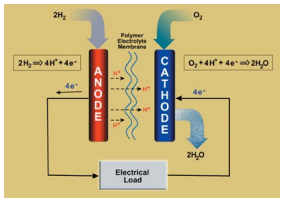
$O_2 + 4H^+ + 4e^- \rightarrow 2H_2O$ **ORR**

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

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

$E^0 = 1.23$ V

PEM Fuel cells



Electrochemistry: a quick overview

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

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

ORR

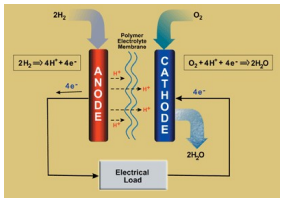
$O_2 + 4H^+ + 4e^- \rightarrow 2H_2O$

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

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

$E^0 = 1.23$ V

PEM Fuel cells



OER

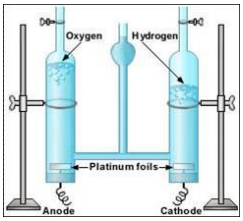
$2H_2O \rightarrow O_2 + 4H^+ + 4e^-$

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

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

$E^0 = -1.23$ V

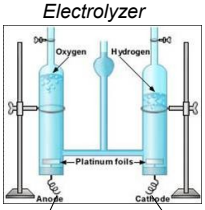
Electrolysis



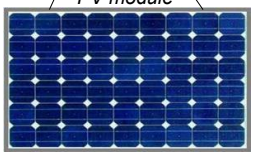
Artificial photosynthesis: using light to make fuels

Goal: storing solar energy through water splitting

Electrolyzer



PV module



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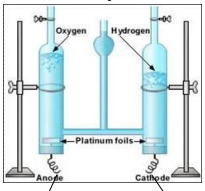
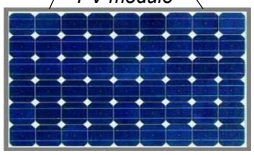
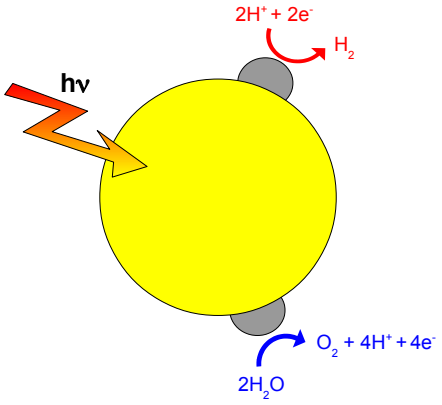


PV module

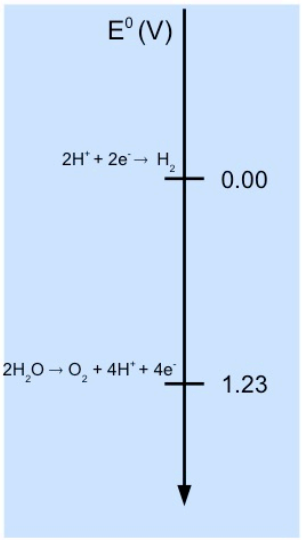


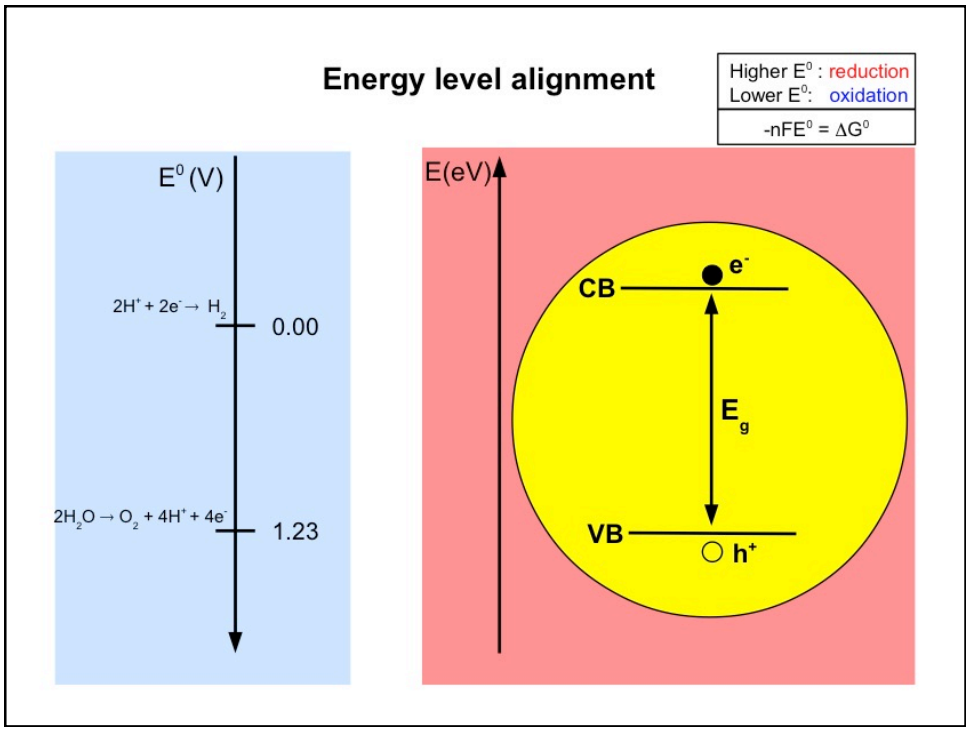
Integrated photo-catalyst

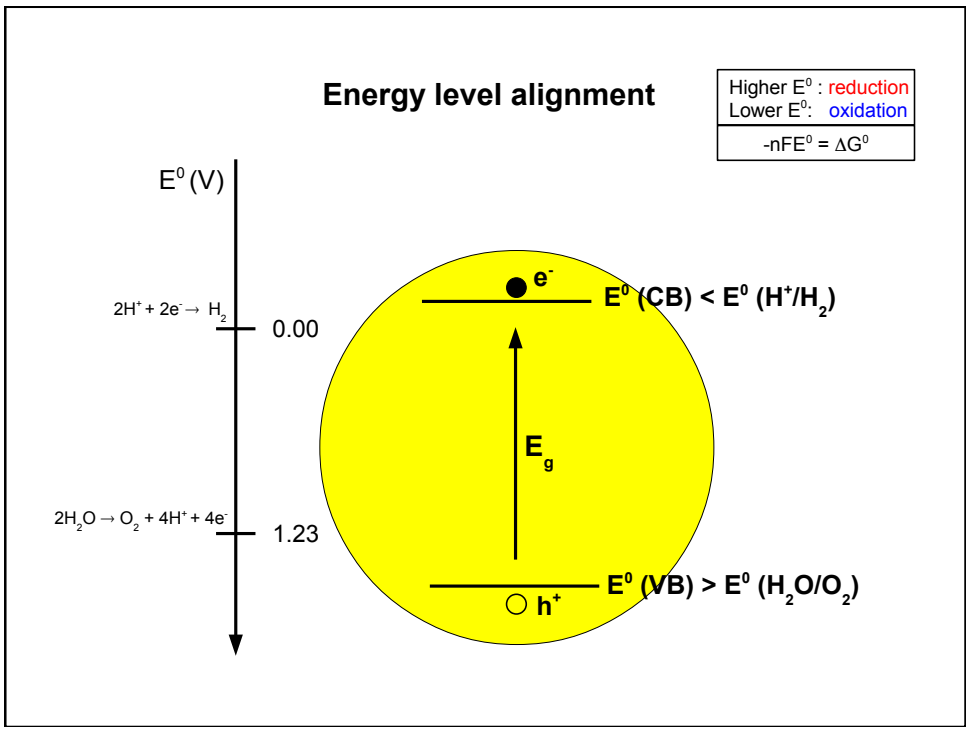


Energy level alignment

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

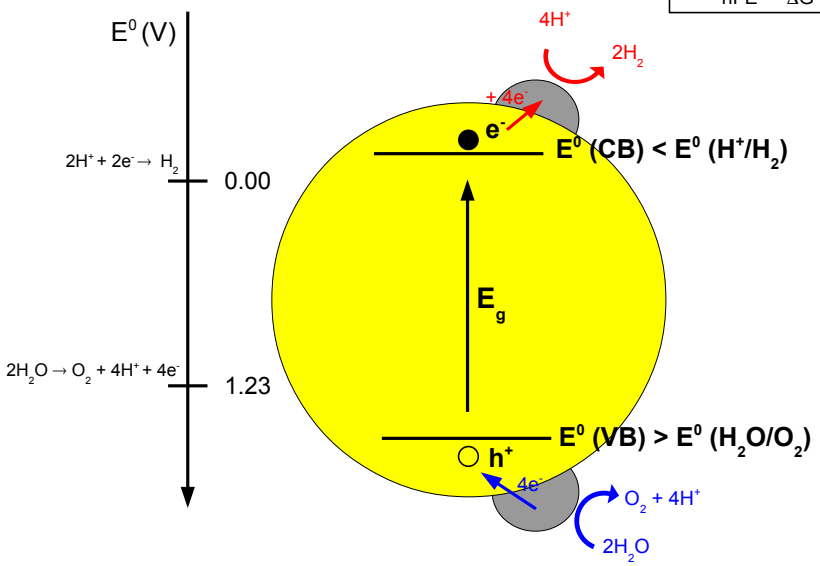



Energy level alignment
Higher E⁰ : reduction
Lower E⁰: oxidation
-nFE⁰ = ΔG⁰
E⁰ (V)
2H⁺ + 2e⁻ → H₂
0.00
2H₂O → O₂ + 4H⁺ + 4e⁻
1.23
E(eV)
CB
e⁻
Eg
VB
h⁺


Energy level alignment
Higher E⁰ : reduction
Lower E⁰: oxidation
-nFE⁰ = ΔG⁰
E⁰ (V)
2H⁺ + 2e⁻ → H₂
0.00
2H₂O → O₂ + 4H⁺ + 4e⁻
1.23
e⁻
E⁰ (CB) < E⁰ (H⁺/H₂)
Eg
h⁺
E⁰ (VB) > E⁰ (H₂O/O₂)

Energy level alignment

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



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:

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

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

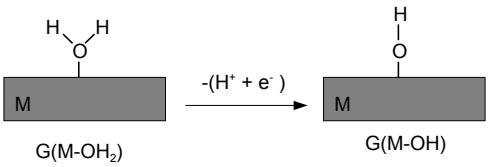
Therefore, using NHE as reference, we can compute the chemical potential of the $(H^+ + e^-)$ pair from the chemical potential of gas phase H_2

No need to estimate $\mu(H^+) + \mu(e^-)$ separately

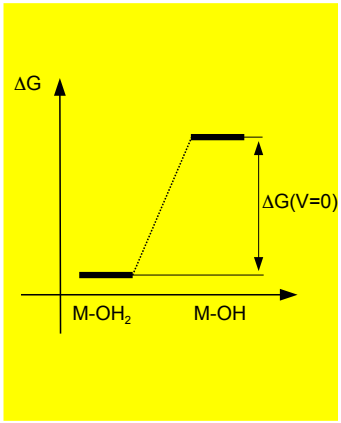
Nørskov's approach: Computational NHE

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

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



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



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

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

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

Nørskov's approach: Computational NHE

Finite V:

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

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

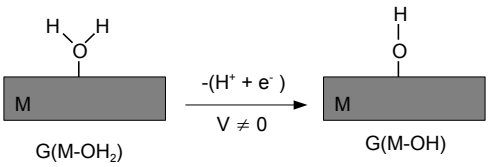
$\mu(H^+)+ \mu(e^-) = 1/2\mu(H_2) - eV$

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

Nørskov's approach: Computational NHE

Example: $V \neq 0$

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



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

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

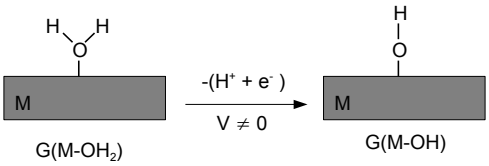
$= G(M\text{-}OH_2) + 1/2\mu(H_2) - eV - G(M\text{-}OH)$

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

Nørskov's approach: Computational NHE

Example: $V \neq 0$

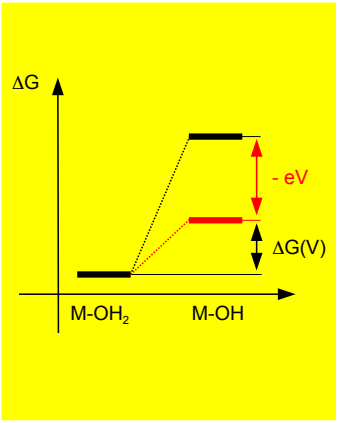
$M\text{-}OH_2 \rightarrow M\text{-}OH + H^+ + e^-$



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

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

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



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

Nørskov's approach: Computational NHE

Finite pH:

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

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

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

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

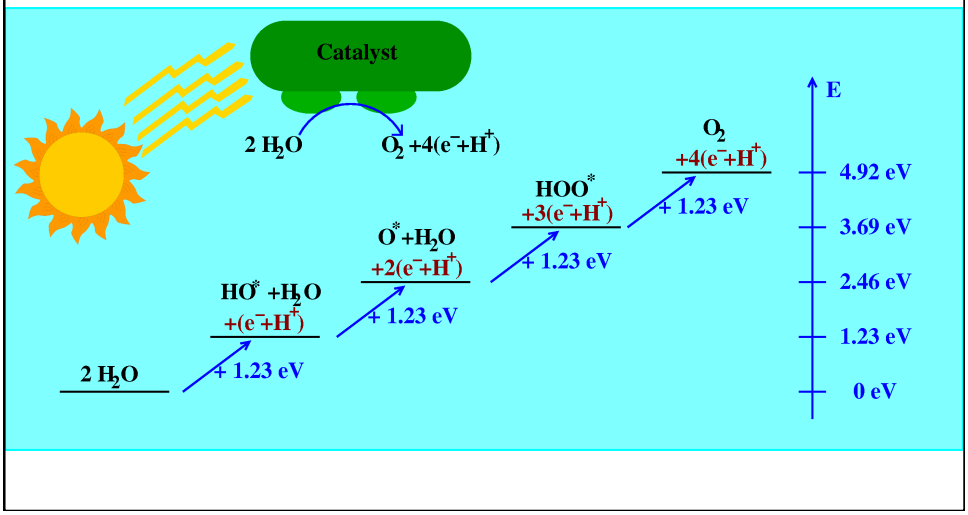
Limits: *only ($H^+ + e^-$) pairs (PCET). No ET nor PT steps*

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.

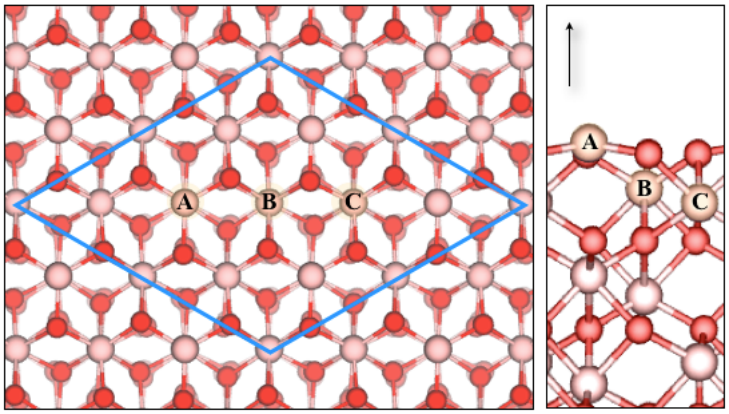
Limits: thermodynamics only. No kinetics.

Splitting water: what it takes

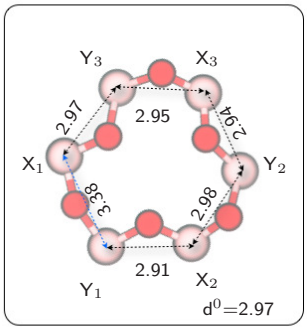
$$
\begin{aligned}
2H_2O + ()^* &\xrightarrow{A} HO^* + H_2O + H^+ + e^- \\
&\xrightarrow{B} O^* + H_2O + 2(H^+ + e^-) \\
&\xrightarrow{C} HOO^* + 3(H^+ + e^-) \\
&\xrightarrow{D} O_2 + 4(H^+ + e^-) + ()^*
\end{aligned}
$$



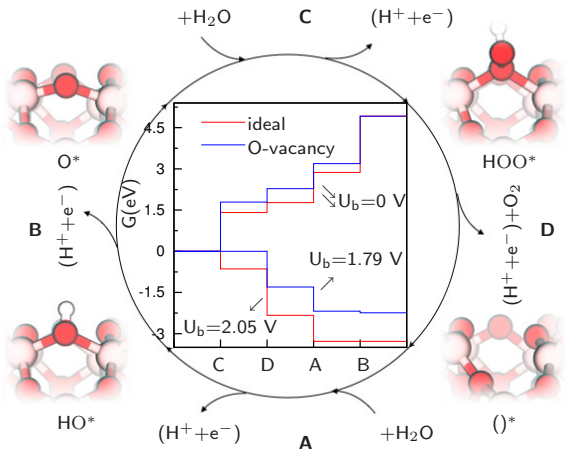
Computational model of hemaite (0001)-slab



The four PCET steps on ideal surfaces and with O-vacancy

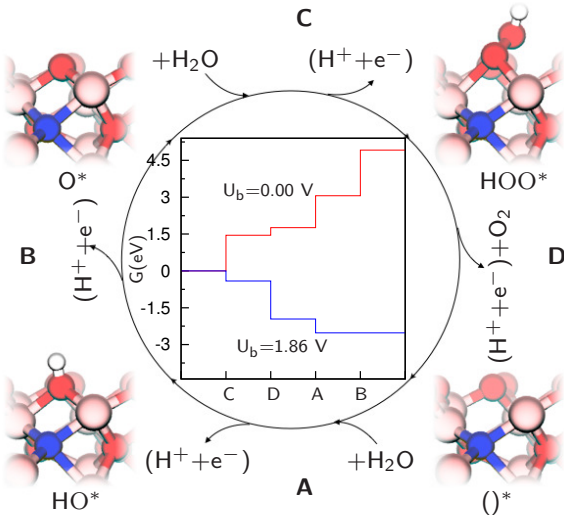


(a)



(b)

... and with N-doping:



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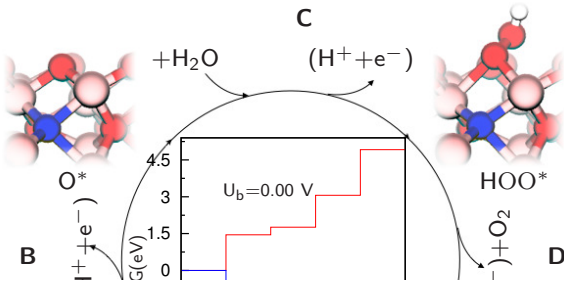
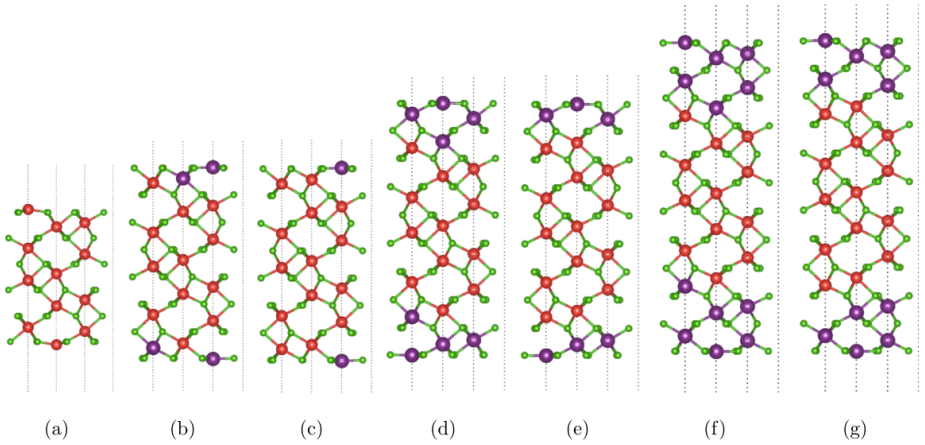
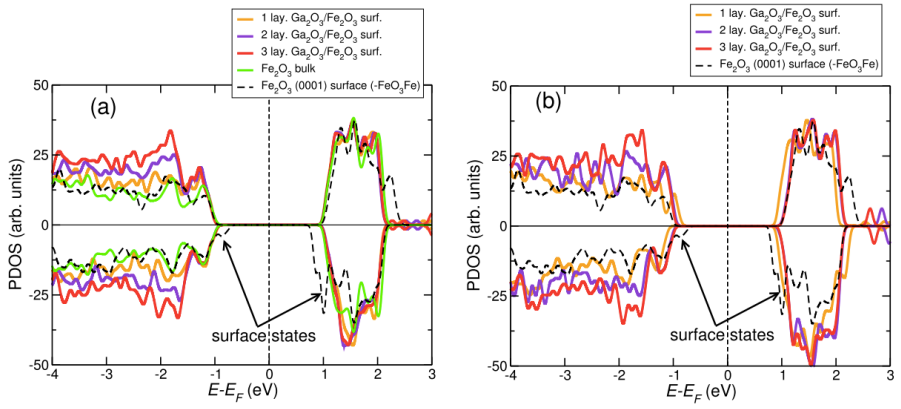


	ideal	O-va	Fe-va	N-doped
η	0.82	0.56	0.98	0.63
ΔE_O	−2.22	−2.73	−0.98	−2.21
ΔE_{OH}	−2.41	−2.60	−1.30	−2.21
ΔE_{OOH}	−0.92	−0.94	−0.54	−0.78

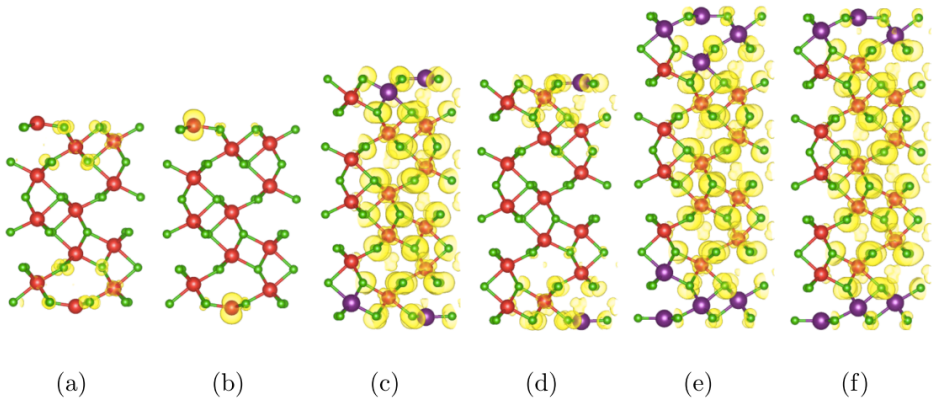
Role of surface states: covering with Ga layers



Role of surface states: covering with Ga layers



Role of surface states: covering with Ga layers



(a) (b) (c) (d) (e) (f)

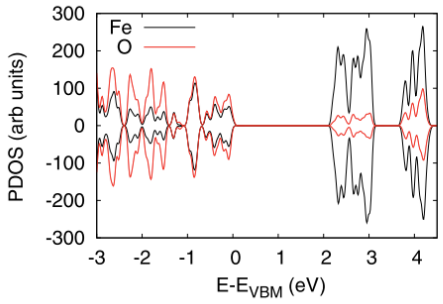
Which level of theory for hematite?

TABLE I. Kohn-Sham gap in bulk Fe_2O_3 as a function of the fraction of exact exchange (X) included in the PBE0 functional.

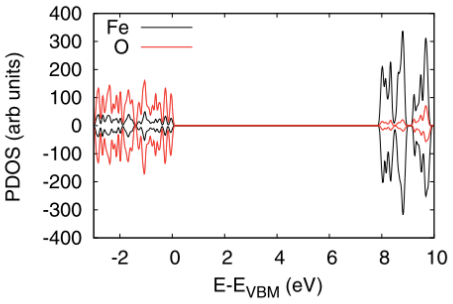
X(%)	E_{gap} (eV)
0	0.91
5	1.54
10	2.21
15	2.90
20	3.60
25	4.31
50	7.96
100	15.61

Functional: PBE0 with X % of HF exchange

Which level of theory for hematite?

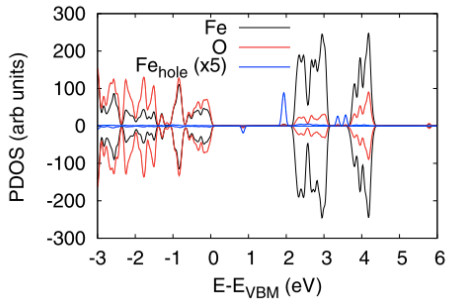


10% HF exchange

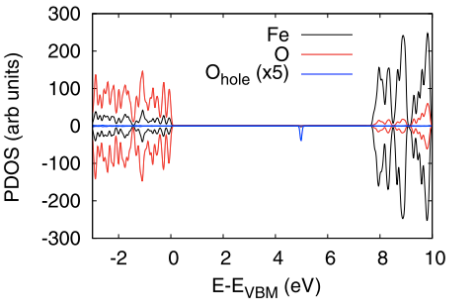


50% HF exchange

What about holes and polarons in hematite?

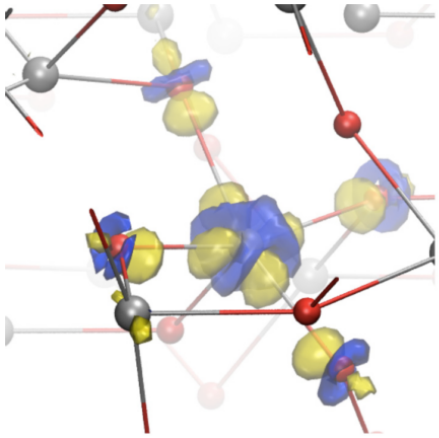


10% HF exchange

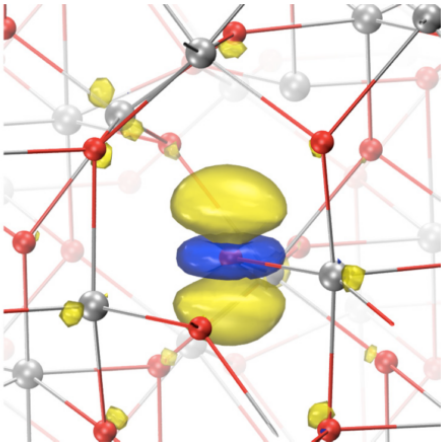


50% HF exchange

What about holes and polarons in hematite?



10% HF exchange



50% HF exchange

Trying to answer this problem by going towards higher levels of theory

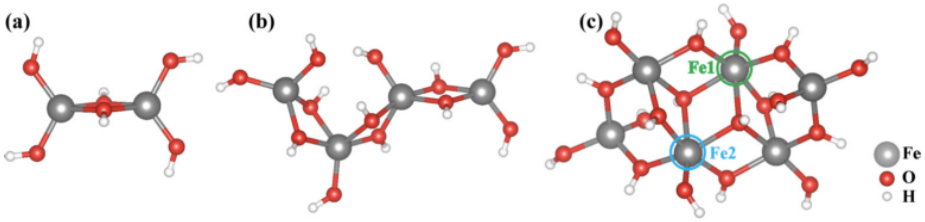


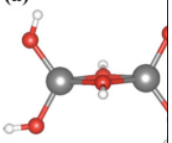
FIG. 4. Geometry of the neutral (a) $Fe_2O_6H_6$, (b) $Fe_4O_{12}H_{12}$, and (c) $Fe_6O_{18}H_{18}$ clusters.

wards

TABLE III. Change in the magnetic moments on the O and Fe atoms with respect to the neutral system of the $Fe_2O_6H_6$ (dimer), $Fe_4O_{12}H_{12}$ (tetramer), and $Fe_6O_{18}H_{18}$ (hexamer) clusters, in the presence of a hole, studied with different levels of theory.

	Method	%X	Δμ(O)	Δμ(Fe)
Dimer	PBE0	0	0.08	0.86
		10	0.08	0.80
		25	0.07	0.70
		30	0.95	0.00
		50	0.98	0.01
		100	1.00	0.01
	HF	100	1.18	−0.05
	MP2	100	1.19	−0.05
	CCSD	100	1.00	−0.07
Tetramer	PBE0	0	0.22	0.88
		10	0.10	0.84
		25	0.22	0.70
		30	1.14	−0.05
		50	1.13	−0.06
		100	1.09	−0.05
	HF	100	1.19	−0.08
	MP2	100	1.14	−0.09
Hexamer	PBE0	0	0.18	0.85
		10	0.21	0.77
		25	0.32	0.64
		30	1.13	−0.03
		50	1.19	−0.04
		100	1.14	−0.03
	HF	100	1.21	−0.11

(a)



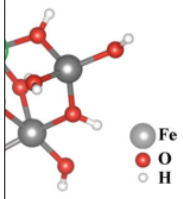


FIG. 4. Ge

H_{18} clusters.

Conclusions

Solar hydrogen as an important ingredient for clean energy solutions

OER very challenging: 4-electron process

“Computational hydrogen electrode” as a useful tool for simulations

Hematite interesting material for OER, but many issues are still open

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