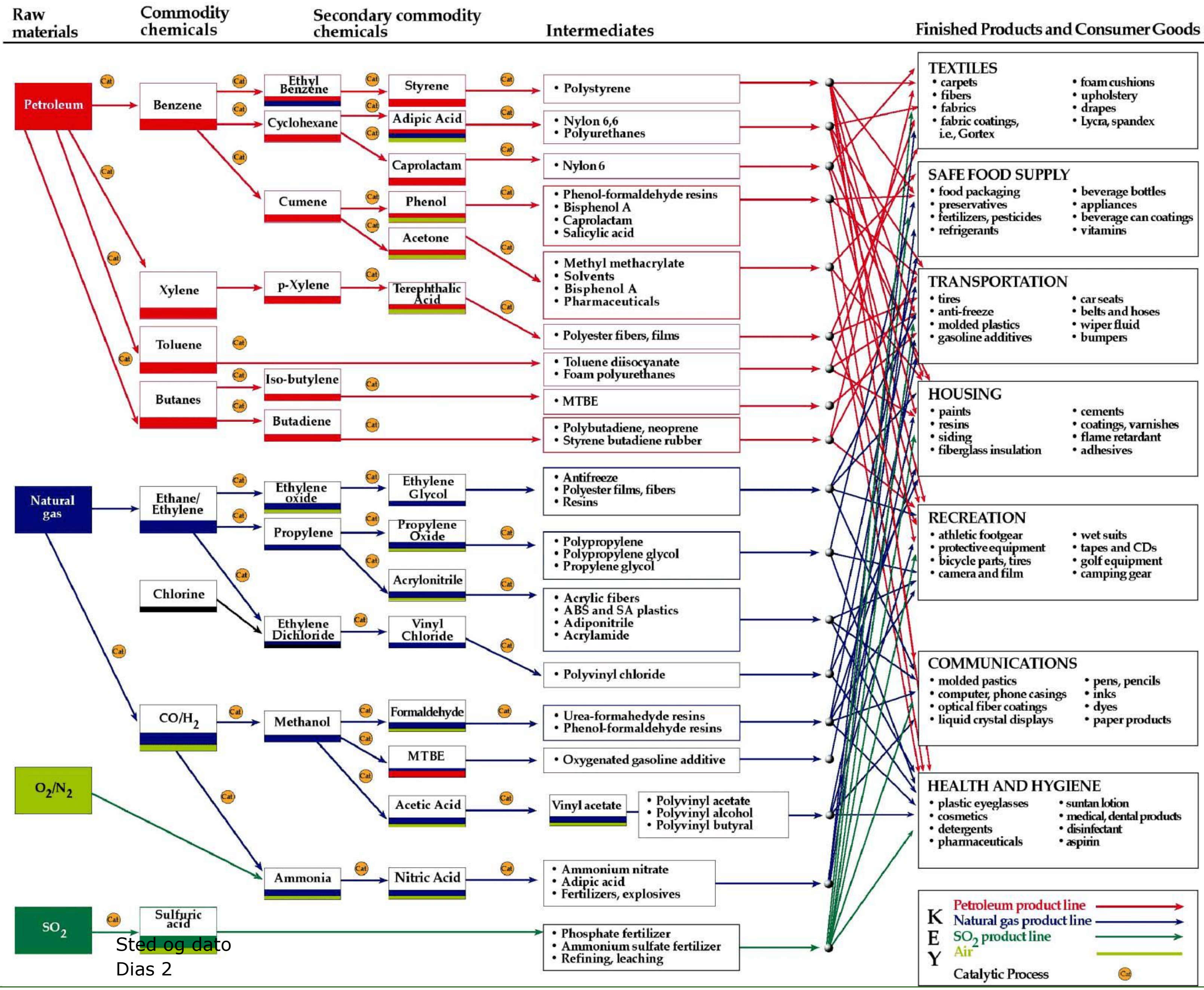
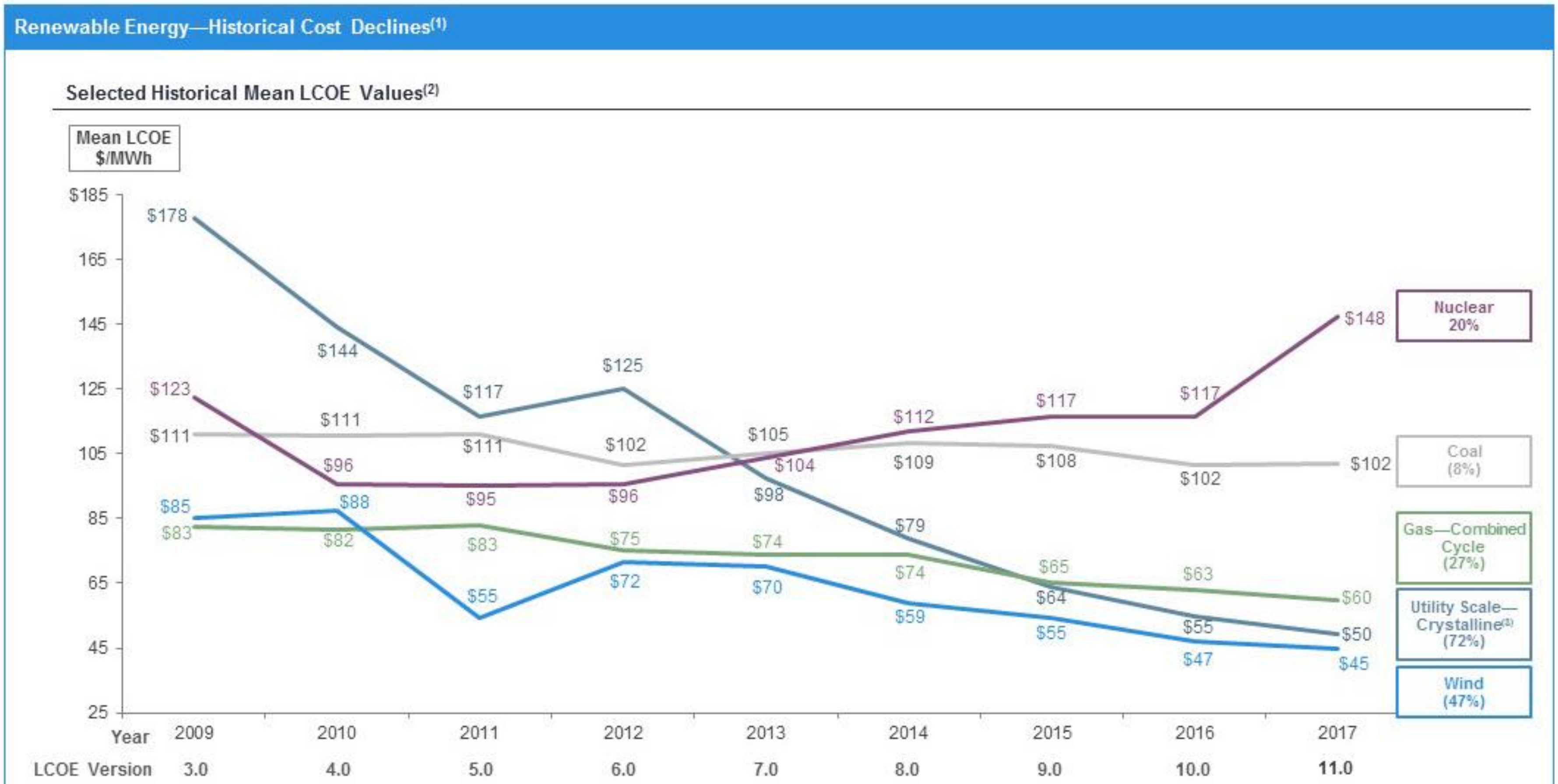
(Towards)-Modelling the Electrochemical Interface

Jan Rossmeisl.
Department of Chemistry
University of Copenhagen


Raw materials
Commodity chemicals
Secondary commodity chemicals
Intermediates
Finished Products and Consumer Goods
Petroleum
Benzene
Ethyl Benzene
Styrene
• Polystyrene
Cyclohexane
Adipic Acid
• Nylon 6,6
• Polyurethanes
Caprolactam
• Nylon 6
Cumene
Phenol
• Phenol-formaldehyde resins
• Bisphenol A
• Caprolactam
• Salicylic acid
Acetone
• Methyl methacrylate
• Solvents
• Bisphenol A
• Pharmaceuticals
Xylene
p-Xylene
Terephthalic Acid
• Polyester fibers, films
Toluene
• Toluene diisocyanate
• Foam polyurethanes
Butanes
Iso-butylene
• MTBE
Butadiene
• Polybutadiene, neoprene
• Styrene butadiene rubber
Natural gas
Ethane/ Ethylene
Ethylene oxide
Ethylene Glycol
• Antifreeze
• Polyester films, fibers
• Resins
Propylene
Propylene Oxide
• Polypropylene
• Polypropylene glycol
• Propylene glycol
Acrylonitrile
• Acrylic fibers
• ABS and SA plastics
• Adiponitrile
• Acrylamide
Chlorine
Ethylene Dichloride
Vinyl Chloride
• Polyvinyl chloride
CO/H2
Methanol
Formaldehyde
• Urea-formahedyde resins
• Phenol-formaldehyde resins
MTBE
• Oxygenated gasoline additive
Acetic Acid
Vinyl acetate
• Polyvinyl acetate
• Polyvinyl alcohol
• Polyvinyl butyral
O2/N2
Ammonia
Nitric Acid
• Ammonium nitrate
• Adipic acid
• Fertilizers, explosives
SO2
Sulfuric acid
• Phosphate fertilizer
• Ammonium sulfate fertilizer
• Refining, leaching
TEXTILES
• carpets
• fibers
• fabrics
• fabric coatings, i.e., Gortex
• foam cushions
• upholstery
• drapes
• Lycra, spandex
SAFE FOOD SUPPLY
• food packaging
• preservatives
• fertilizers, pesticides
• refrigerants
• beverage bottles
• appliances
• beverage can coatings
• vitamins
TRANSPORTATION
• tires
• anti-freeze
• molded plastics
• gasoline additives
• car seats
• belts and hoses
• wiper fluid
• bumpers
HOUSING
• paints
• resins
• siding
• fiberglass insulation
• cements
• coatings, varnishes
• flame retardant
• adhesives
RECREATION
• athletic footgear
• protective equipment
• bicycle parts, tires
• camera and film
• wet suits
• tapes and CDs
• golf equipment
• camping gear
COMMUNICATIONS
• molded pastics
• computer, phone casings
• optical fiber coatings
• liquid crystal displays
• pens, pencils
• inks
• dyes
• paper products
HEALTH AND HYGIENE
• plastic eyeglasses
• cosmetics
• detergents
• pharmaceuticals
• suntan lotion
• medical, dental products
• disinfectant
• aspirin
KEY
Petroleum product line
Natural gas product line
SO2 product line
Air
Catalytic Process
Cat

Future: cheap (free) electricity



Source: Lazard estimates.

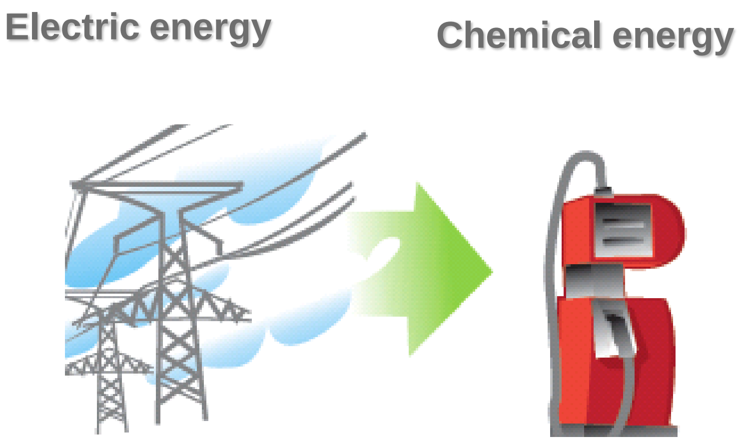
Note: Reflects average of unsubsidized high and low LCOE range for given version of LCOE study.

(1) Primarily relates to North American alternative energy landscape, but reflects broader/global cost declines.

(2) Reflects total decrease in mean LCOE since the later of Lazard's LCOE—Version 3.0 or the first year Lazard has tracked the relevant technology.

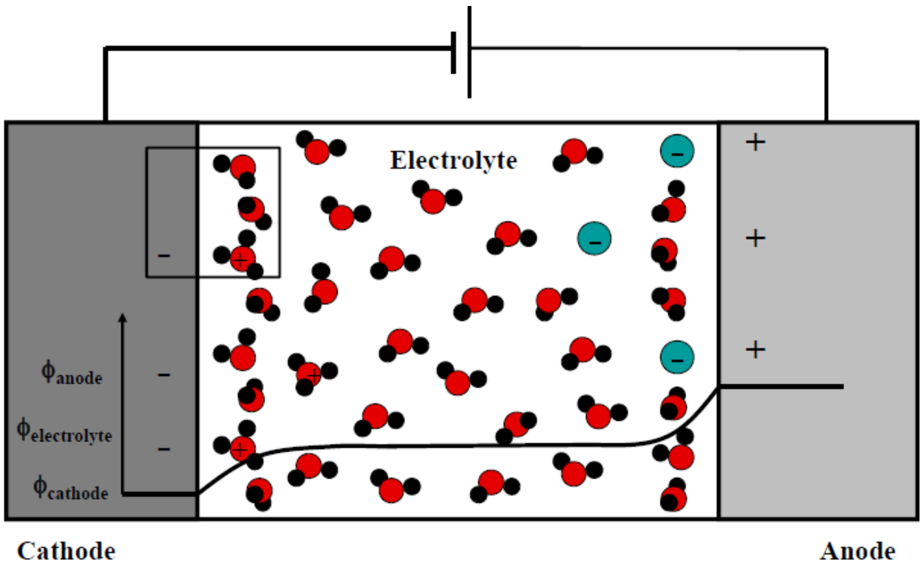
(3) Reflects mean of fixed tilt (high end) and single axis tracking (low end) crystalline PV installations.

Electrochemical Energy Conversion

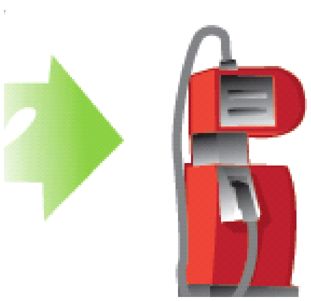


Challenge, control the surface chemistry

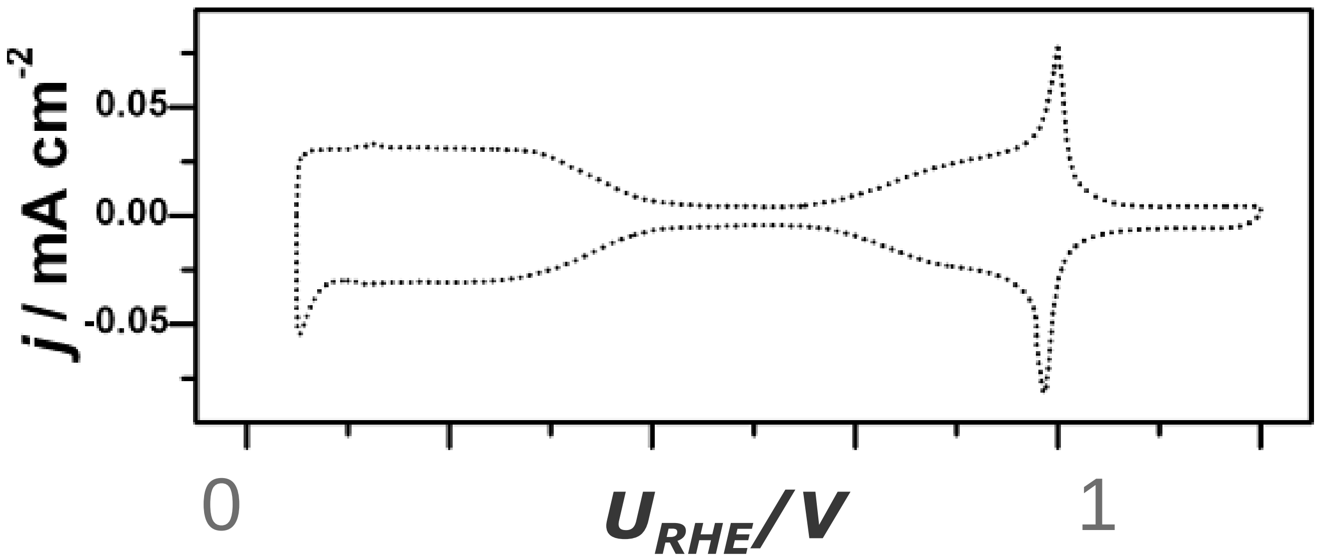
Electric energy

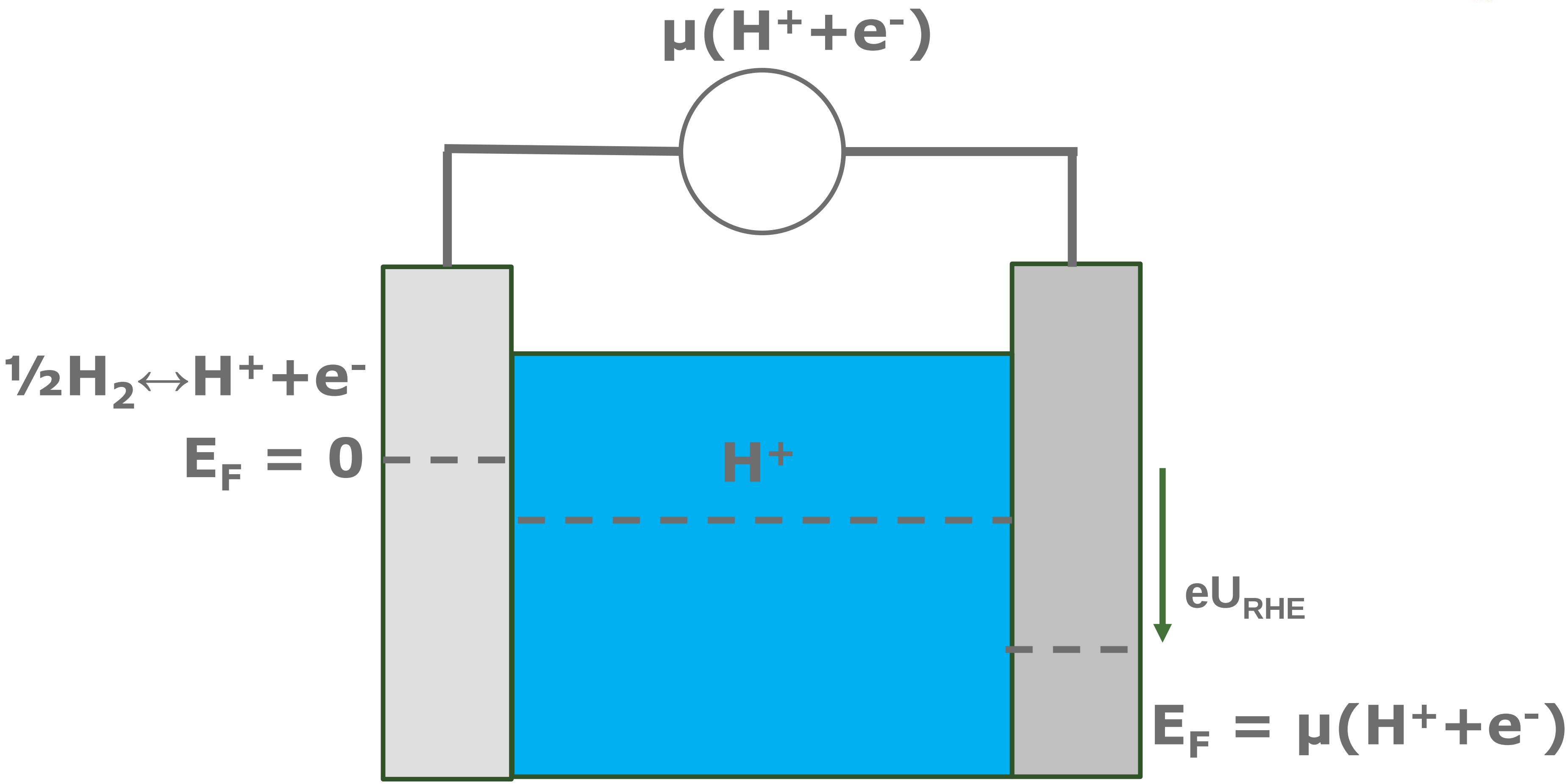


Chemical energy



Why use DFT



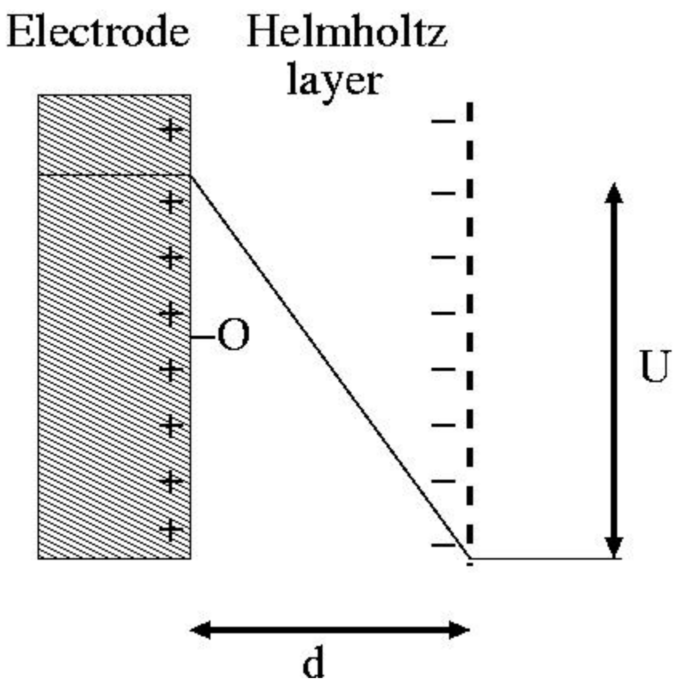


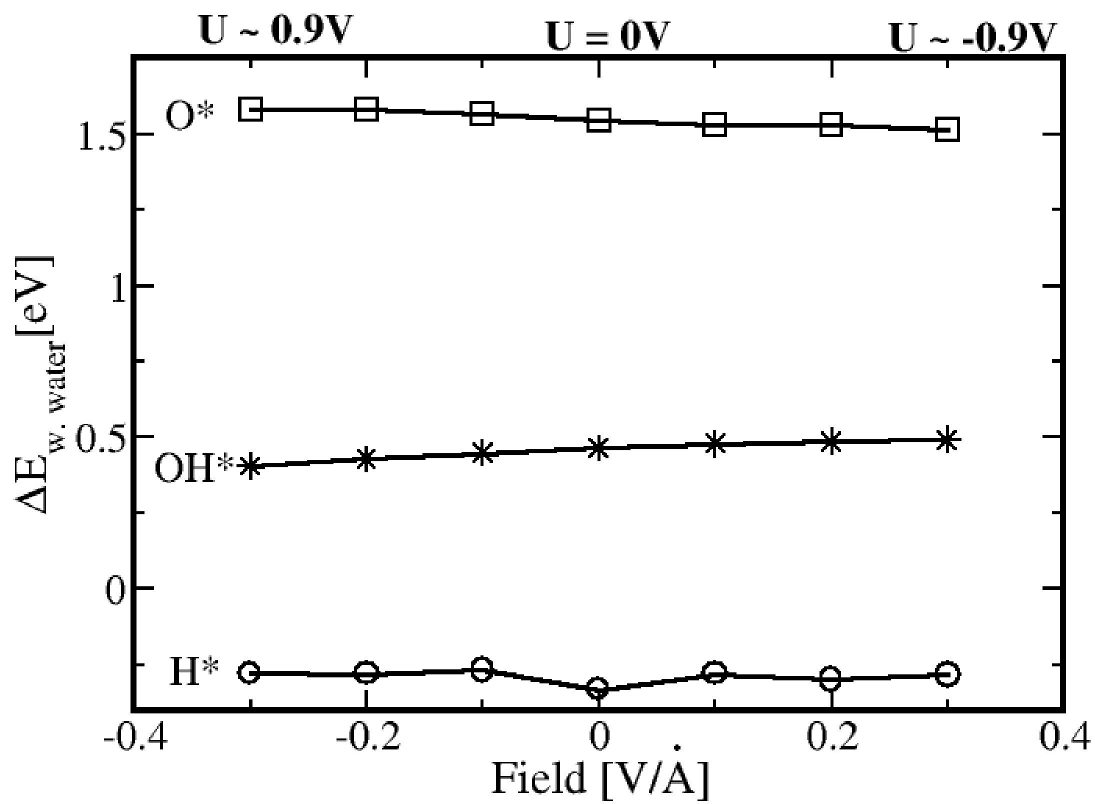
$$\mu = -eU_{RHE}$$

Computational Hydrogen Electrode

Nørskov, Rossmeisl, Logadottir, Lindqvist, Kitchin, Bligaard Jónsson, *J. Phys. Chem. B*, **108**, (2004)

Field effects



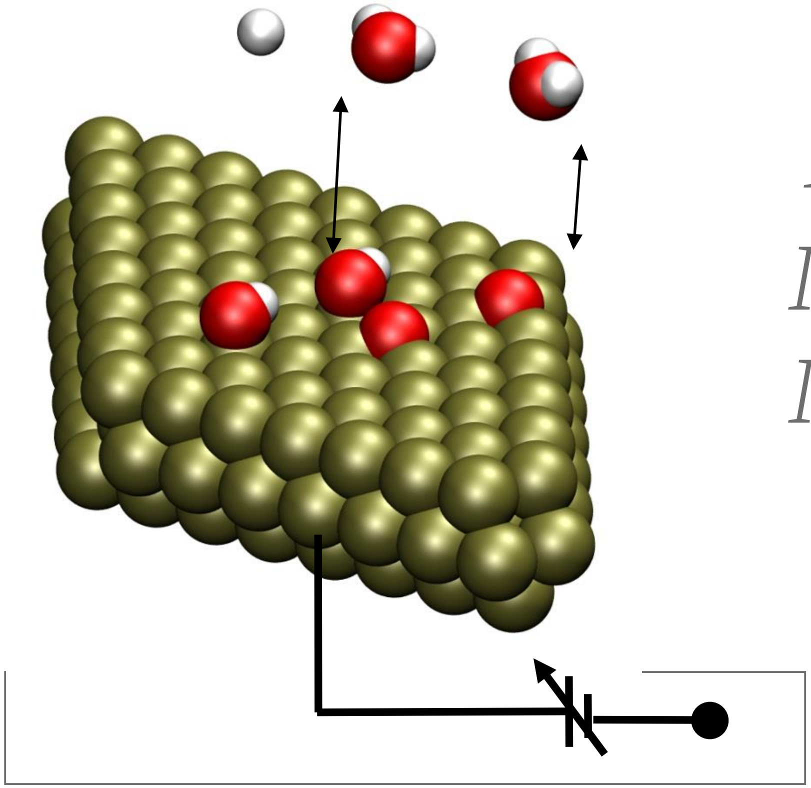


Rossmeisl, Nørskov, Taylor, Janik, Neurock. *J. Phys. Chem. B* **110**, (2006), 21833-21839

Karlberg, Rossmeisl, Nørskov, PCCP, 9 (2007) 5158

Evaluate energy of the surface as function of the potential

$$E_N(U_{RHE})=E(N)-E(0)-½NG(H_2)-½NeU_{RHE}$$



U vs. RHE

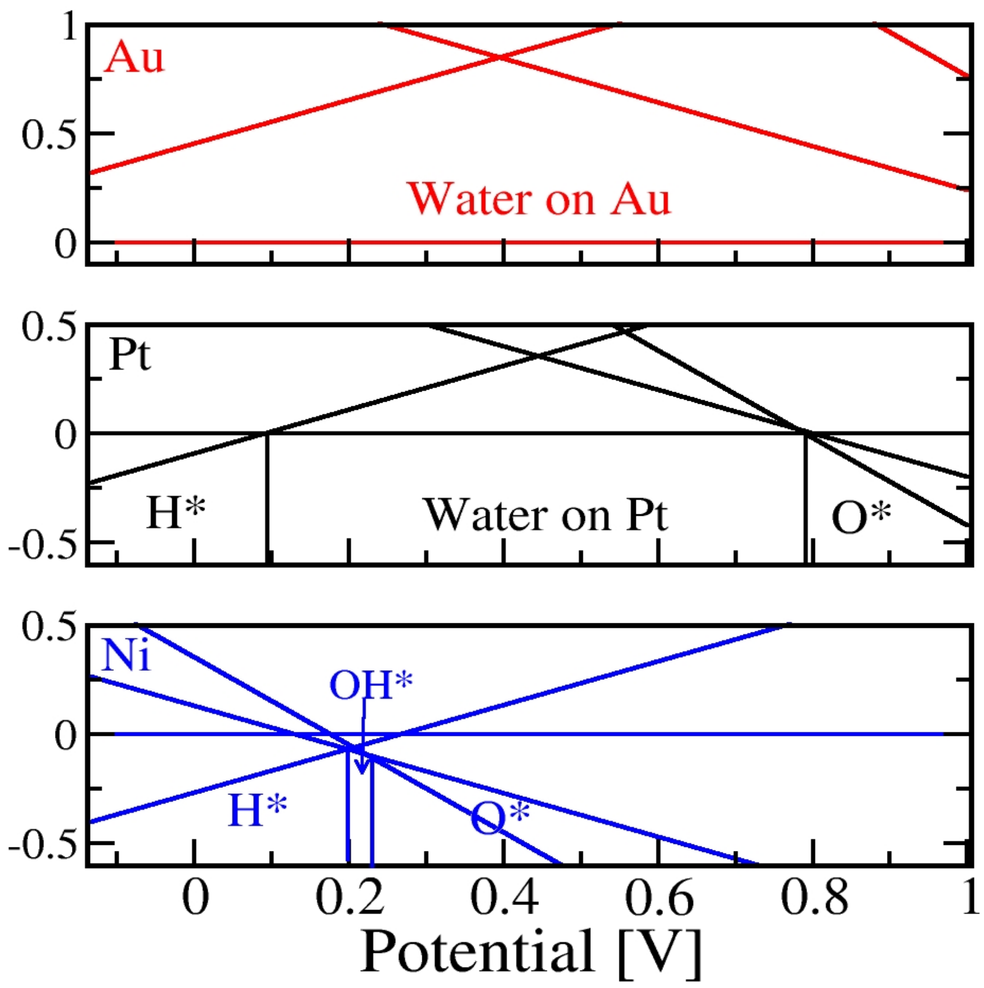
$N=1 \qquad H^+ + e^- + * \leftrightarrow H*$

$N=-1 \qquad H_2O + * \rightleftarrows *OH + H^+ + e^-$

$N=-2 \qquad *OH \rightleftarrows O* + H^+ + e^-$

Phase-diagrams

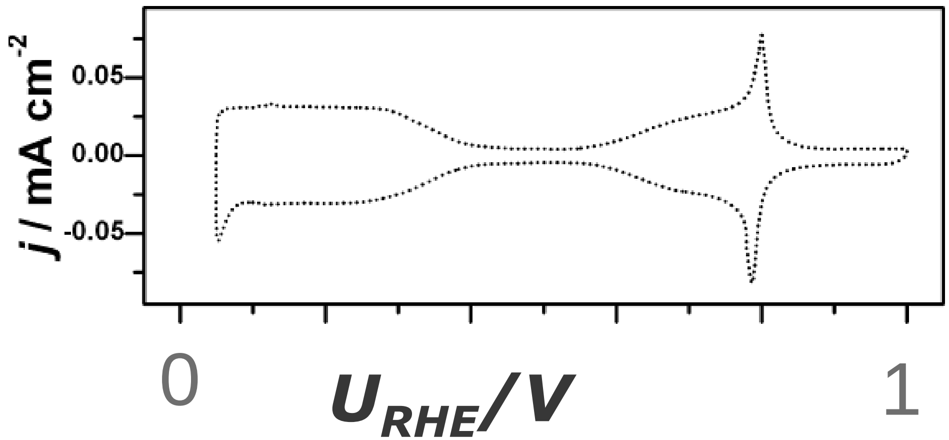
$E_N(U_{RHE})$

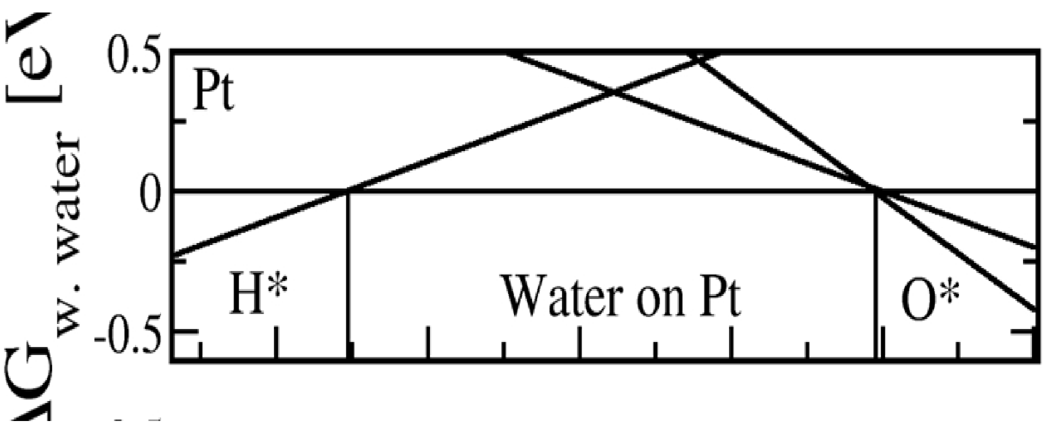


Rossmeisl, Nørskov, Taylor, Janik, Neurock. *J. Phys. Chem. B* **110**, (2006)

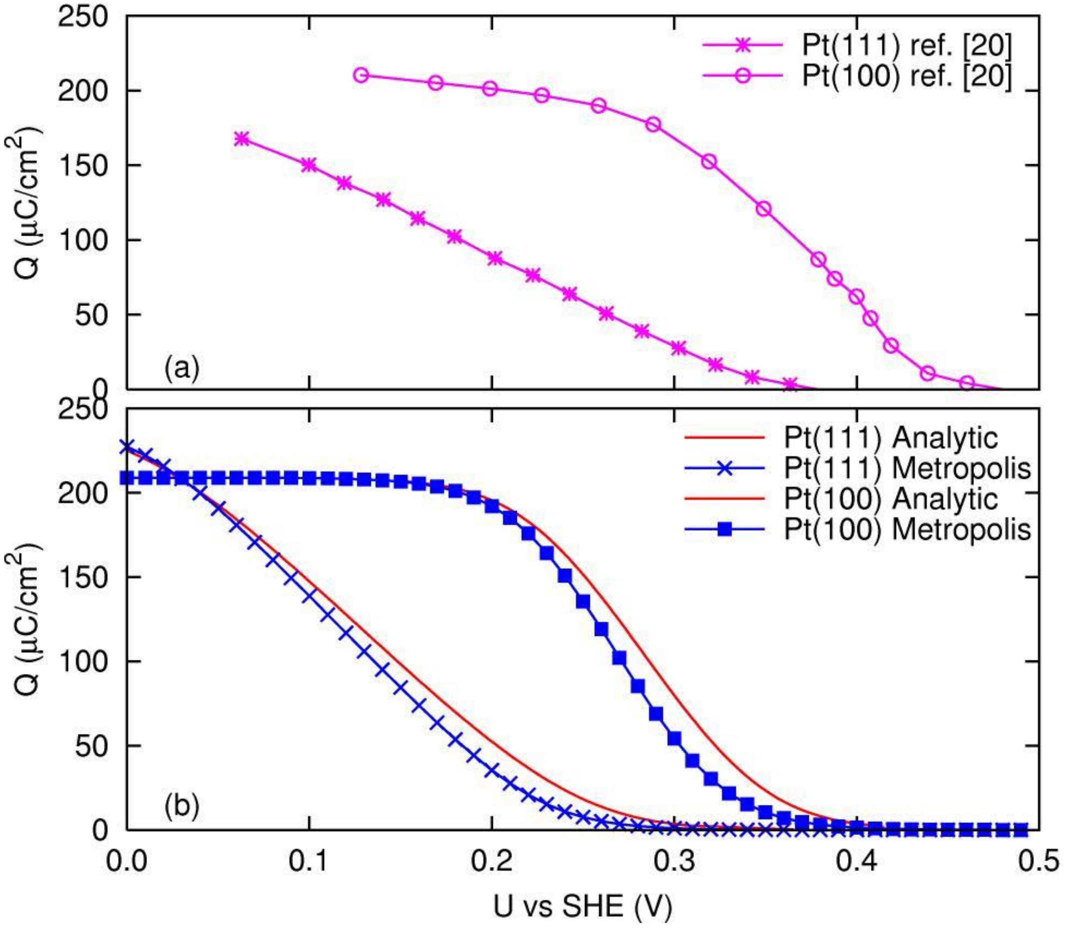
Cyclic voltammetry

CV for Pt(111)





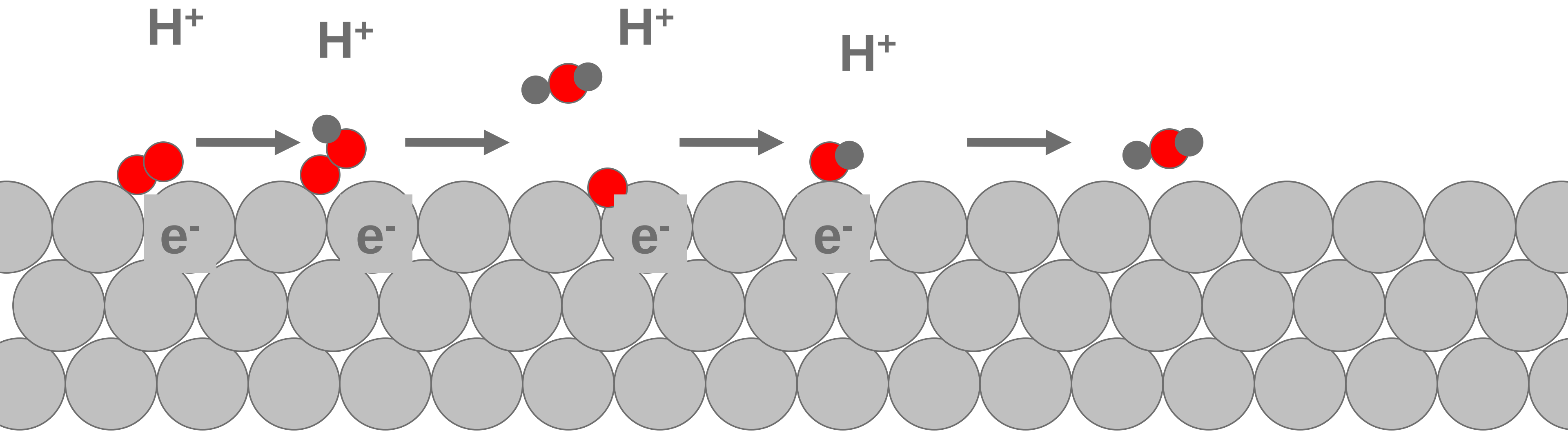
$H^+ + e^- \rightarrow H^*$

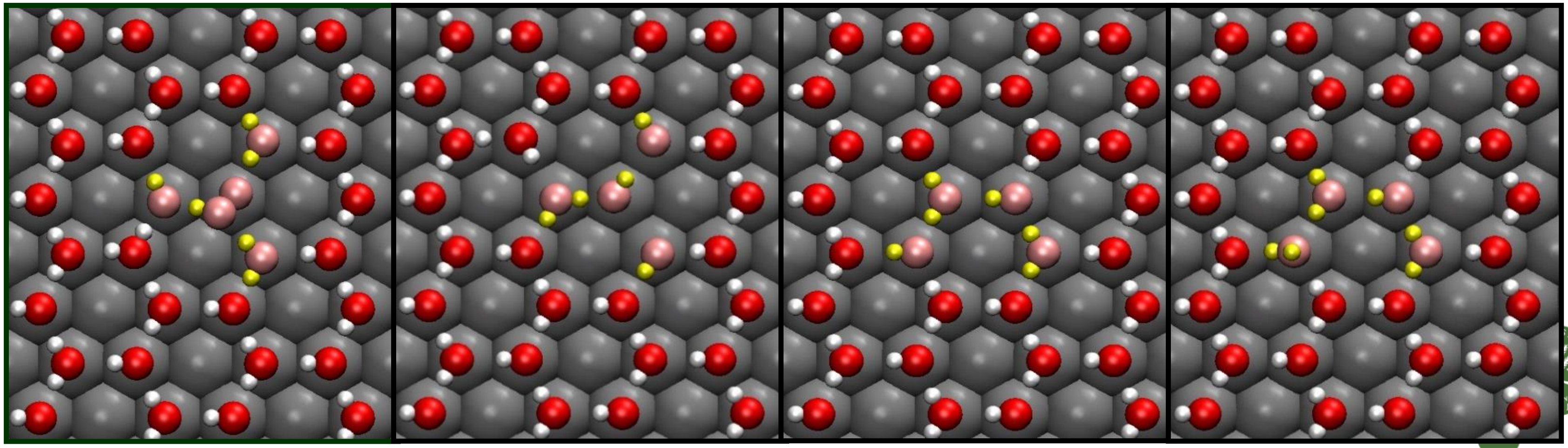


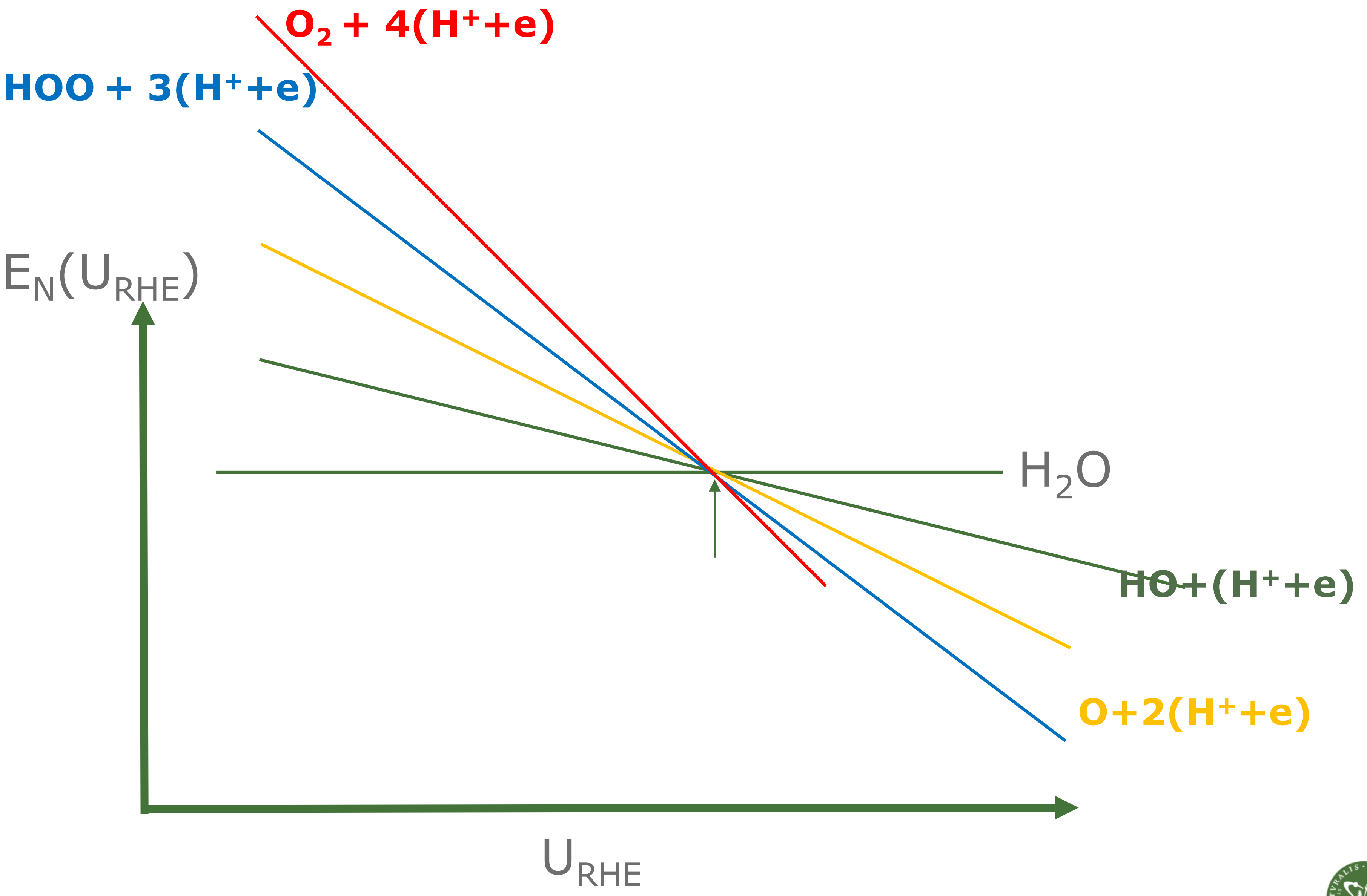
Markovic et al J. Phys. Chem. **101**, 5405 (1997)

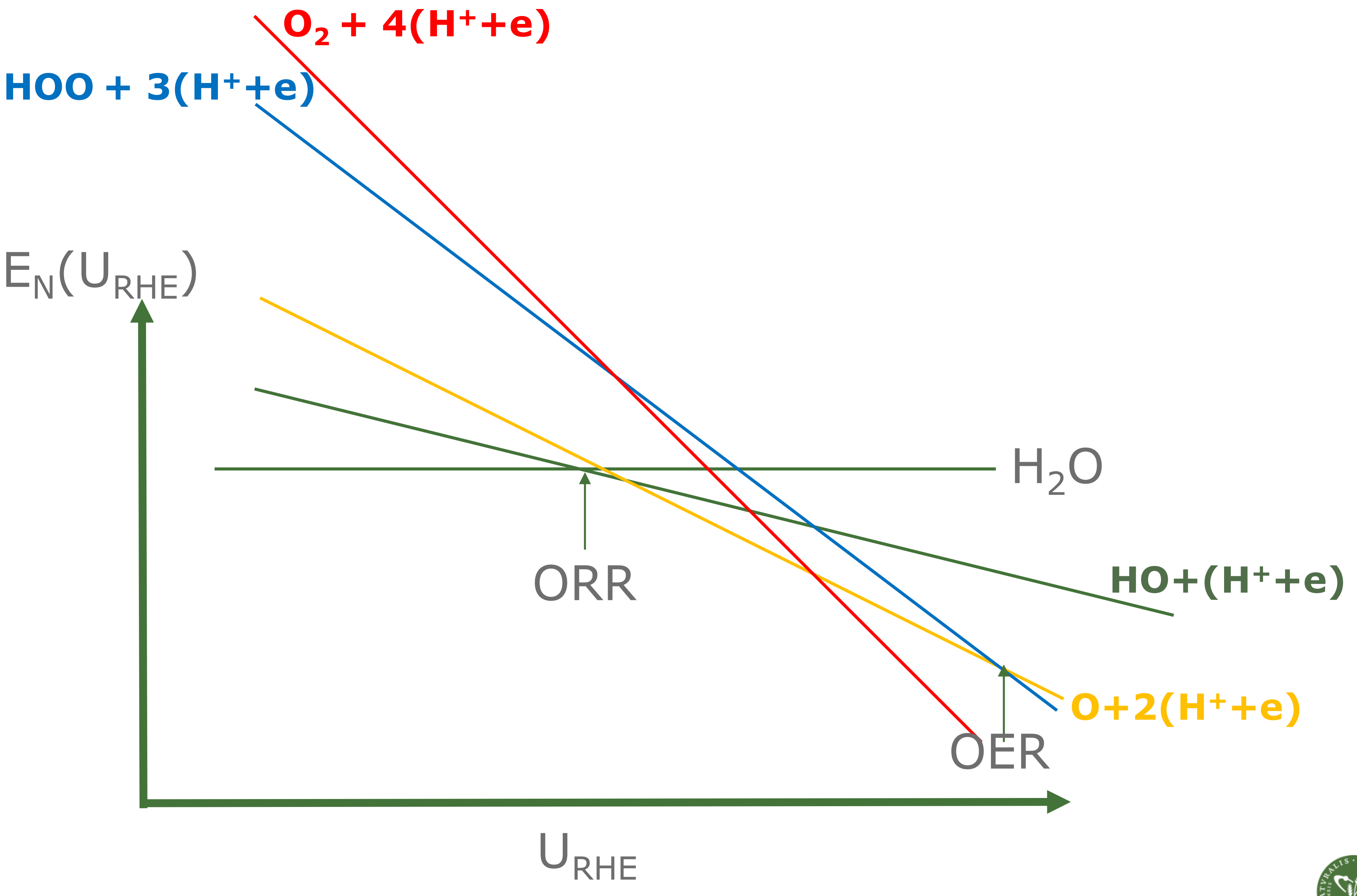
G.S. Karlberg, T. Jaramillo, E.Skulason, J. Rossmeisl, T. Bligaard, J.K. Nørskov. *PRL*, 99, (2007)

ORR and OER intermediates





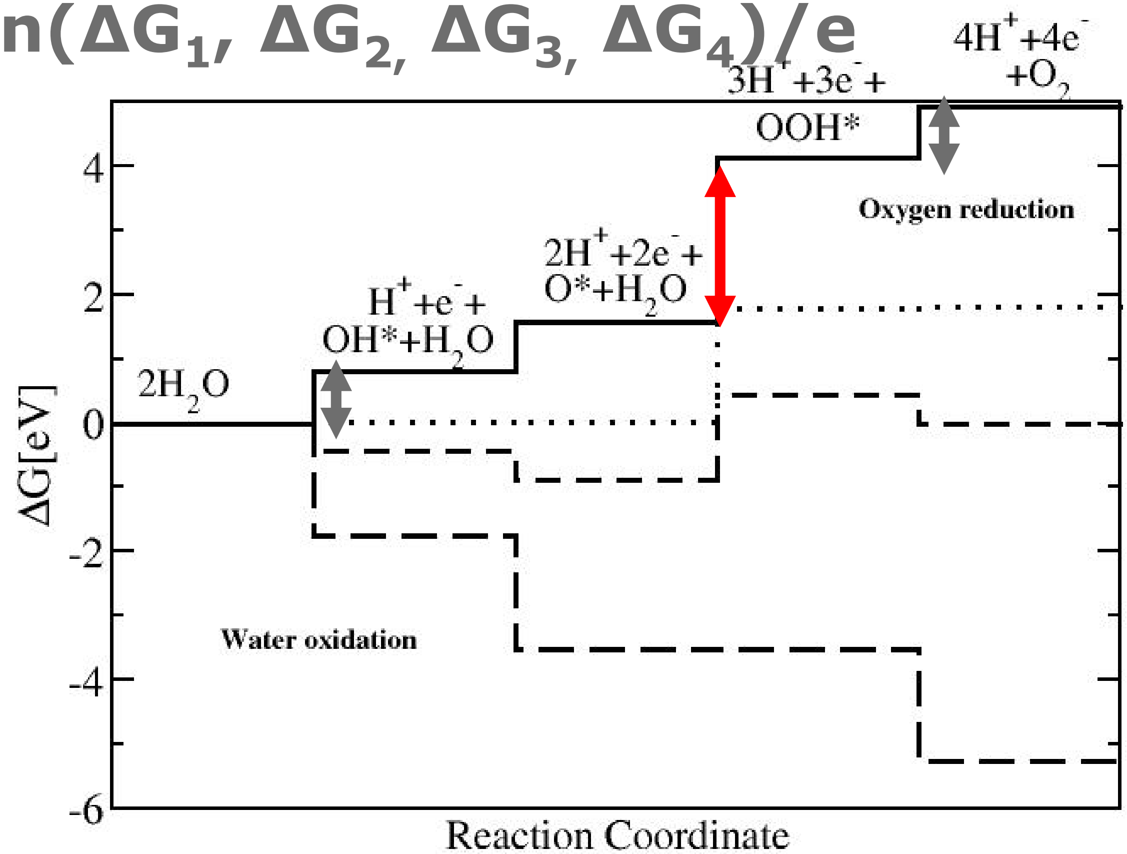

O2 + 4(H+ +e)
HOO + 3(H+ +e)
EN(URHE)
H2O
HO+(H+ +e)
O+2(H+ +e)
URHE


$O_2 + 4(H^+ + e)$
$HOO + 3(H^+ + e)$
$E_N(U_{RHE})$
H_2O
ORR
$HO + (H^+ + e)$
$O + 2(H^+ + e)$
OER
U_{RHE}

U_{ORR} and U_{OER}

$U_{OER}=\max(\Delta G_1, \Delta G_2, \Delta G_3, \Delta G_4)/e$

$U_{ORR}=\min(\Delta G_1, \Delta G_2, \Delta G_3, \Delta G_4)/e$

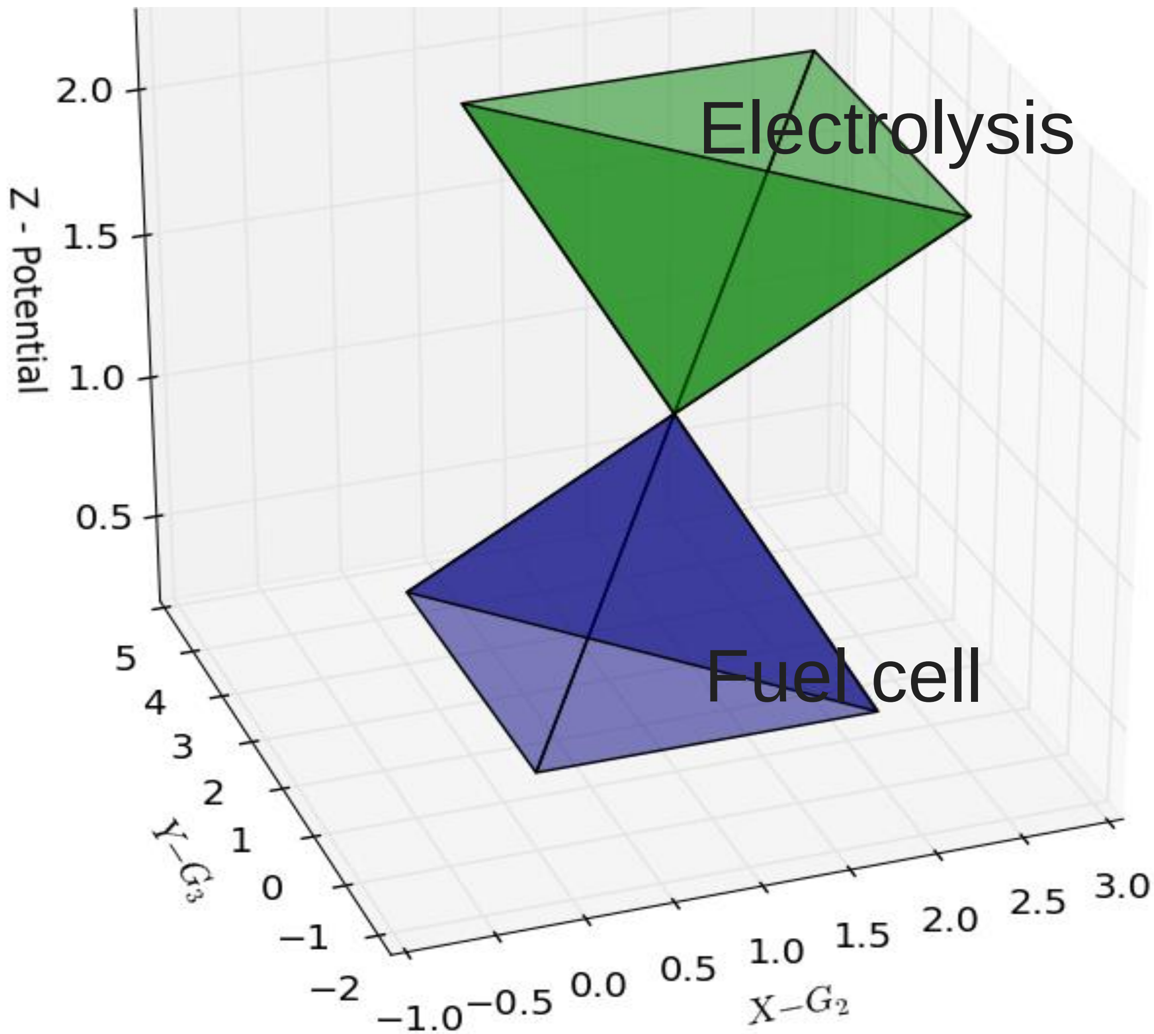


$\Delta G_1 \rightarrow \Delta G_2 \rightarrow \Delta G_3 \rightarrow \Delta G_4$

OER and ORR double pyramide

$\Delta G_2 \sim \Delta G_1$
4.92 eV= $\Delta G_1 + \Delta G_1 + \Delta G_3 + \Delta G_4$
$\Delta G_4 = 4.92\text{eV} - 2\Delta G_1 - \Delta G_3$

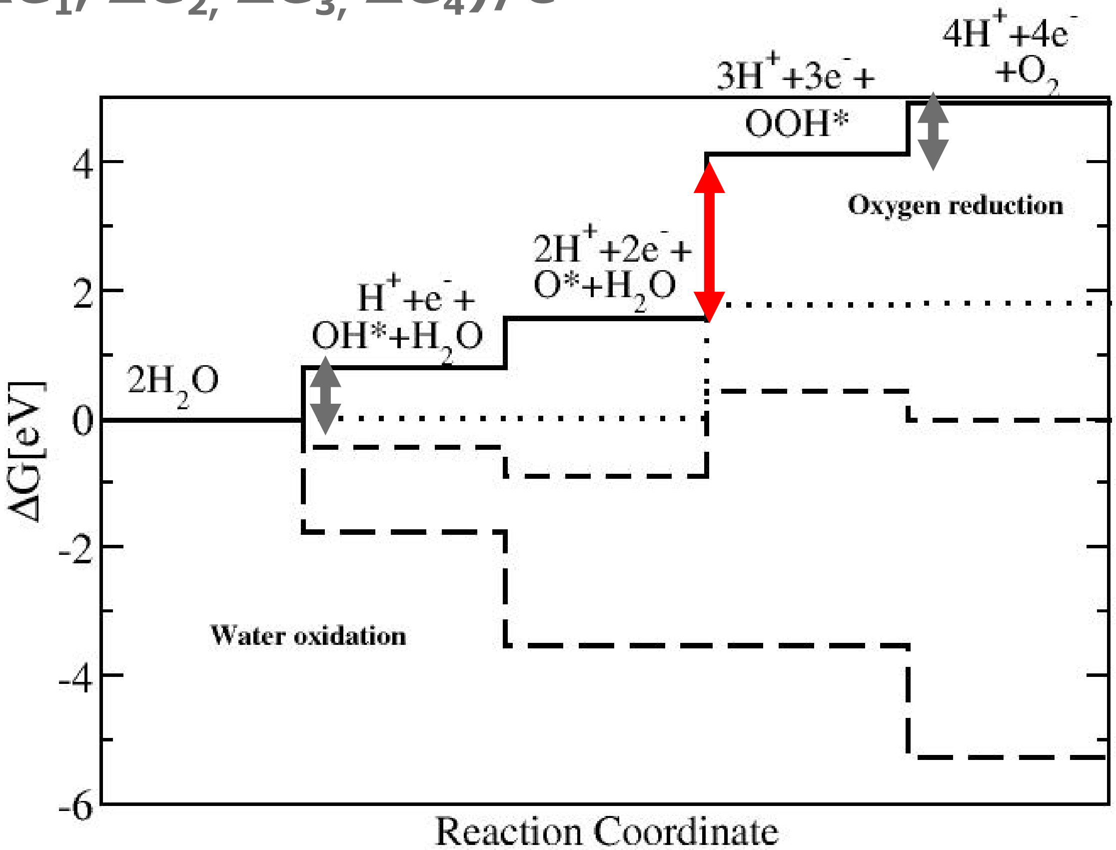
$\mathbf{U_{ORR}(\Delta G_1, \Delta G_3)}$
$\mathbf{U_{OER}(\Delta G_1, \Delta G_3)}$



U_{ORR} and U_{OER}

$U_{OER}=\max(\Delta G_1, \Delta G_2, \Delta G_3, \Delta G_4)/e$

$U_{ORR}=\min(\Delta G_1, \Delta G_2, \Delta G_3, \Delta G_4)/e$

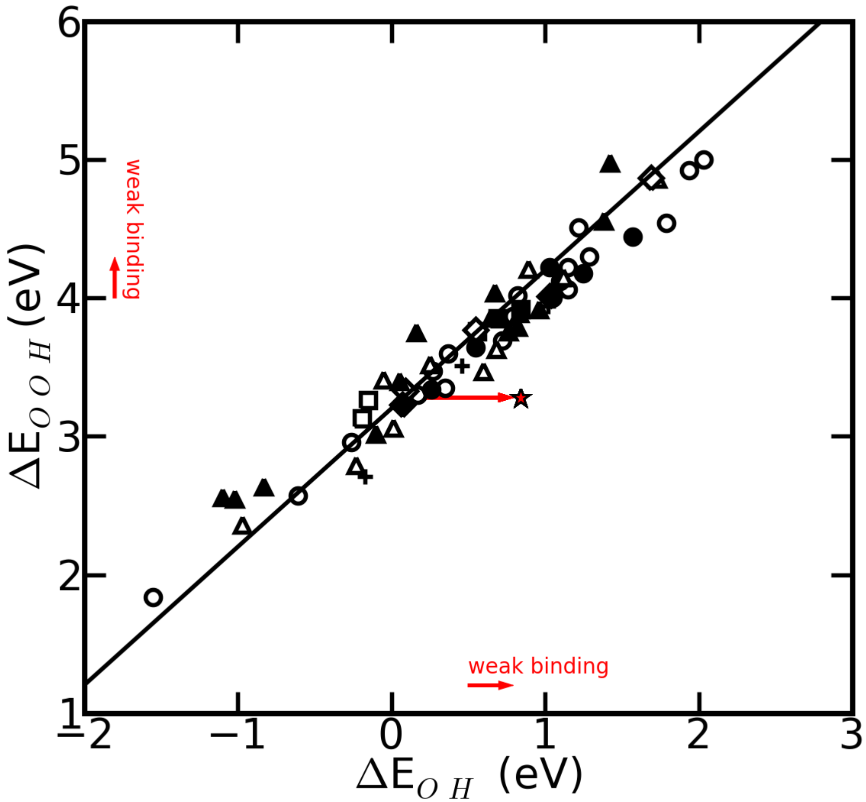


$$\Delta G_1 \rightarrow \Delta G_2 \rightarrow \Delta G_3 \rightarrow \Delta G_4$$

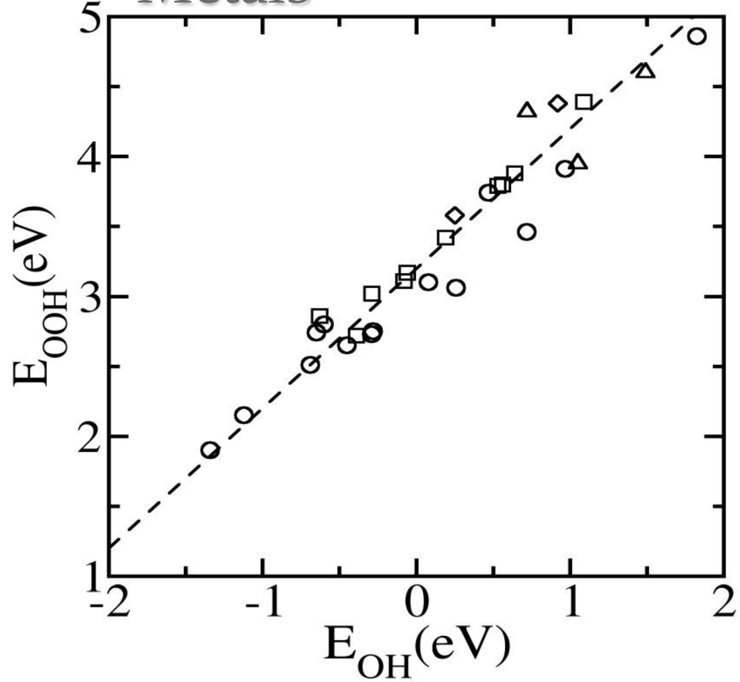
Universal scaling

$$E_{OOH} = E_{OH} + 3.2 \pm 0.2\ eV$$

Oxides



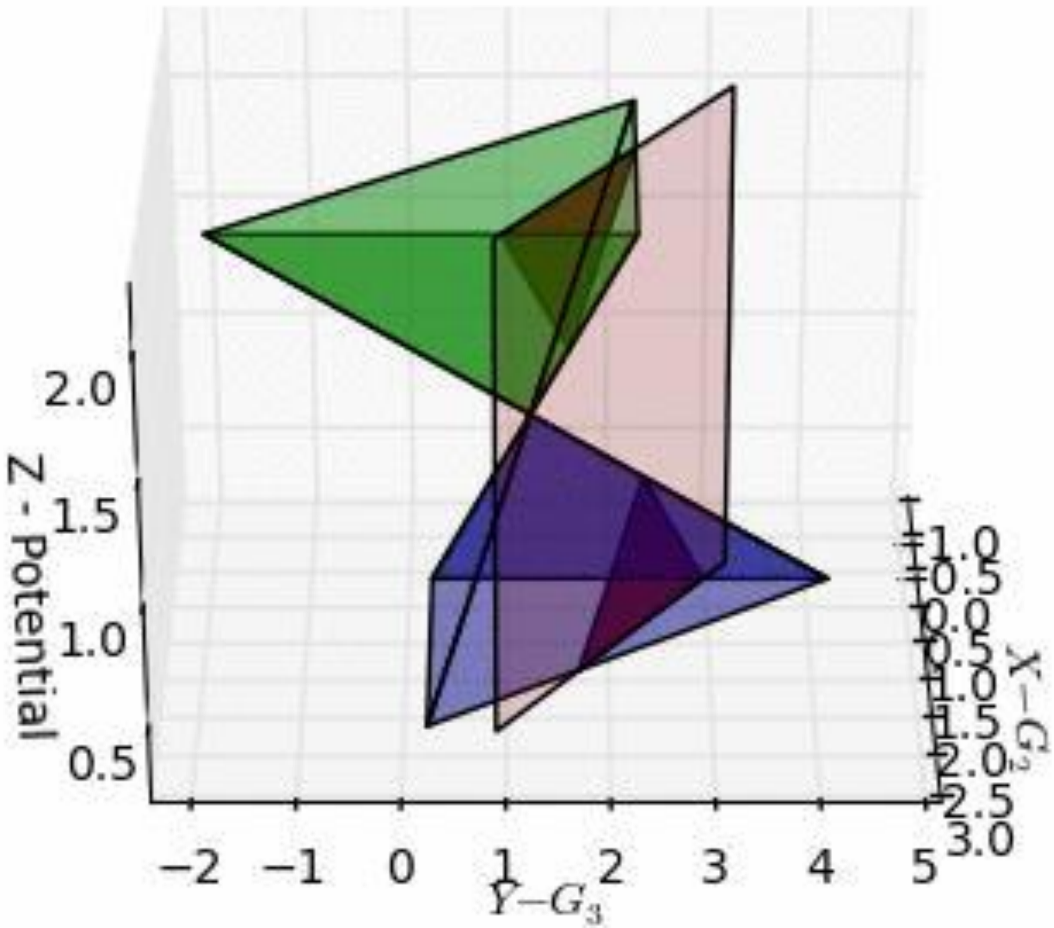
Metals



M. Koper, Journal of Electroanalytical Chemistry 2011
Man, Su, Calle-Vallejo, Hansen, Martinez, Inoglu, Kitchin, Nørskov, Rossmeisl ChemCatChem 2011

Scaling: $\Delta G_1 + 3.2eV = 2\Delta G_2 + \Delta G_3$

$$\Leftrightarrow \Delta G_3 = 3.2eV - \Delta G_1$$

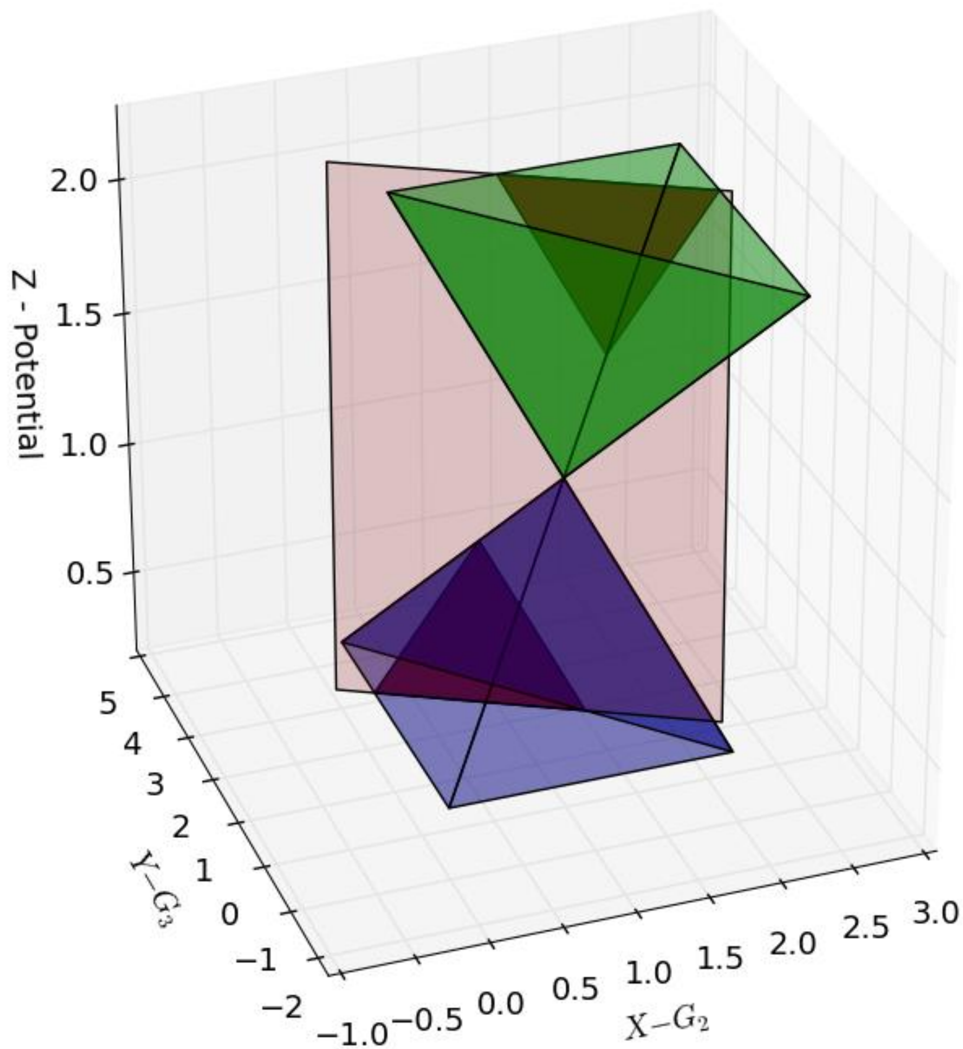


OER

ORR

Busch Halck, Kramm, Siahrostami Krtil and Rossmeisl, Nano Energy 2016

Scaling → Volcanos

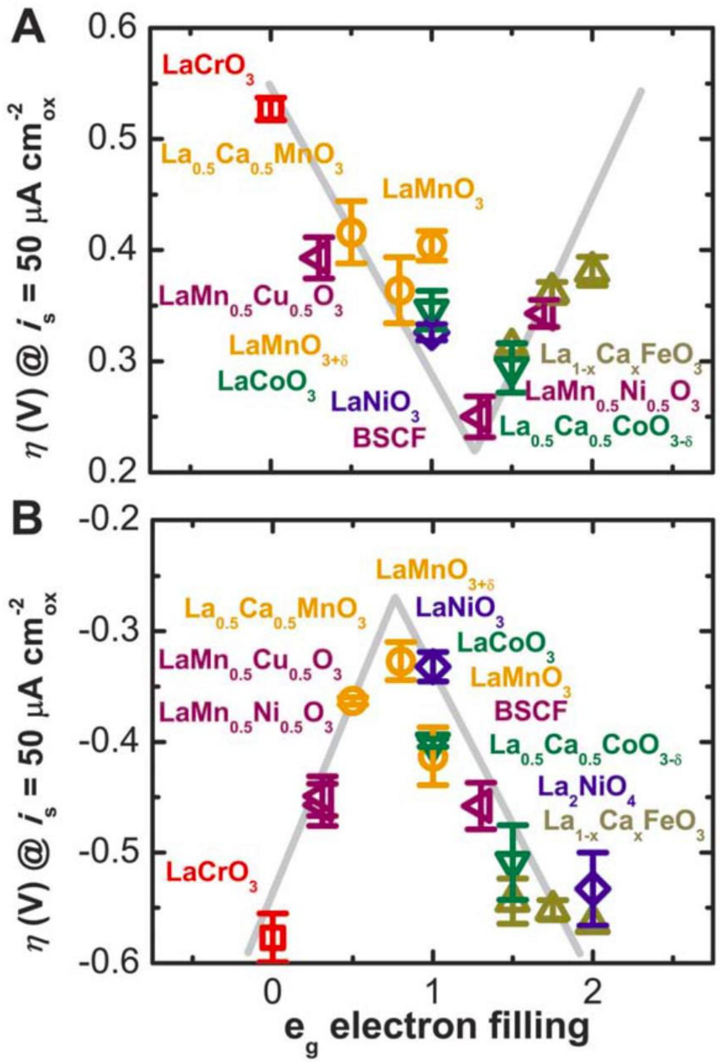


OER

ORR

Double Volcano

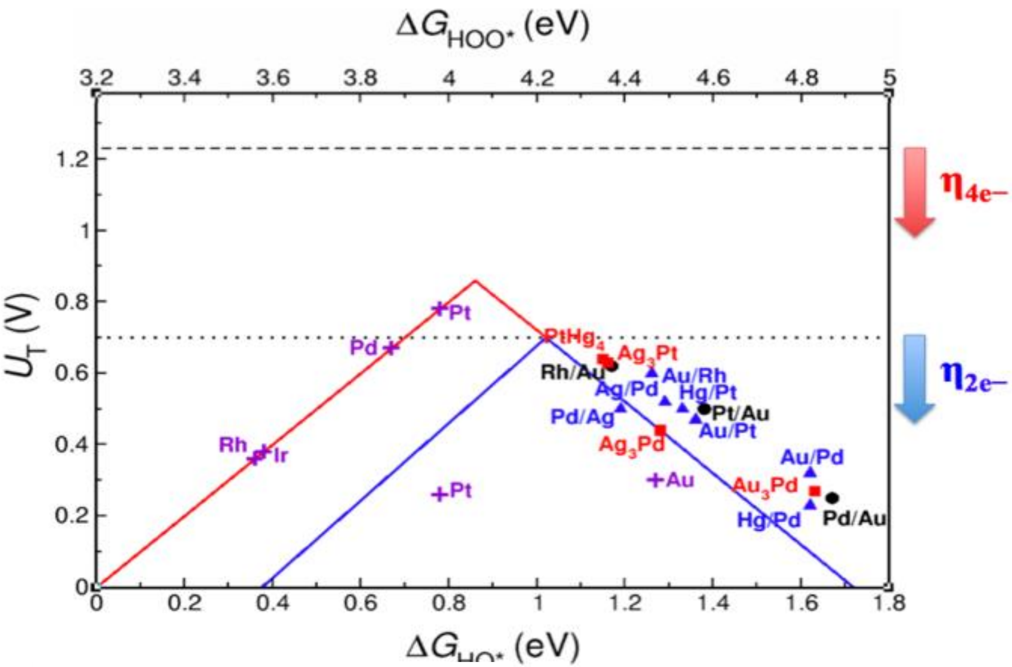
Suntivich, May,Gasteiger, Goodenough, Shao-Horn *Science* **334**, 1383 (2011)

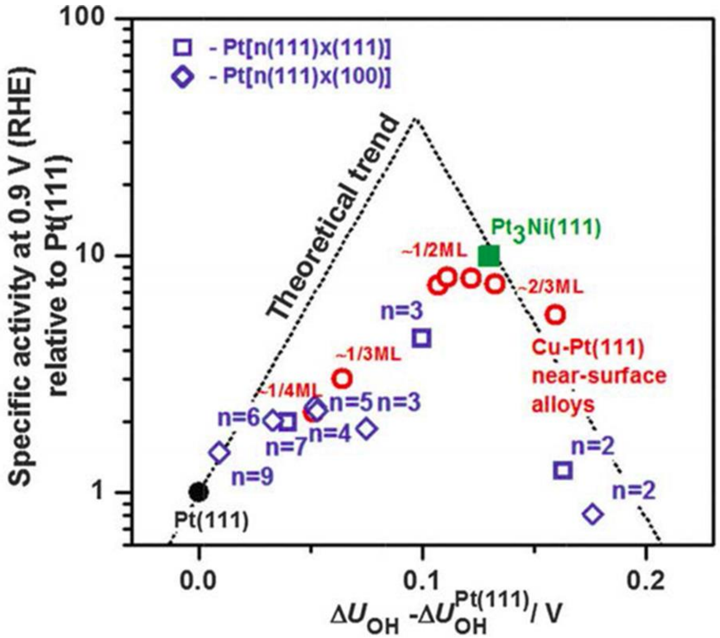


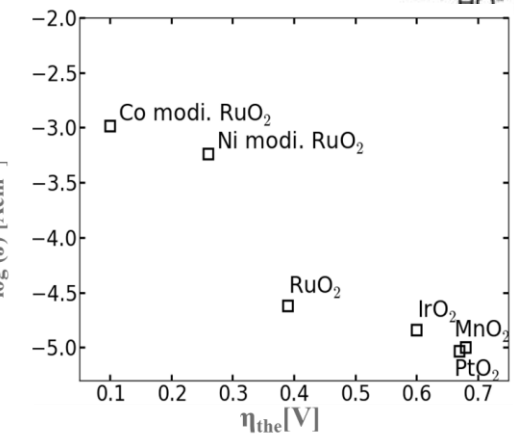
OER

ORR

The role of the surface

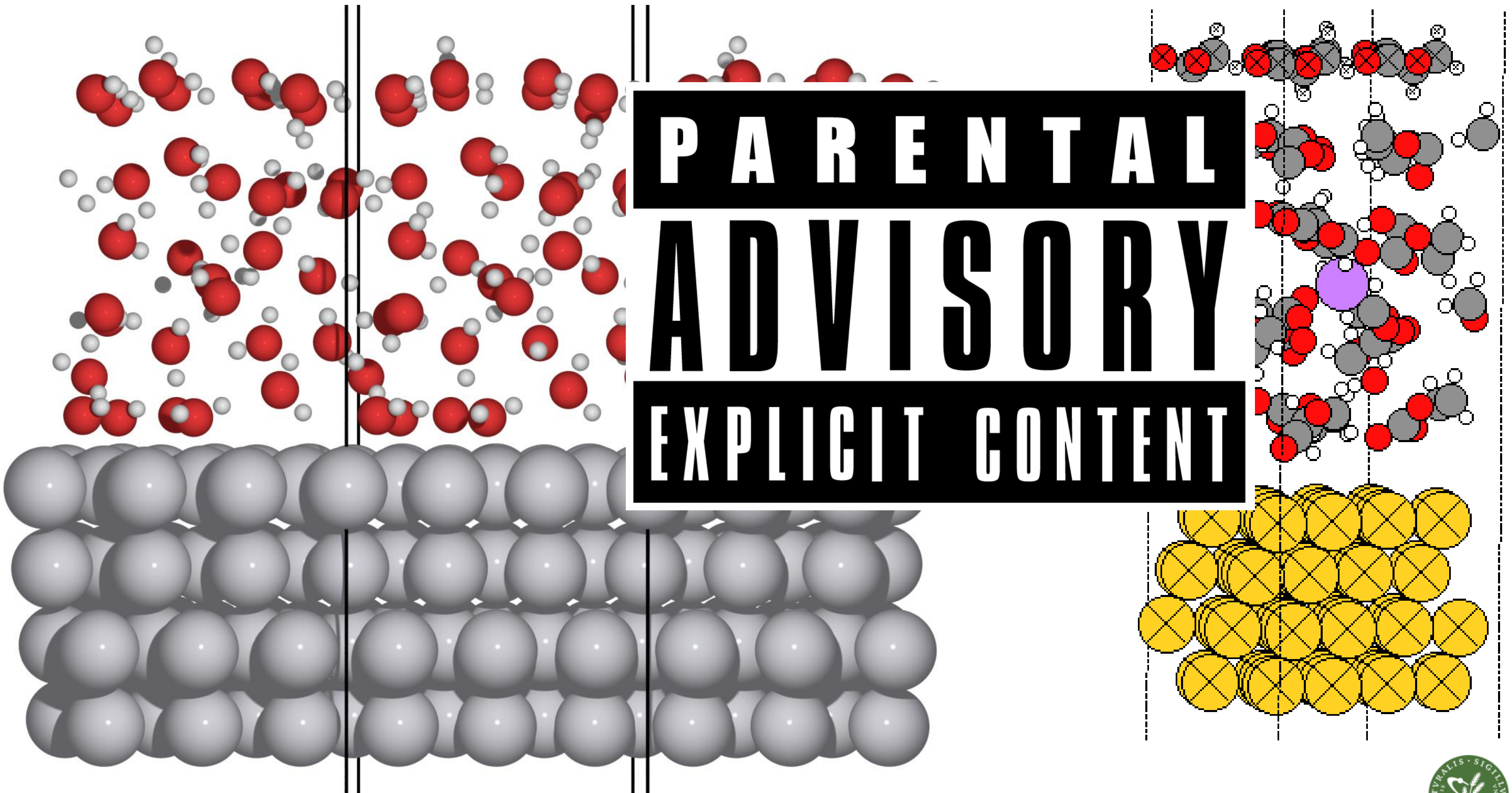




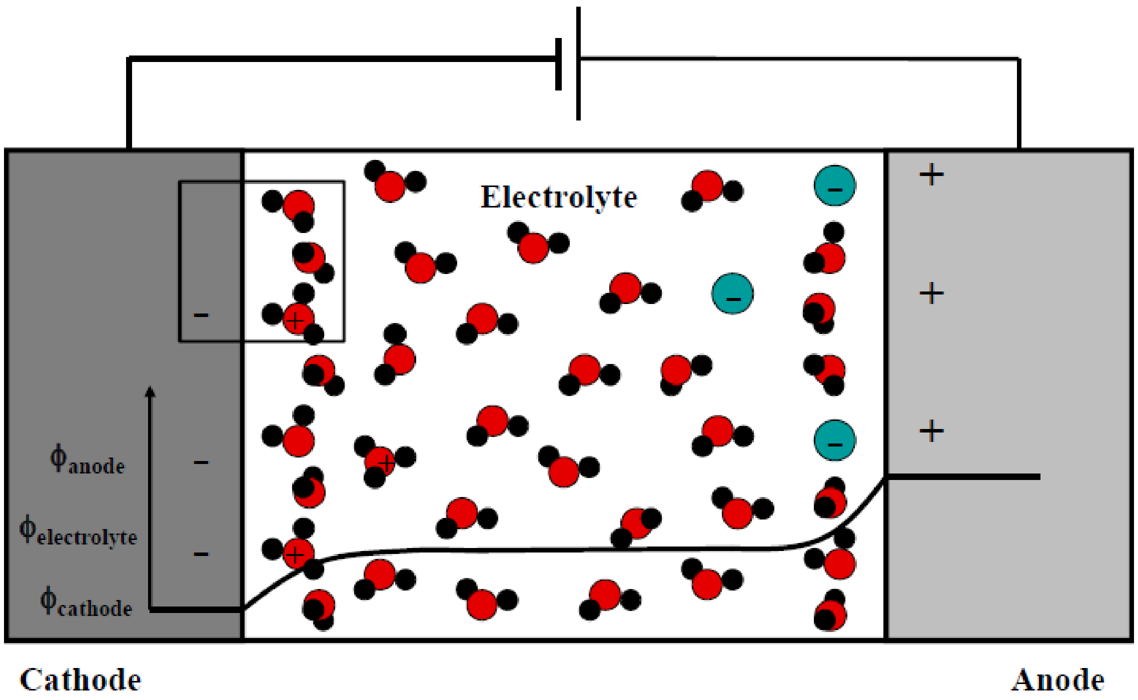


What is the role of the electrolyte?

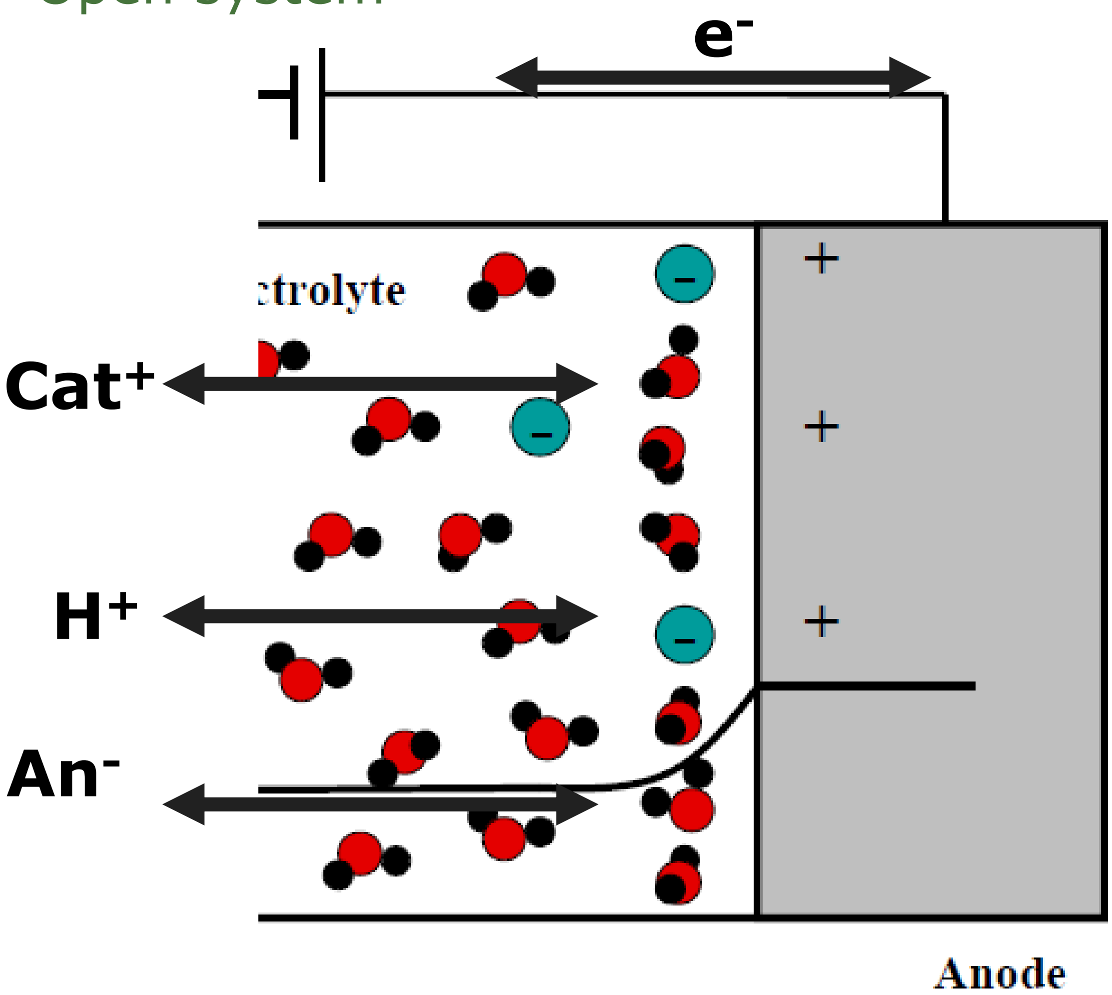
Towards Electrochemical interfaces



Open system

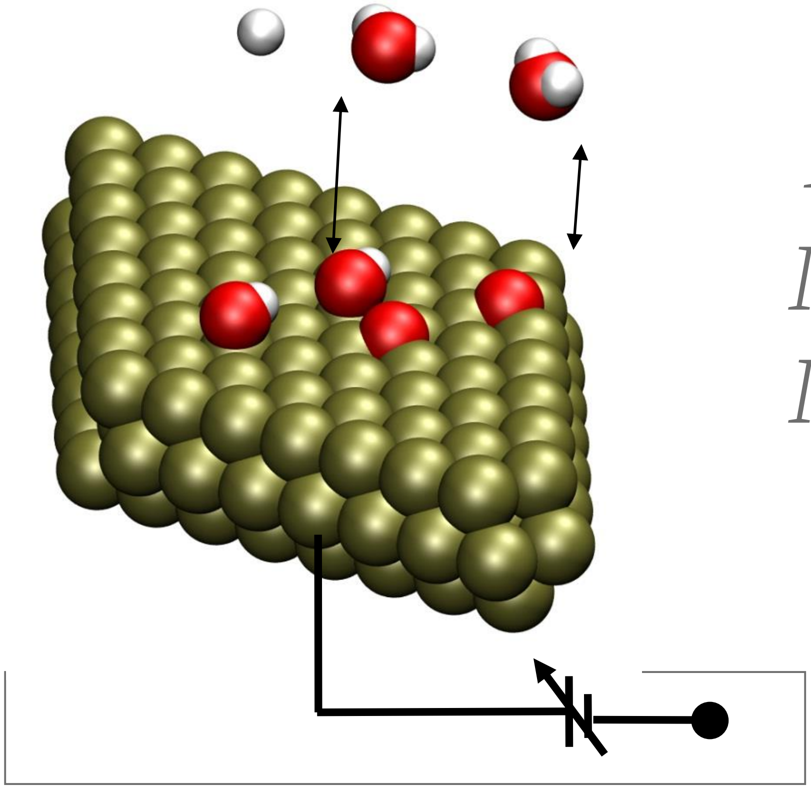


Open system



Evaluate energy of the surface as function of the potential

$$E_N(U_{RHE})=E(N)-E(0)-½NG(H_2)-½NeU_{RHE}$$



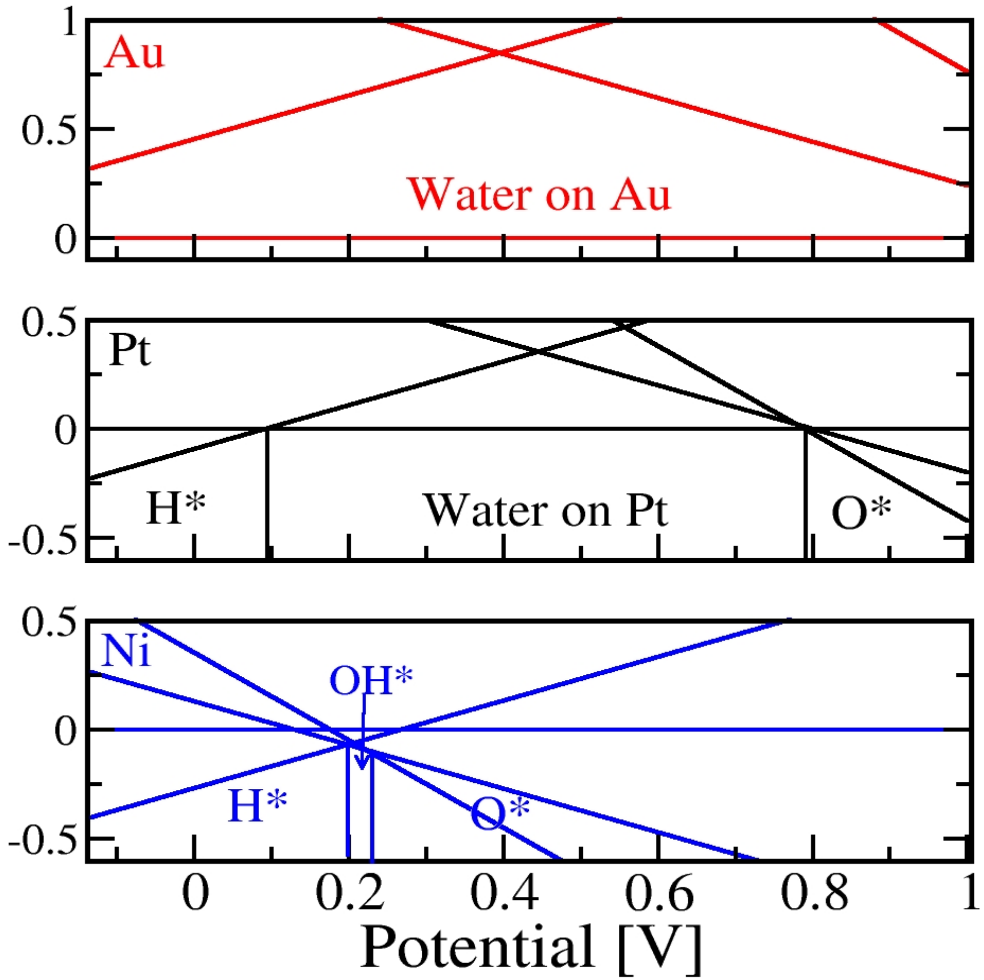
$N=1$ $\quad H^+ + e^- + * \leftrightarrow H*$

$N=-1$ $\quad H_2O + * \rightleftarrows *OH + H^+ + e^-$

$N=-2$ $\quad *OH \rightleftarrows O* + H^+ + e^-$

Phase-diagrams

$E_N(U_{RHE})$



Rossmeisl, Nørskov, Taylor, Janik, Neurock. *J. Phys. Chem. B* **110**, (2006)

What have we done

U=E(N)-E(0)-½NG_{H2}

In an open system with constant μ , Min(U(N))

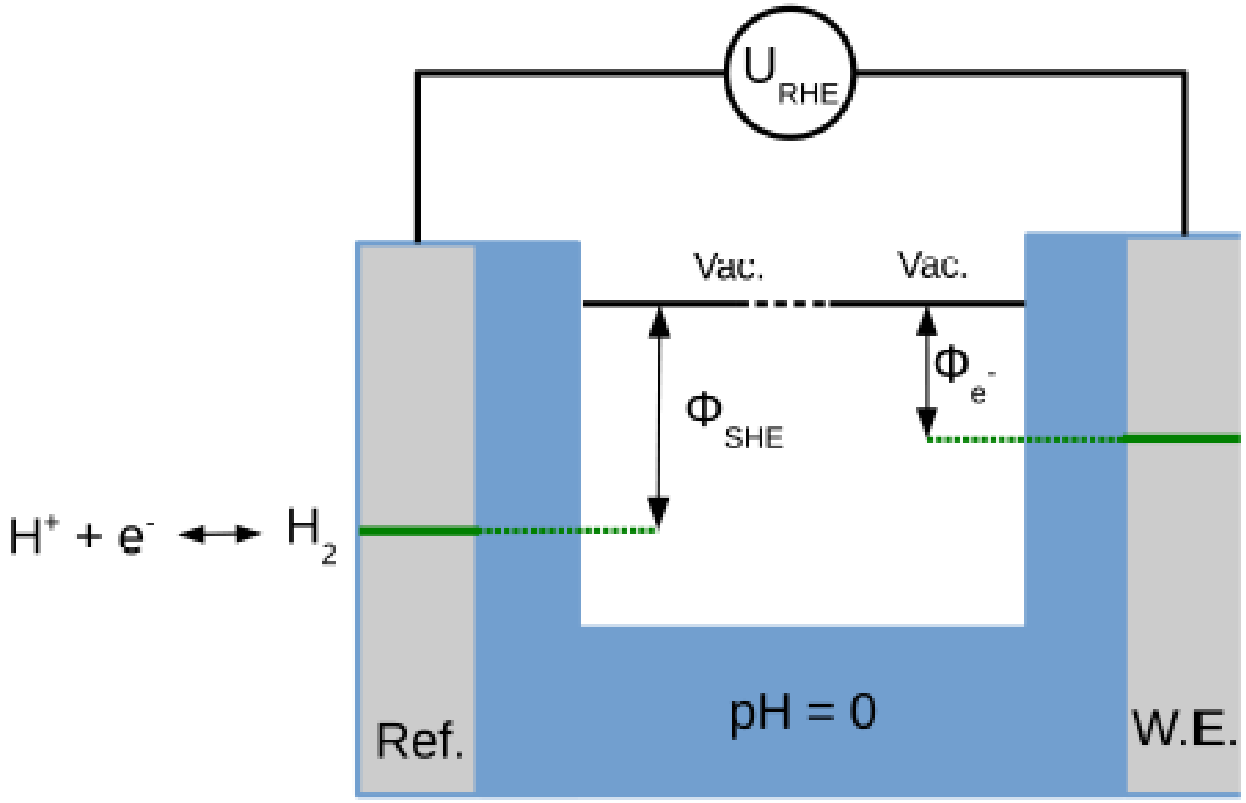
d(U) = μdN

In a closed system with constant N, γ=U-μN, Min(γ(μ))

d(U-μN) = -Ndμ

$$E_N(U_{RHE})=E(N)-E(0)-½NG(H_2)-½NeU_{RHE}$$

Generalized Computational electrode
Workfunction is linked to the potential



Martin Hangaard Hansen, Chengjun Jin, Kristian S. Thygesen, Jan Rossmeisl, JPC 2016

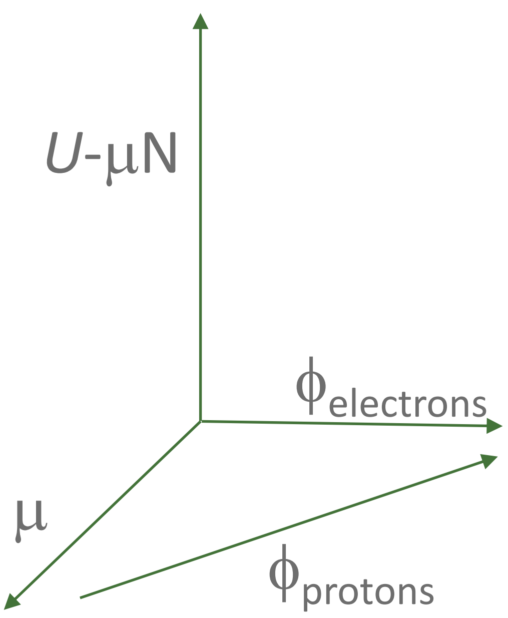
What can we do with pH?

$\mu = \phi_{electrons} + \phi_{protons}$ $\quad$ $pH \sim \phi_{protons}$

$d(U) = \mu dN = \phi_{electrons}\, dN + \phi_{protons}\, dN$

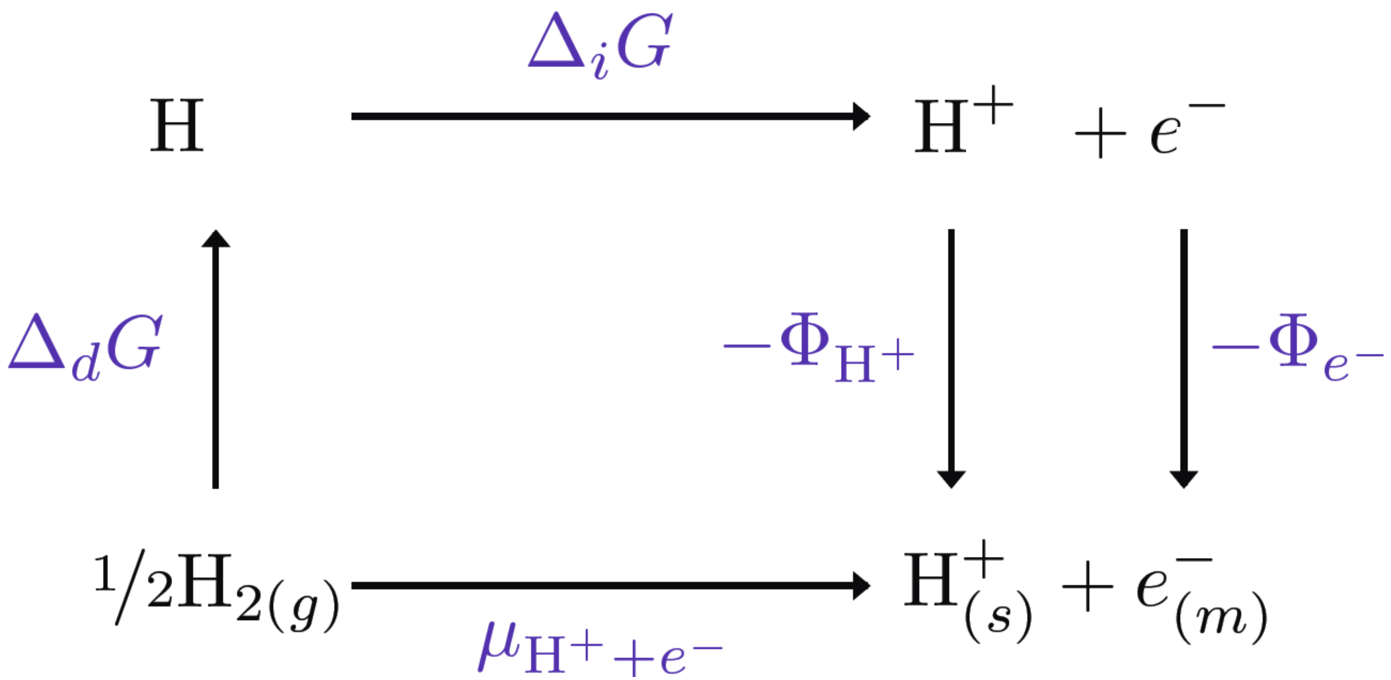
$d(\gamma) = d(U - \mu N) = -N d\mu = -N d\phi_{electrons} - N d\phi_{protons}$

$Min(\gamma(\mu, \phi_{electrons}))$

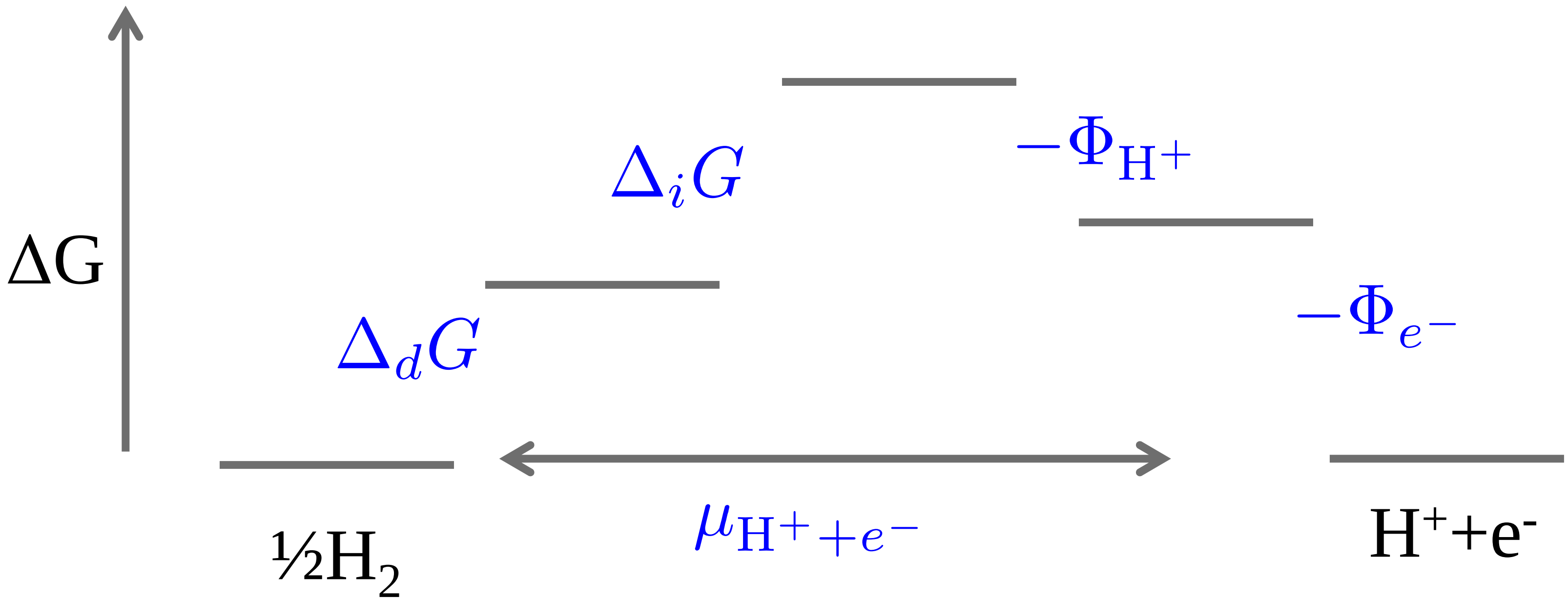


Rossmeisl, Bagger, Arnarson in preparation

Born-Haber-cycle



Born-Haber

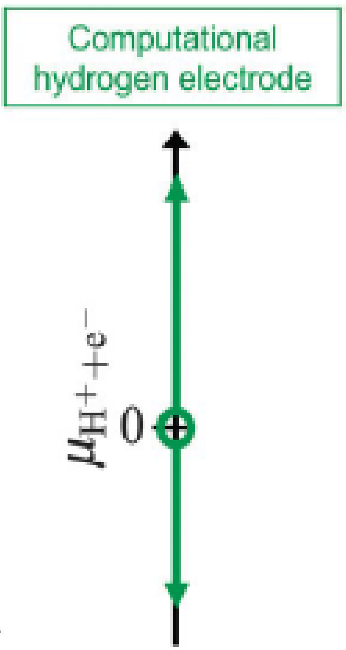


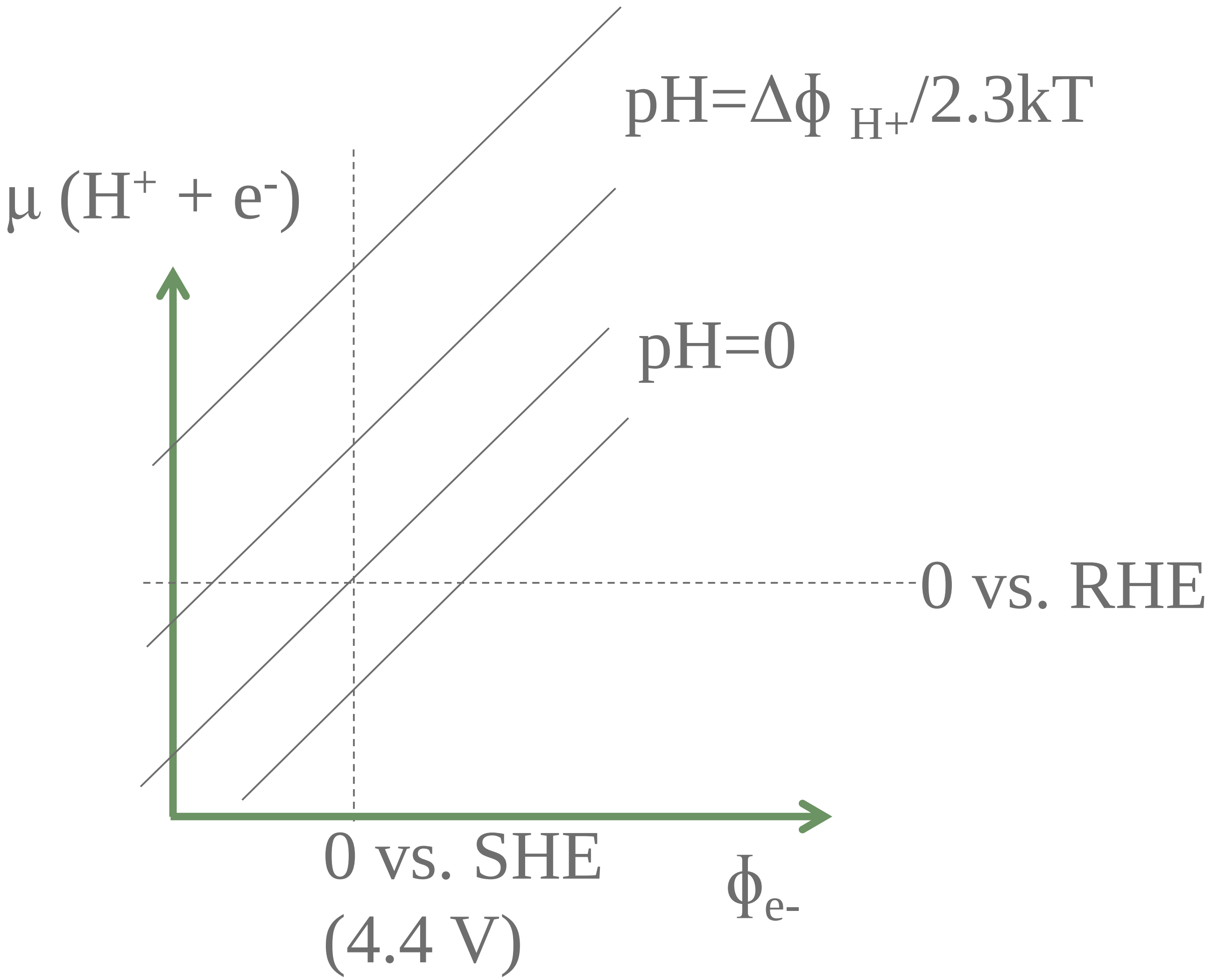
From experiments ϕ_{e-} ~ 4.4 eV at pH=0

$\Delta\phi_{H+}$ = kT ln [a_{H+}] = 0.059eV/pH

Knowing $\mu_{H+ + e-}$ and ϕ_{e-} means that pH is known as well

pH and potential

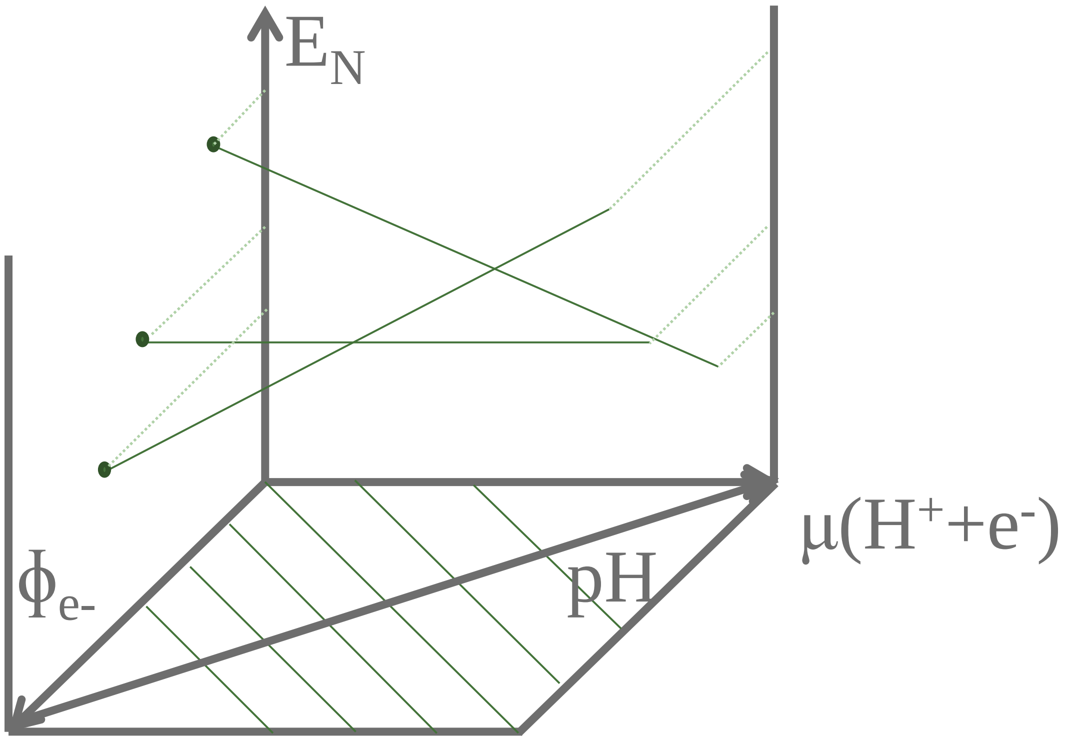




The energy of the interface

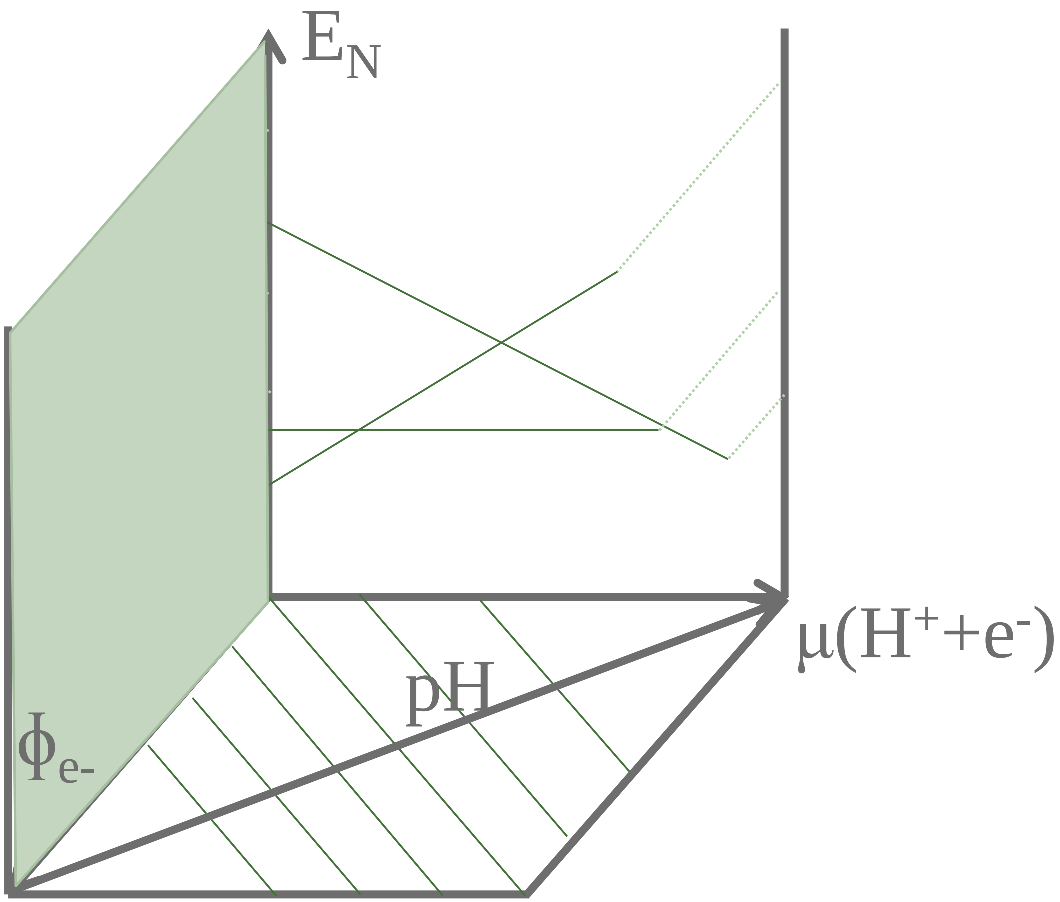
$$E_N(U_{RHE})=E(N)-E(0)-½NG(H_2)-½NeU_{RHE}$$

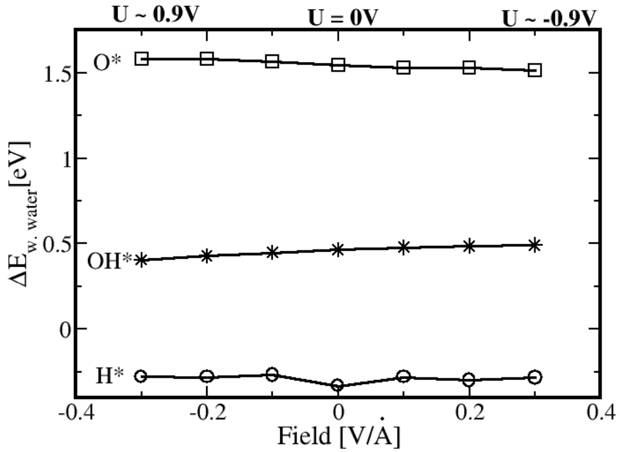
$$E_N(\phi_{e-},U_{RHE})=E(N,\phi_{e-})-E(0)-½NG(H_2)-½NeU_{RHE}$$



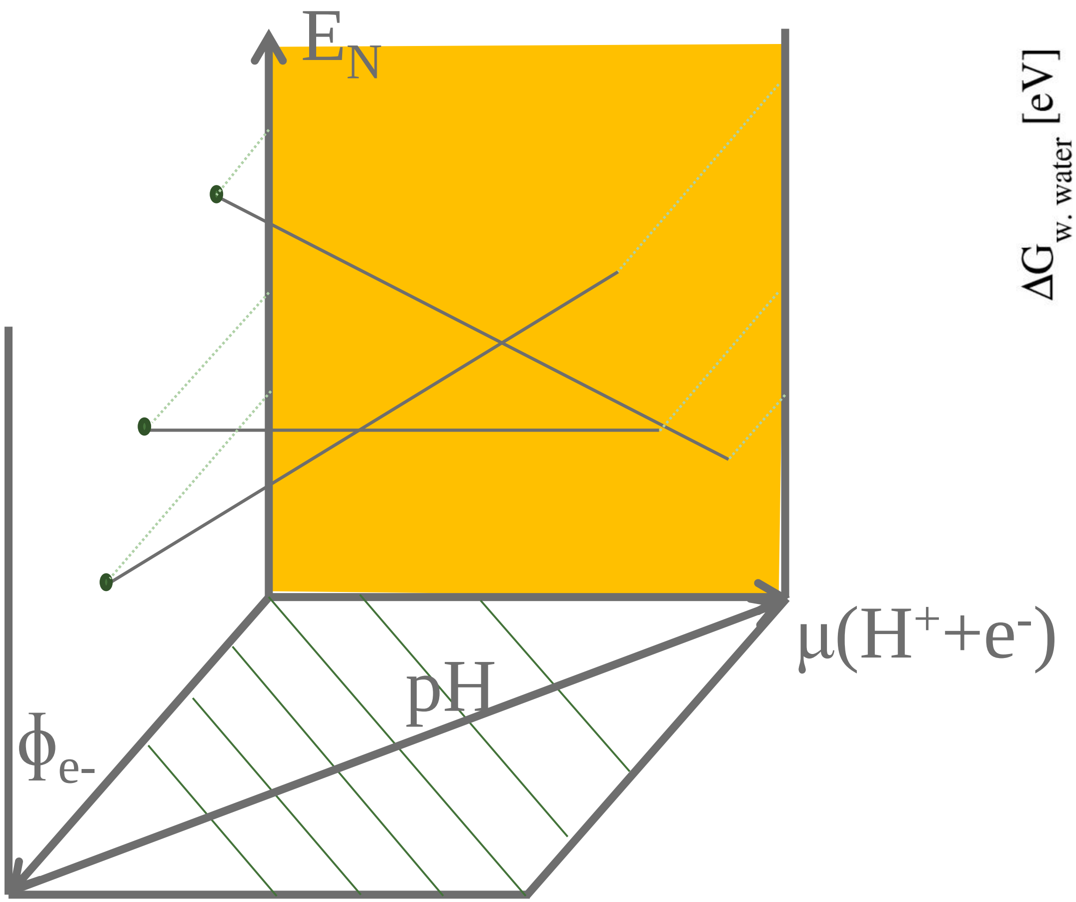
Rossmeisl, Chan, Ahmed, Tripkovic, Bjorketun, PCCP 2013

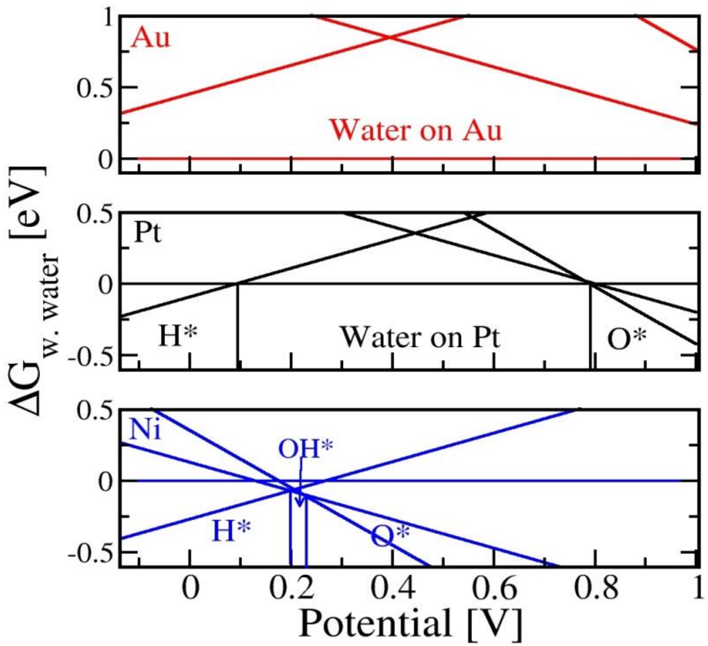
Projections



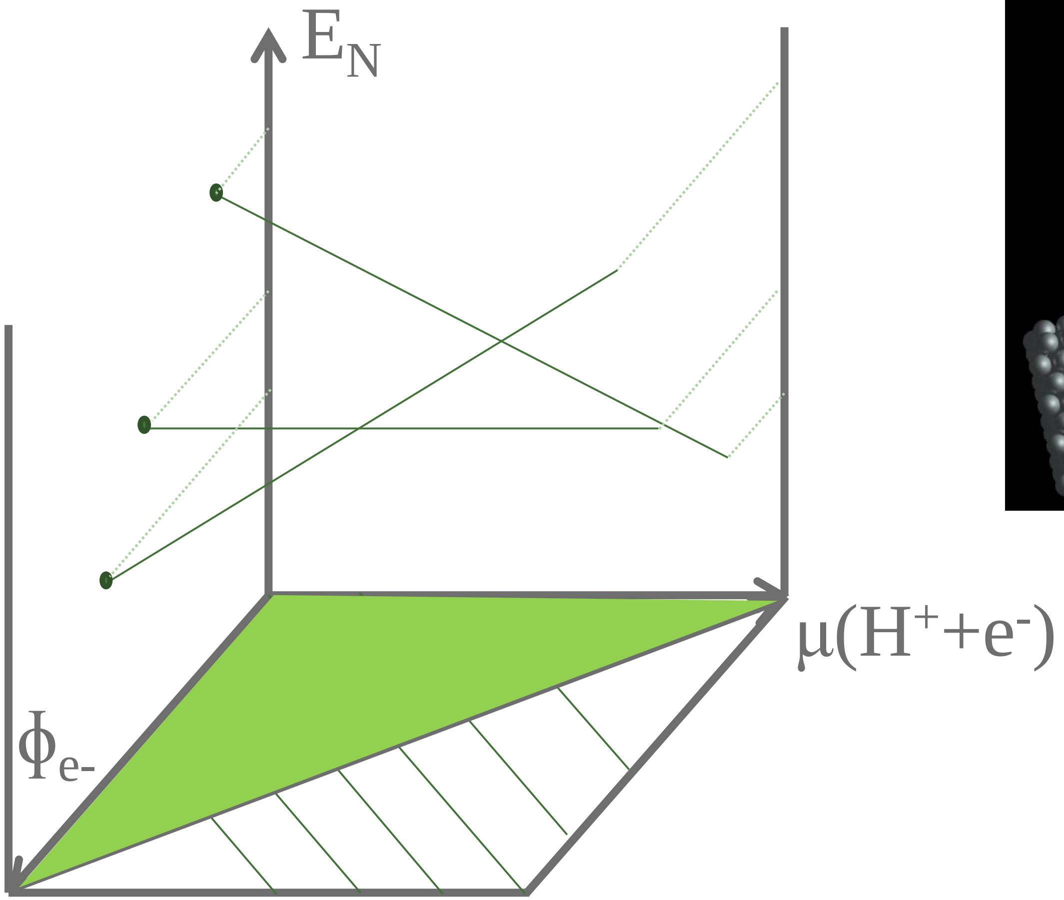


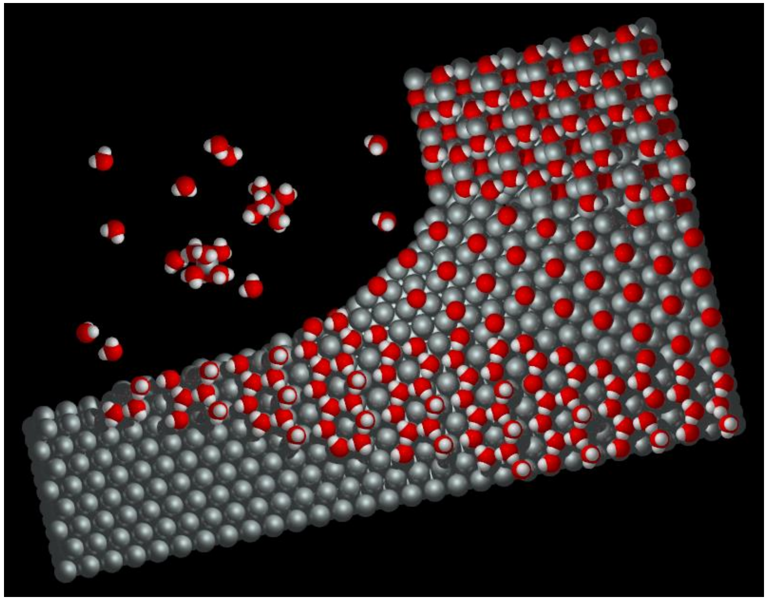
Projections



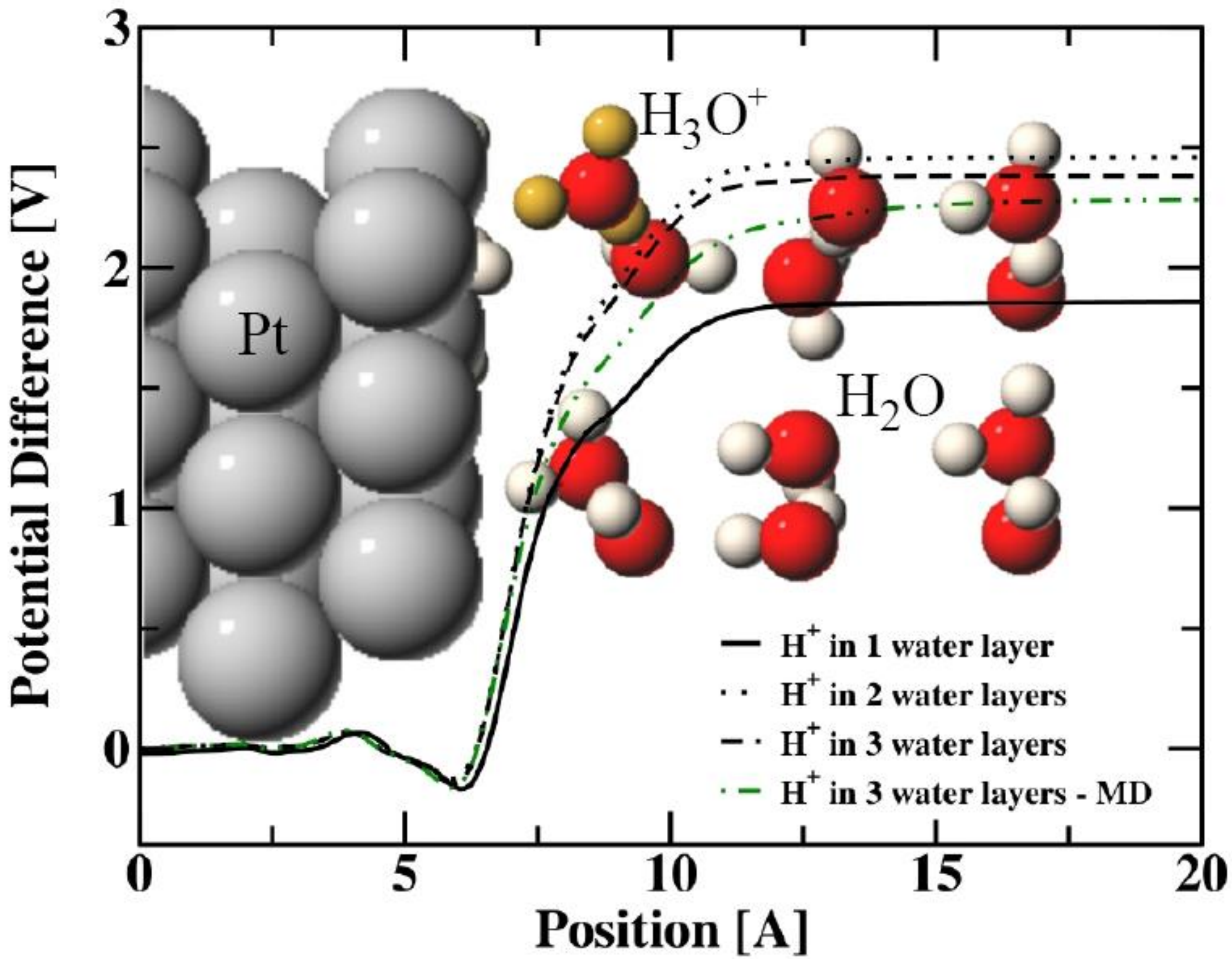


Projections



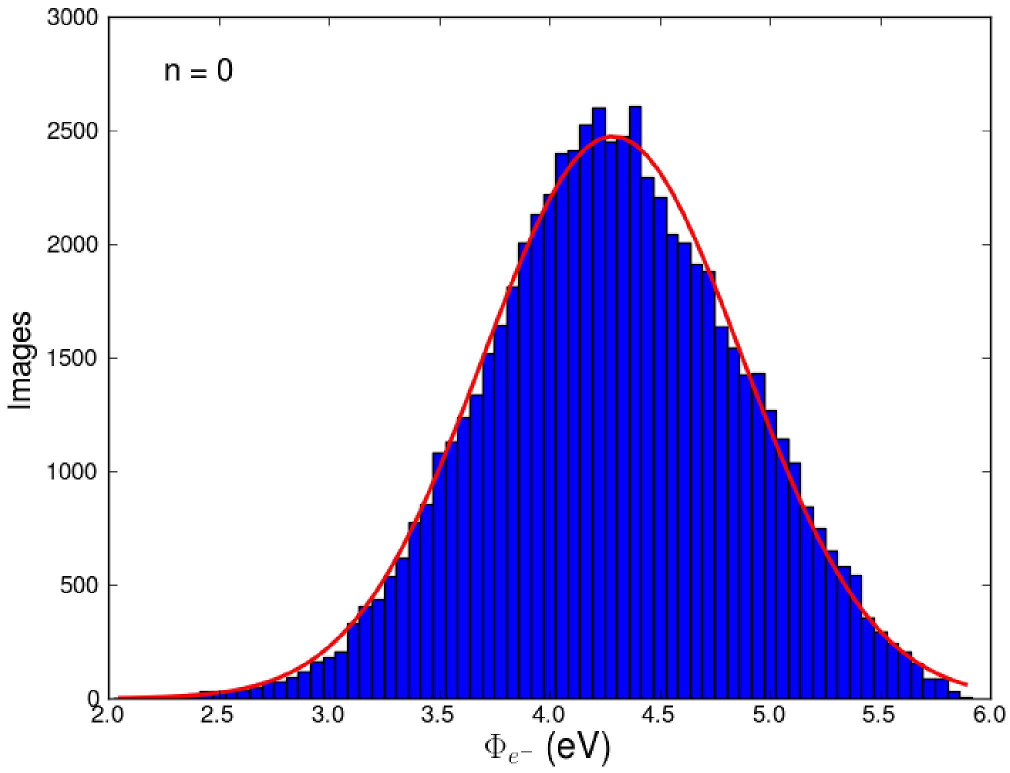


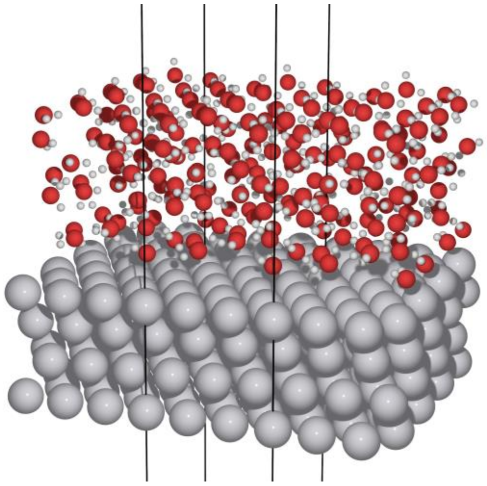
Adding hydrogen to the electrolyte E_N



Rossmeisl, Skúlason, Björketun, Tripkovic, Nørskov. *Chem. Phys. Lett.* **466**. (2008) 68-71

Work function as order parameter
Normal distribution $E_N(\phi_{e-})$

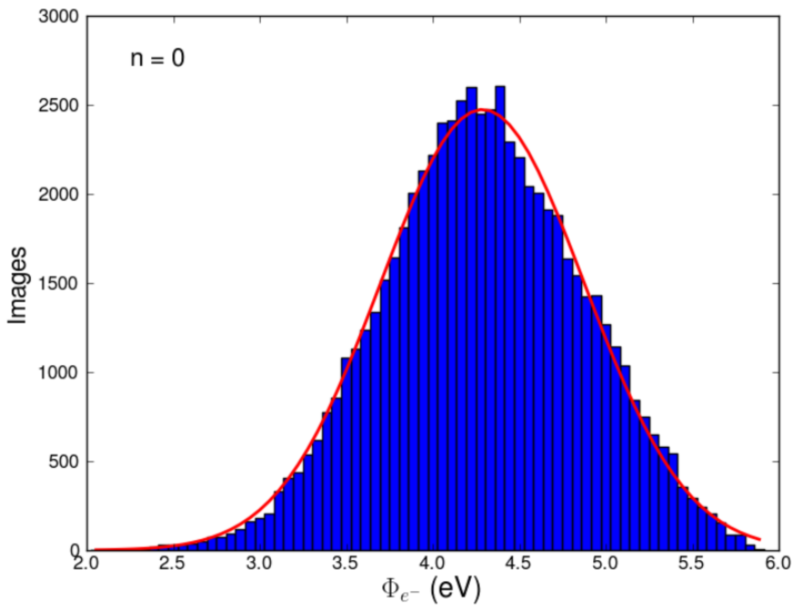


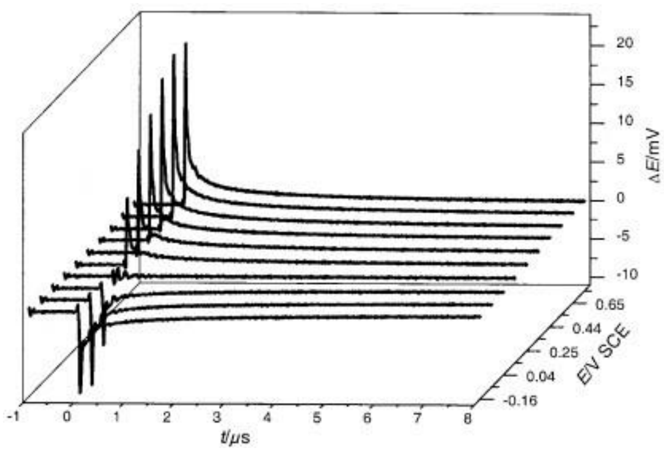


Hansen, Nilsson, Rossmeisl, PCCP, 2017

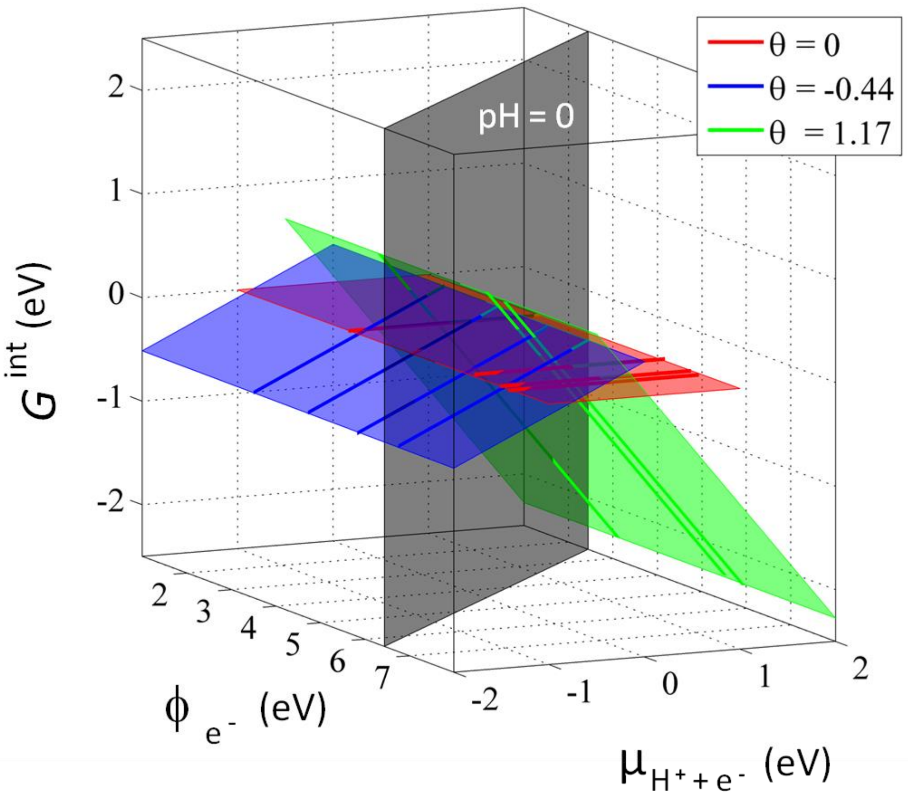
Potential of maximum entropy

$$\left(\frac{\partial U}{\partial T}\right)_T = -\left(\frac{\partial \Delta S}{\partial q^M}\right)_q$$

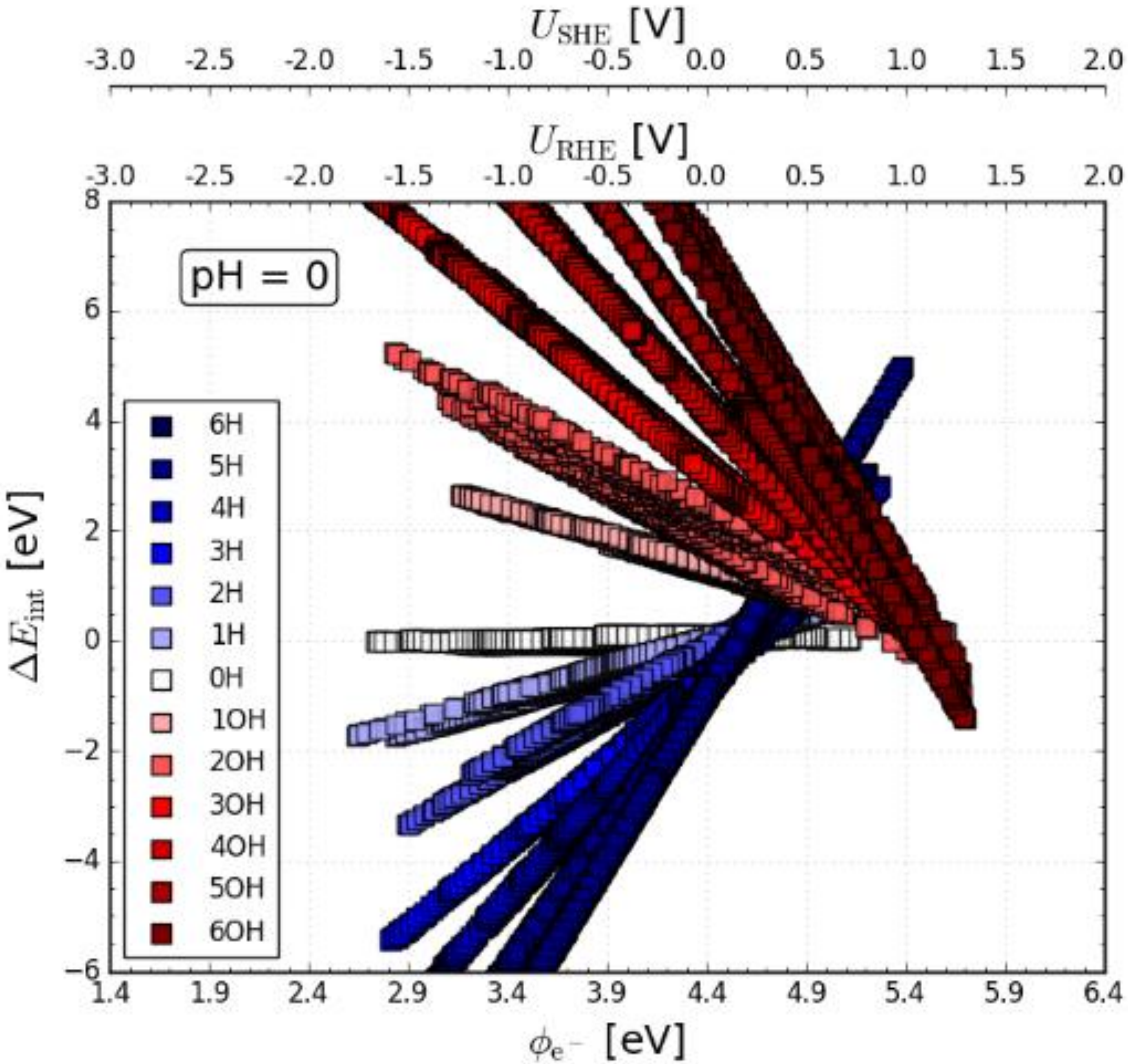




Climent, V.; Coles, B. A.; Compton, R. G. *Laser-Induced Potential Transients on a Au(111) Single-Crystal Electrode. Determination of the Potential of Maximum Entropy of Double-Layer Formation.* J. Phys. Chem. B **2002**, 106, 5258–5265


pH = 0
θ = 0
θ = -0.44
θ = 1.17
G^int (eV)
2
1
0
-1
-2
2 3 4 5 6 7
ϕ e- (eV)
-2 -1 0 1 2
μ H+ + e- (eV)

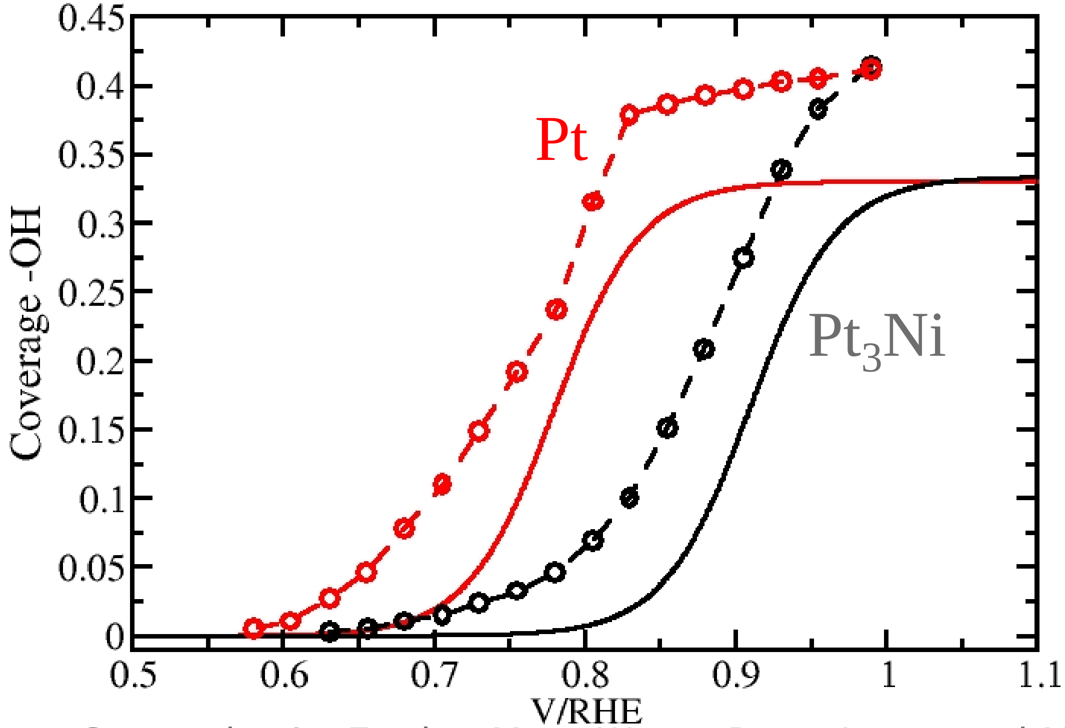
$\gamma_N(\mu,\phi_e)$

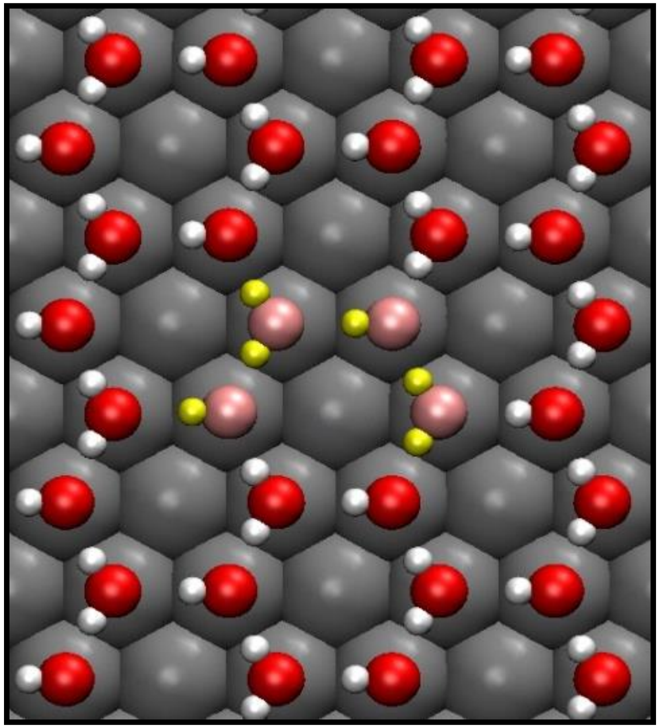


OH-coverage
$H_2O \leftrightarrow OH^* + H^+ + e^-$

Langmuir isotherm

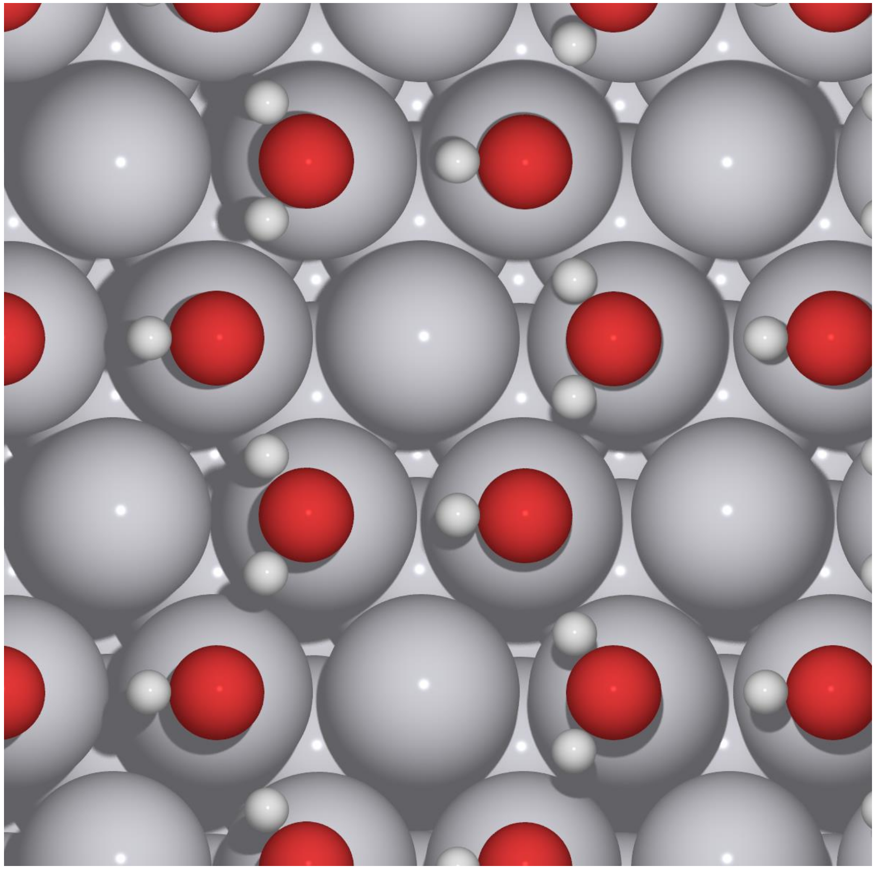
$\Theta_{OH} = 1/3\ 1/(1+\exp((\Delta G_{OH} - eU)/kT))$

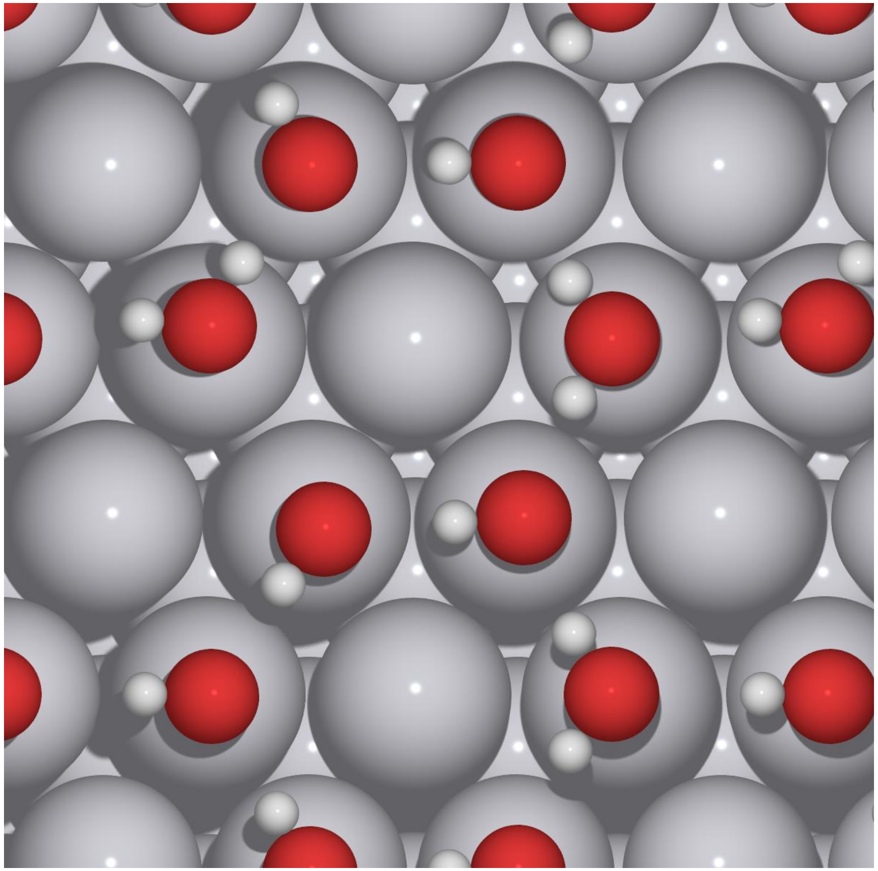




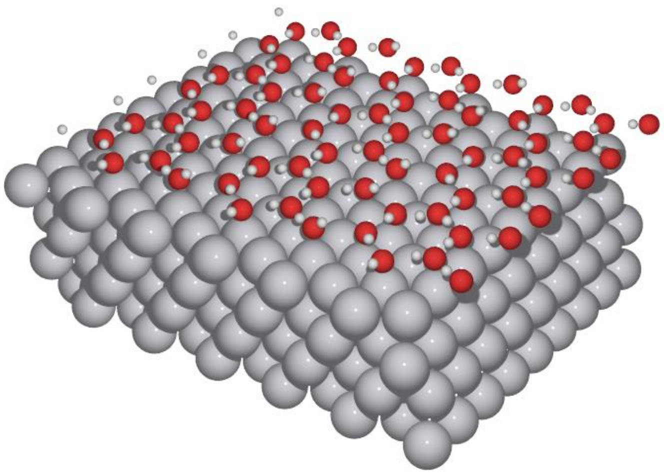
Stamenkovic, Fowler, Mun, Wang, Ross, Lucas and Markovic, *Science*, 2007, **315**, 493-4

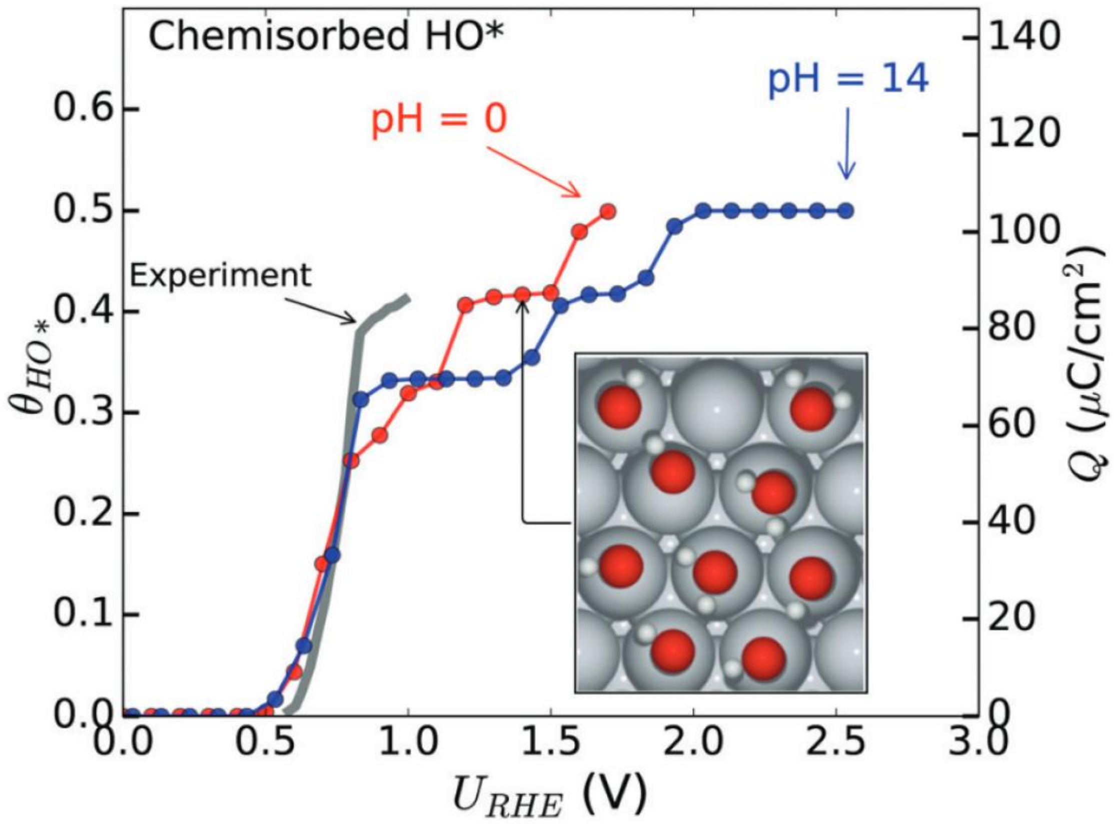
Rossmeisl, Karlberg, Jaramillo, Nørskov. *Faraday Discussions* **140**, (2008) 337-346



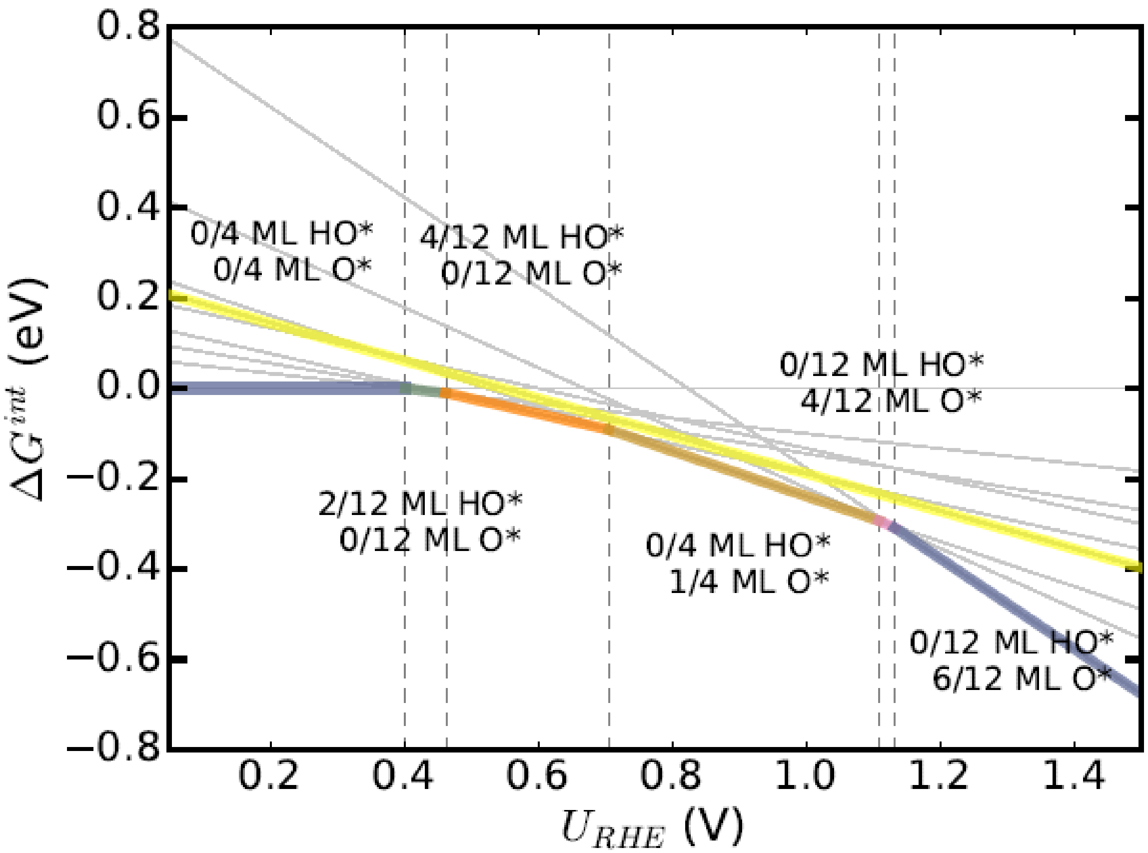


Structure of OH and H_2O on Pt(111)

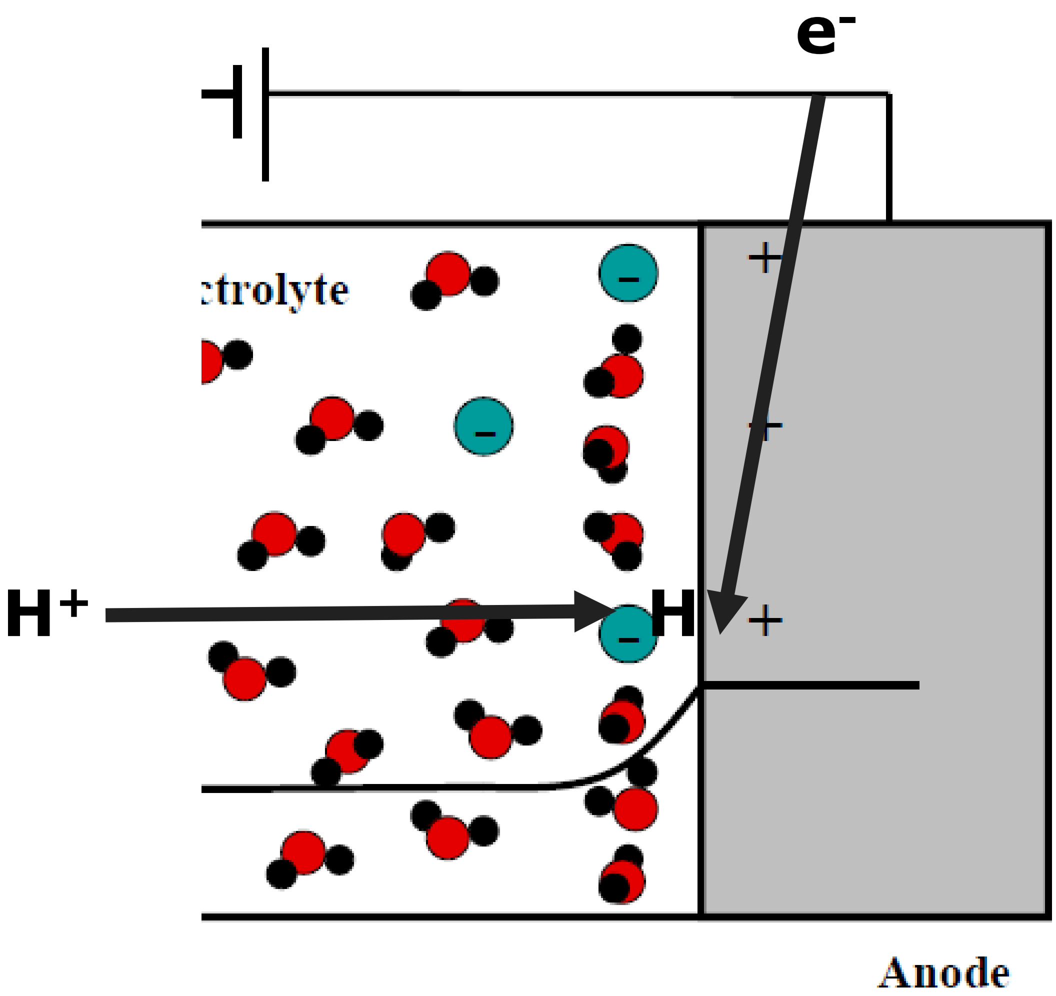


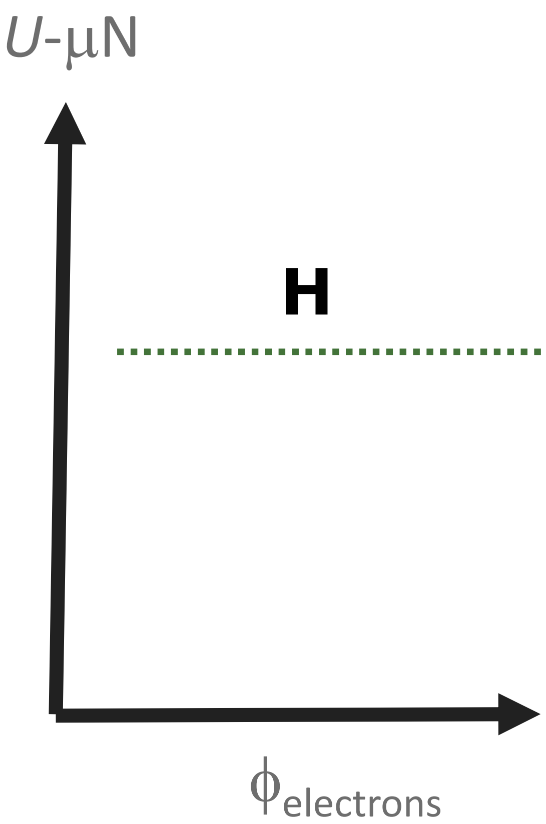


Hansen, Nilsson, Rossmeisl, PCCP, 2017

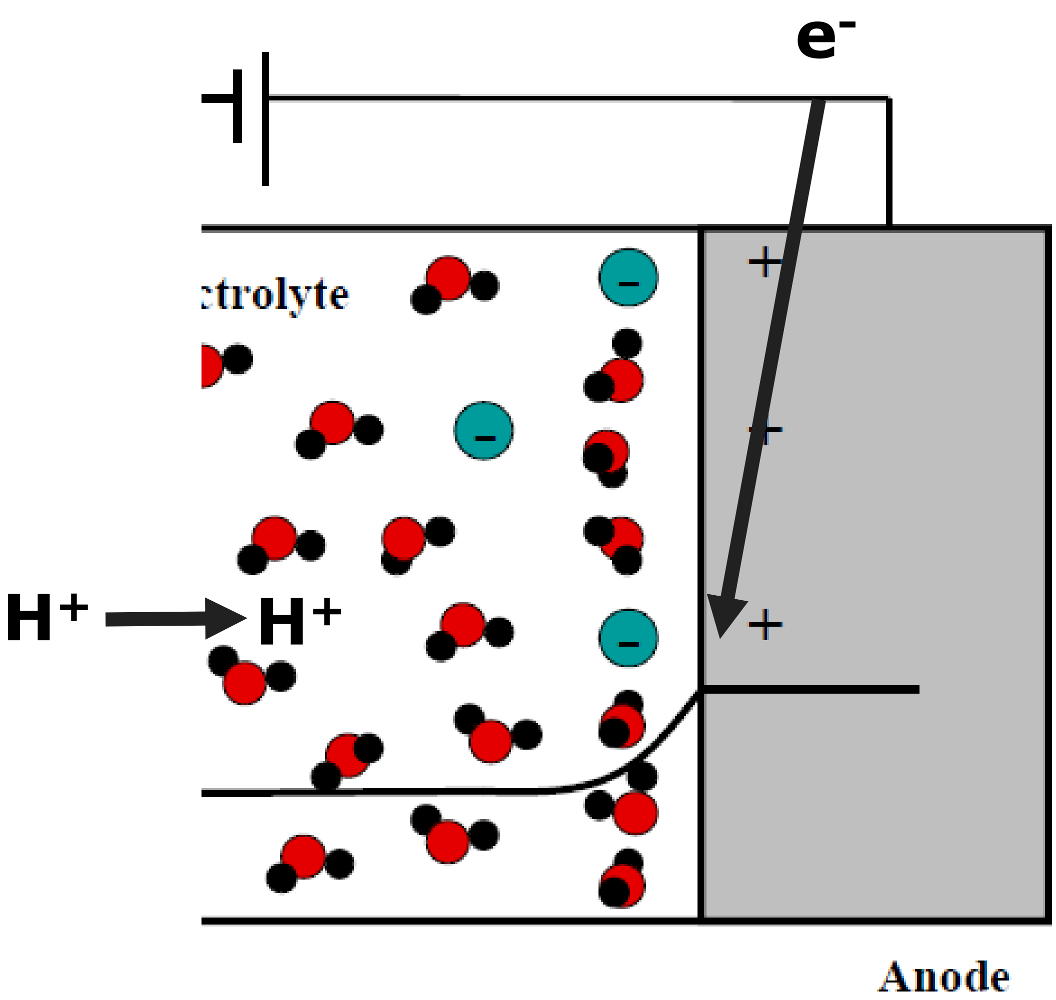

0.8
0.6
0.4
0.2
0.0
−0.2
−0.4
−0.6
−0.8
ΔG^{int} (eV)
0.2
0.4
0.6
0.8
1.0
1.2
1.4
U_{RHE} (V)
0/4 ML HO*
0/4 ML O*
4/12 ML HO*
0/12 ML O*
0/12 ML HO*
4/12 ML O*
2/12 ML HO*
0/12 ML O*
0/4 ML HO*
1/4 ML O*
0/12 ML HO*
6/12 ML O*

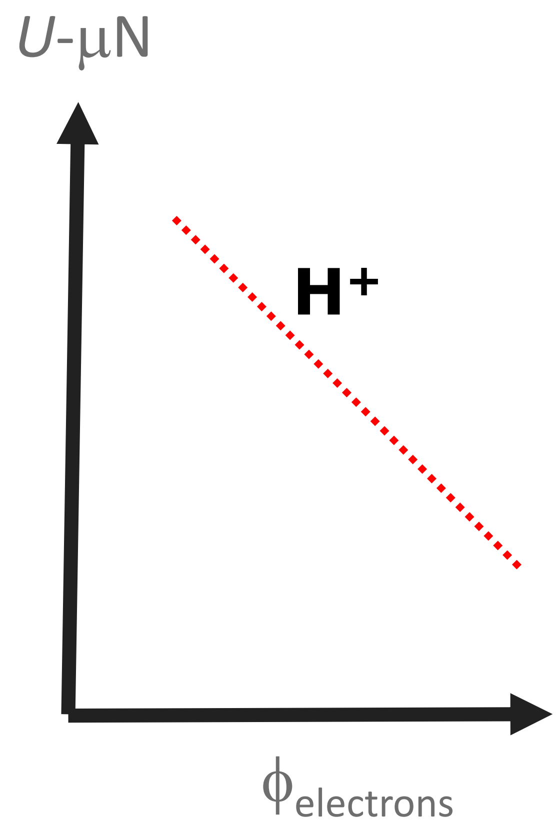
Charge tranfer?



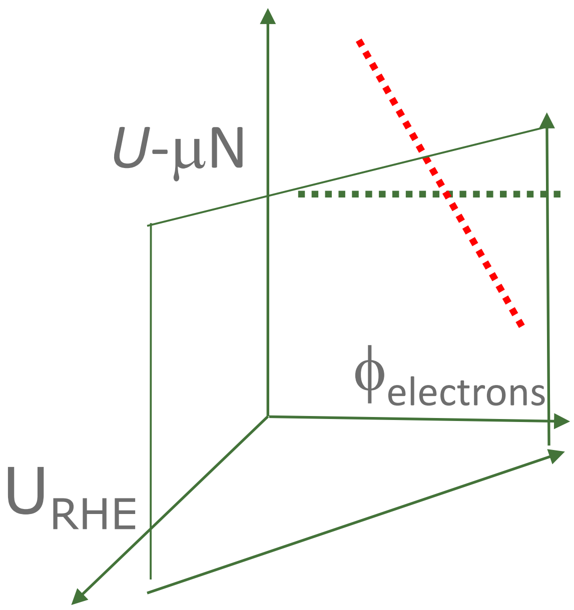


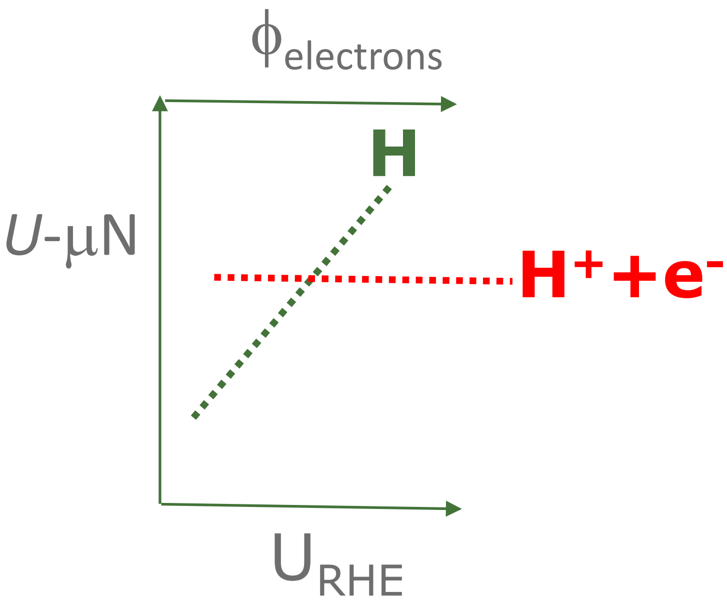
Open system

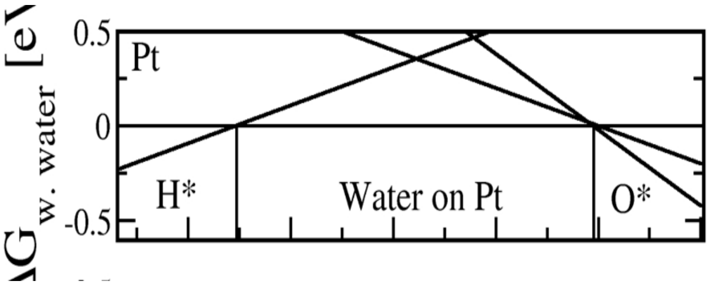




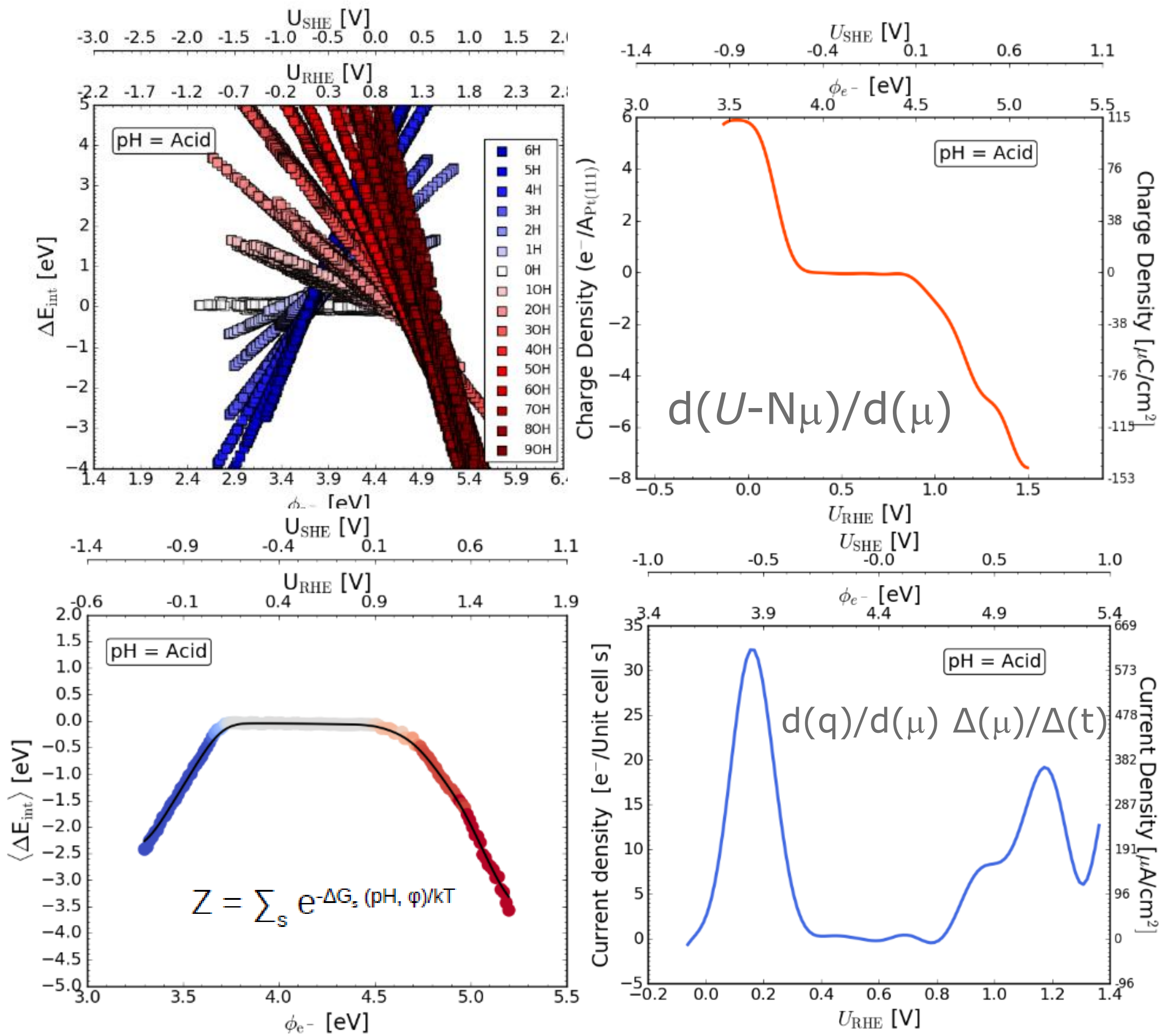
Coupled proton electron transfer?



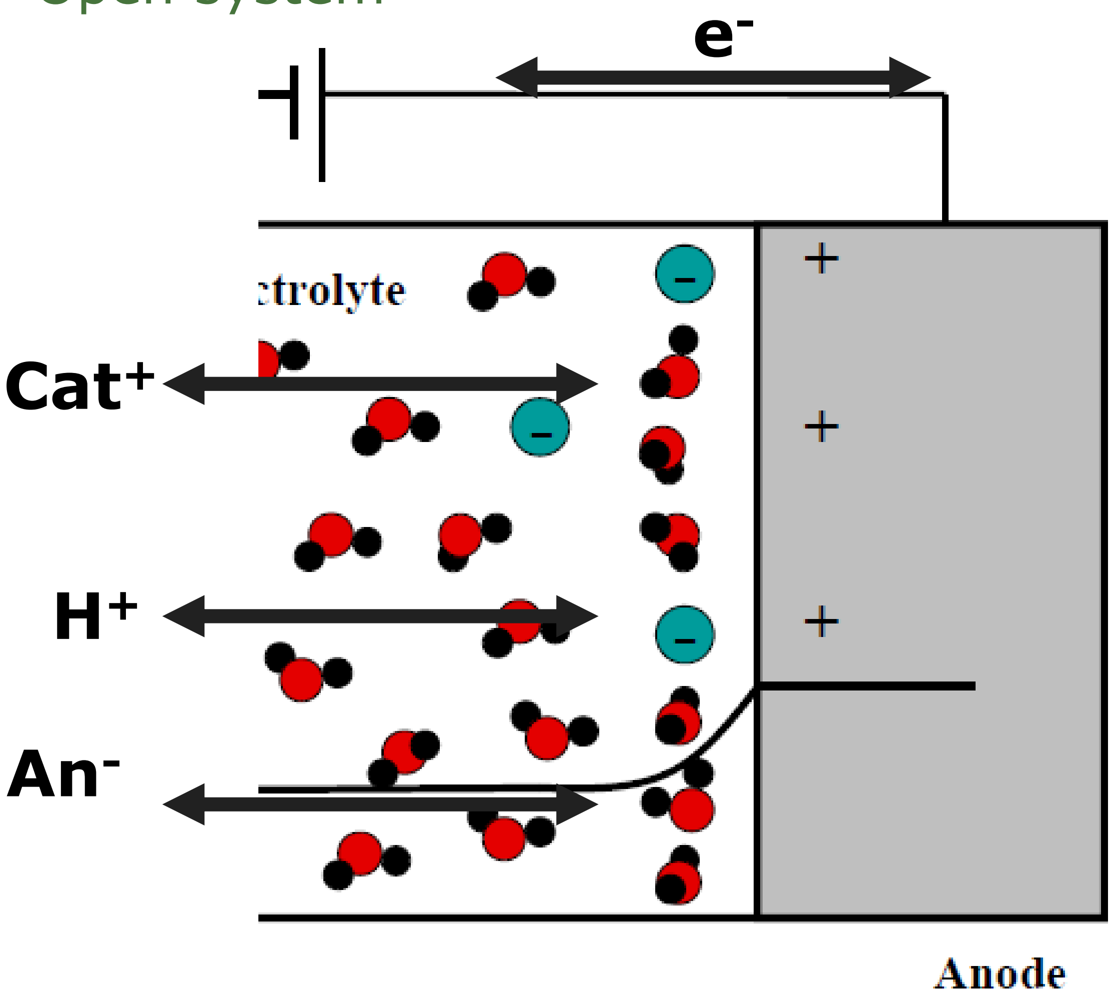




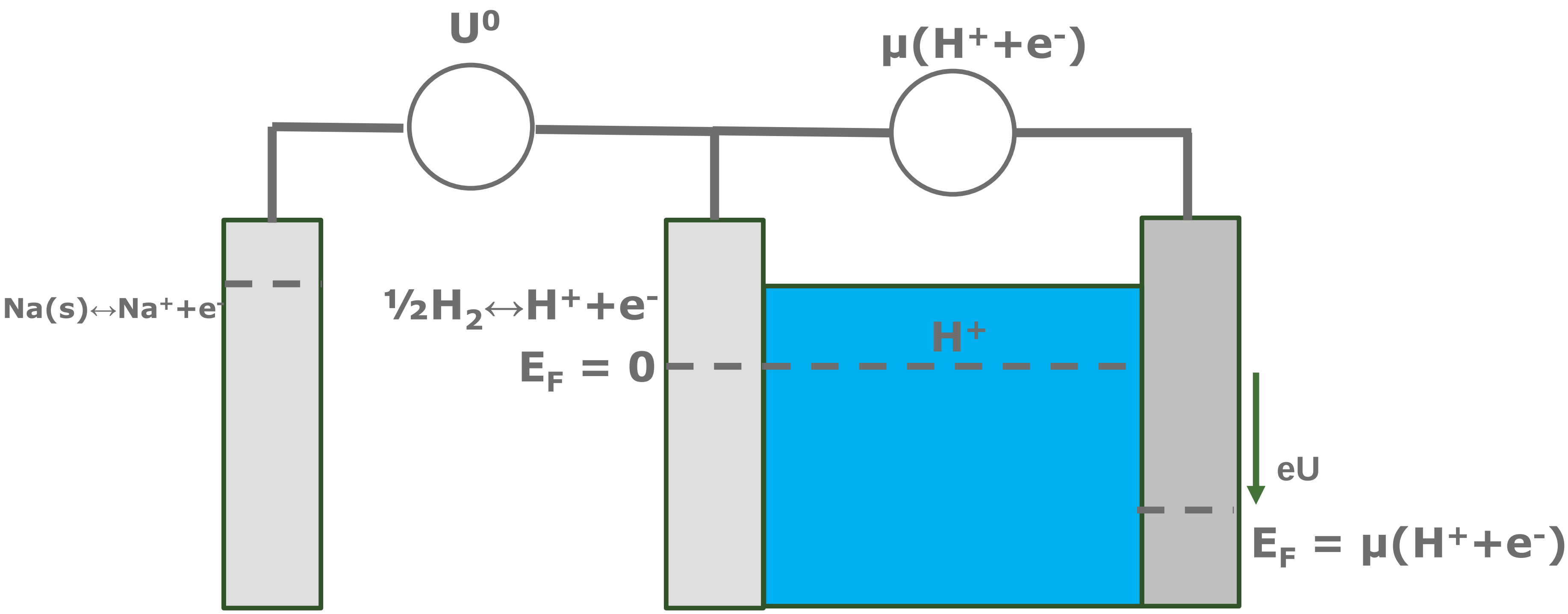
From simulations to CV's



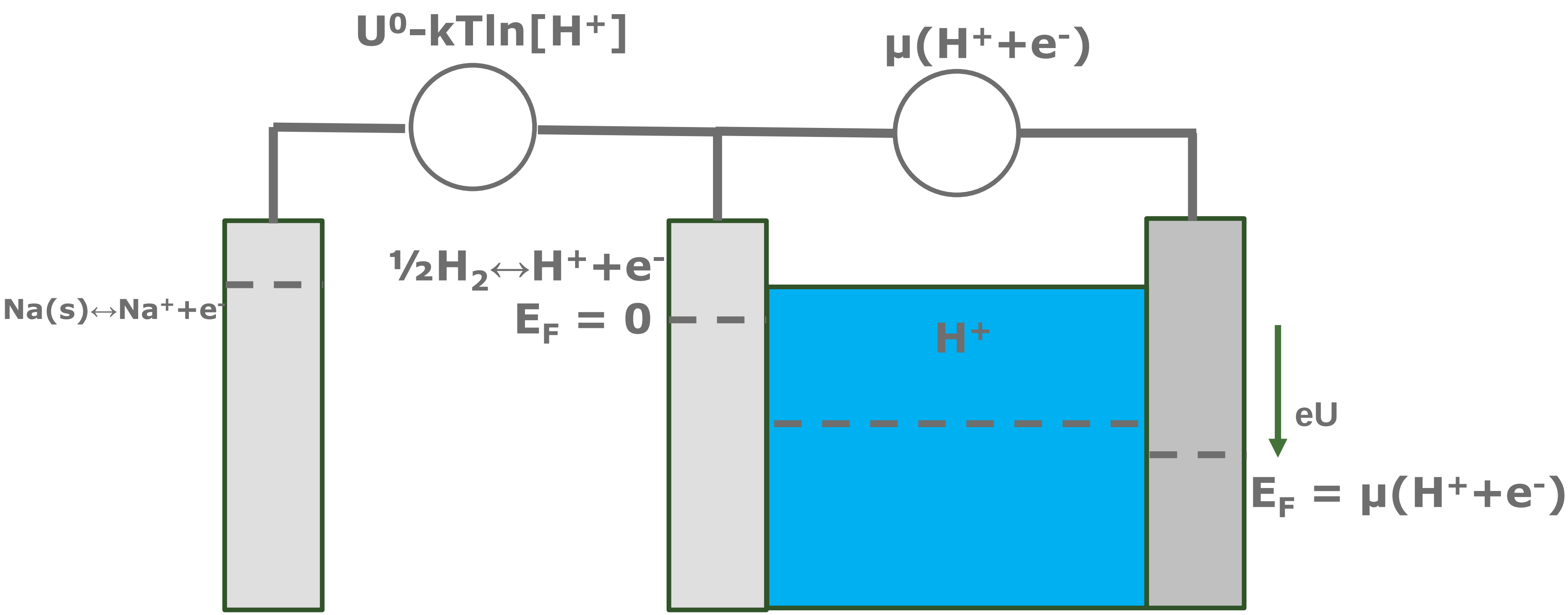
Open system



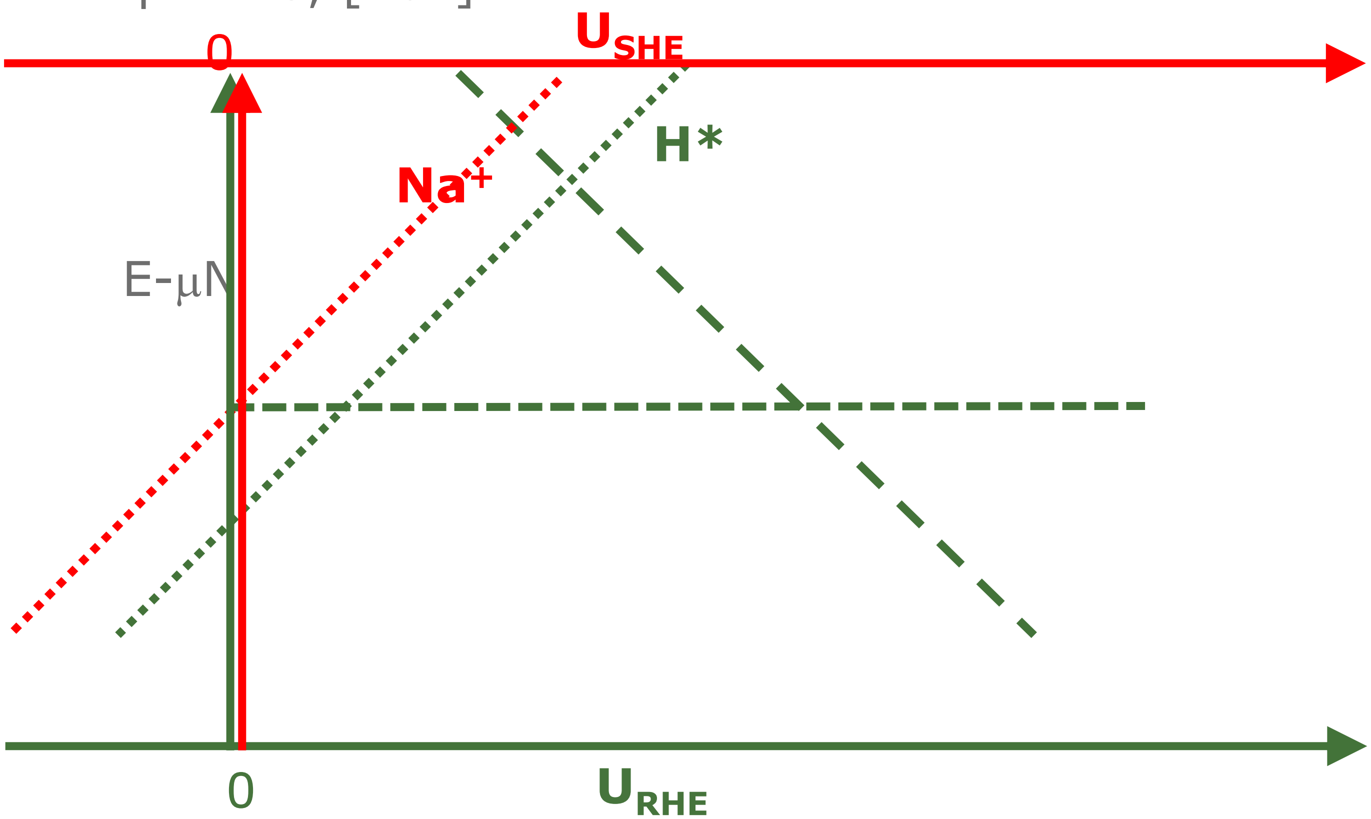
pH = 0, [Na^+] = 1M



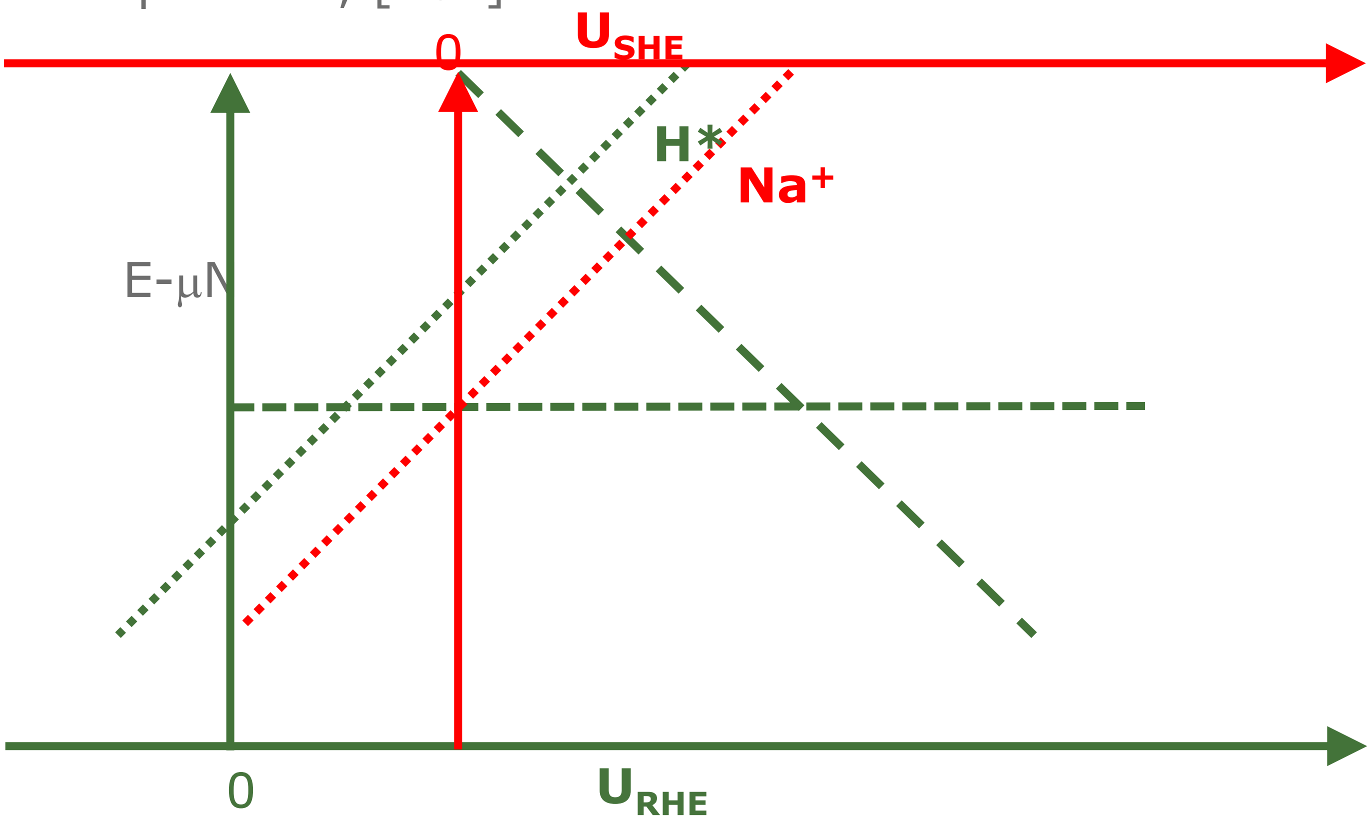
$pH = 14$, $[Na^+] = 1M$

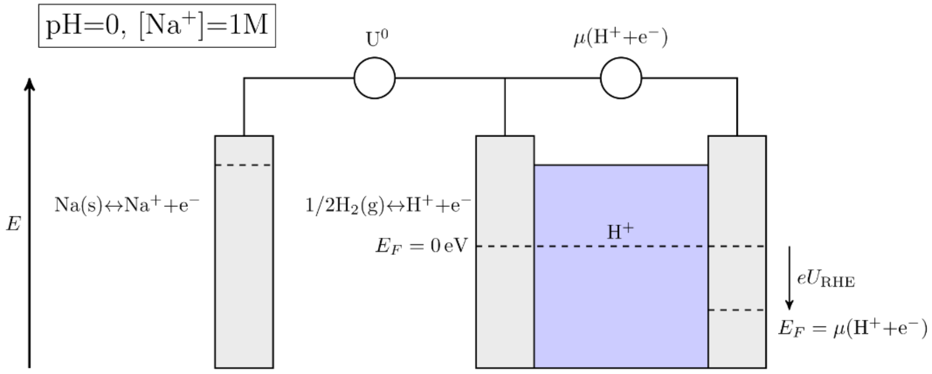


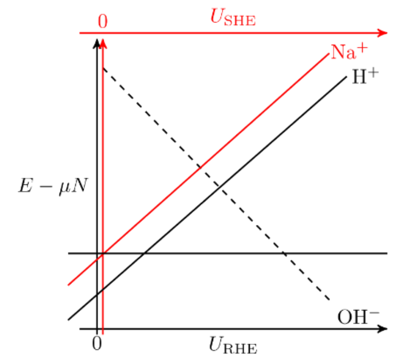
pH = 0, [Na+] = 1M

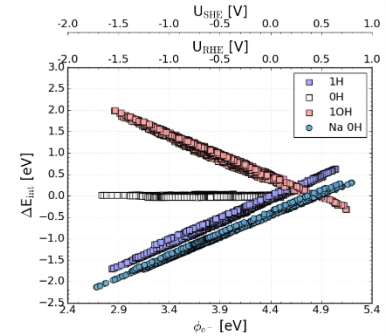


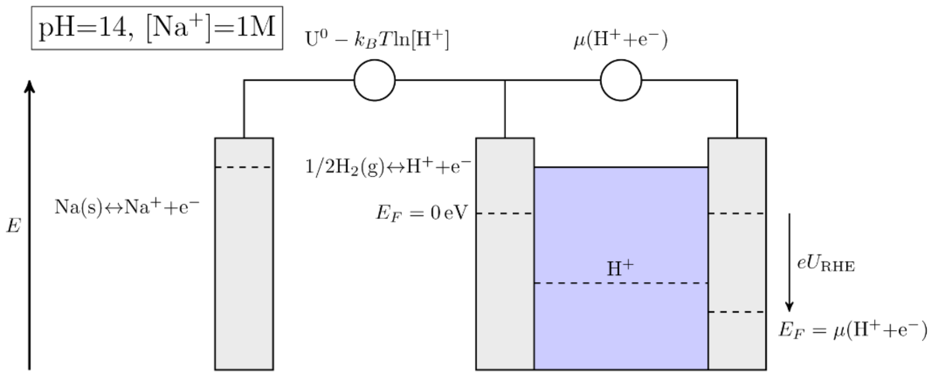
pH = 14, [Na+] = 1M

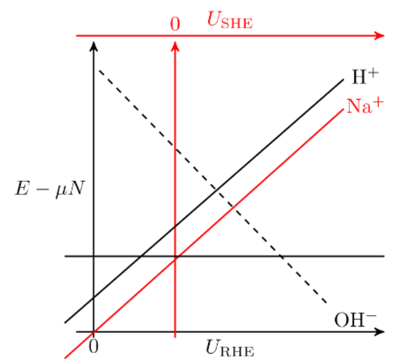


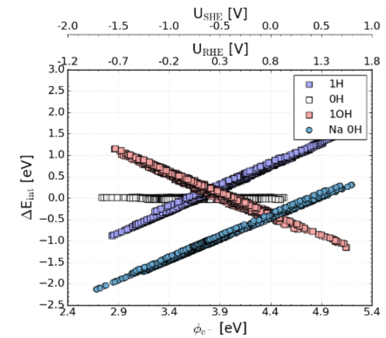

pH=0, [Na$^+$]=1M
U^0
μ(H$^+$+e$^-$)
E
Na(s)↔Na$^+$+e$^-$
1/2H$_2$(g)↔H$^+$+e$^-$
$E_F = 0\,\mathrm{eV}$
H$^+$
eU_{RHE}
$E_F = \mu(\mathrm{H^+ + e^-})$

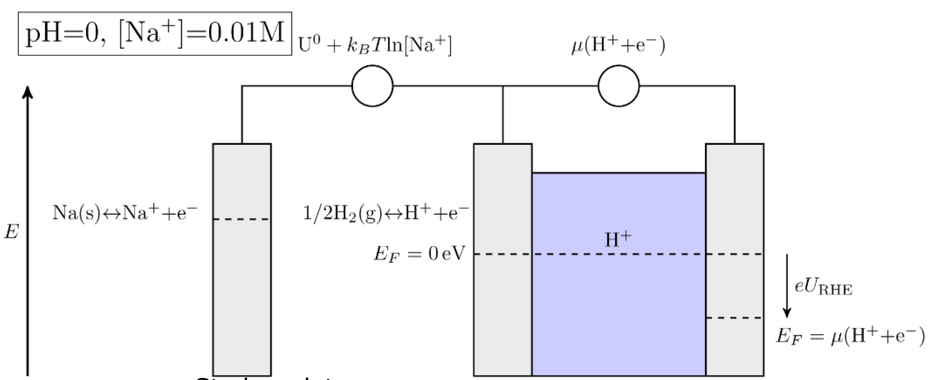

0
U_{SHE}
Na$^+$
H$^+$
$E - \mu N$
OH$^-$
0
U_{RHE}

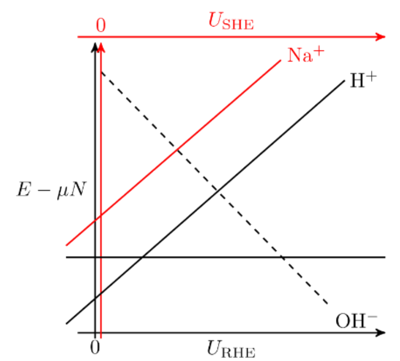

U$_{\mathrm{SHE}}$ [V]
U$_{\mathrm{RHE}}$ [V]
1H
0H
1OH
Na 0H
ΔE_{int} [eV]
ϕ_{e^-} [eV]

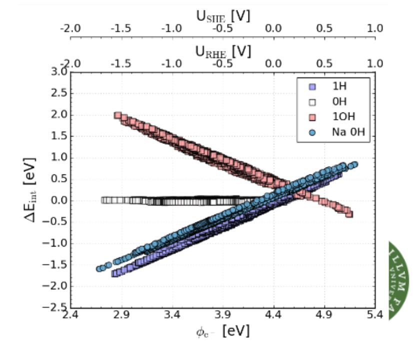

pH=14, [Na$^+$]=1M
U^0 − $k_BT\ln$[H$^+$]
μ(H$^+$+e$^-$)
E
Na(s)↔Na$^+$+e$^-$
1/2H$_2$(g)↔H$^+$+e$^-$
$E_F = 0\,\mathrm{eV}$
H$^+$
eU_{RHE}
$E_F = \mu(\mathrm{H^+ + e^-})$


0
U_{SHE}
H$^+$
Na$^+$
$E - \mu N$
OH$^-$
0
U_{RHE}

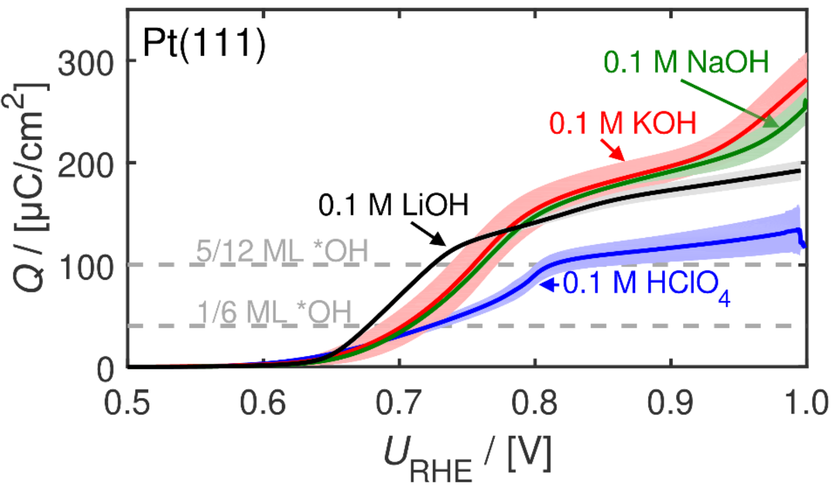

U$_{\mathrm{SHE}}$ [V]
U$_{\mathrm{RHE}}$ [V]
1H
0H
1OH
Na 0H
ΔE_{int} [eV]
ϕ_{e^-} [eV]

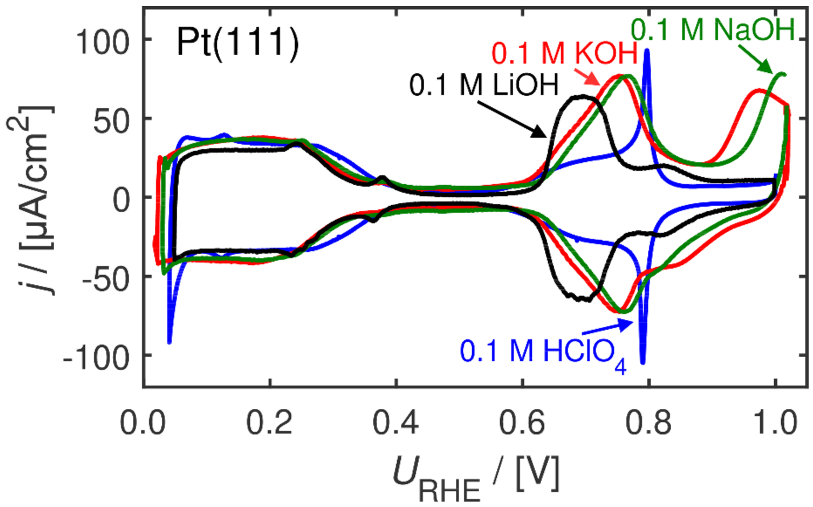

pH=0, [Na$^+$]=0.01M
U^0 + $k_BT\ln$[Na$^+$]
μ(H$^+$+e$^-$)
E
Na(s)↔Na$^+$+e$^-$
1/2H$_2$(g)↔H$^+$+e$^-$
$E_F = 0\,\mathrm{eV}$
H$^+$
eU_{RHE}
$E_F = \mu(\mathrm{H^+ + e^-})$


0
U_{SHE}
Na$^+$
H$^+$
$E - \mu N$
OH$^-$
0
U_{RHE}


U$_{\mathrm{SHE}}$ [V]
U$_{\mathrm{RHE}}$ [V]
1H
0H
1OH
Na 0H
ΔE_{int} [eV]
ϕ_{e^-} [eV]

Pt (111) in Acid and Base





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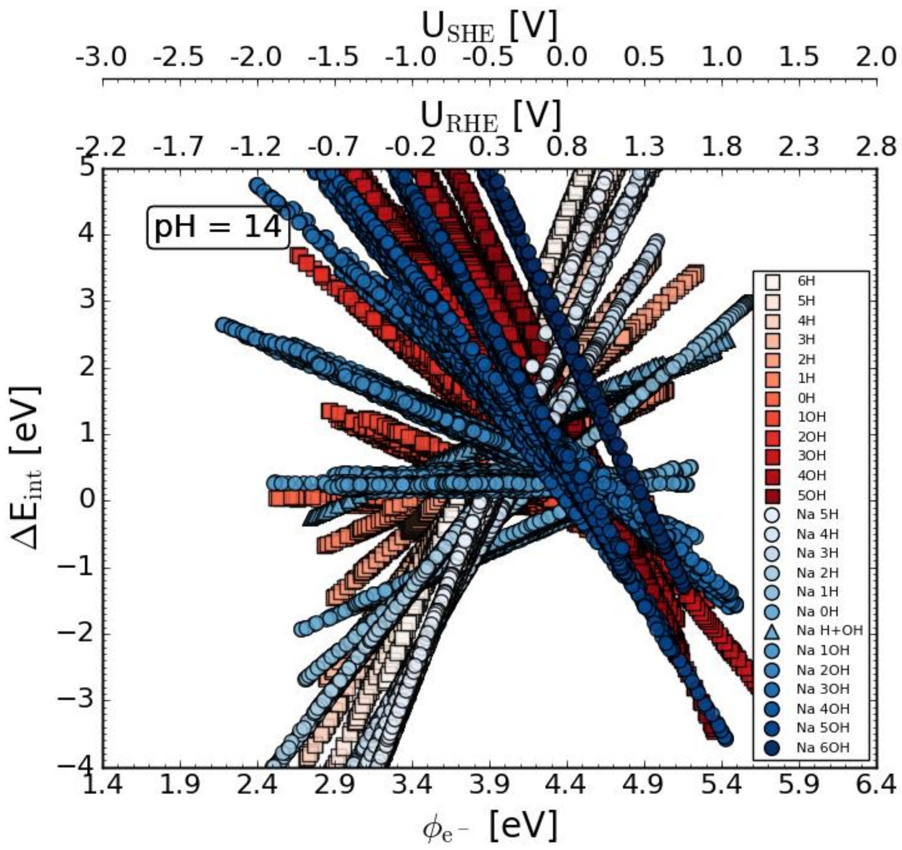
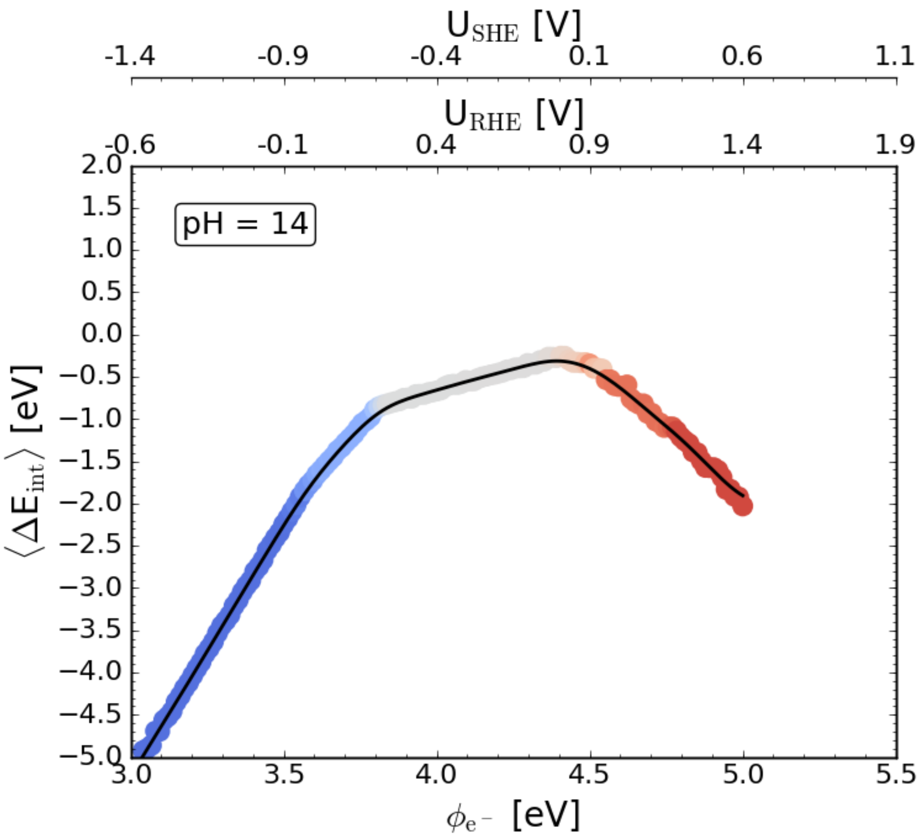
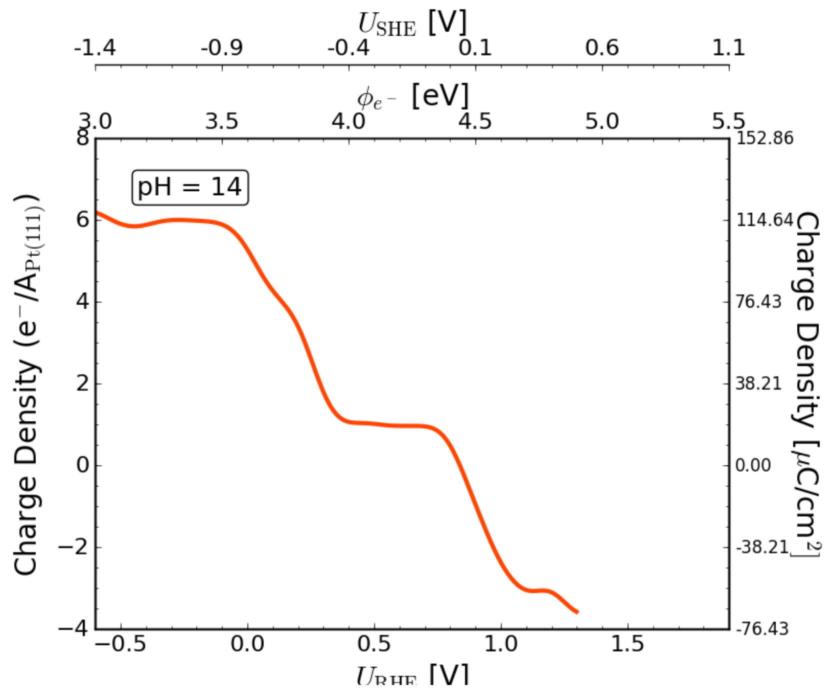
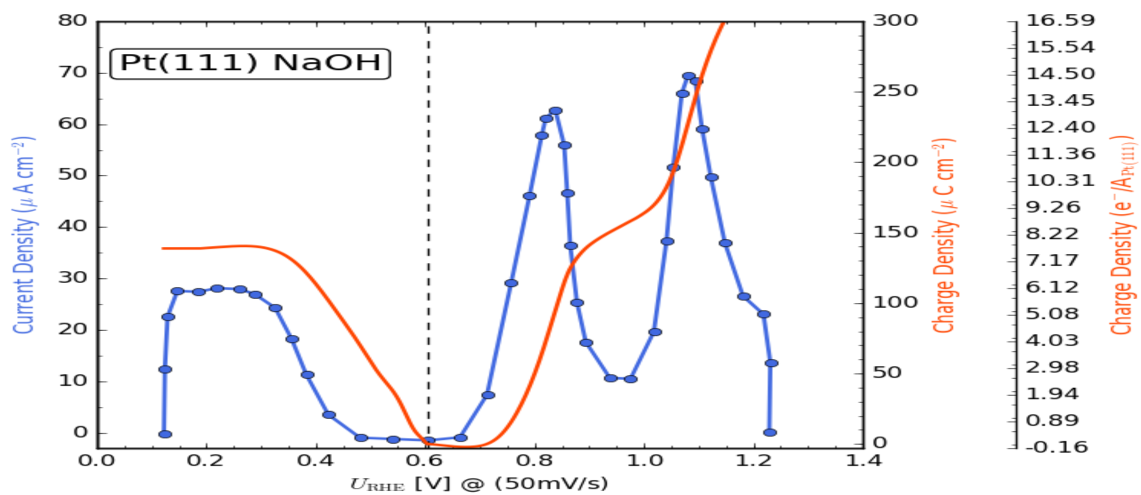
Pt(111) NaOH


U_SHE [V]
-3.0 -2.5 -2.0 -1.5 -1.0 -0.5 0.0 0.5 1.0 1.5 2.0
U_RHE [V]
-2.2 -1.7 -1.2 -0.7 -0.2 0.3 0.8 1.3 1.8 2.3 2.8
pH = 14
6H
5H
4H
3H
2H
1H
0H
1OH
2OH
3OH
4OH
5OH
Na 5H
Na 4H
Na 3H
Na 2H
Na 1H
Na 0H
Na H+OH
Na 1OH
Na 2OH
Na 3OH
Na 4OH
Na 5OH
Na 6OH
ΔE_int [eV]
φ_e- [eV]
1.4 1.9 2.4 2.9 3.4 3.9 4.4 4.9 5.4 5.9 6.4

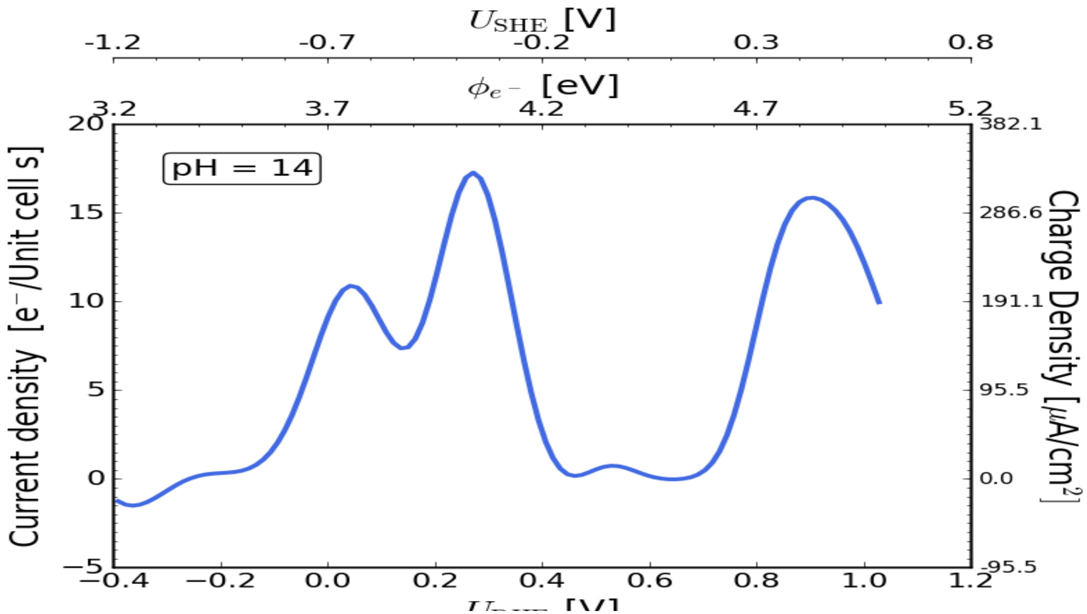

U_SHE [V]
-1.4 -0.9 -0.4 0.1 0.6 1.1
U_RHE [V]
-0.6 -0.1 0.4 0.9 1.4 1.9
pH = 14
⟨ΔE_int⟩ [eV]
φ_e- [eV]
3.0 3.5 4.0 4.5 5.0 5.5

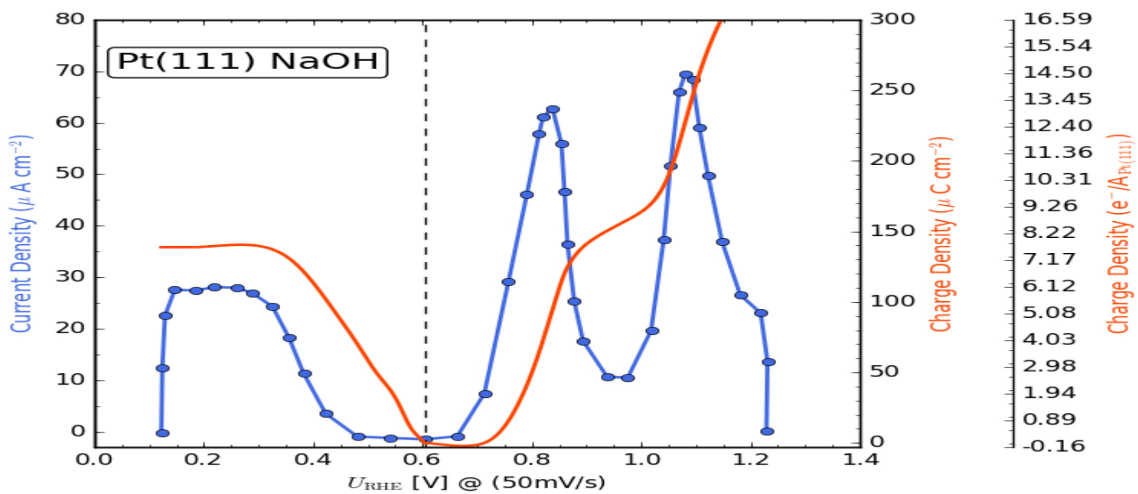
Pt 111 in NaOH



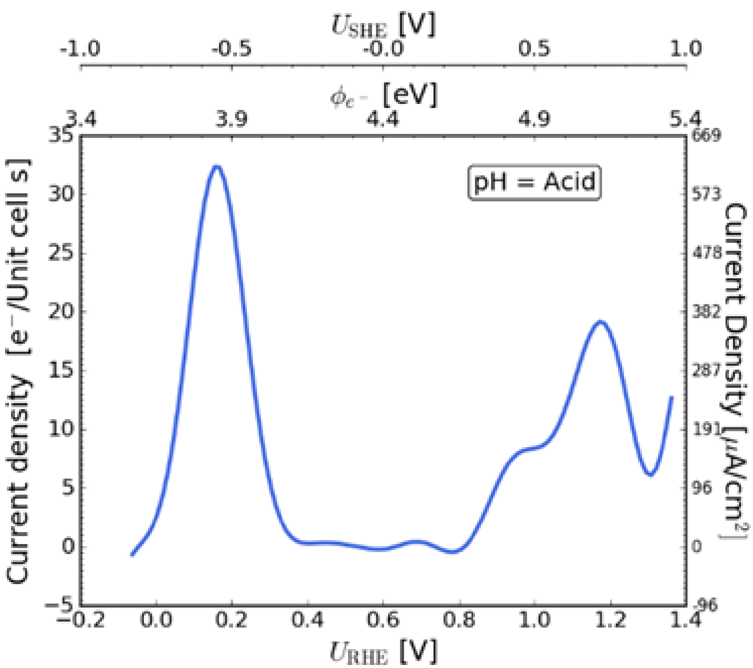


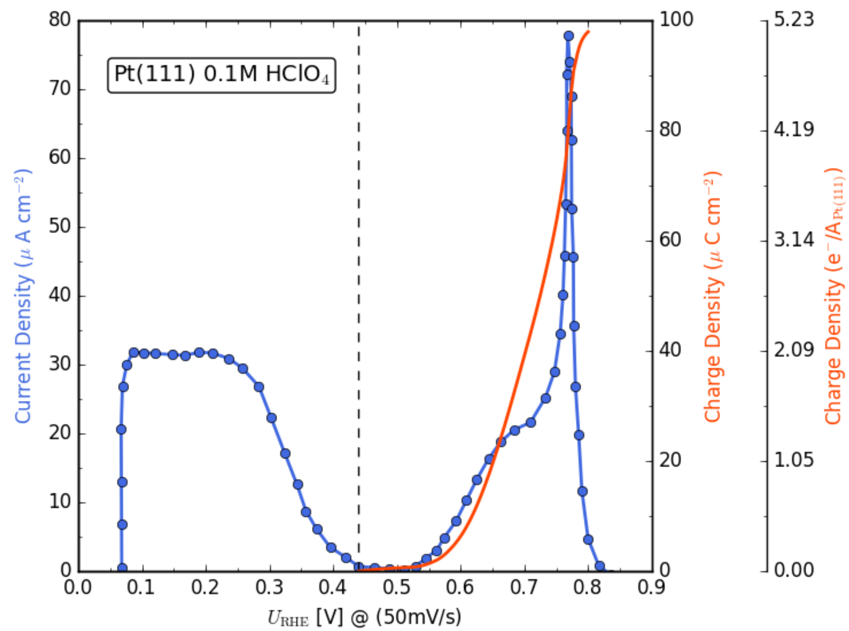
Pt (111) in NaOH





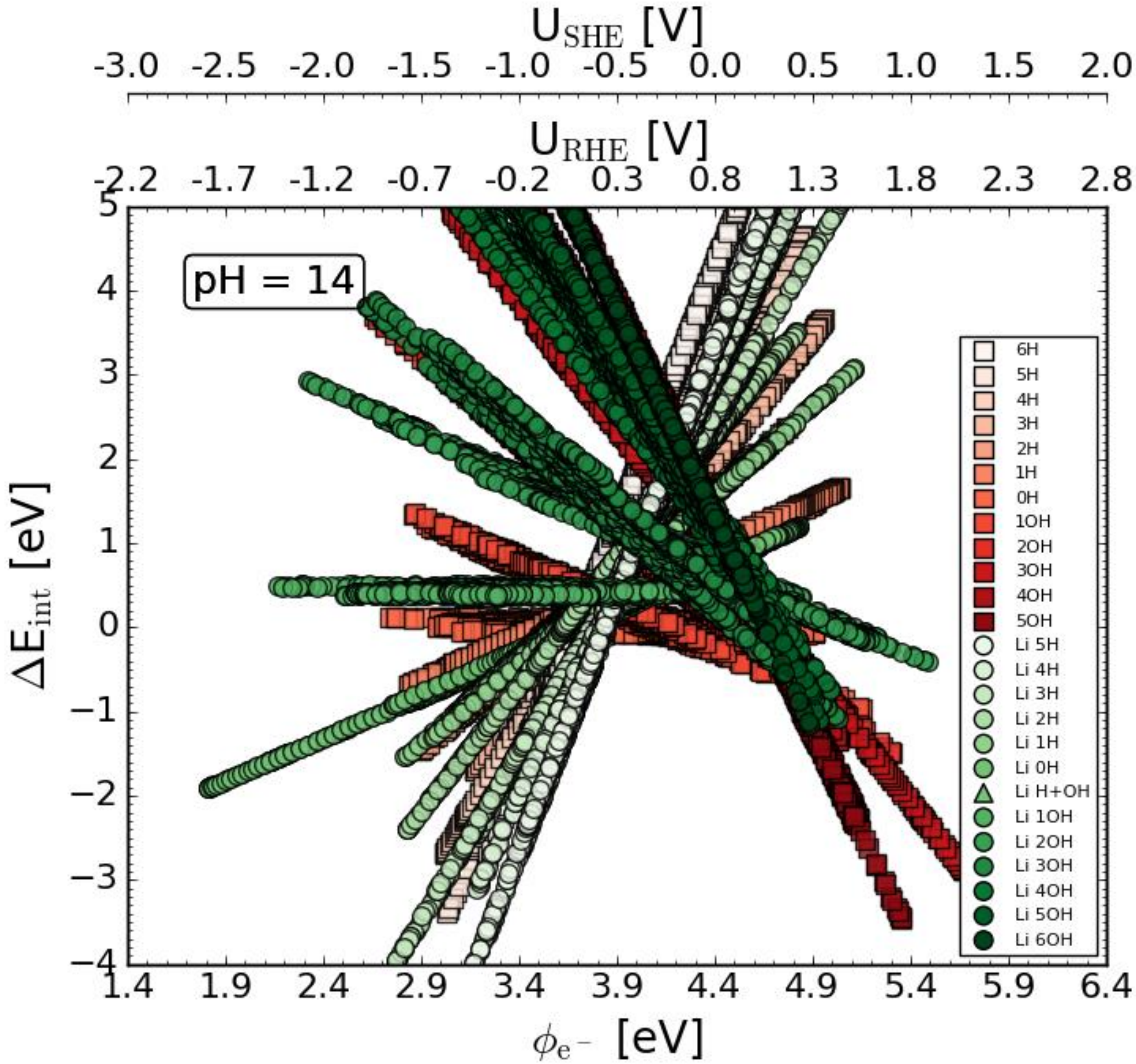
CV – in acid


U_{SHE} [V]
-1.0
-0.5
-0.0
0.5
1.0
ϕ_{e^-} [eV]
3.4
3.9
4.4
4.9
5.4
pH = Acid
Current density [e⁻/Unit cell s]
35
30
25
20
15
10
5
0
−5
Current Density [μA/cm²]
669
573
478
382
287
191
96
0
-96
−0.2
0.0
0.2
0.4
0.6
0.8
1.0
1.2
1.4
U_{RHE} [V]

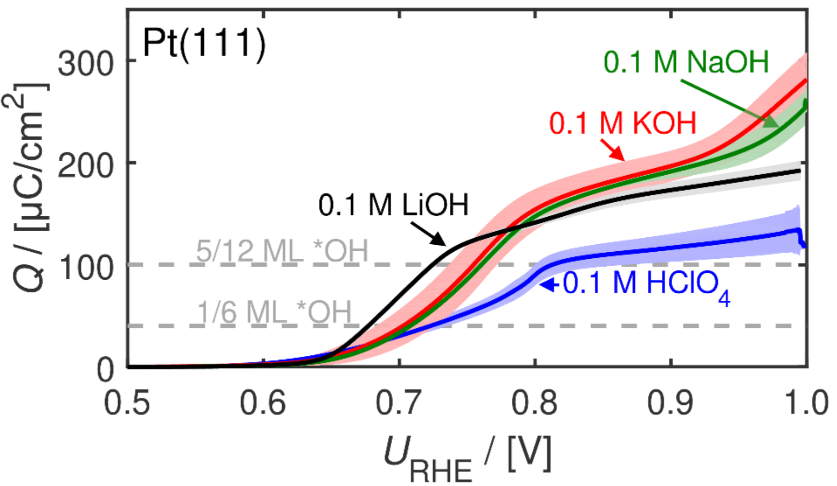

Pt(111) 0.1M $HClO_4$
Current Density (μ A cm⁻²)
80
70
60
50
40
30
20
10
0
Charge Density (μ C cm⁻²)
100
80
60
40
20
0
Charge Density (e⁻/A$_{Pt(111)}$)
5.23
4.19
3.14
2.09
1.05
0.00
0.0
0.1
0.2
0.3
0.4
0.5
0.6
0.7
0.8
0.9
U_{RHE} [V] @ (50mV/s)

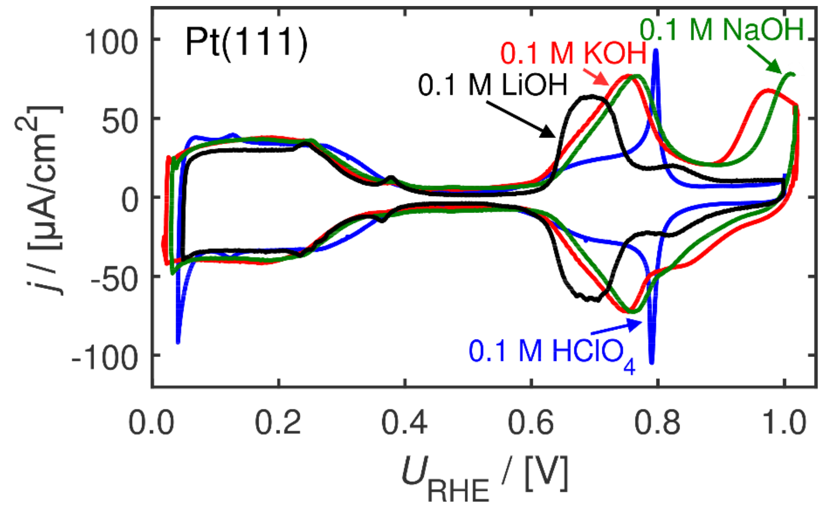
o

Pt (111) in LiOH



Pt (111) in Acid and Base
LiOH similar to acid





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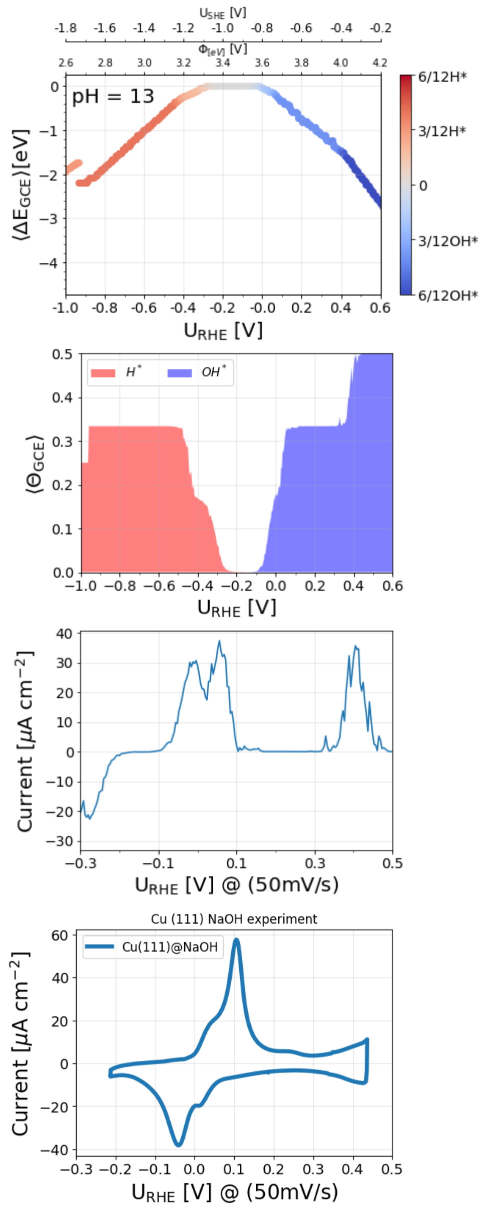
<table>
<tr><th></th><th>Cu(111)</th><th>Cu(100)</th><th>Cu(110)</th></tr>
<tr><td>Alkaline (Aquous) pH=13,

0.1 [M] NaOH</td>
<td>
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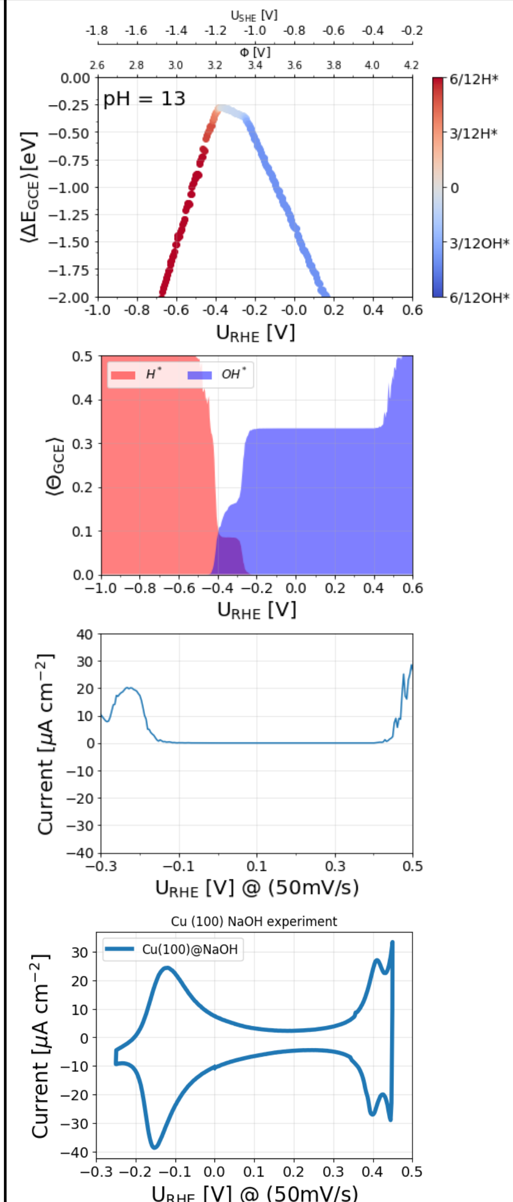
<td>
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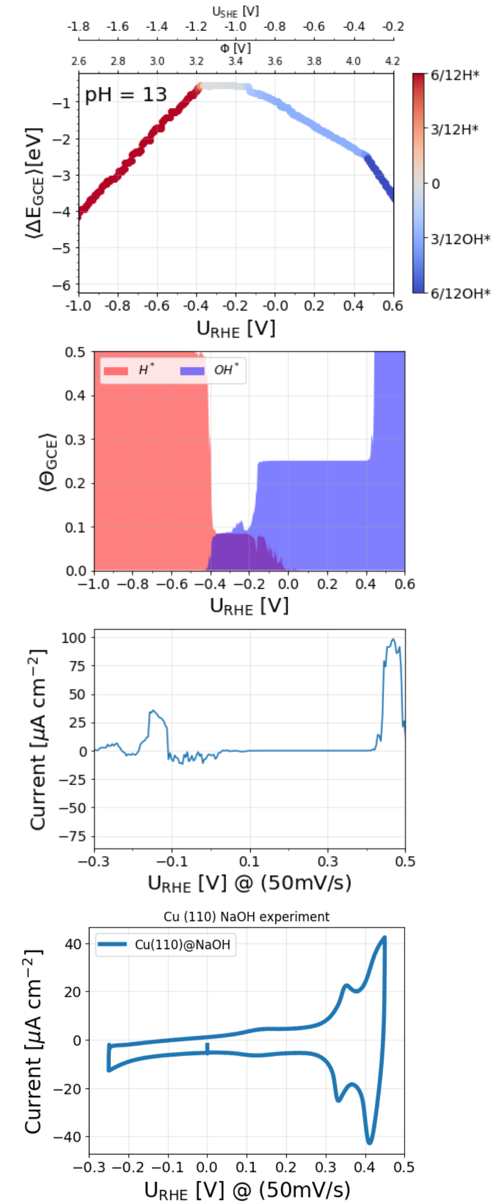
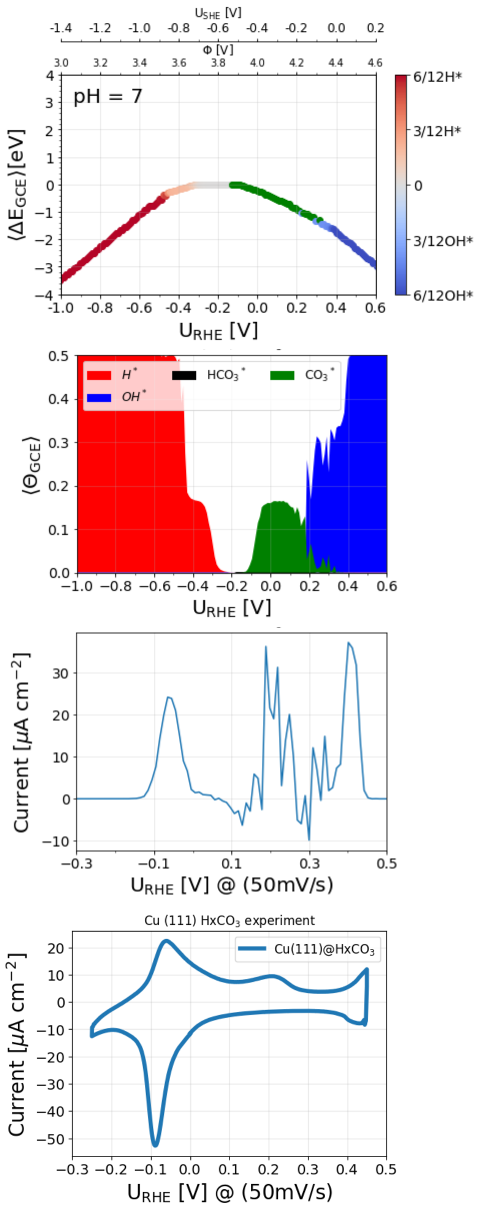
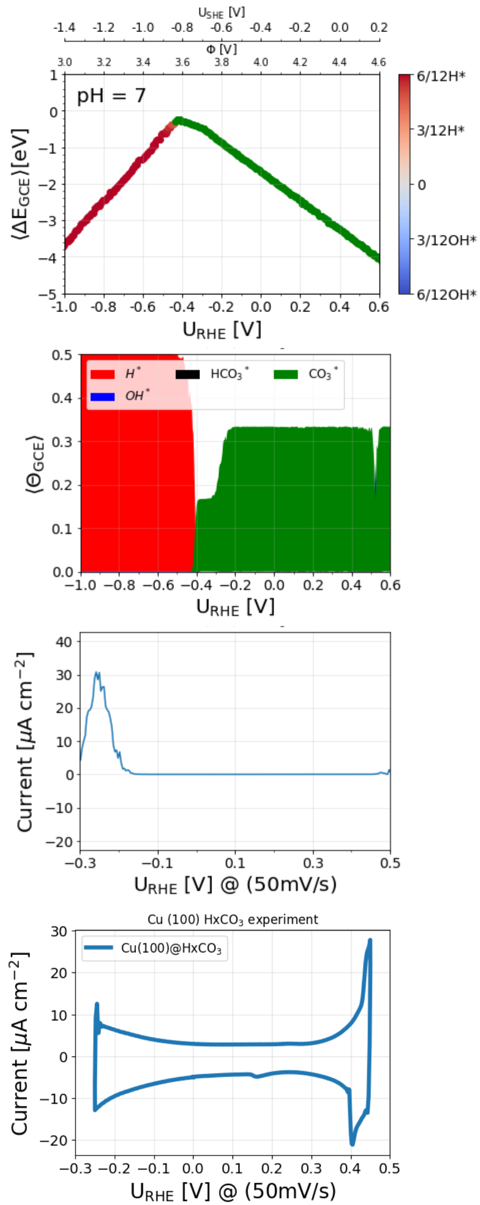
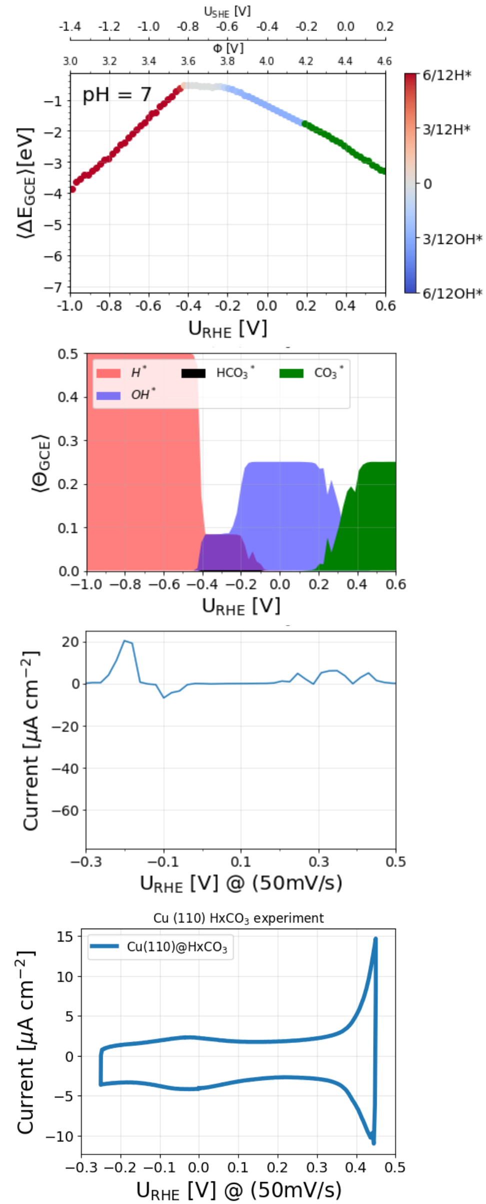
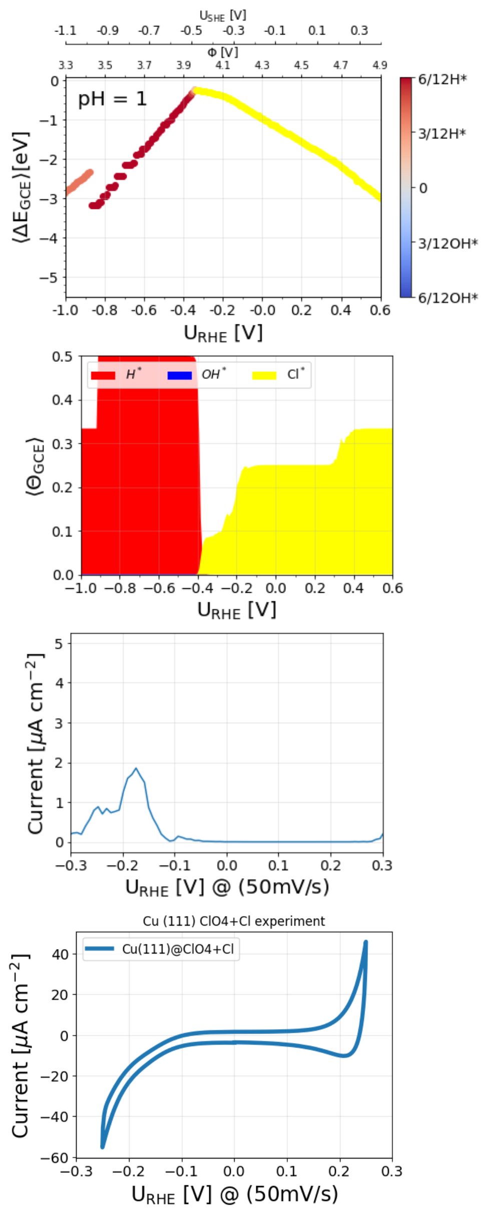
<td>
</td></tr>
</table>

	Cu(111)	Cu(100)	Cu(110)
Neutral pH=7, **0.1 [M] H_xCO_3**			

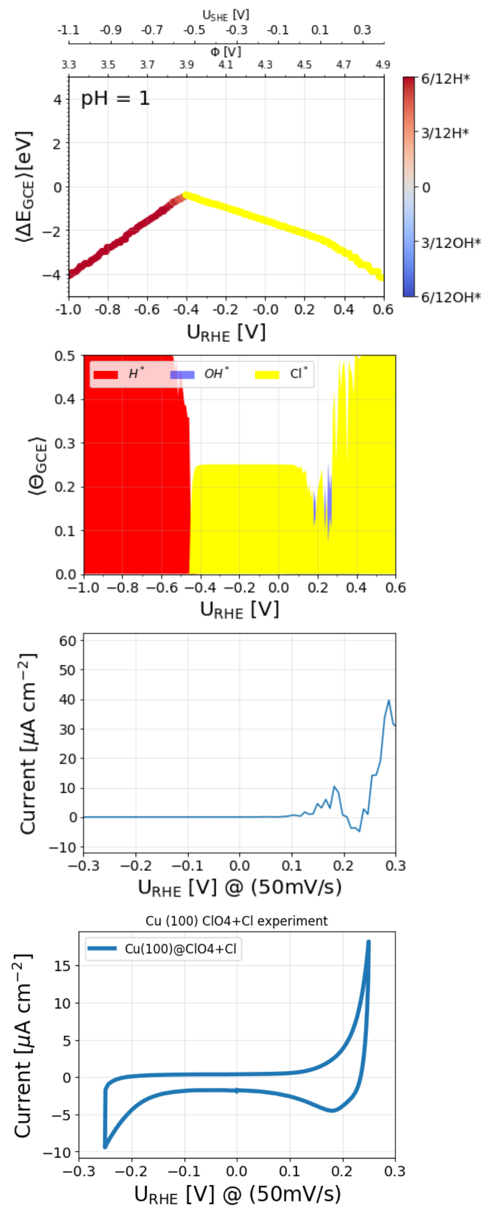
Acidic pH=1,

0.1M [$HClO_4$] + [Cl]

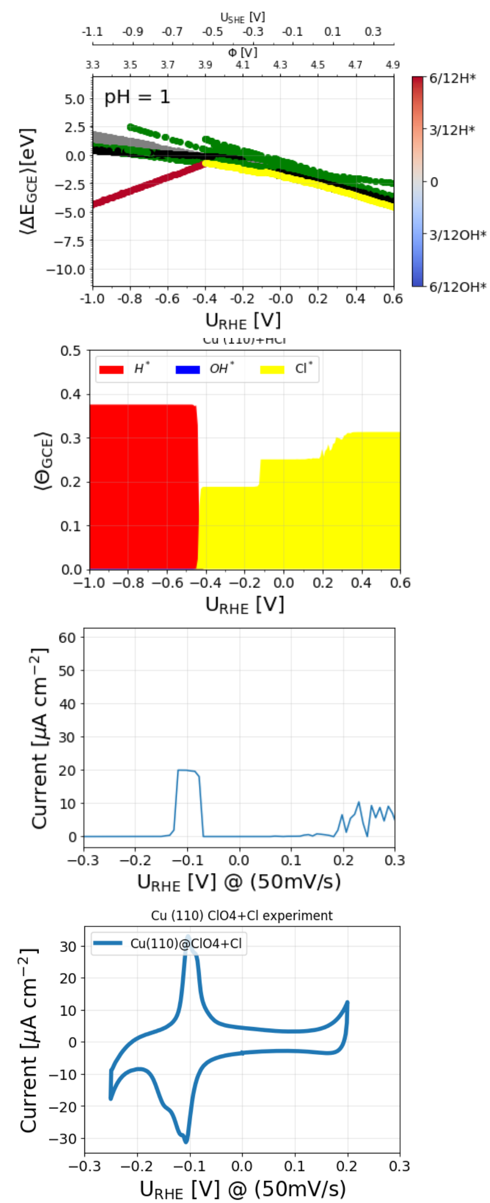
Cu(111)



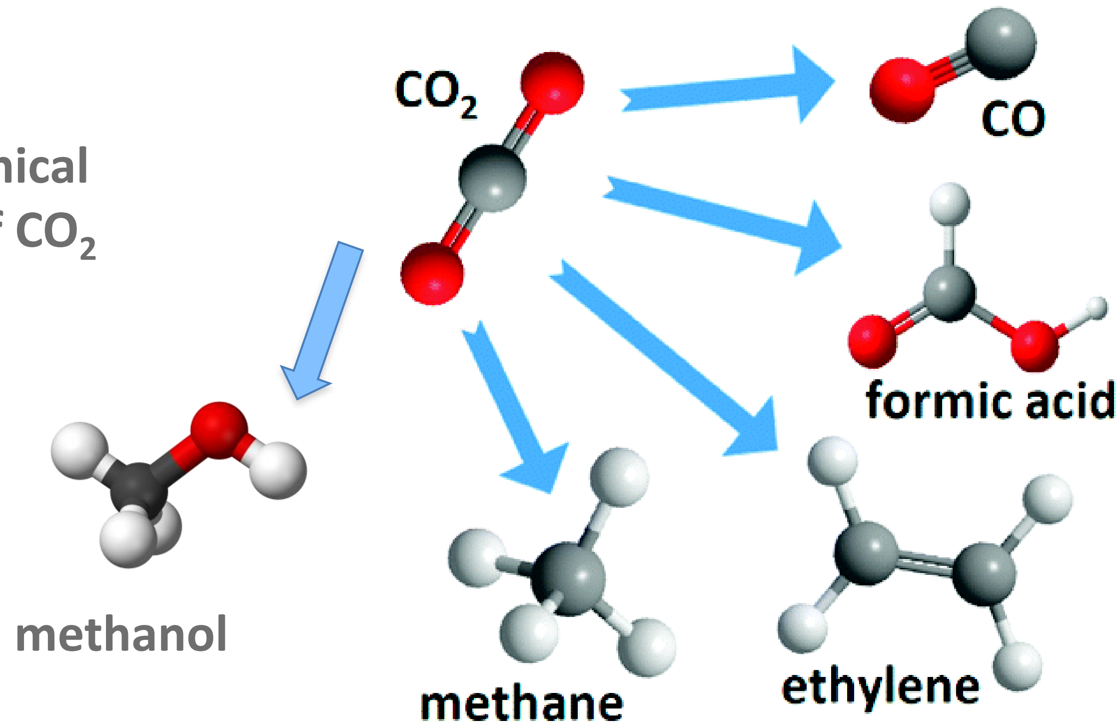
Cu(100)



Cu(110)



Electrochemical reduction of CO_2



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Two Pathways for the Formation of Ethylene in CO Reduction on Single-Crystal Copper Electrodes

Klaas Jan P. Schouten, Zisheng Qin, Elena Pérez Gallent, and Marc T. M. Koper*

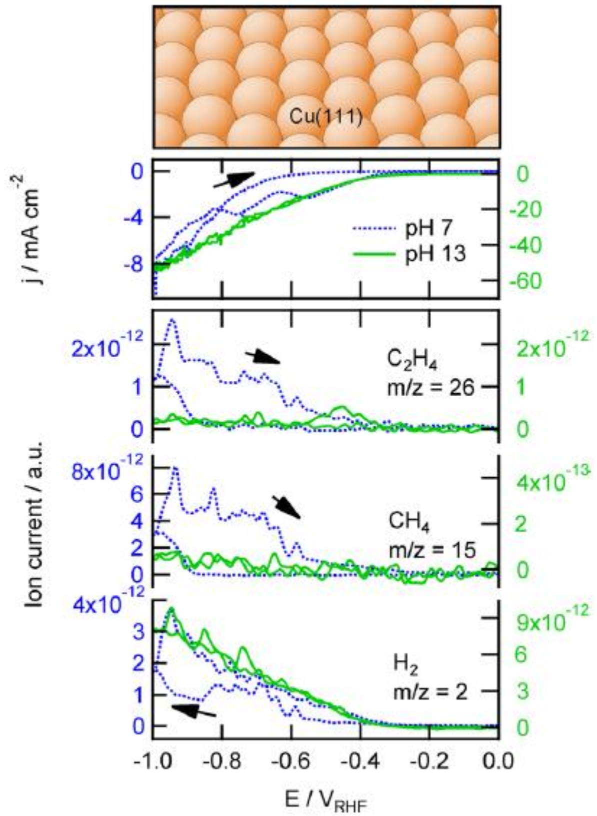


Figure 1. Top: (111) facet of the copper fcc crystal. Middle: cyclic voltammograms for the reduction of a saturated solution of CO (~1 mM) on Cu(111) in phosphate buffer (pH 7) and NaOH solution (pH 13). Bottom: associated mass fragments of volatile products measured with OLEMS. Data for pH 7 are shown with blue dotted lines and plotted against the left axis, and data for pH 13 are shown with green solid lines and plotted against the right axis.

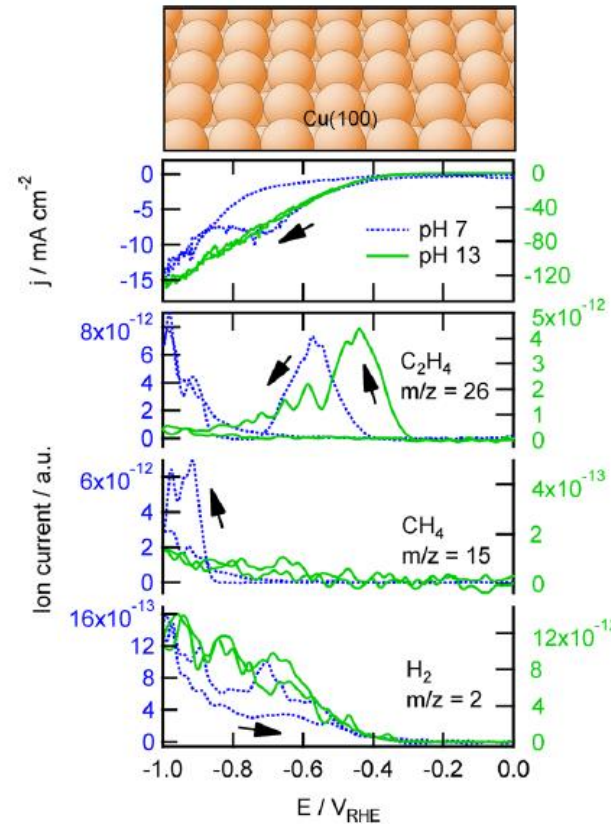
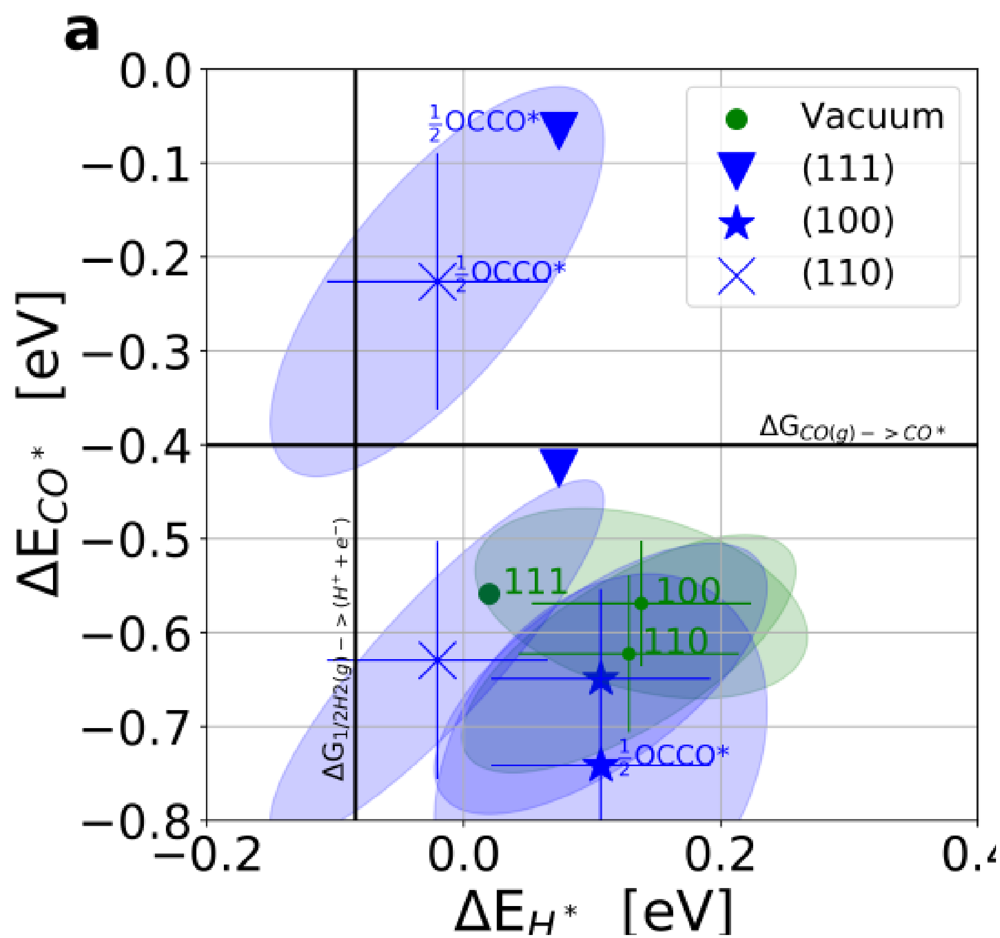
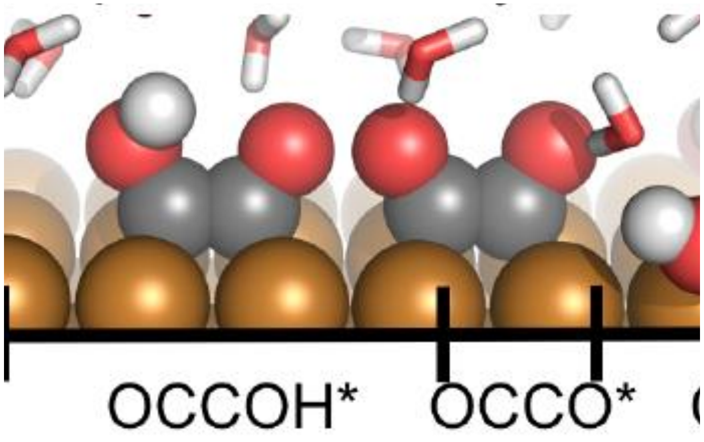
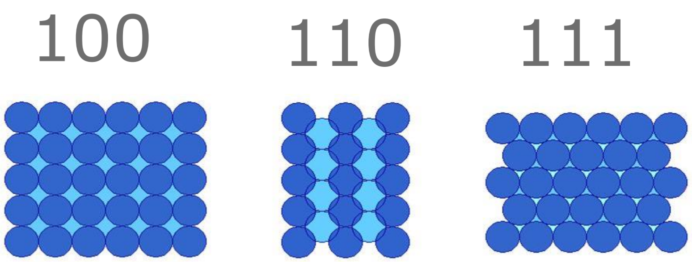


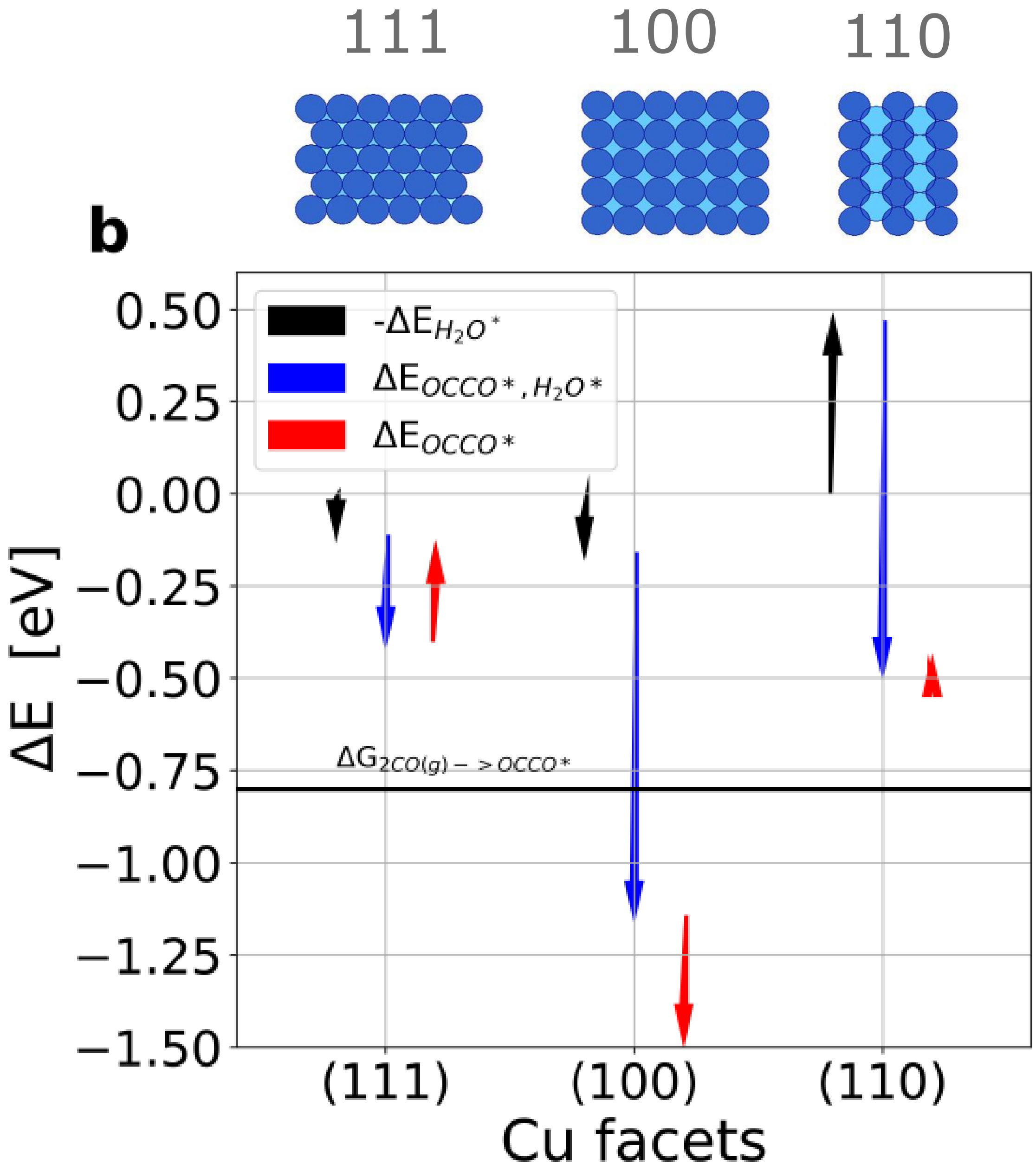
Figure 2. Top: (100) facet of the copper fcc crystal. Middle: cyclic voltammograms for the reduction of a saturated solution of CO (~1 mM) on Cu(100) in phosphate buffer (pH 7) and NaOH solution (pH 13). Bottom: associated mass fragments of volatile products measured with OLEMS. Data for pH 7 are shown with blue dotted lines and plotted against the left axis, and data for pH 13 are shown with green solid lines and plotted against the right axis.

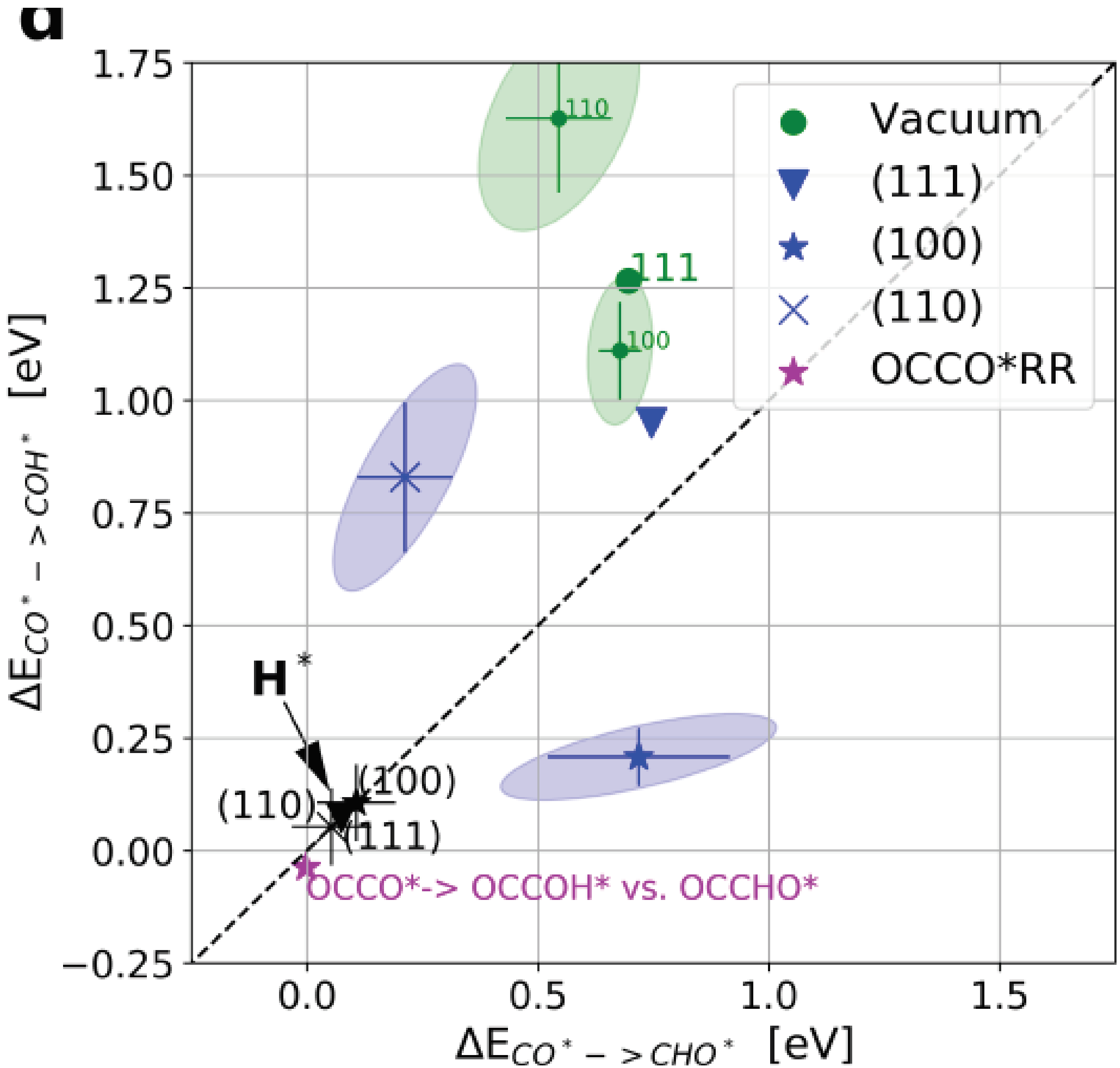
OCCO


a
Vacuum
(111)
(100)
(110)
½OCCO*
½OCCO*
111
100
110
½OCCO*
ΔG_CO(g)−>CO*
ΔG_1/2H2(g)−>(H⁺+e⁻)
ΔE_CO* [eV]
ΔE_H* [eV]
0.0
−0.1
−0.2
−0.3
−0.4
−0.5
−0.6
−0.7
−0.8
−0.2
0.0
0.2

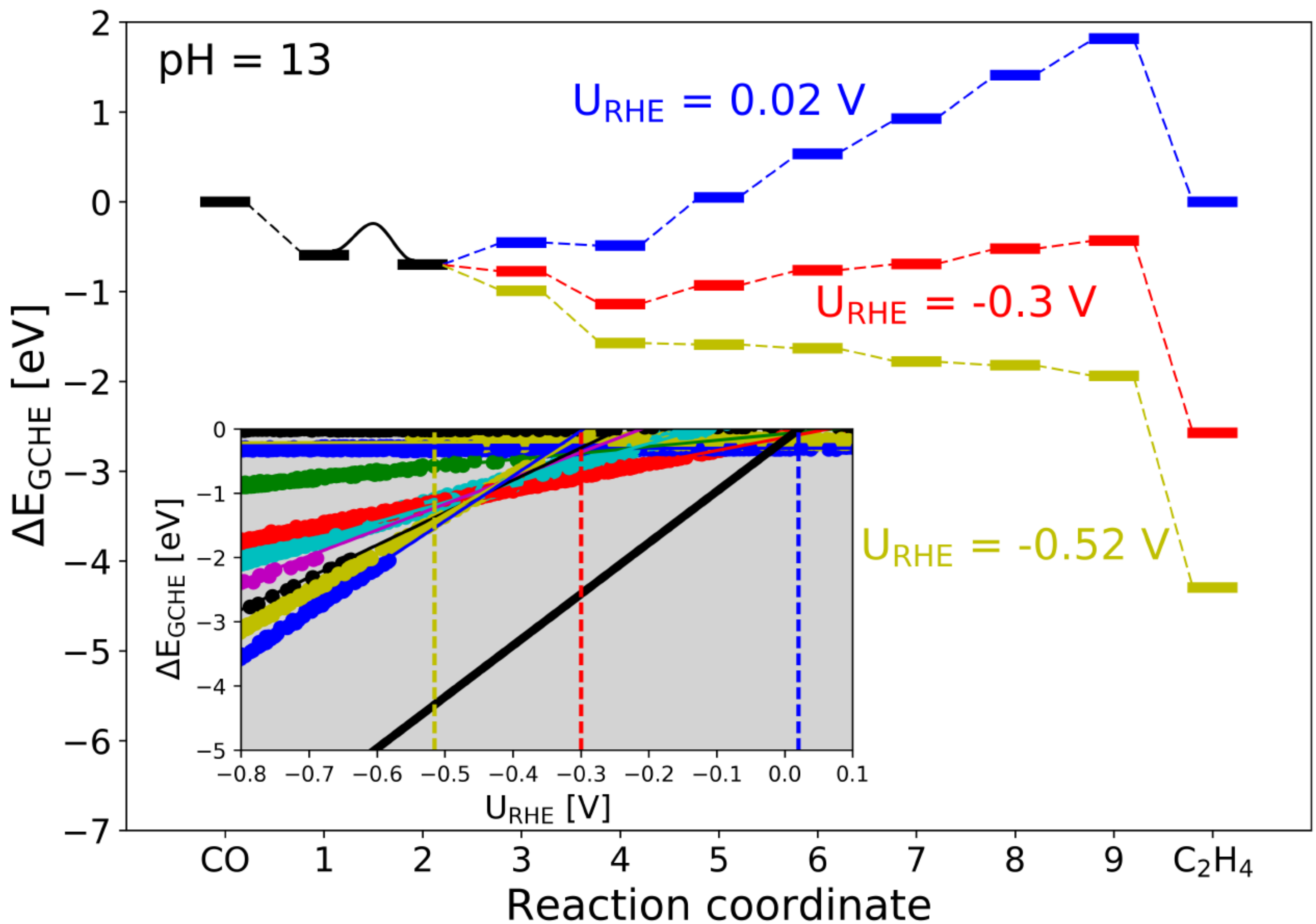

OCCOH*
OCCO*


100
110
111


111
100
110
b
0.50
0.25
0.00
−0.25
−0.50
−0.75
−1.00
−1.25
−1.50
ΔE [eV]
-ΔE$_{H_2O^*}$
ΔE$_{OCCO*,H_2O*}$
ΔE$_{OCCO*}$
ΔG$_{2CO(g)->OCCO*}$
(111)
(100)
(110)
Cu facets


d
1.75
1.50
1.25
1.00
0.75
0.50
0.25
0.00
−0.25
0.0
0.5
1.0
1.5
ΔE_{CO* −> COH*} [eV]
ΔE_{CO* −> CHO*} [eV]
Vacuum
(111)
(100)
(110)
OCCO*RR
110
111
100
H*
(100)
(110)
(111)
OCCO*-> OCCOH* vs. OCCHO*

C-C coupling


pH = 13
U_{RHE} = 0.02 V
U_{RHE} = -0.3 V
U_{RHE} = -0.52 V
ΔE_{GCHE} [eV]
2
1
0
−1
−2
−3
−4
−5
−6
−7
CO
1
2
3
4
5
6
7
8
9
C_2H_4
Reaction coordinate
ΔE_{GCHE} [eV]
0
−1
−2
−3
−4
−5
−0.8 −0.7 −0.6 −0.5 −0.4 −0.3 −0.2 −0.1 0.0 0.1
U_{RHE} [V]

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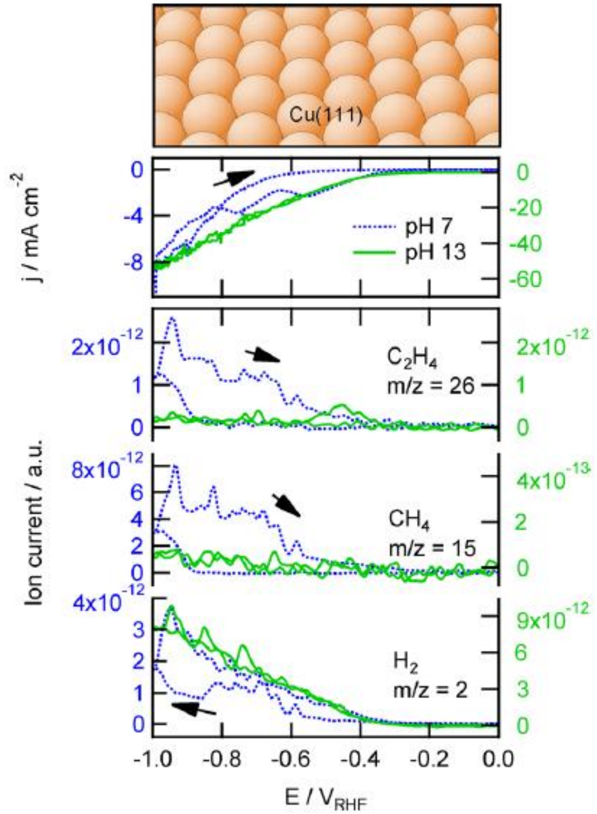


Figure 1. Top: (111) facet of the copper fcc crystal. Middle: cyclic voltammograms for the reduction of a saturated solution of CO (~1 mM) on Cu(111) in phosphate buffer (pH 7) and NaOH solution (pH 13). Bottom: associated mass fragments of volatile products measured with OLEMS. Data for pH 7 are shown with blue dotted lines and plotted against the left axis, and data for pH 13 are shown with green solid lines and plotted against the right axis.

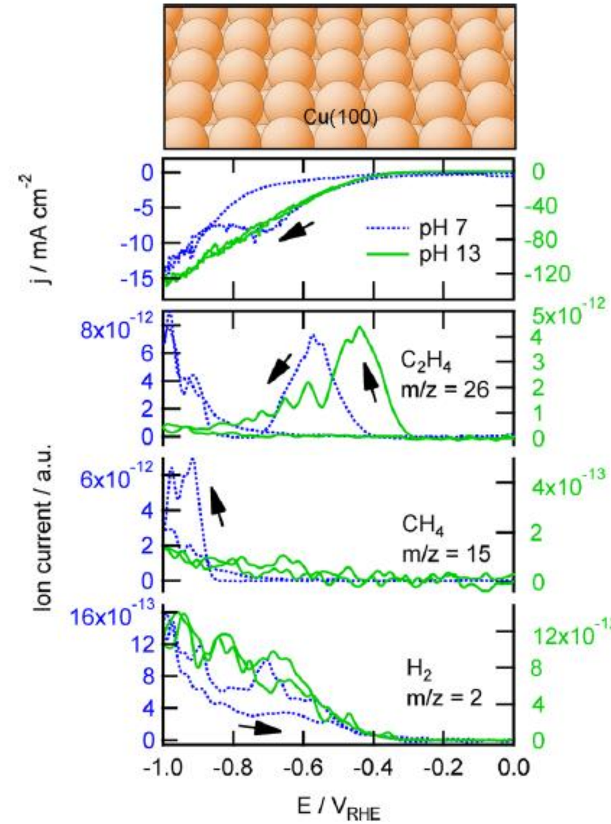
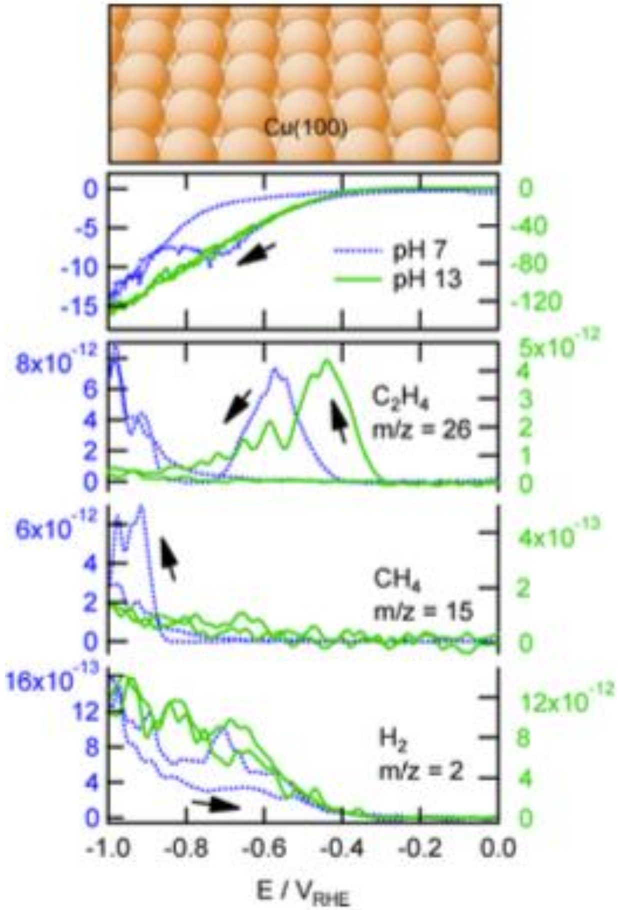


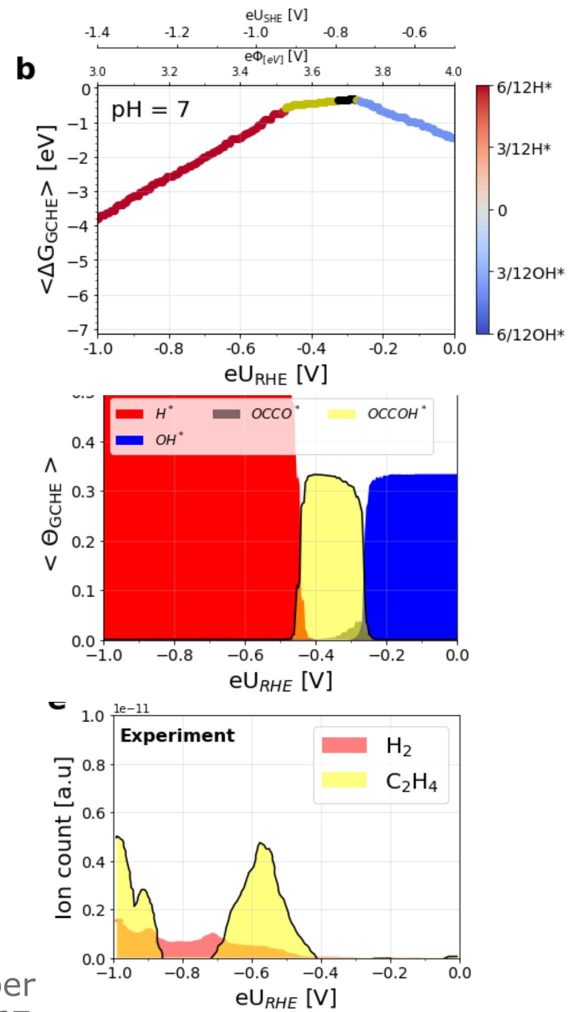
Figure 2. Top: (100) facet of the copper fcc crystal. Middle: cyclic voltammograms for the reduction of a saturated solution of CO (~1 mM) on Cu(100) in phosphate buffer (pH 7) and NaOH solution (pH 13). Bottom: associated mass fragments of volatile products measured with OLEMS. Data for pH 7 are shown with blue dotted lines and plotted against the left axis, and data for pH 13 are shown with green solid lines and plotted against the right axis.

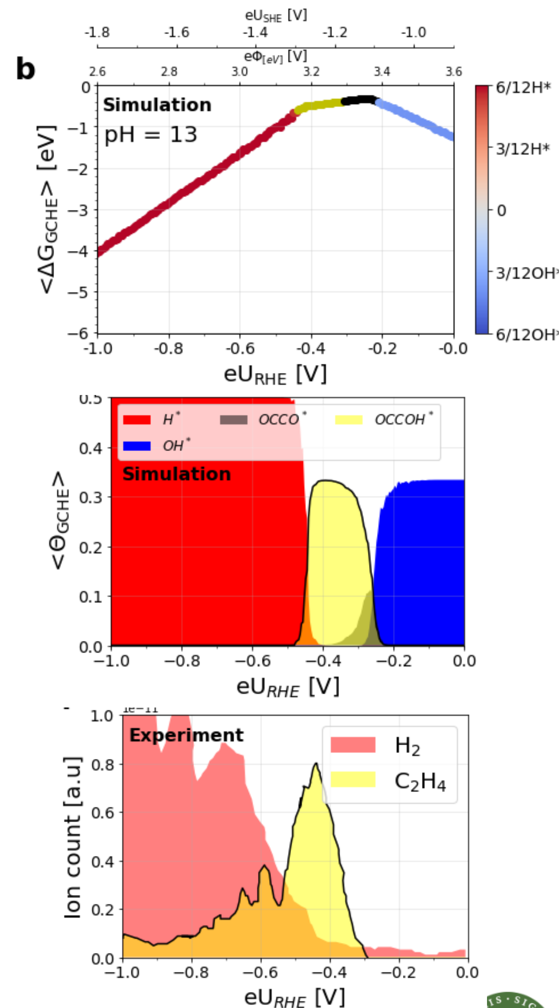
pH 7 = Phosphate buffer
pH 13 = NaOH electrolyte

Water Electrolyte

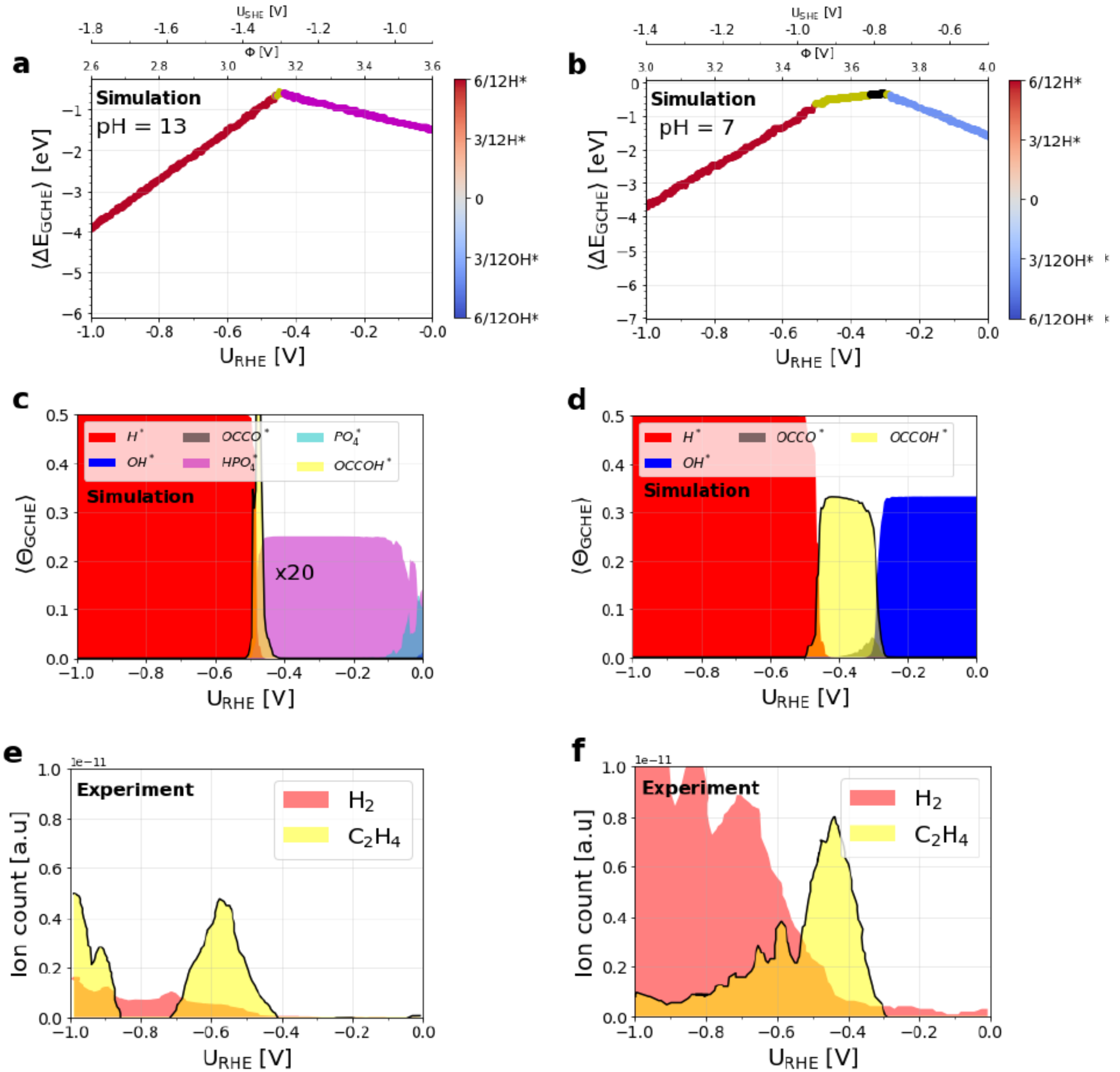
Water Electrolyte

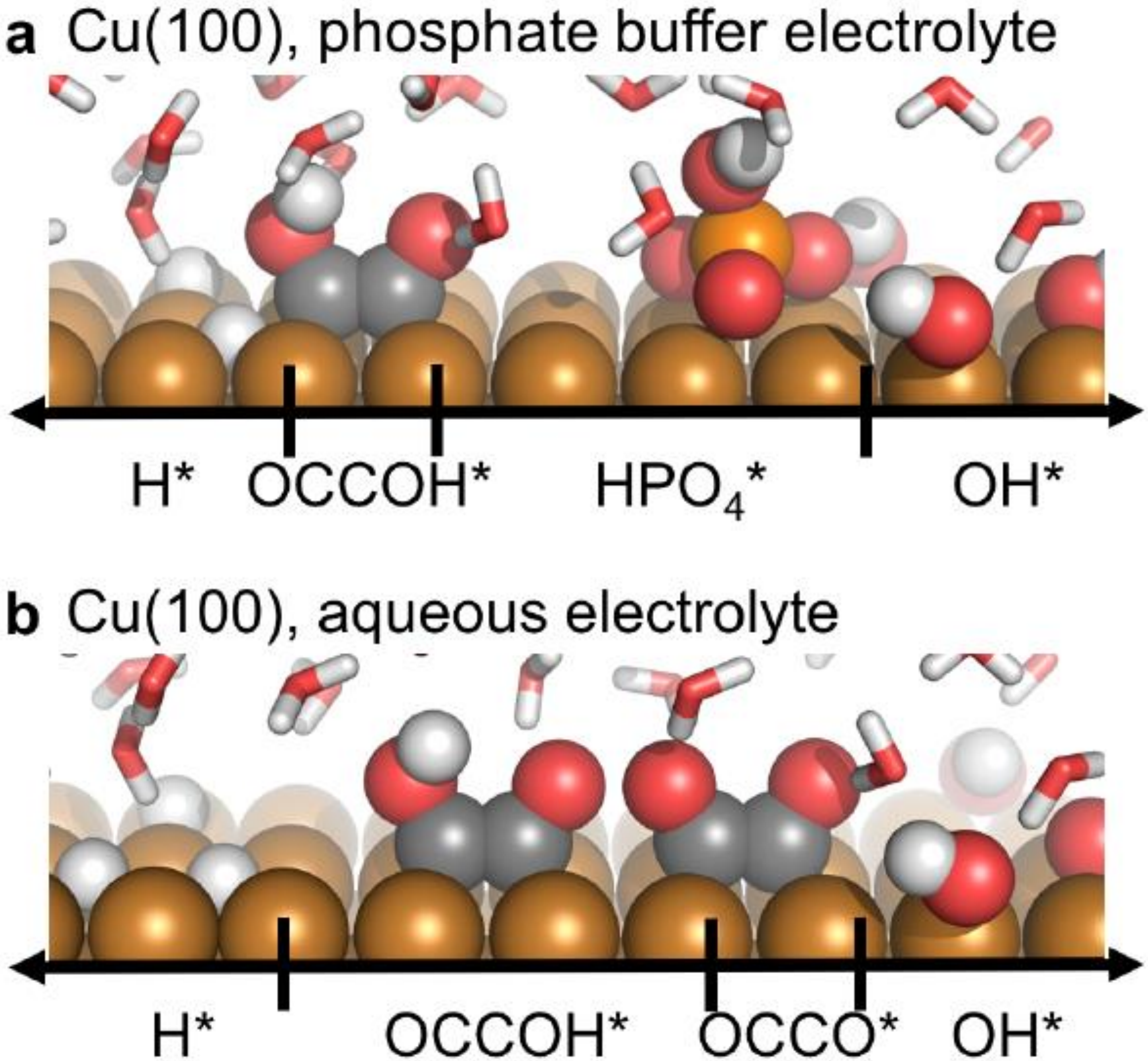






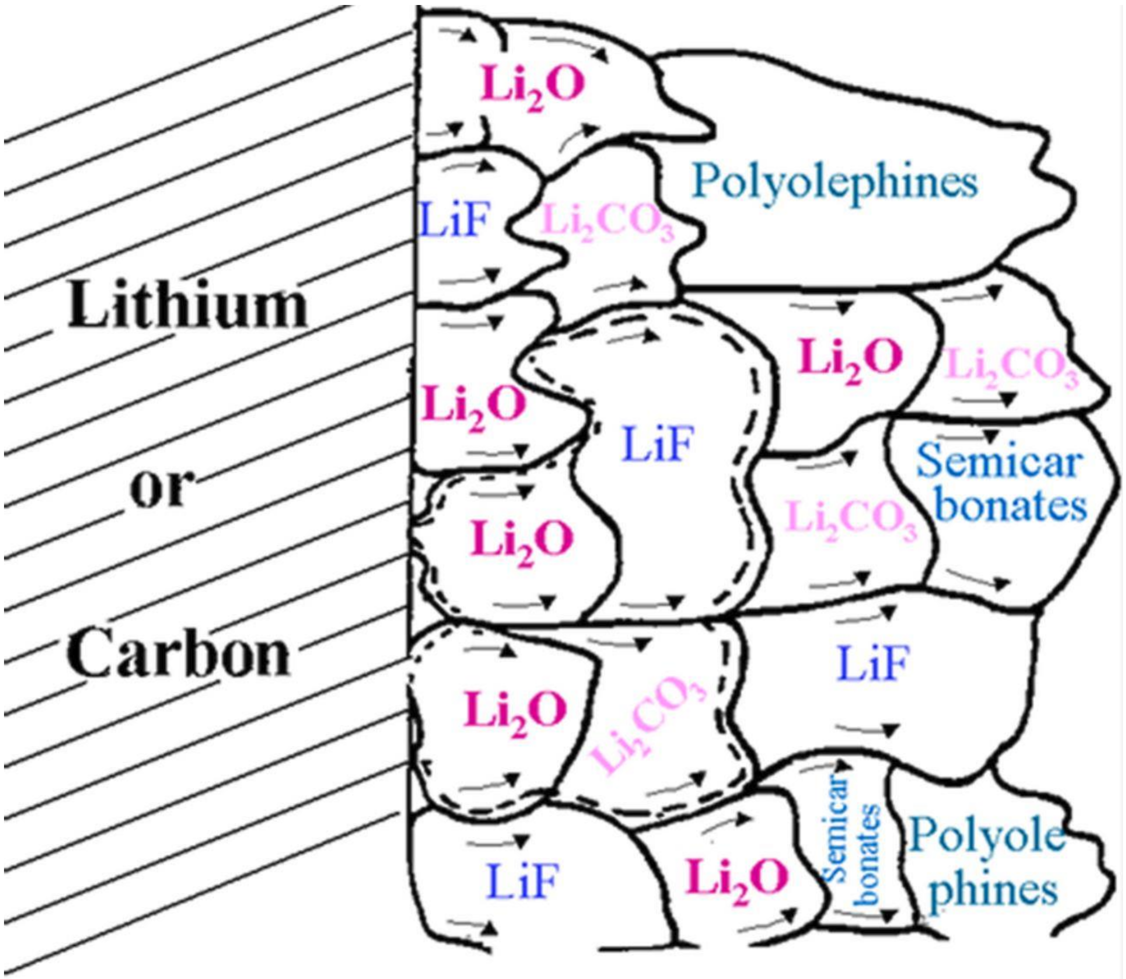
Klaas Jan P. Schouten, …., Marc M.T. Koper
J. Am. Chem. Soc. 2012, 134, 9864−9867


a
b
c
d
e
f
Simulation
pH = 13
pH = 7
U_{SHE} [V]
Φ [V]
⟨ΔE_GCHE⟩ [eV]
U_{RHE} [V]
6/12H*
3/12H*
0
3/12OH*
6/12OH*
⟨Θ_GCHE⟩
H*
OH*
OCCO*
HPO4*
PO4*
OCCOH*
x20
Experiment
Ion count [a.u]
1e−11
H_2
C_2H_4



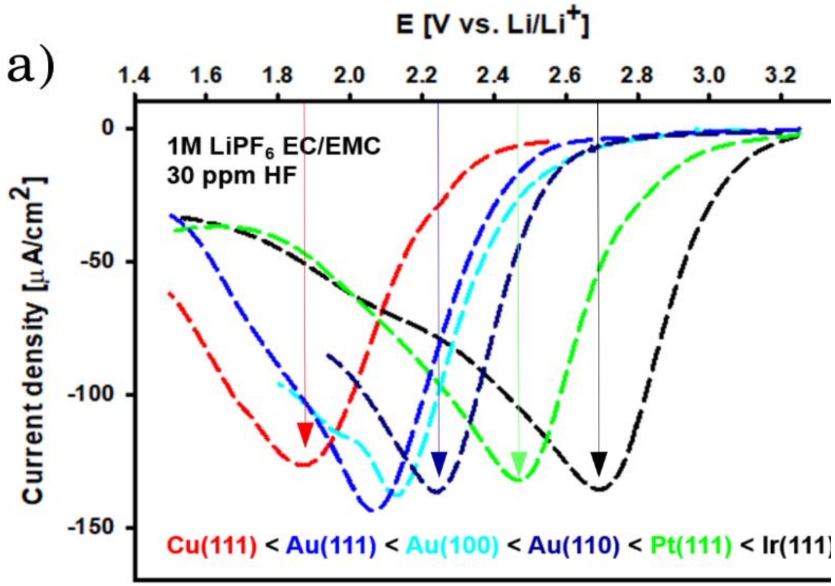
A. Bagger, L. Arnarson, MH. Hansen, E Spohr, J Rossmeisl. submitted

SEI-layer formation (LiF)



The Electrochemical Response of Electrodes in LP57

Voltammetry in LP57



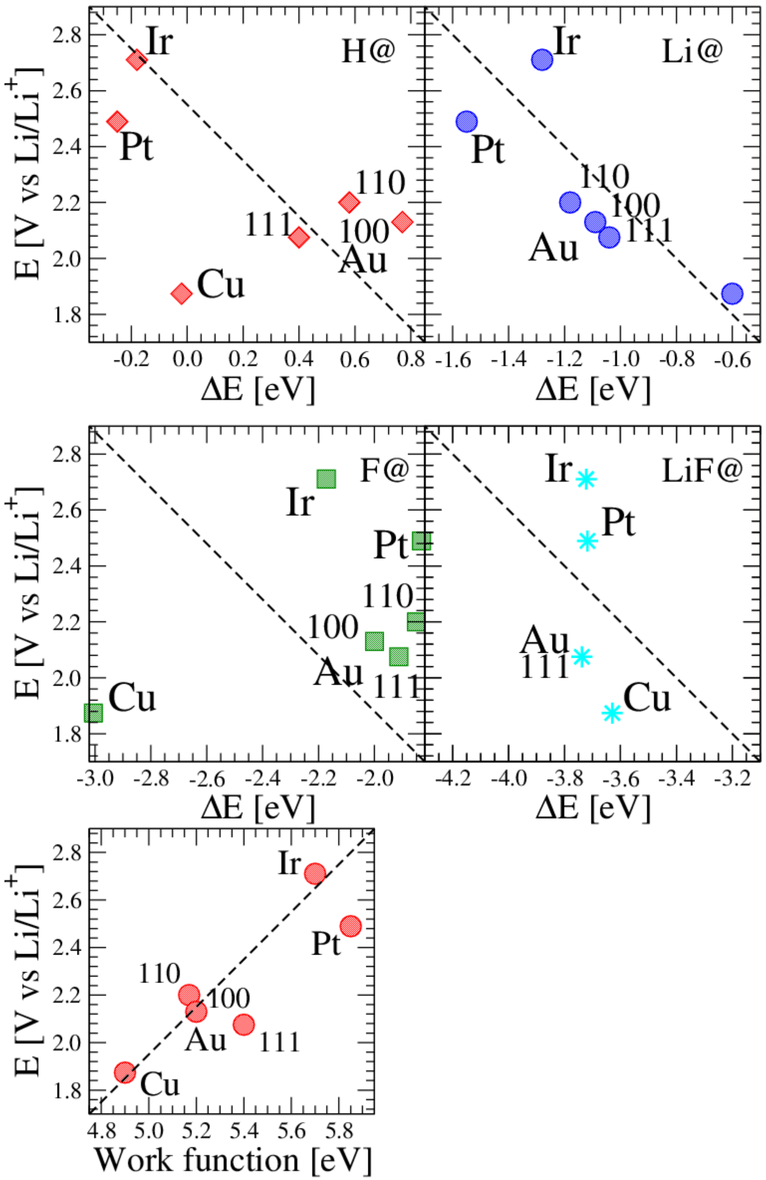
$2Li^+ + 2e^- + 2HF \rightarrow 2LiF + H_2$

$2(Li^+_{(aq)} + e^-) \rightarrow 2Li^*$

$2Li^* + 2HF^* \rightarrow 2H^* + 2\ LiF^* \rightarrow H_{2(g)} + 2LiF_{(s)}$

D. Strmcnik, I.E. Castelli, J.G. Connell, D. Haering, M. Zorko, P. Martins, P.P. Lopes, B. Genorio, T. Østergaard, H. Gasteiger, F. Maglia, B.K. Antonopoulos, V.R. Stamenkovic, J. Rossmeisl and N.M. Markovic. Nature Catalysis 2018

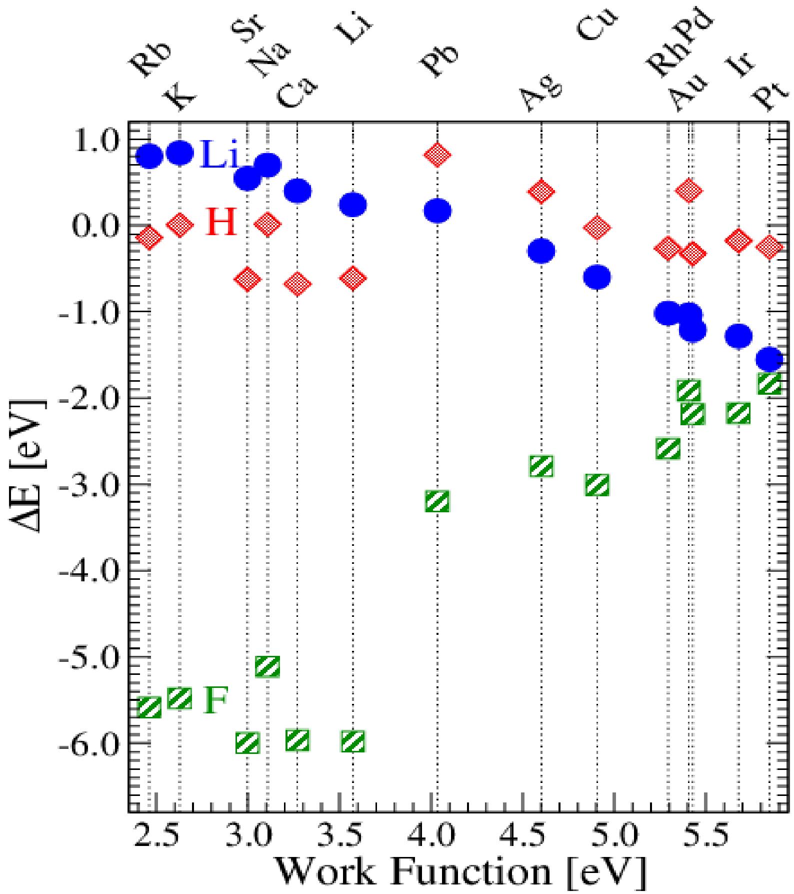
Possible Descriptors

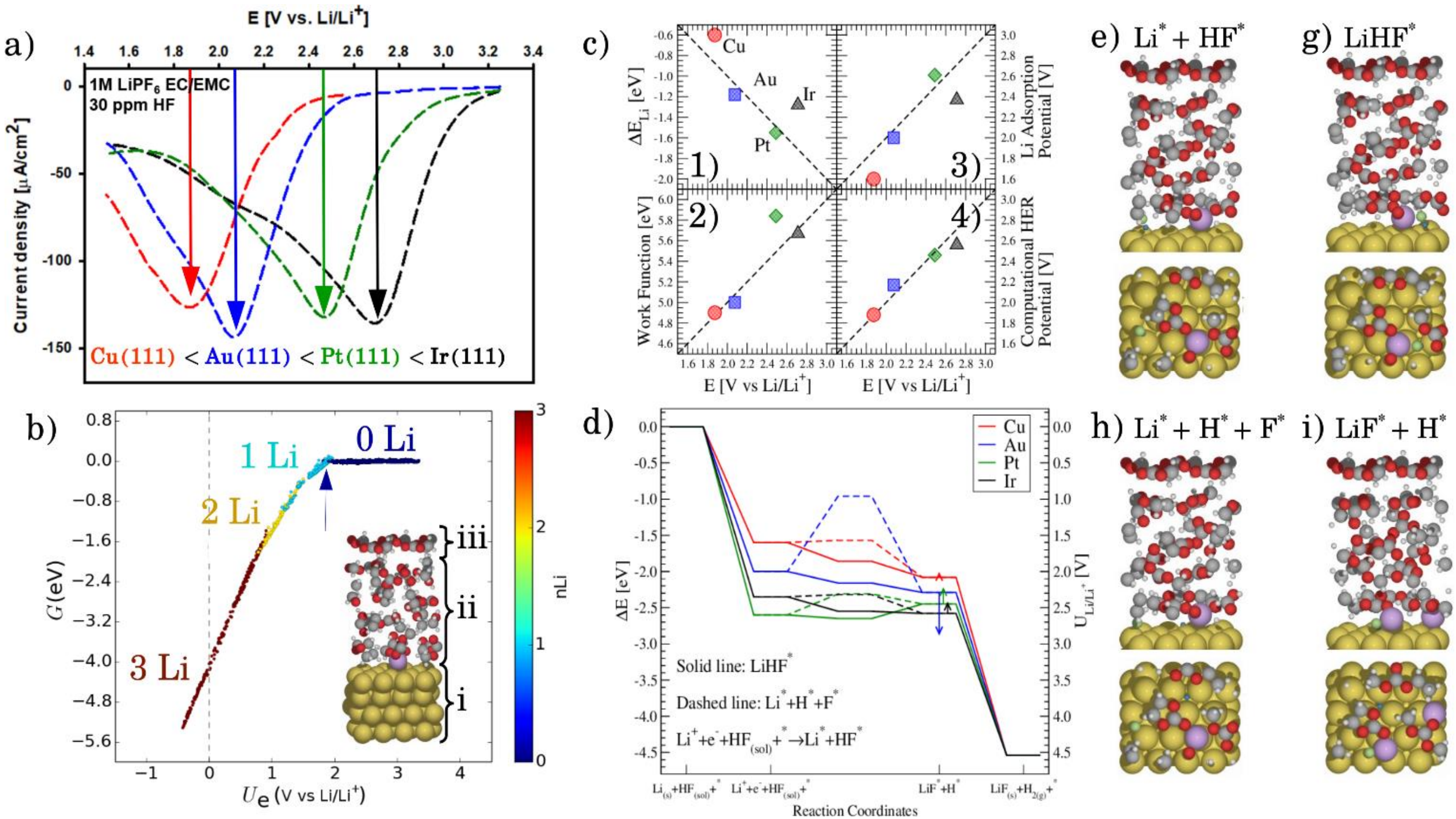


Adsorption energies and **work functions** can be *descriptors* for the **electrostatic response**.

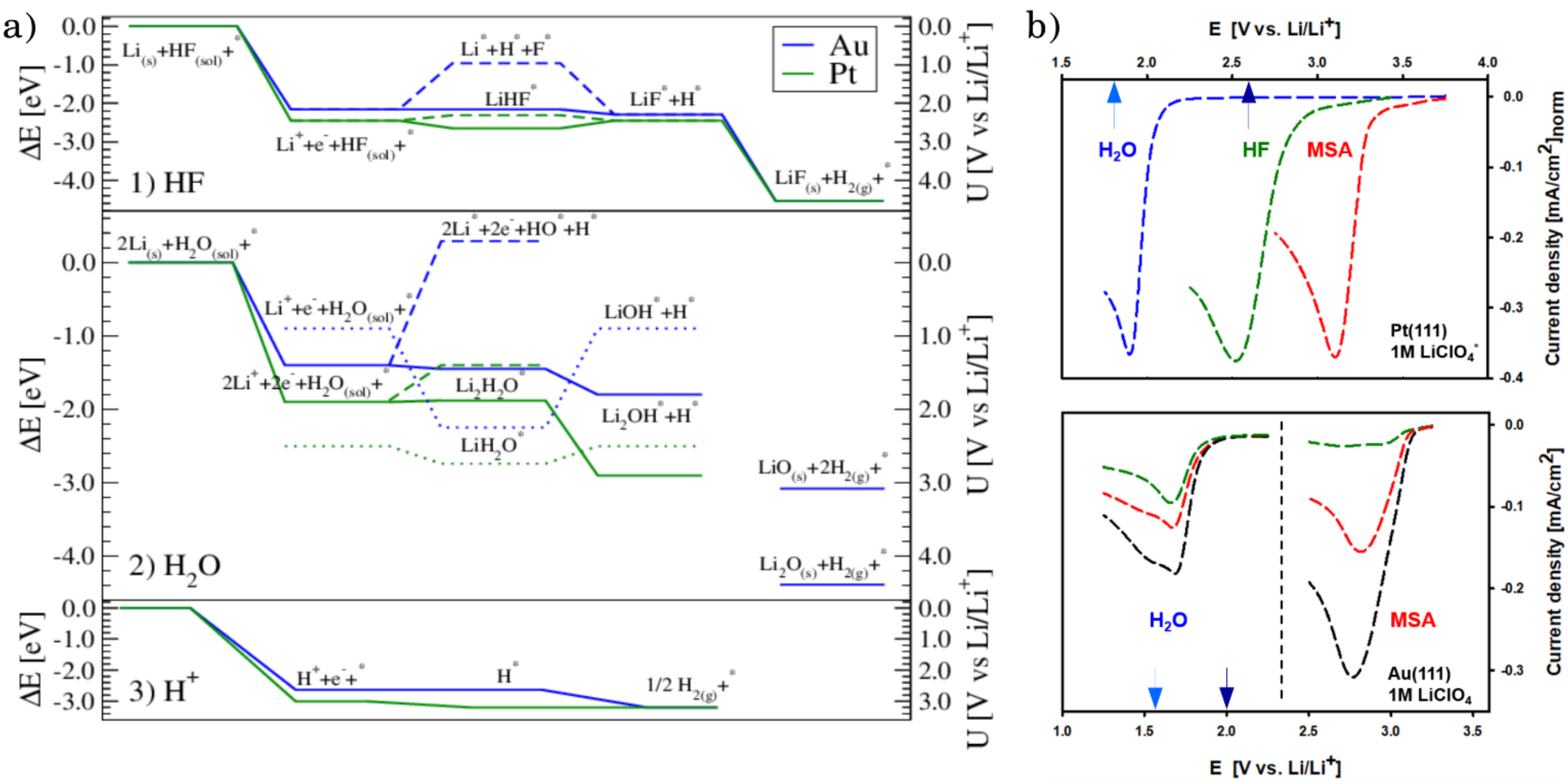
Adsorption of Li, F, and H on Various 111 Surfaces

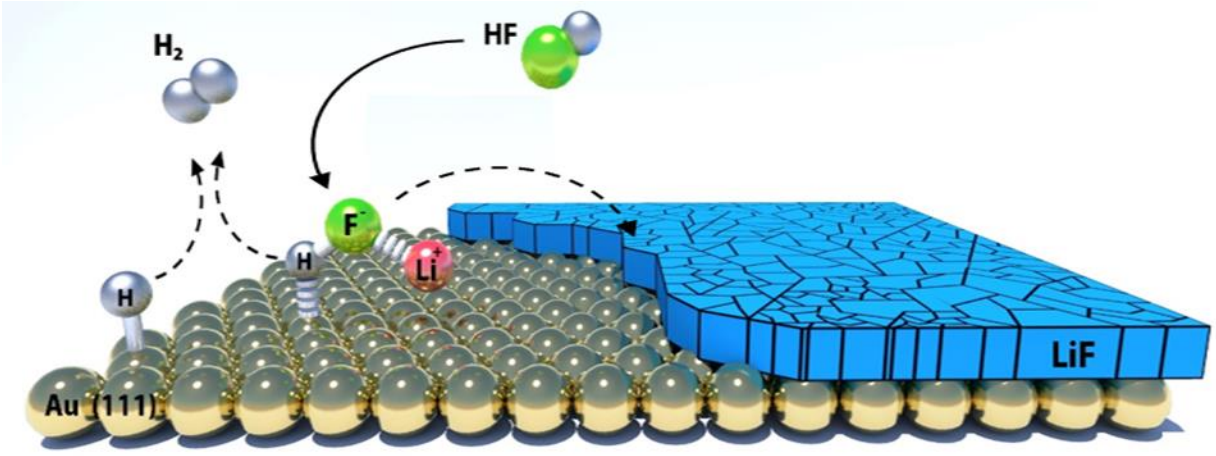
Trends in adsorption energies of **lithium** on various surfaces.
Comparison with other adsorbates, like **hydrogen** and **fluorine**.




a)
E [V vs. Li/Li+]
1M LiPF6 EC/EMC
30 ppm HF
Current density [μA/cm2]
Cu(111) < Au(111) < Pt(111) < Ir(111)
b)
0 Li
1 Li
2 Li
3 Li
iii
ii
i
G(eV)
Ue (V vs Li/Li+)
nLi
c)
Cu
Au
Ir
Pt
1)
2)
3)
4)
ΔELi [eV]
Work Function [eV]
Li Adsorption Potential [V]
Computational HER Potential [V]
E [V vs Li/Li+]
d)
Cu
Au
Pt
Ir
ΔE [eV]
ULi/Li+ [V]
Solid line: LiHF*
Dashed line: Li*+H*+F*
Li++e-+HF(sol)+* →Li*+HF*
Reaction Coordinates
e) Li* + HF*
g) LiHF*
h) Li* + H* + F*
i) LiF* + H*

Other sources of protons.





D. Strmcnik , I.E. Castelli, J.G. Connell, D. Haering, M. Zorko, P. Martins, P.P. Lopes, B. Genorio, T. Østergaard, H. Gasteiger, F. Maglia, B.K. Antonopoulos, V.R. Stamenkovic, J. Rossmeisl and N.M. Markovic. Nature Catalysis 2018

Summary

The Computational Hydrogen Electrode can be generalized to account for pH.

Only standard force/energy calculations.

A posteriori analysis ensures constant chemical potential of protons and electrons.

We obtain the structure of the interface as function of pH and potential.

Which in some cases determine the electrocatalytic properties.

Questions?

There is only a few protons in the electrolyte don’t you have too many protons in the simulations?

Decoupled electron-proton transfer?

Have you included the entropy in the simulations?

Why do you use explicit solvent?