Modeling Electrochemical Systems

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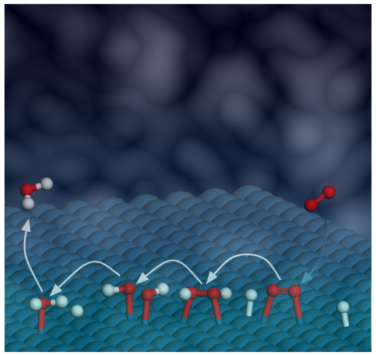
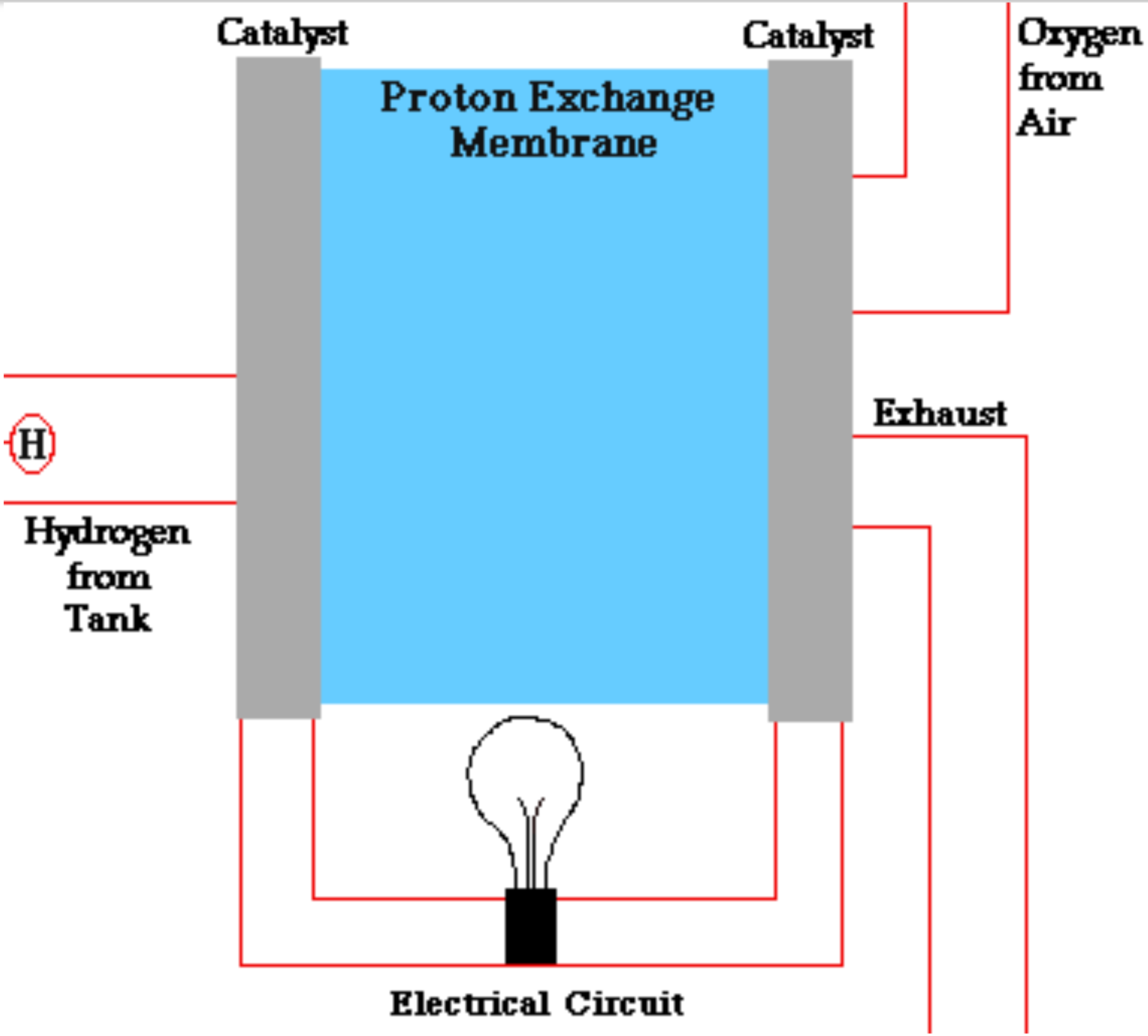


Max-Born-Symposium, Wrocław

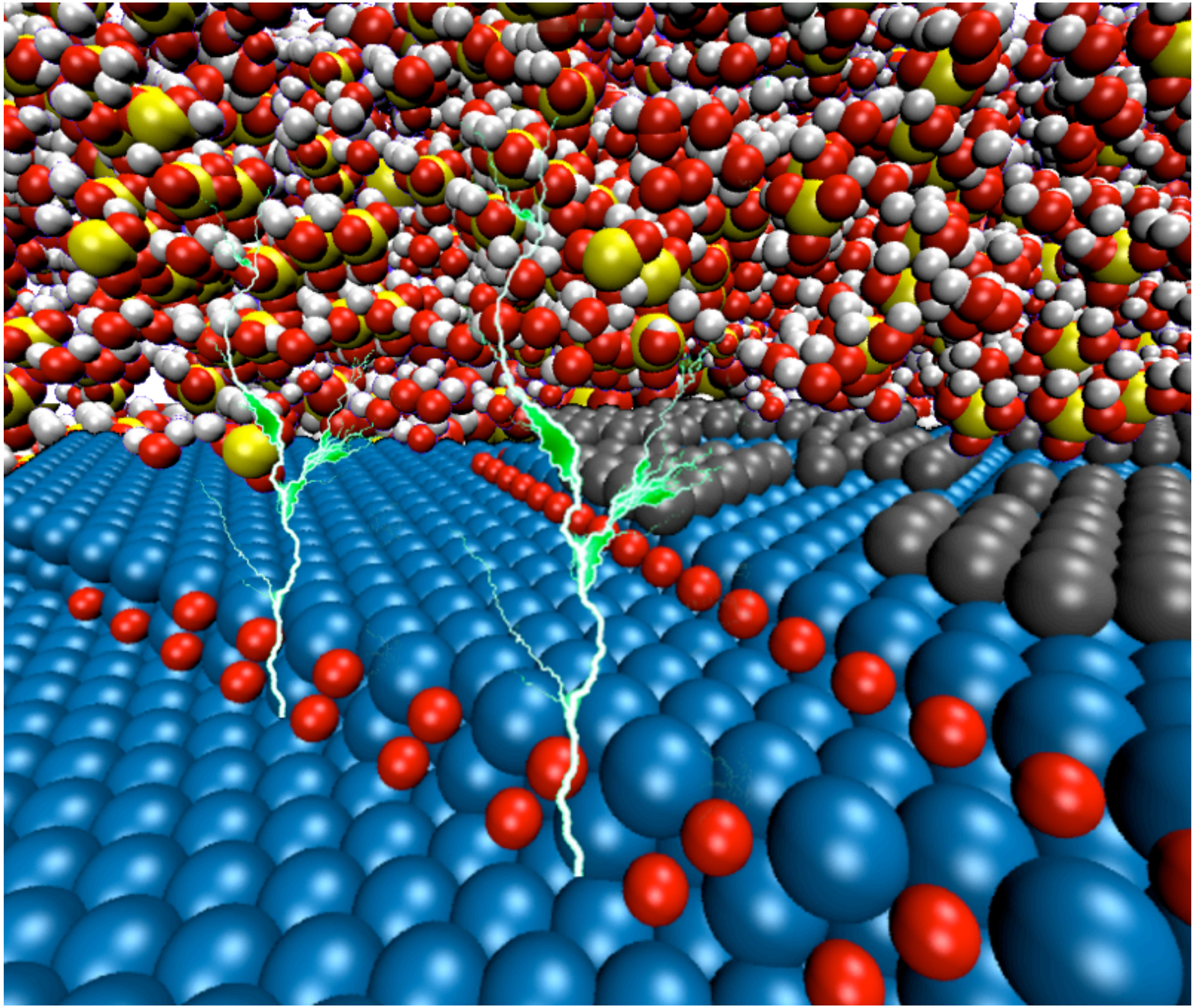
Sept. 20, 2010

Motivation

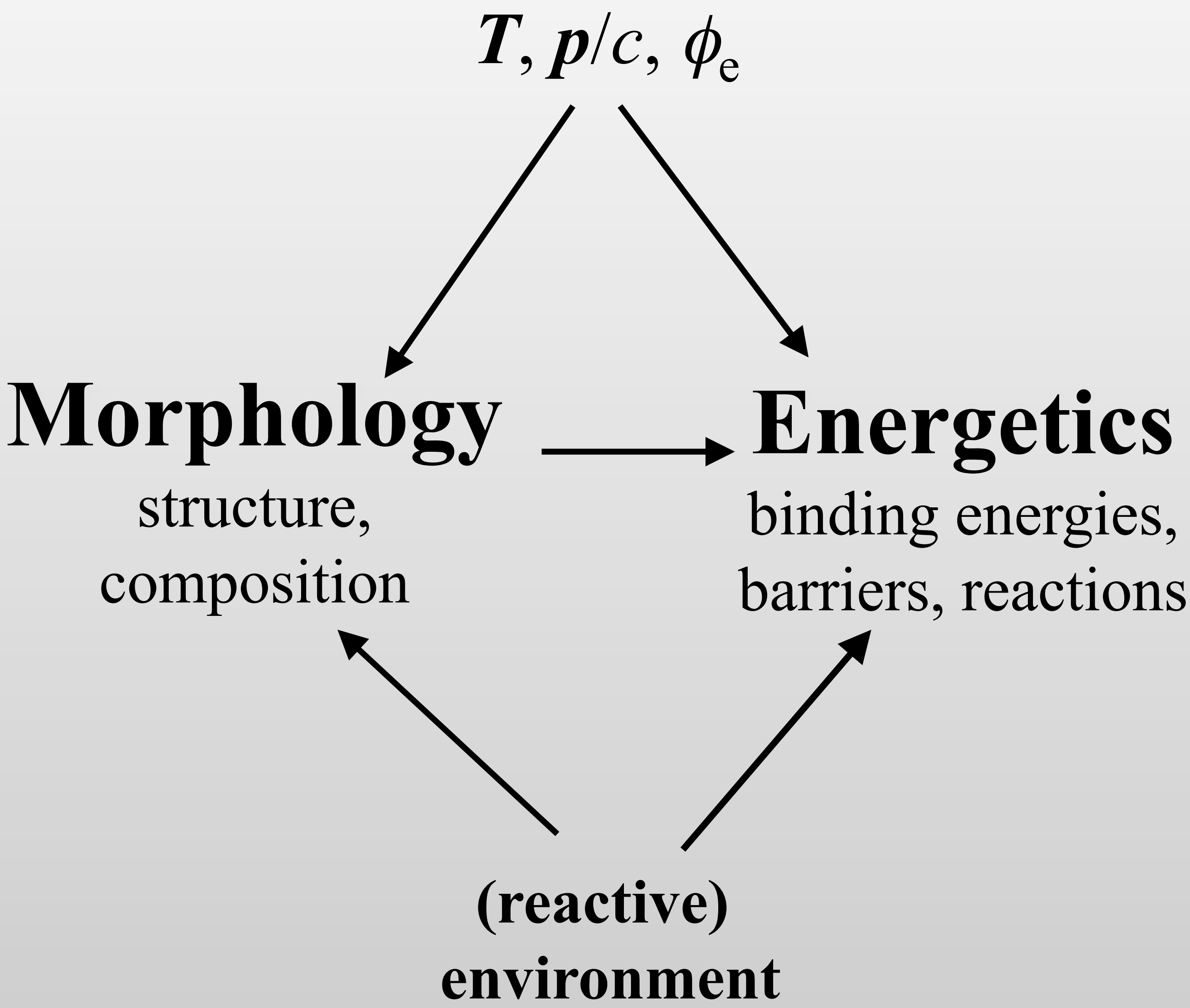


Catalyst
Catalyst
Oxygen from Air
Proton Exchange Membrane
Exhaust
H
Hydrogen from Tank
Electrical Circuit

Electrochemistry

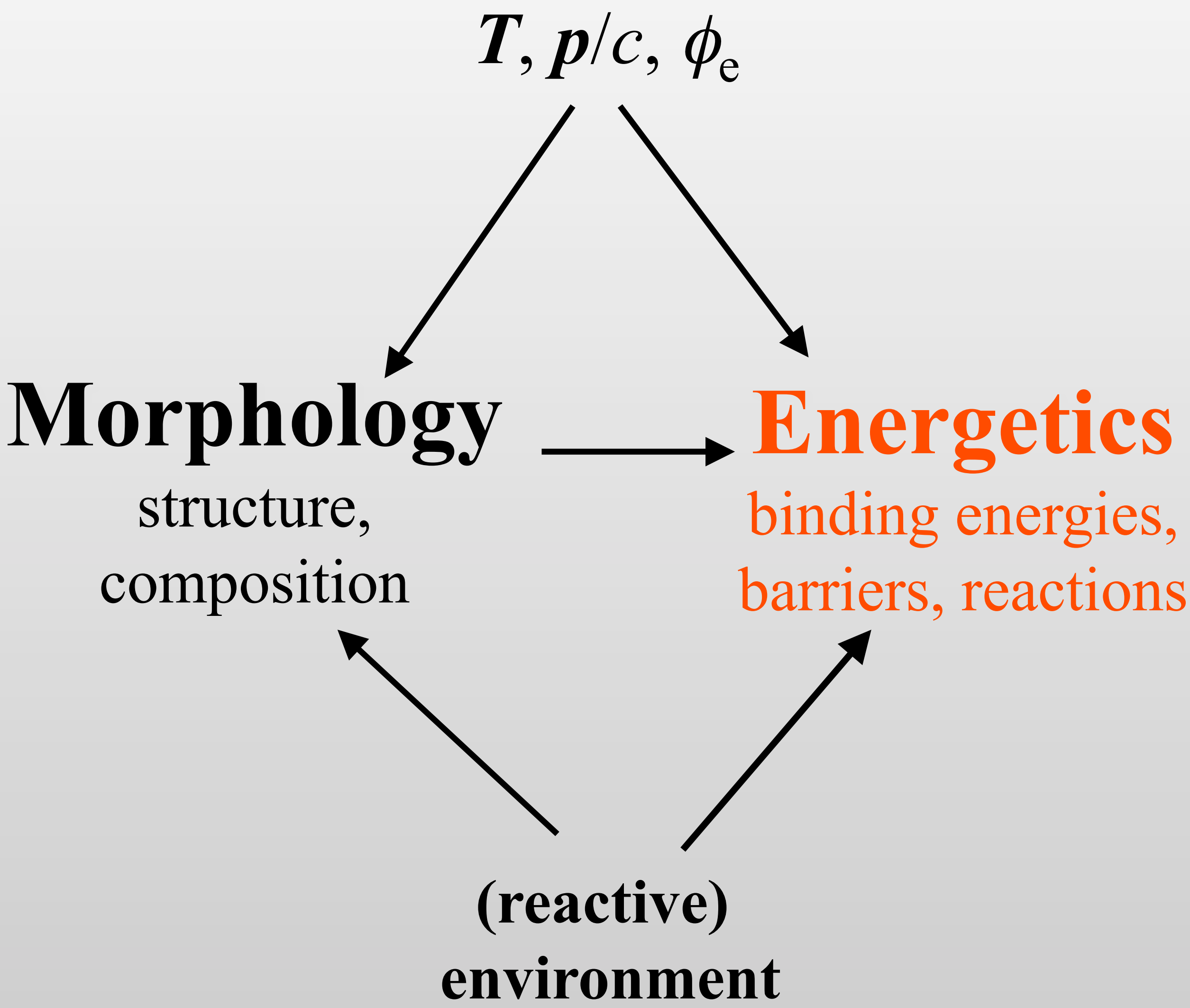


Multiphysics in Electrochemistry



Cathode Reaction on pure Pt(111)

$$H_2 + \frac{1}{2} O_2 \longrightarrow H_2O$$



ORR on Pt

What is known about the ORR:
the first electron transfer is rate determining

$$O_2^* + e^- \rightarrow O_2^{*-}$$

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

Damjanovic, A.; Genshaw, M. A.; Bockris, J. O. M.
J. Phys. Chem. 1964, 45, 4057

ORR on Pt

Google search:
"Damjanovic Genshaw Bockris 4057"

~~Damjanovic, A.; Genshaw, M. A.; Bockris, J. O. M. *J. Phys. Chem.* 1964, 45, 4057~~

~~A. Damjanovic, M. A. Genshaw and J. O'M. Bockris, *J. Chem. Phys.* 45 (1964) 4057~~

A. Damjanovic, M. A. Genshaw, and J. O'M. Bockris, *J. Chem. Phys.*, 45, 4057 (1966)

~~Damjanovic A., Genshaw M.A., Bockris J.O'M., *J. Phys. Chem.* 1996. V. 45. P. 4057~~

~~Damjanovic, A.; Genshaw, M. A.; Bockris, J. O. M. *J. Phys. Chem.* 2001, 45, 4057~~

ORR on Pt

A. Damjanovic, M. A. Genshaw, and J. O'M. Bockris,
J. Chem. Phys., 45, 4057 (1966)

→ doesn't discuss the ORR explicitly

→ describes how to interpret electrochemical kinetic experiments with different reaction pathways

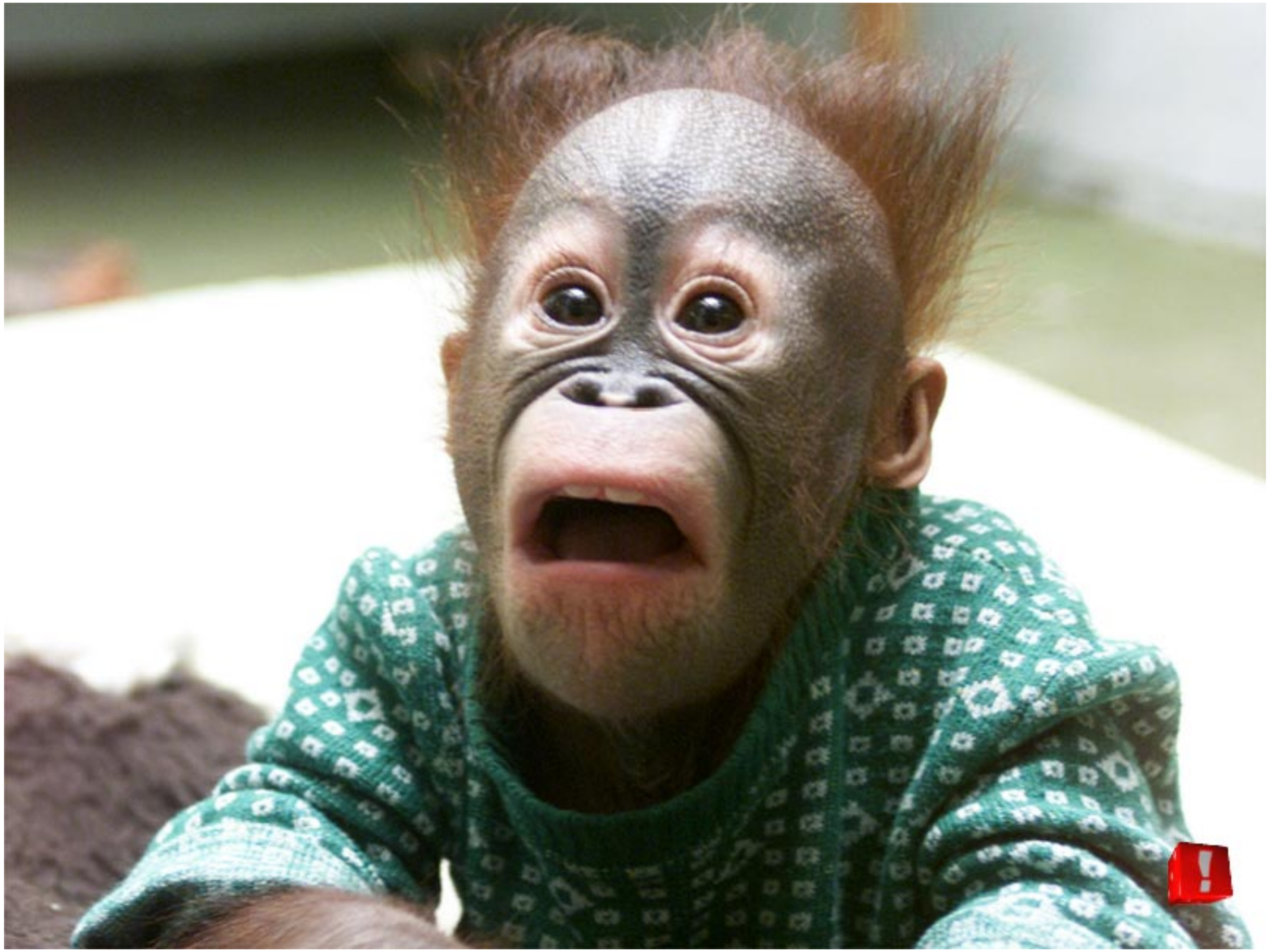
A. Damjanovic and V. Brusic,
***Electrochim. Acta* 1967, 12, 615**

explicitly argues for: $O_2^* + H^+ + e^- \rightarrow OOH^*$

and against: $O_2^* + e^- \rightarrow O_2^{*-}$

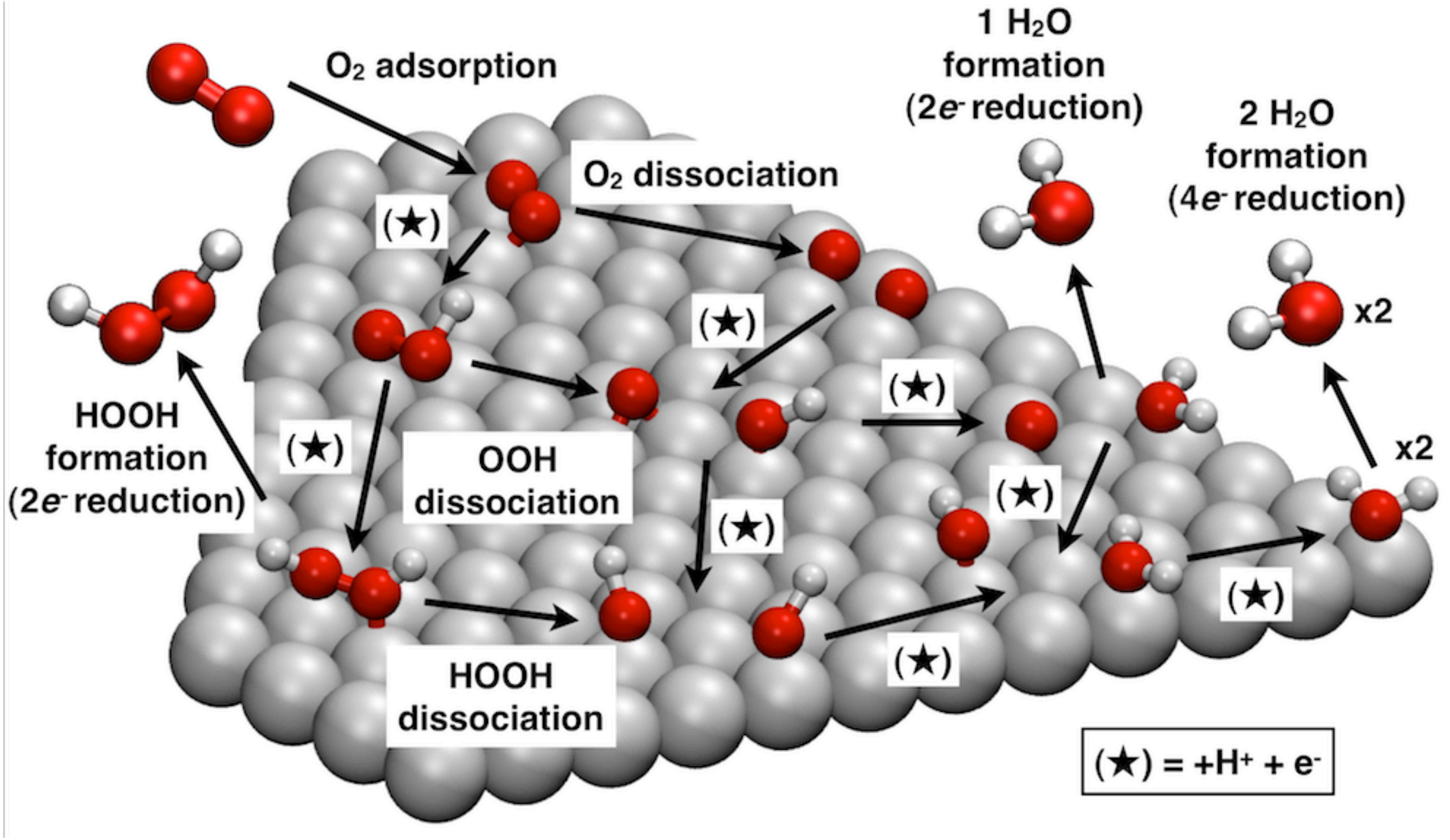
How does the ORR work?

$$H_2 + \frac{1}{2} O_2 \longrightarrow H_2O$$

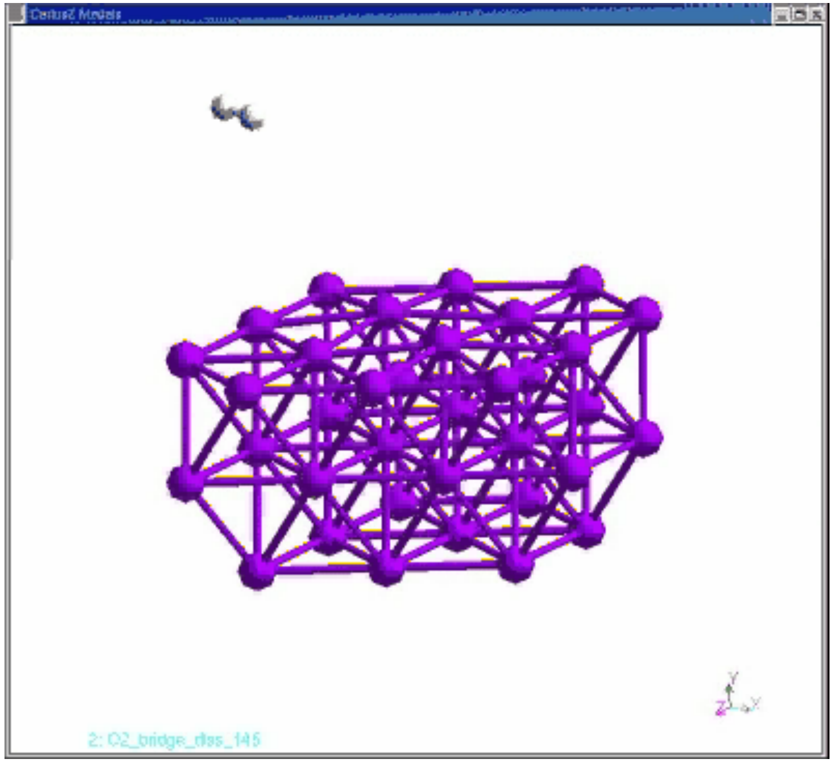


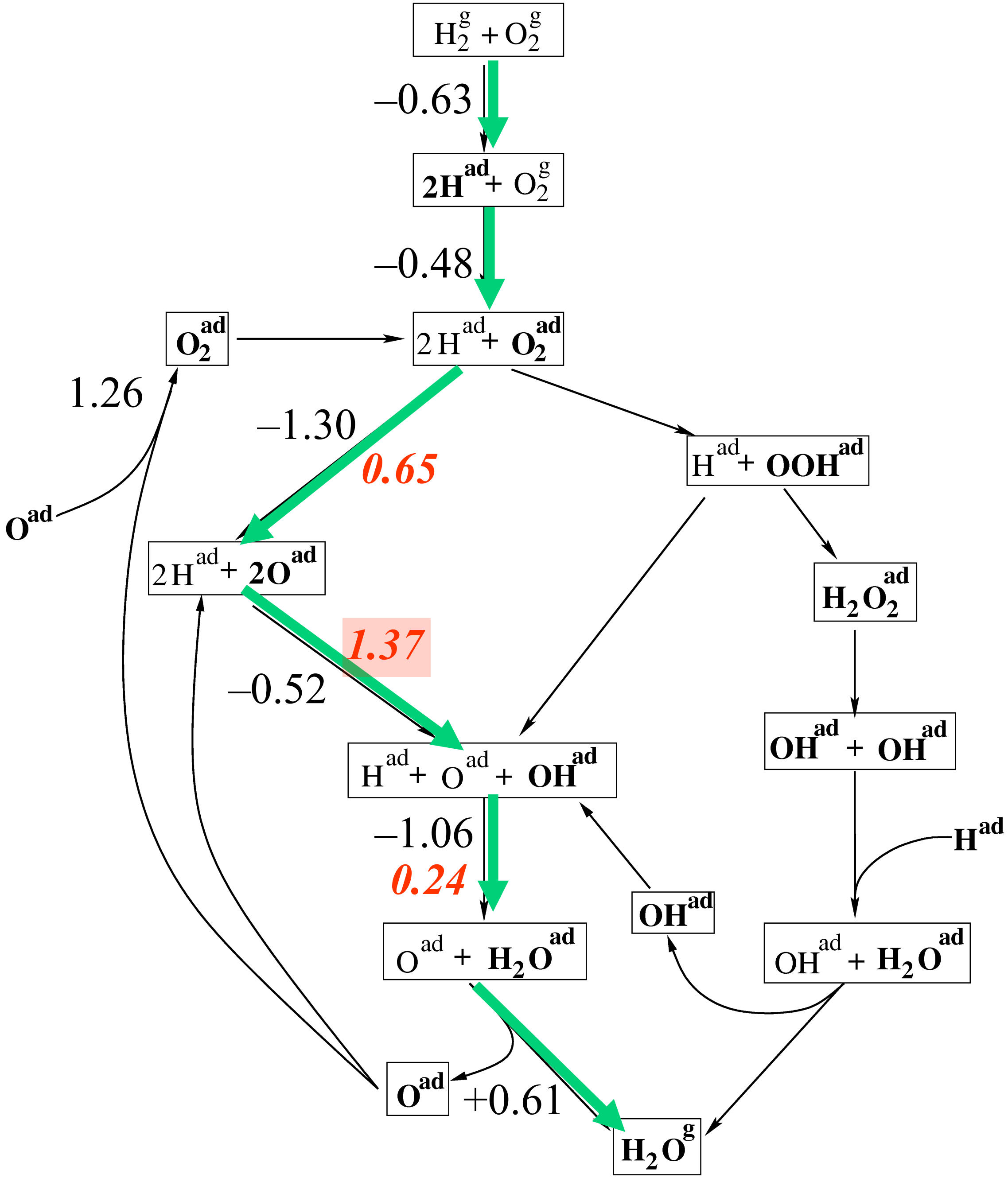
Considered pathways

Determine the actual ORR mechanism dependent on *T, p, U*, and *pH*

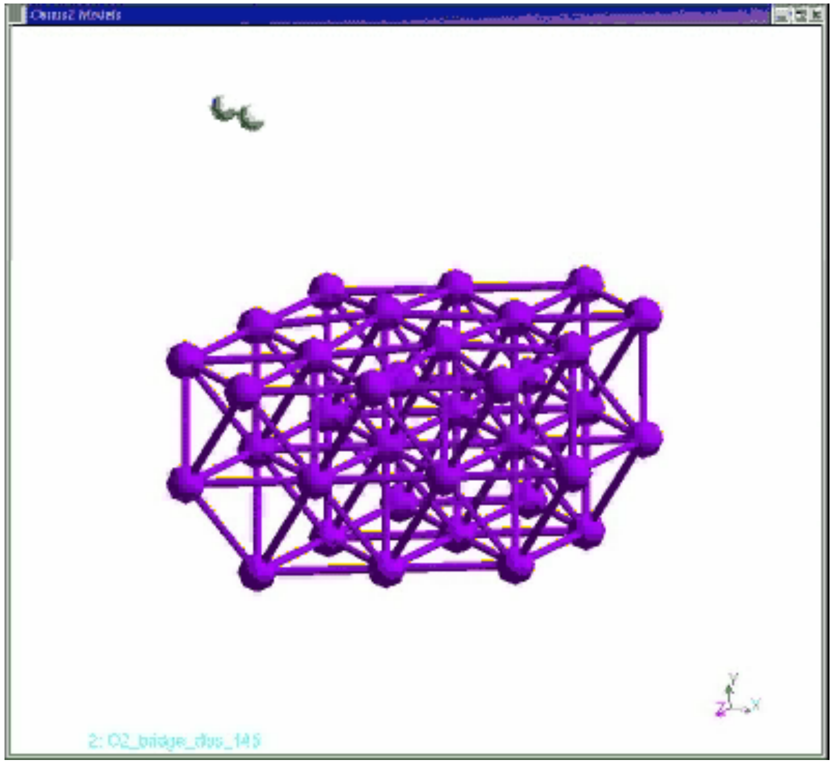


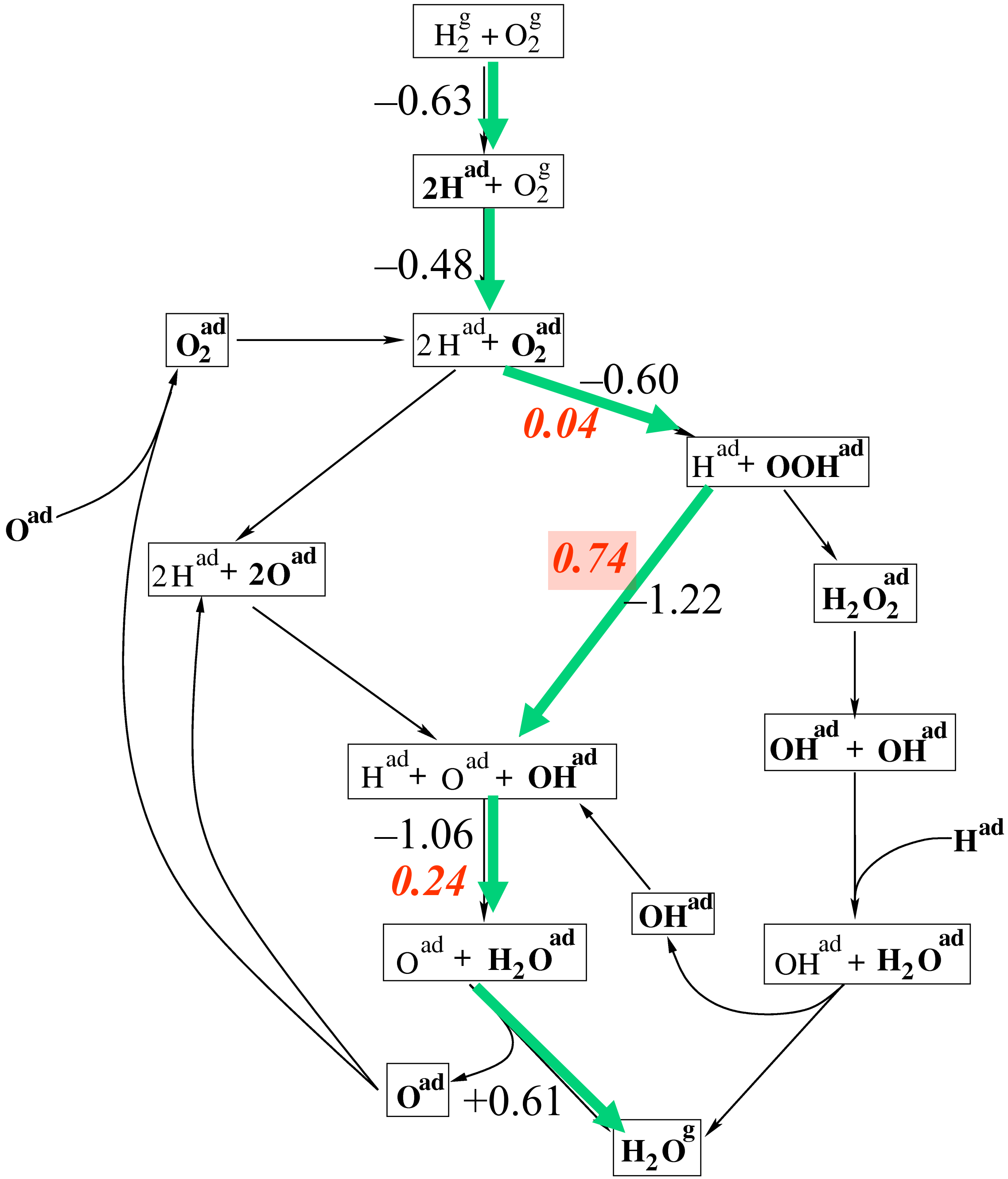
O_2-Dissociation



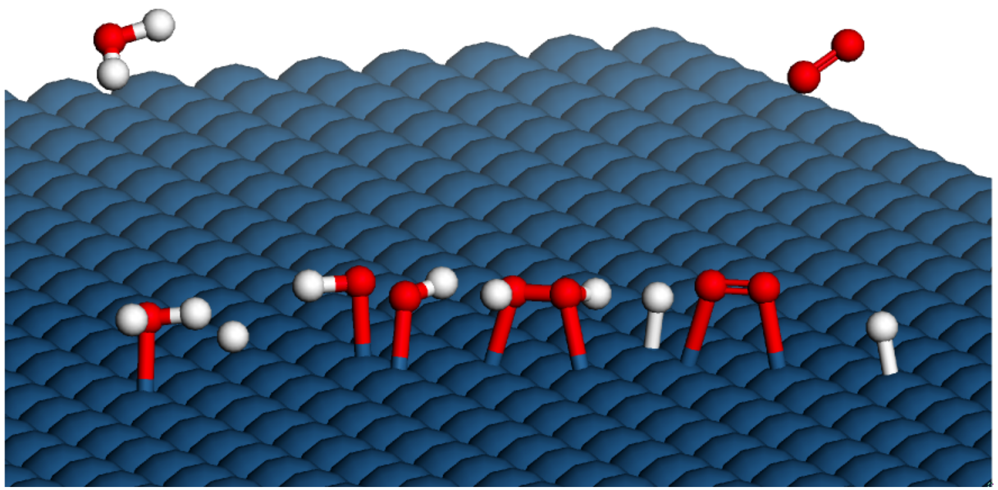


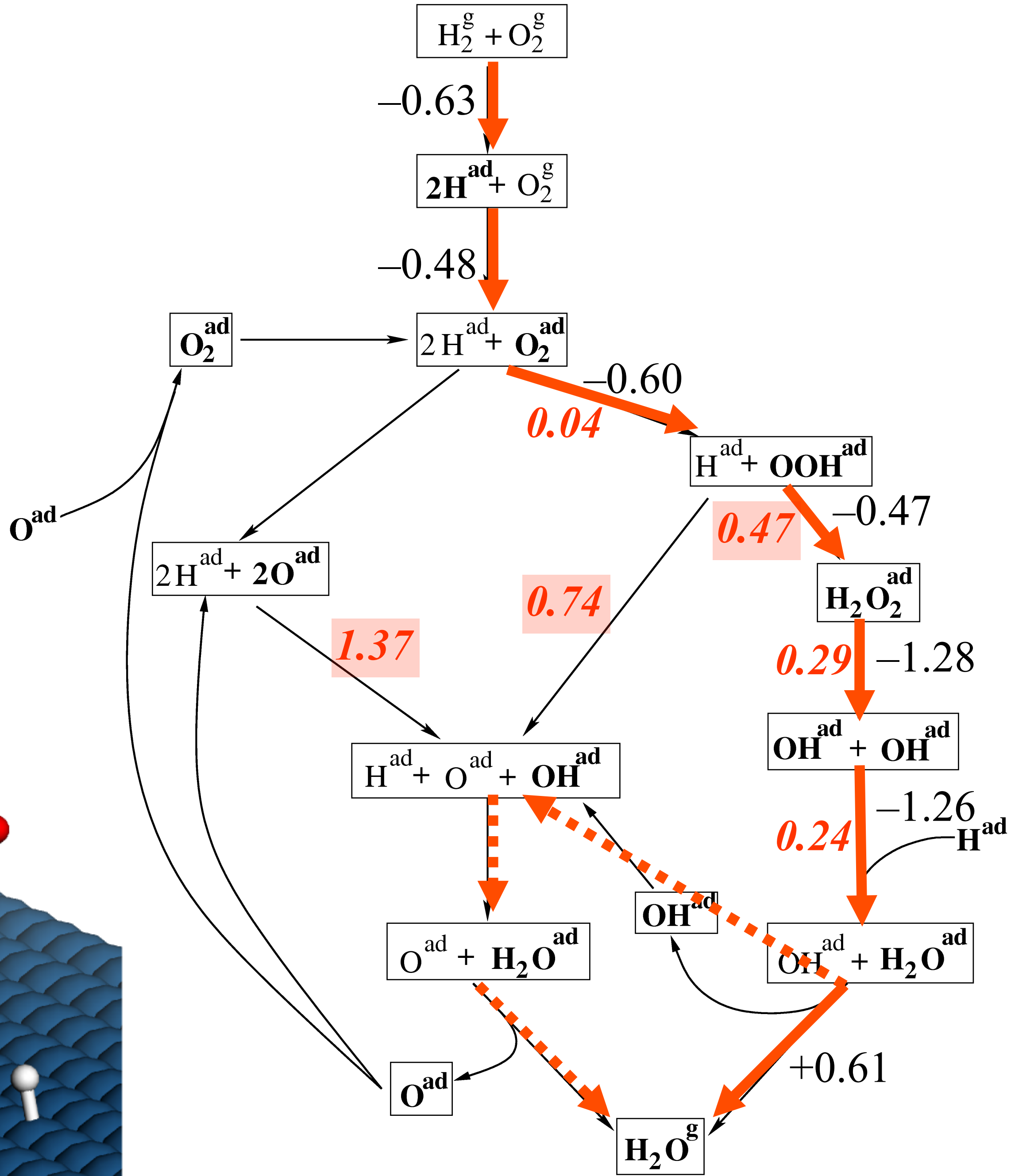
OOH-Formation



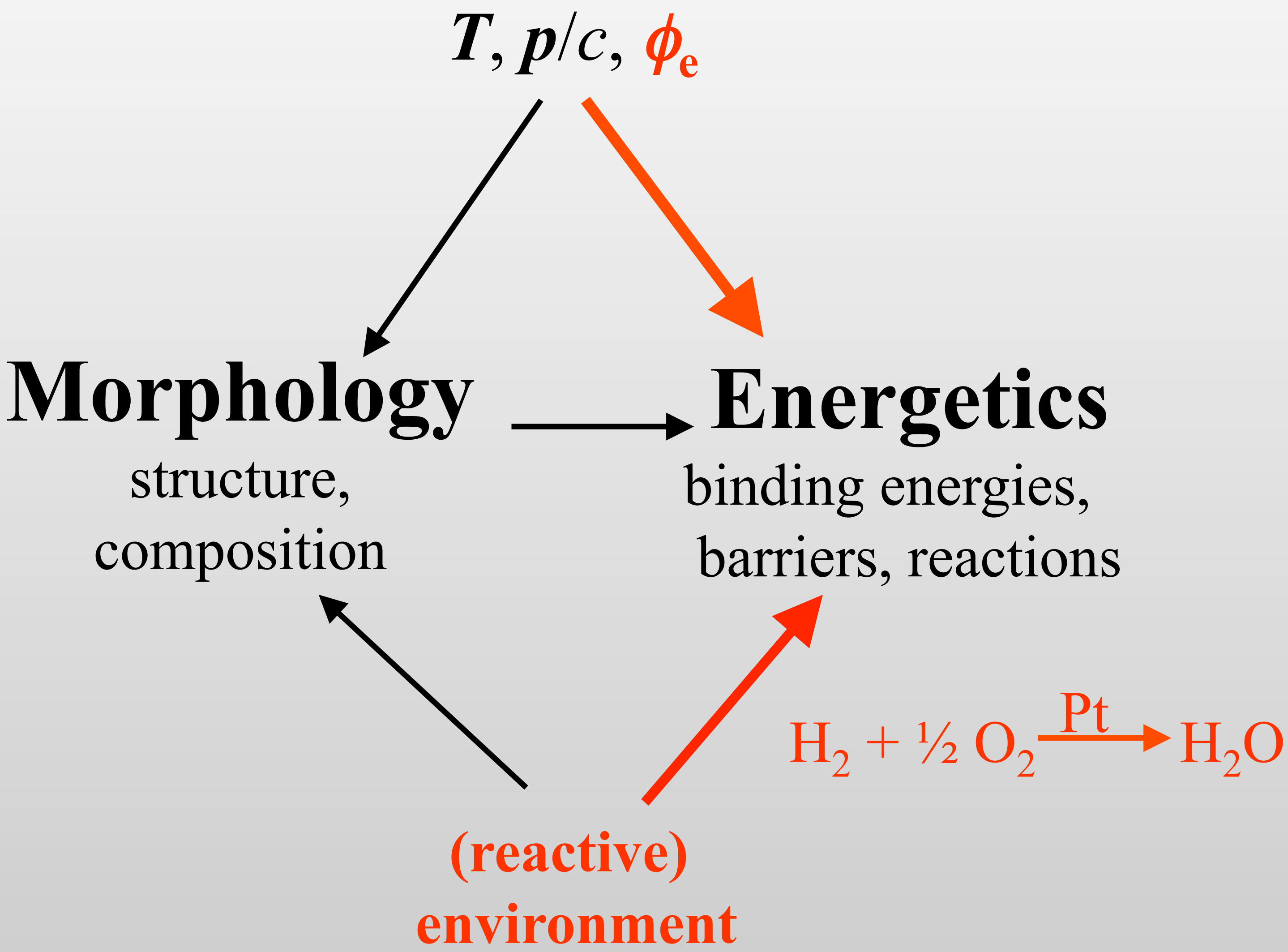


H_2O_2-Formation



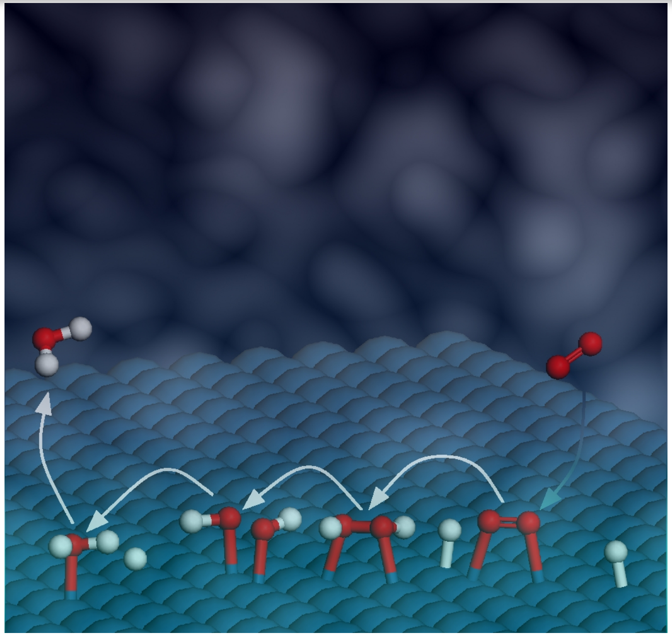


Influence of Environment on the ORR



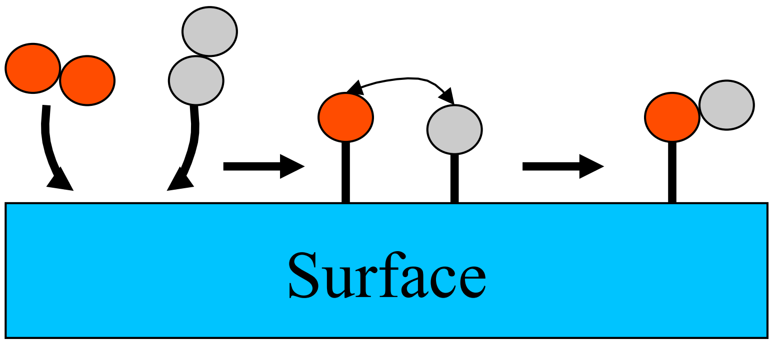
Influence of Environment

Water-Solvent:

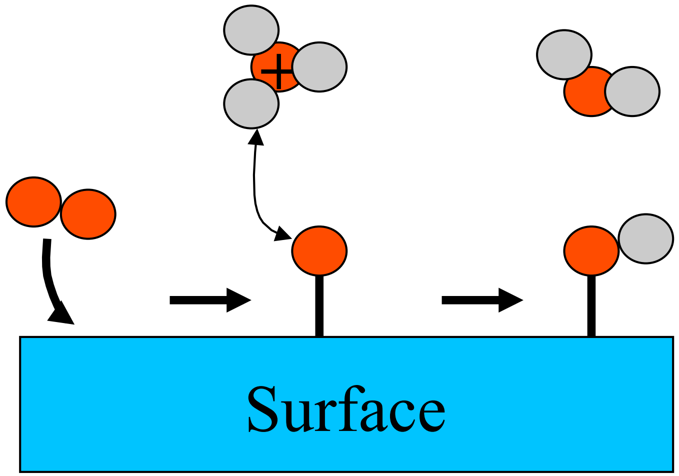


Reaction Mechanism:

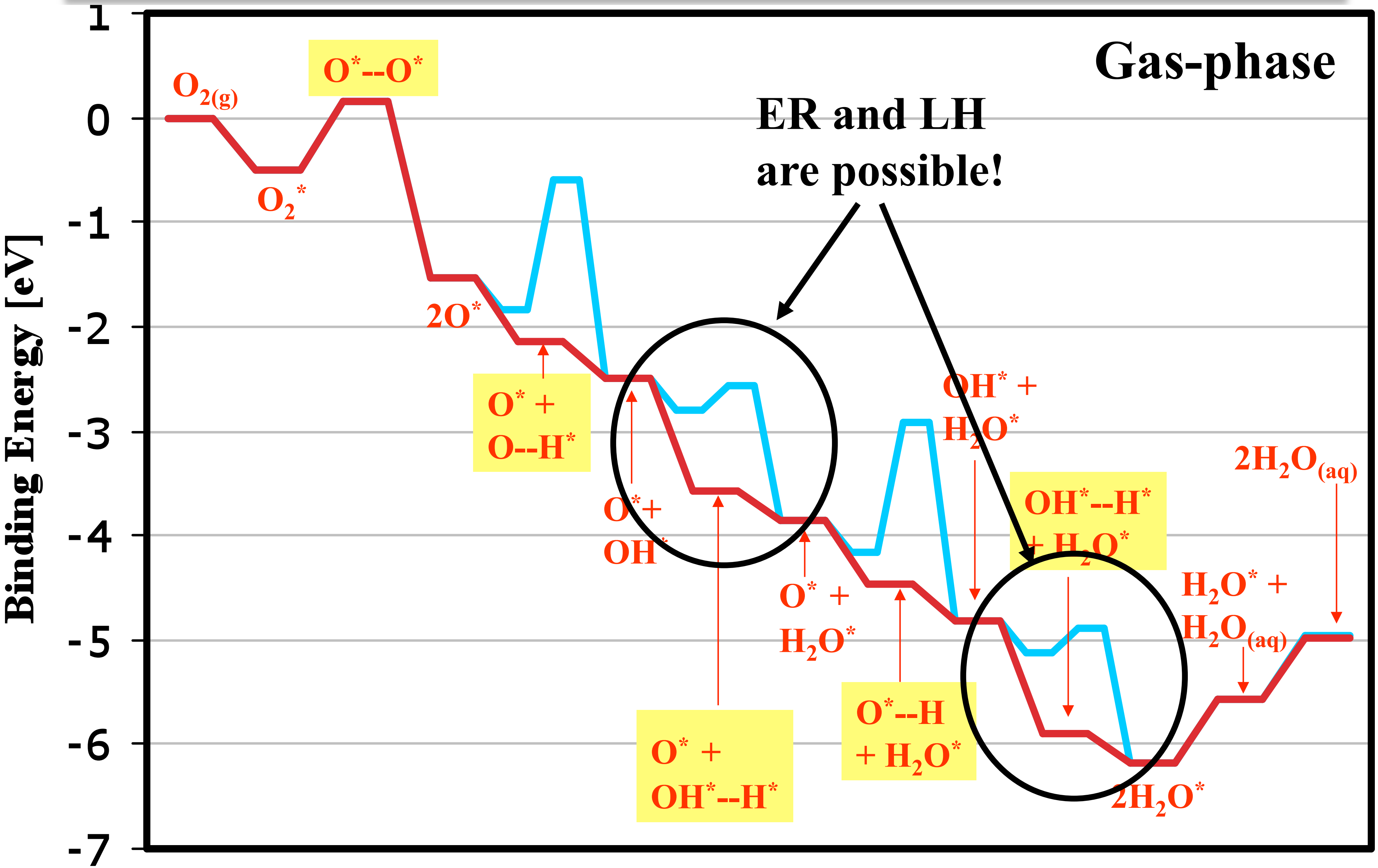
Langmuir–Hinshelwood-type



Eley–Rideal-type



O_2-Dissociation Mechanism (Eley-Rideal + Langmuir Hinshelwood)



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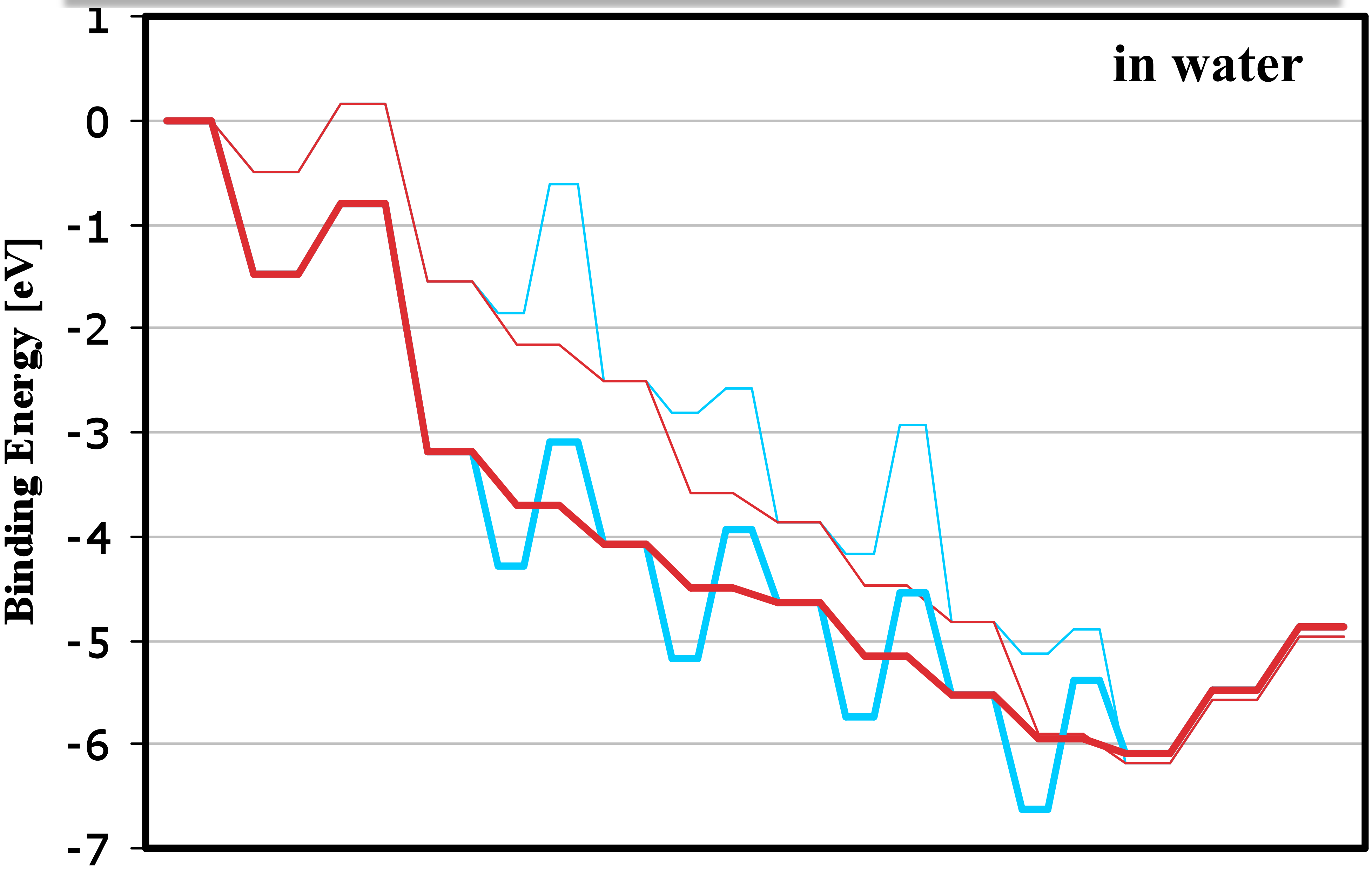
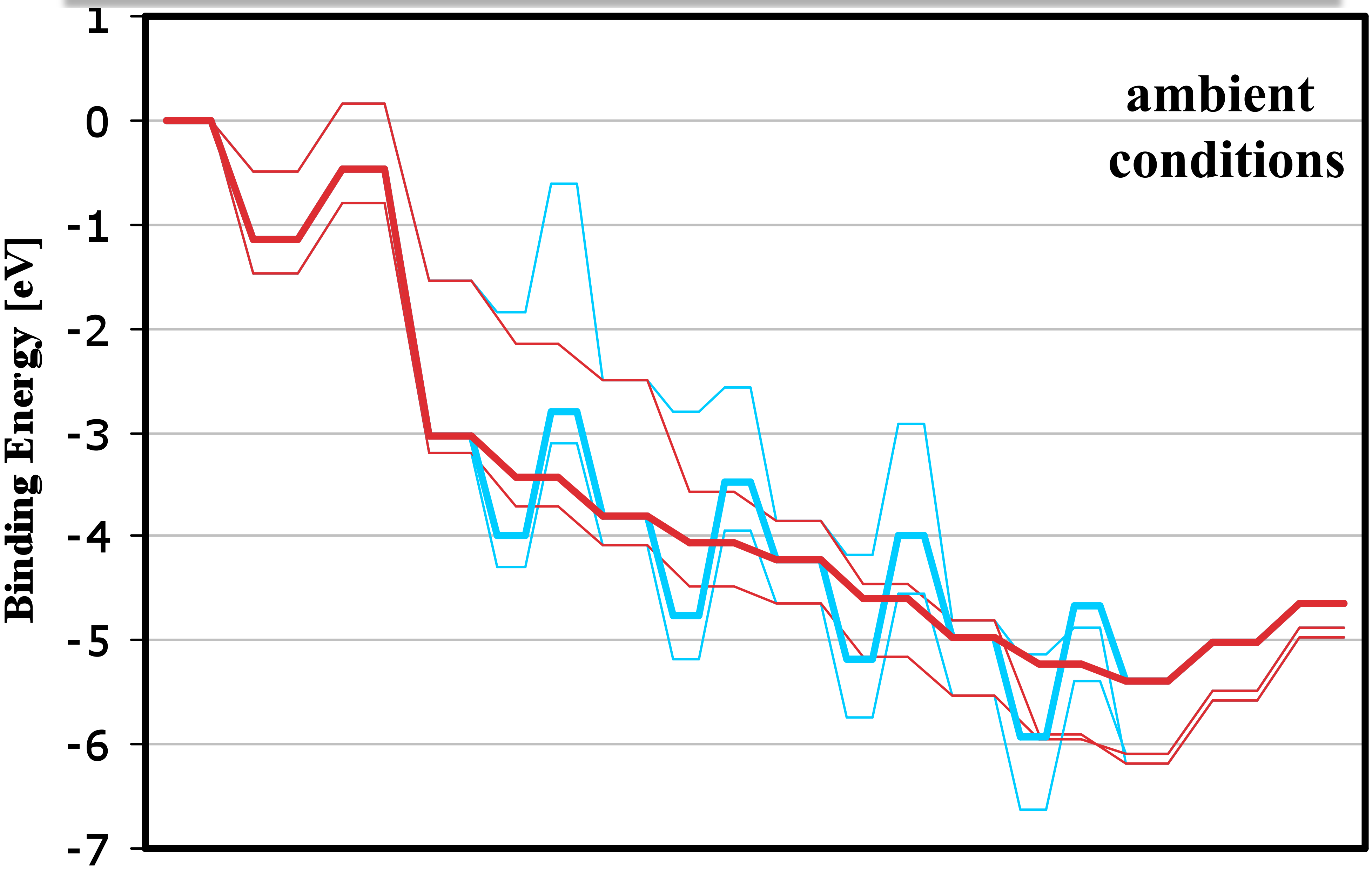


O_2-Dissociation Mechanism
(Eley-Rideal + Langmuir Hinshelwood)



O_2-Dissociation Mechanism
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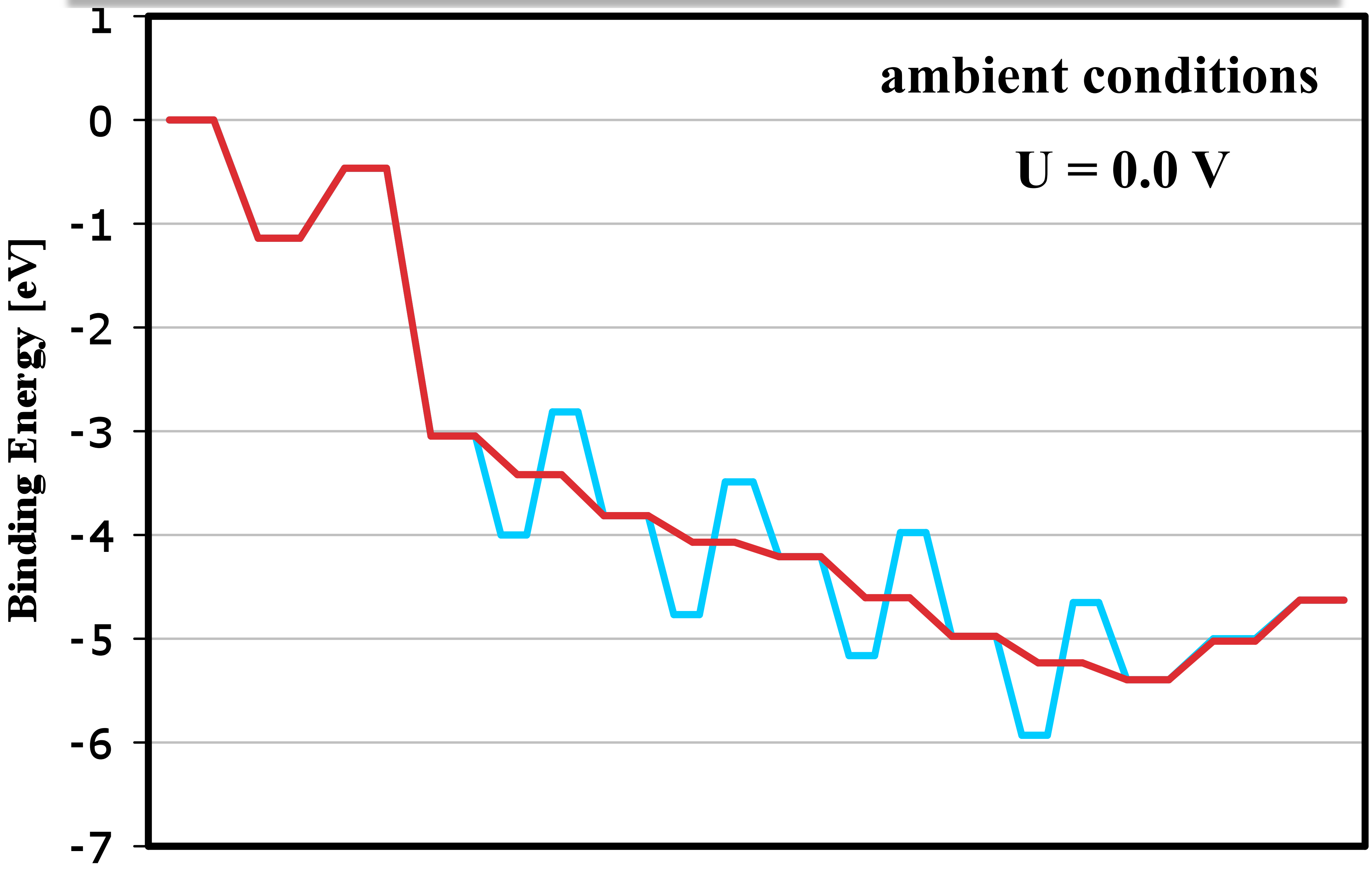
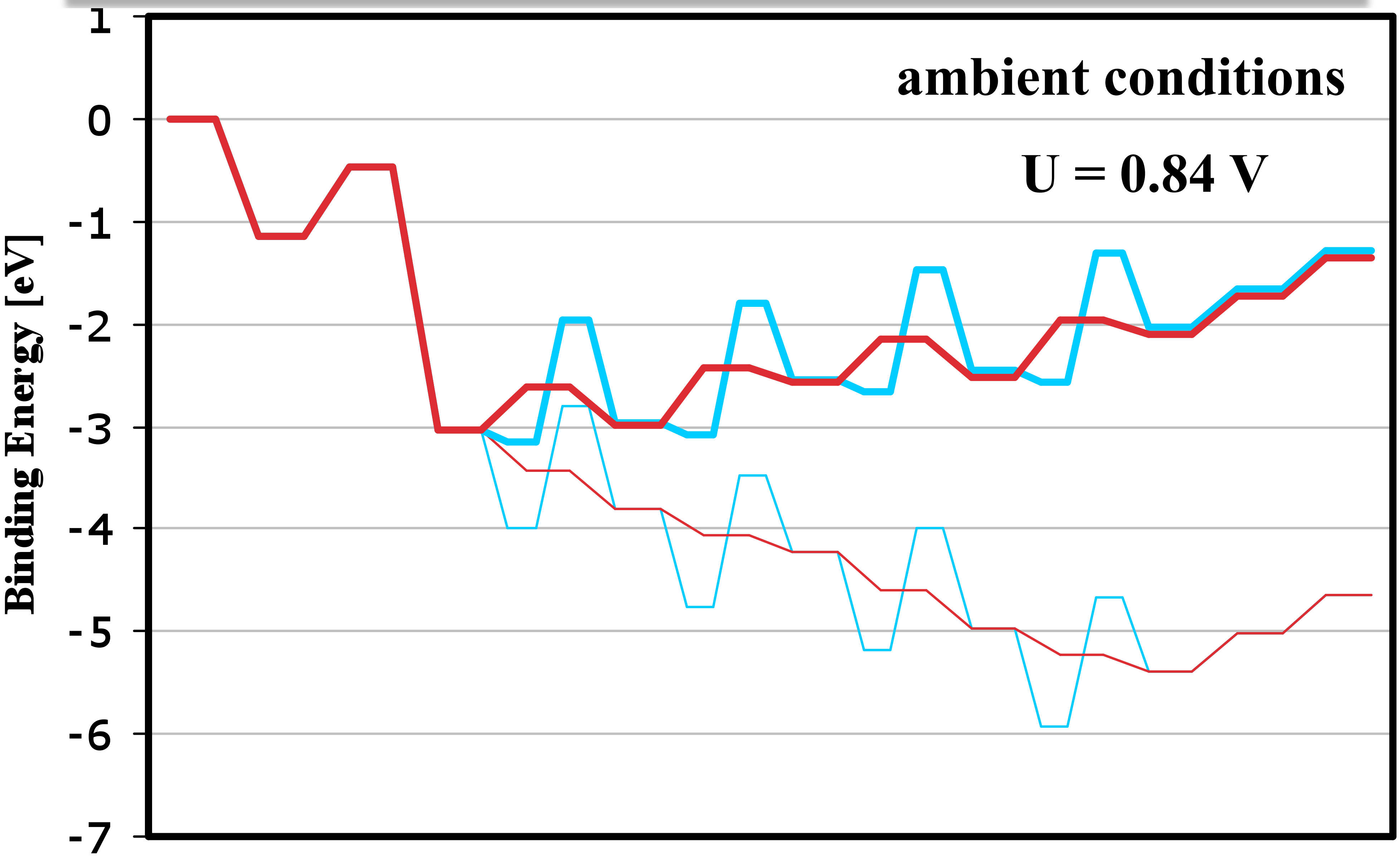


O_2-Dissociation Mechanism (Eley-Rideal + Langmuir Hinshelwood)



O_2-Dissociation Mechanism
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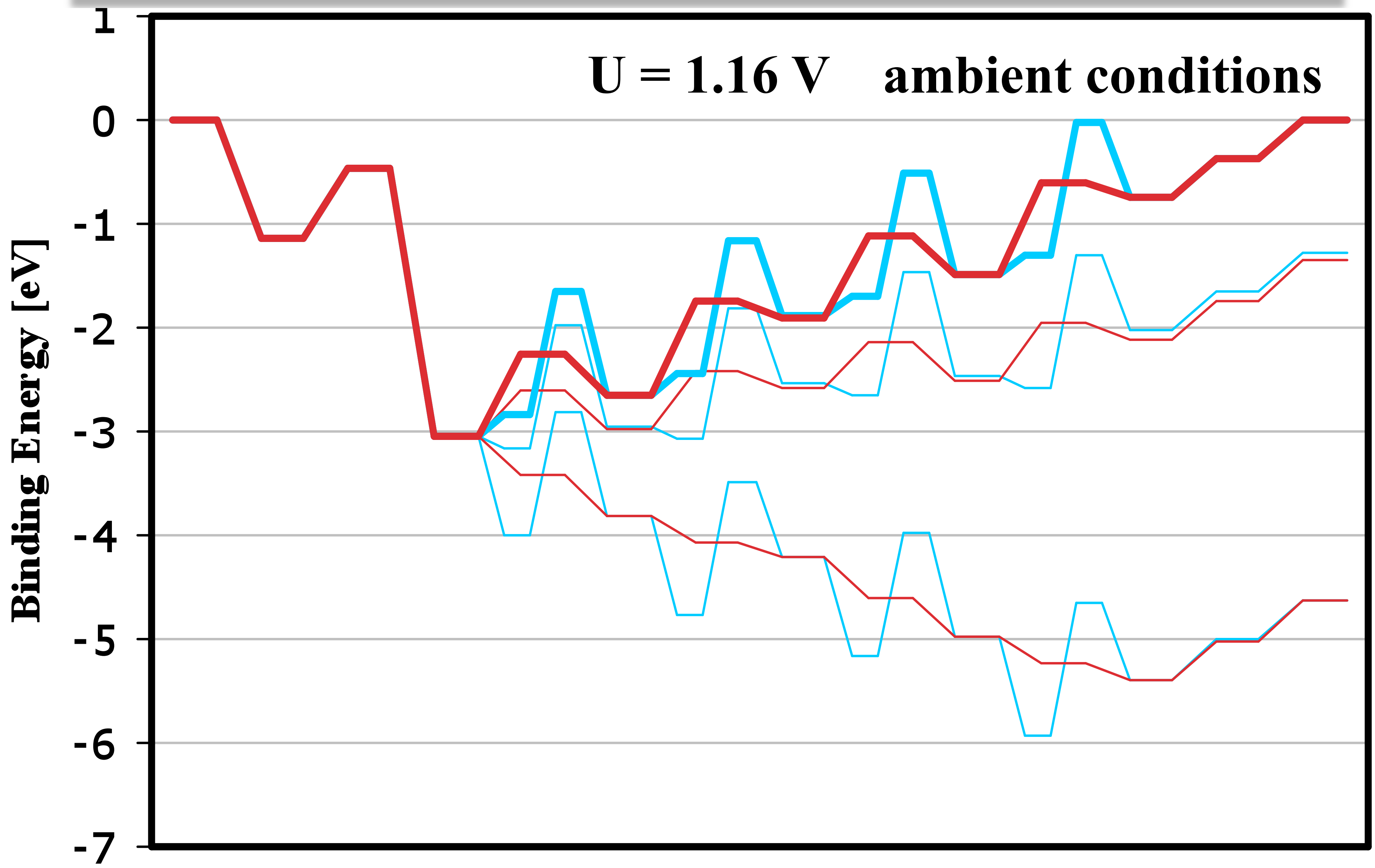
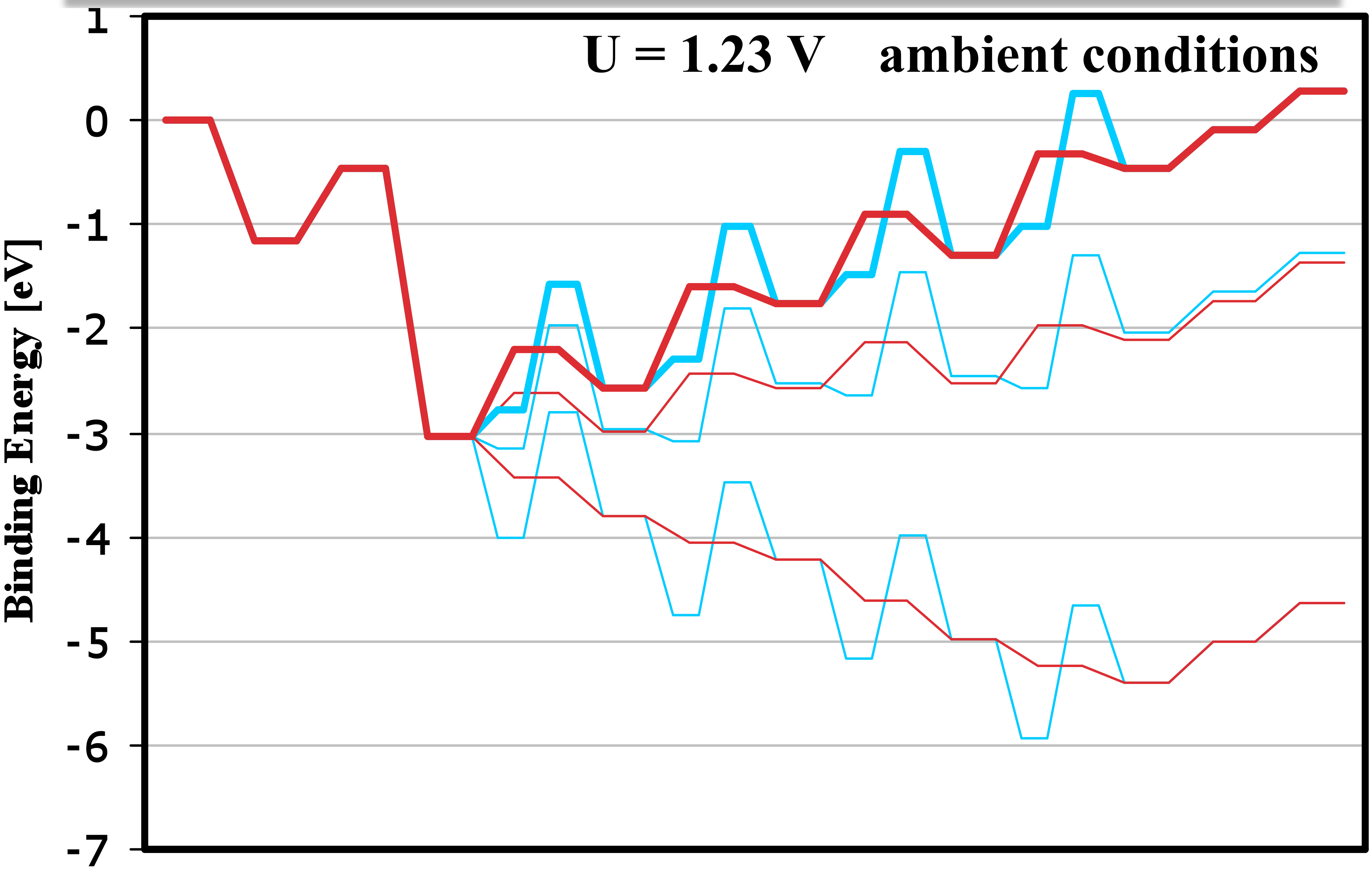
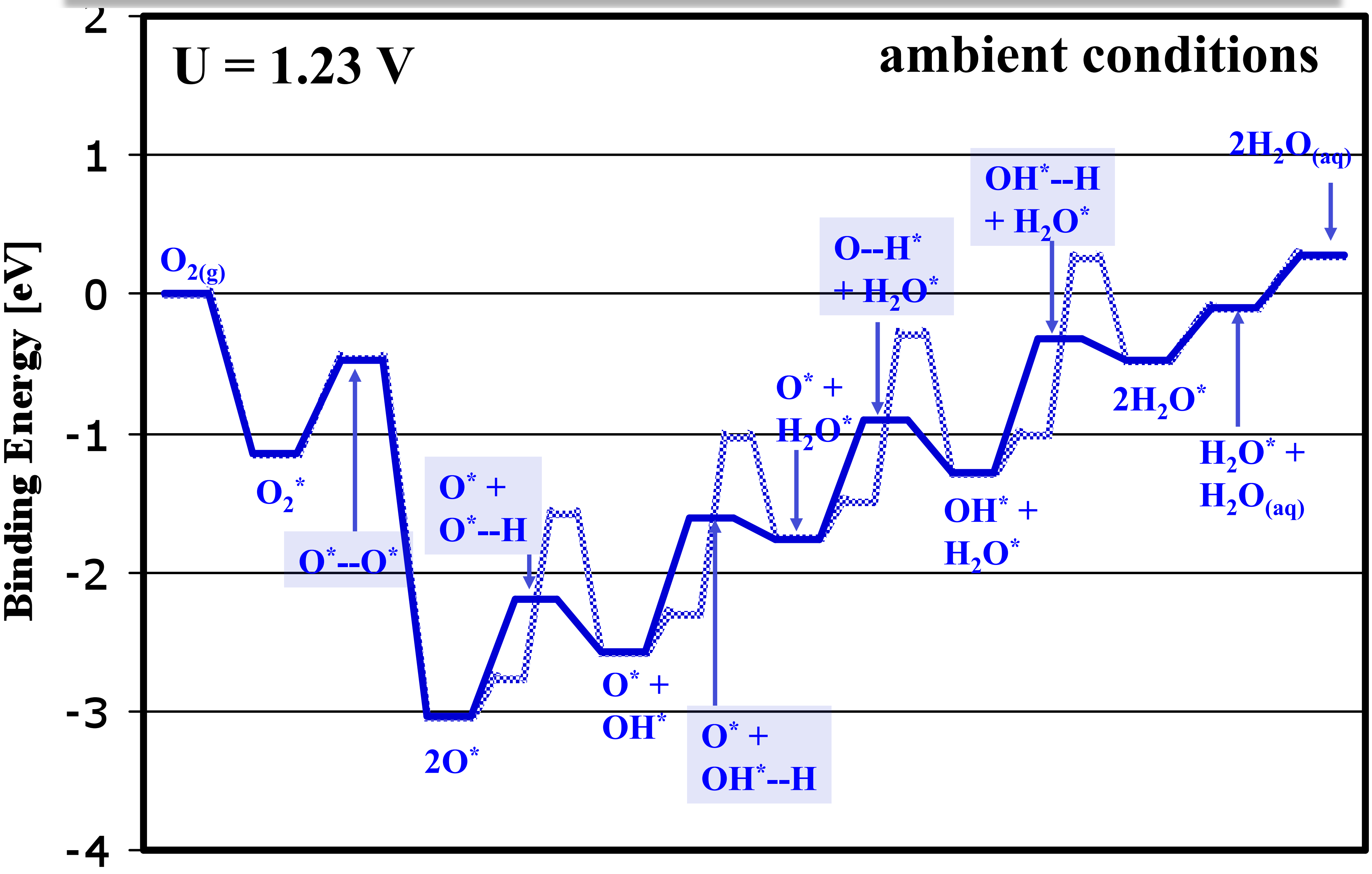


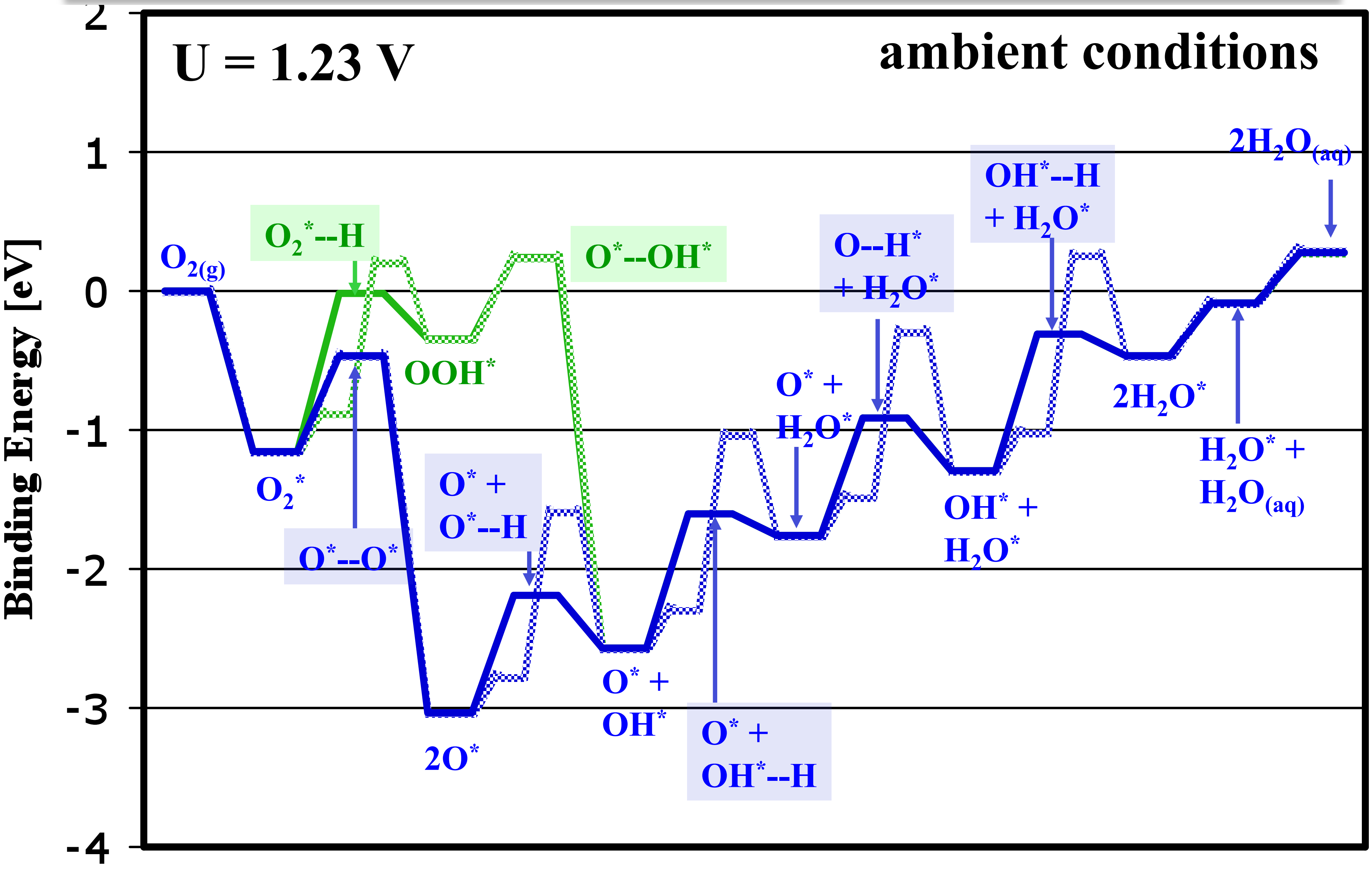
O_2-Dissociation Mechanism (Eley-Rideal + Langmuir Hinshelwood)



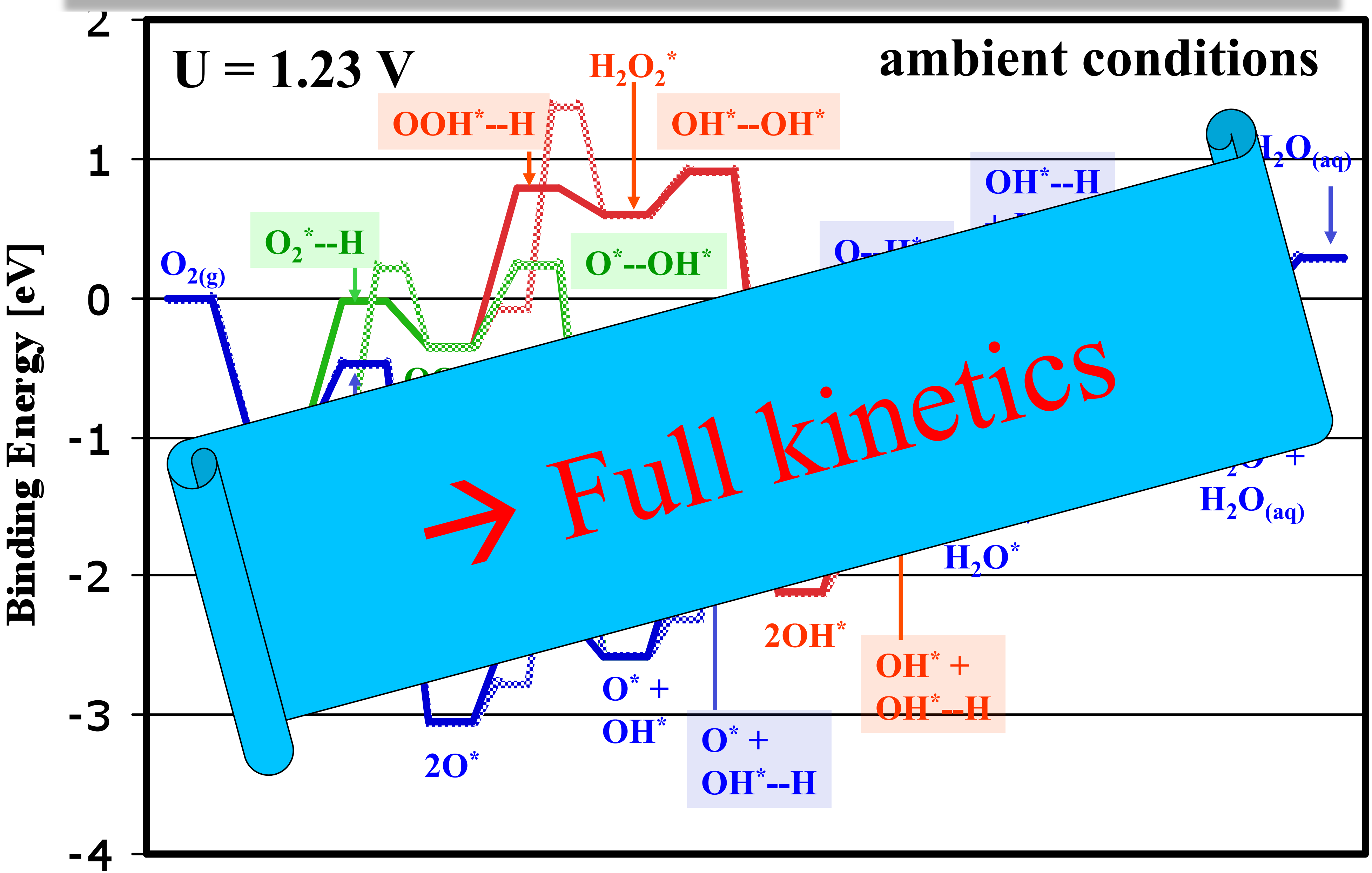
All Mechanisms
(Eley-Rideal + Langmuir-Hinshelwood)



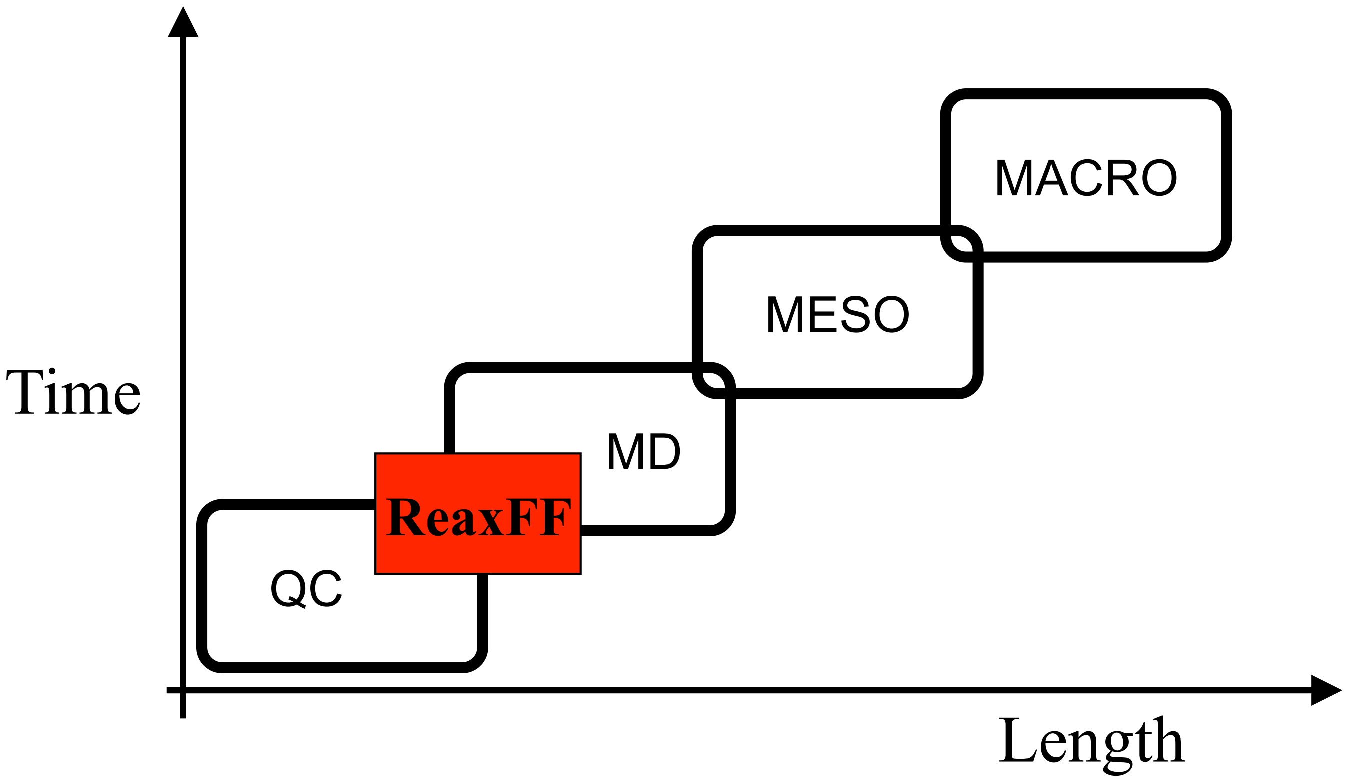
All Mechanisms
(Eley-Rideal + Langmuir-Hinshelwood)



All Mechanisms
(Eley-Rideal + Langmuir-Hinshelwood)



Cathode Reaction with ReaxFF (reactive forcefield)



ReaxFF

non-reactive forcefields (only spheres and springs)

1: x_1 y_1 z_1
2: x_2 y_2 z_2
3: x_3 y_3 z_3
4: x_4 y_4 z_4
5: x_5 y_5 z_5
6: x_6 y_6 z_6

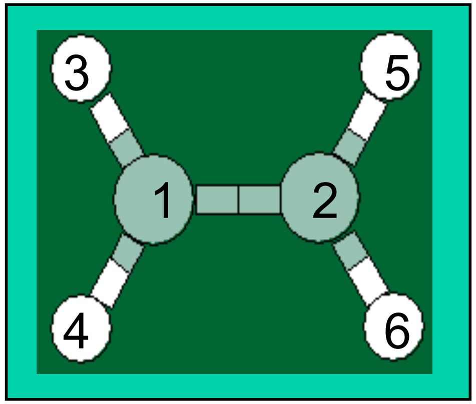
Atom positions

1: 2 3 4
2: 1 5 6
3: 1
4: 1
5: 2
6: 2

Bonding table

fixed

MD Routine



Reactive forcefields

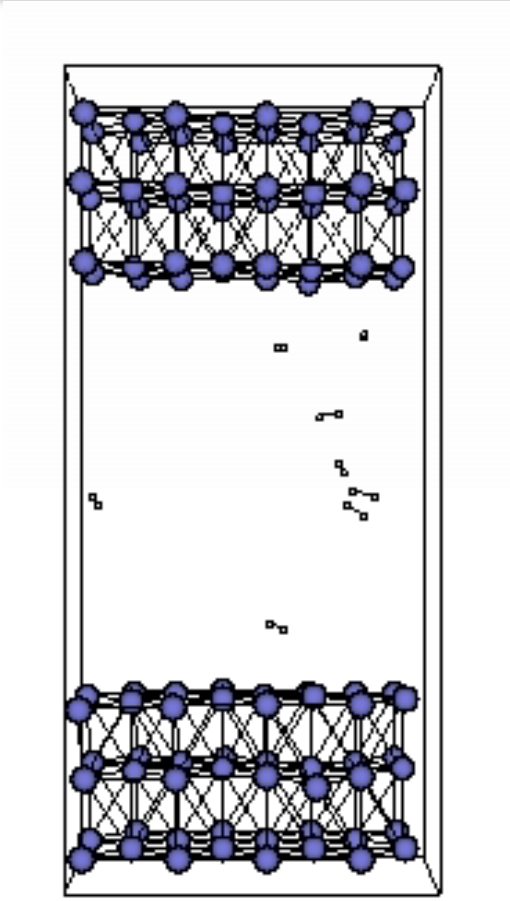
1: x_1 y_1 z_1
2: x_2 y_2 z_2
3: x_3 y_3 z_3
4: x_4 y_4 z_4
5: x_5 y_5 z_5
6: x_6 y_6 z_6

Atom positions

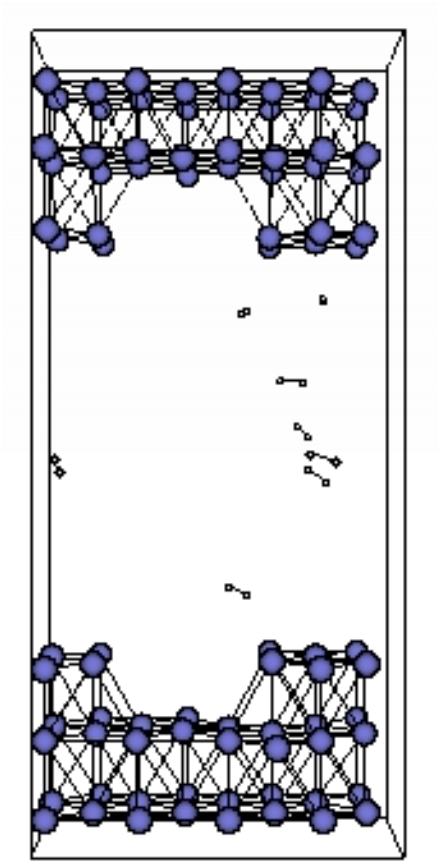
analyzing bonds

MD Routine

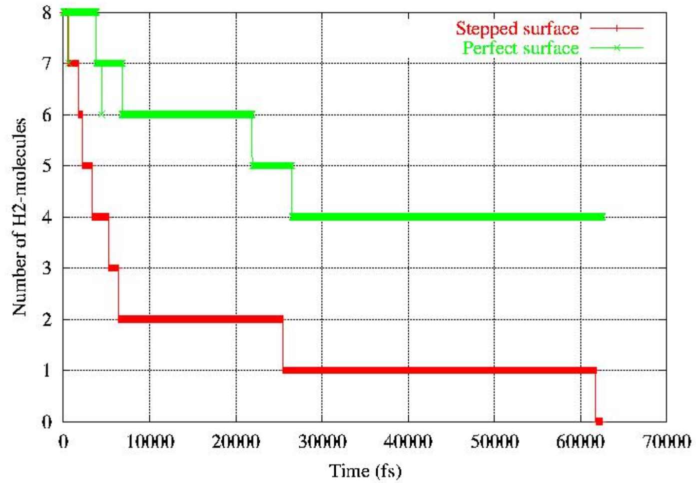
H_2 dissociation on Pt(111)

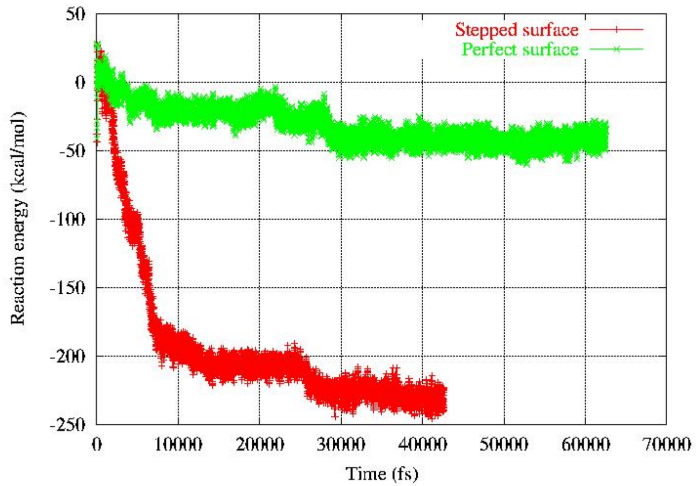


8 H_2-molecules in contact
with a perfect 96-atom (111) Pt-surface.
MD-simulation at 298K



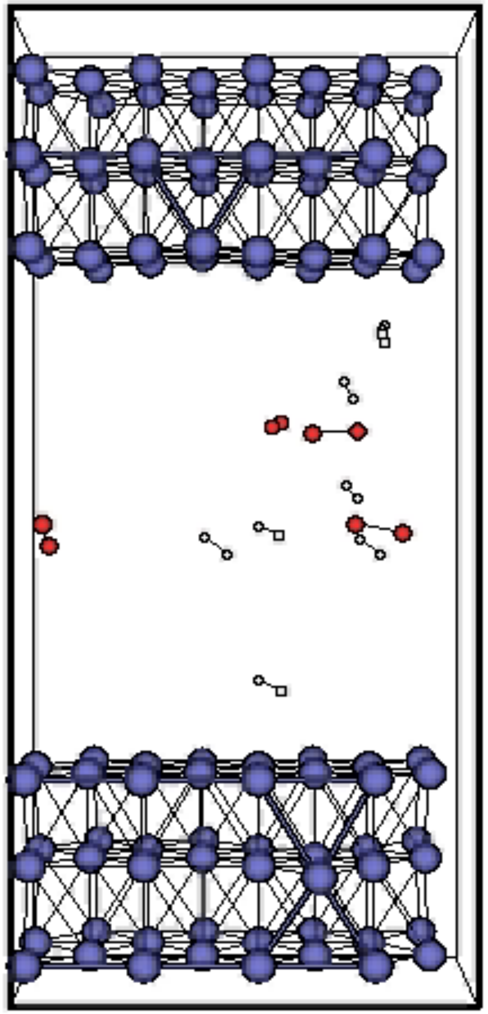
8 H_2-molecules in contact
with a stepped 84-atom (111) Pt-surface.
MD-simulation at 298K



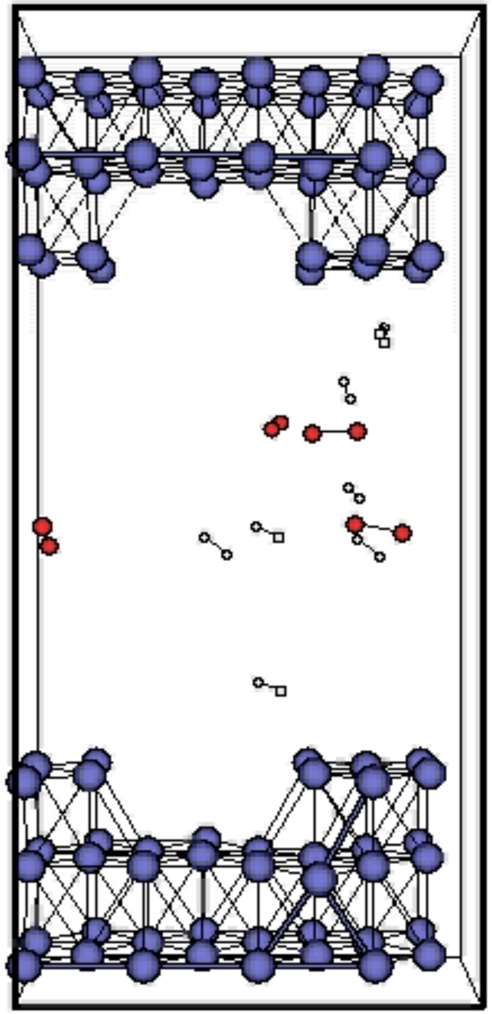


- Surface defects greatly increase reaction rate

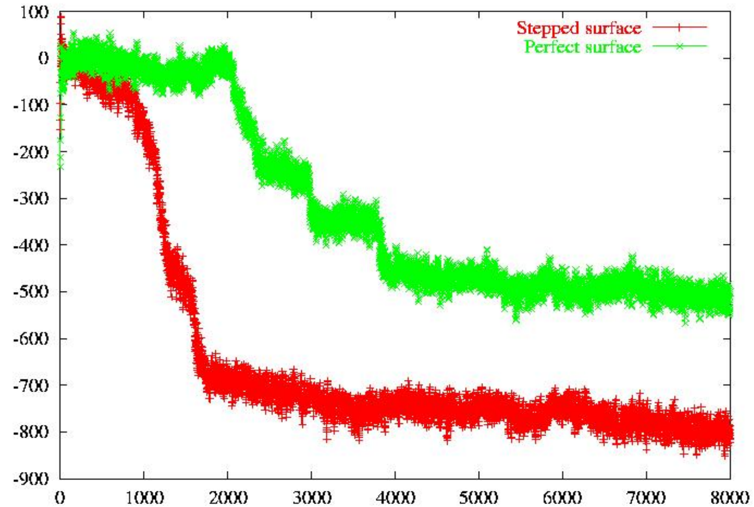
H_2 +O_2 reactions on Pt(111)



8 H_2+ 4 O_2 in contact with a perfect 96-atom (111) Pt-surface. T=1000K



8 H_2 + 4 O_2 in contact with a stepped 84-atom (111) Pt-surface. T=1000K

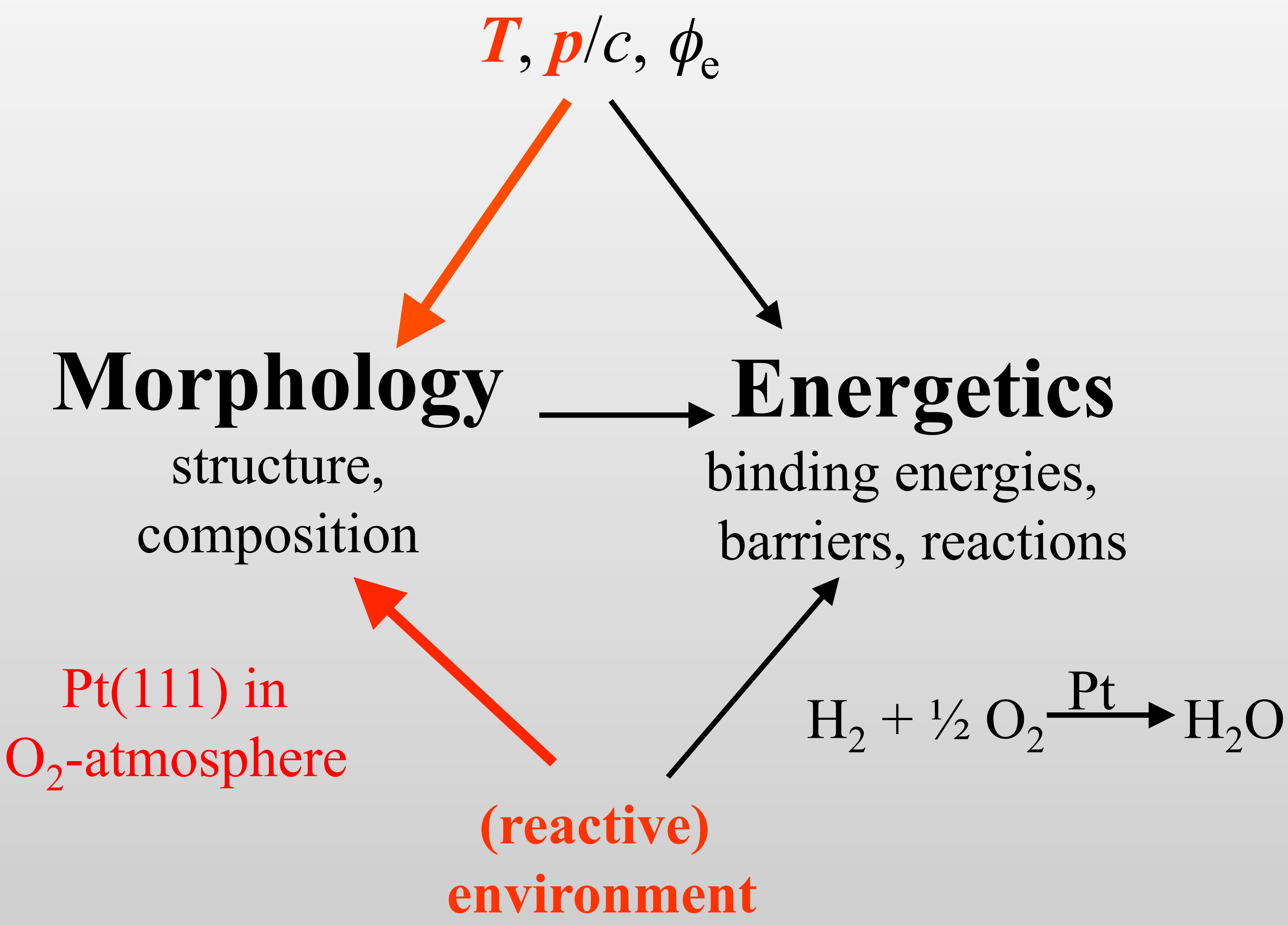


-Perfect surface generates H_2O, stepped surface gets oxidized

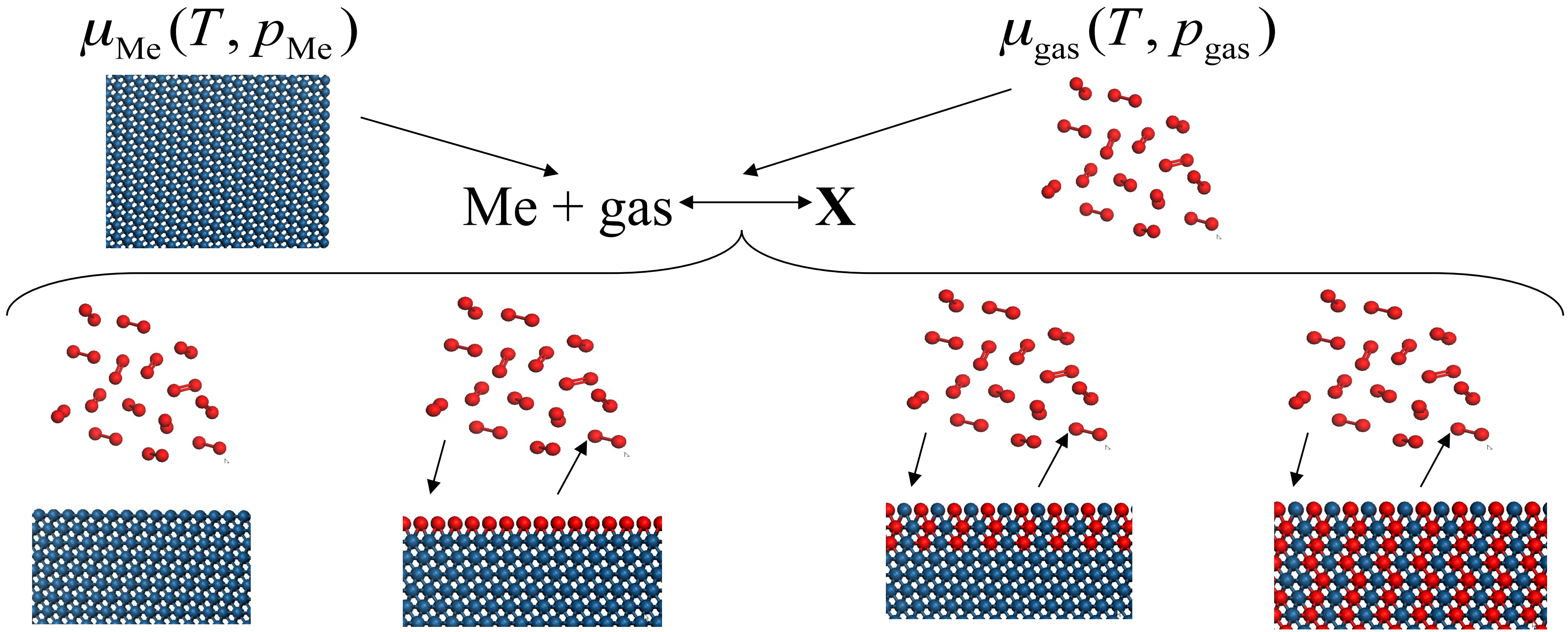
- Need to compare ReaxFF with QC-data for surface defects

- Energy profile for perfect surface clearly shows H_2O generation events

Influence of Atmosphere



The **non-**electrochemical interface



Surface free energy: $$\mu(T, p_{\mathrm{O}}) = \frac{1}{A}\left[G - N_{\mathrm{Pt}}\mu_{\mathrm{Pt}}^{\mathrm{bulk}} - N_{\mathrm{O}}\mu_{\mathrm{O}}^{\mathrm{gas}}(T, p_{\mathrm{O}})\right]$$

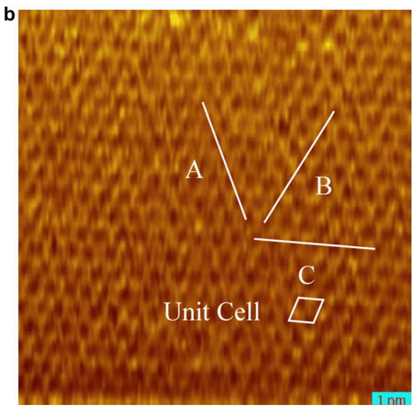
from DFT-calculations

K. Reuter, M. Scheffler, PRB, 68, 045407 (2003)

Pt(111) in Oxygen Atmosphere

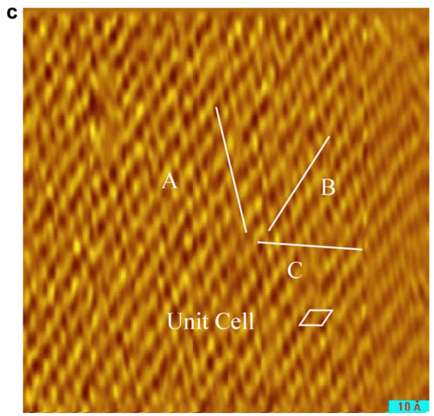
Experiment: HREELS, UPS, AES, LEED, TPD

p(2×2)

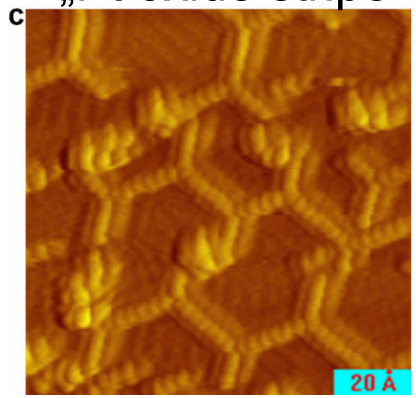


$400K, p=2\cdot10^{-13}$bar

p(2×1)



„Pt oxide stripe“



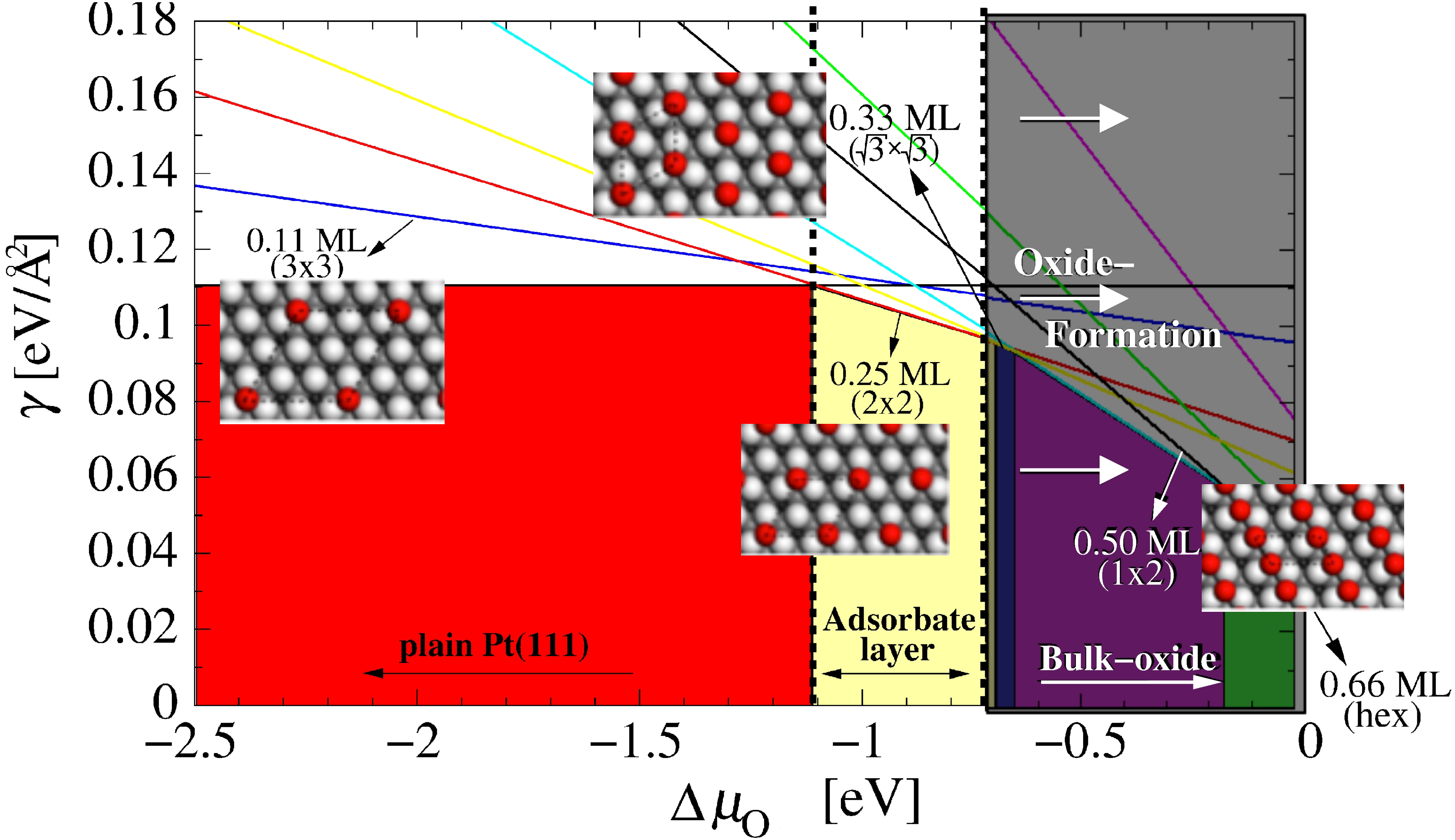
Higher temperatures, atomic oxygen

DFT-calculations:

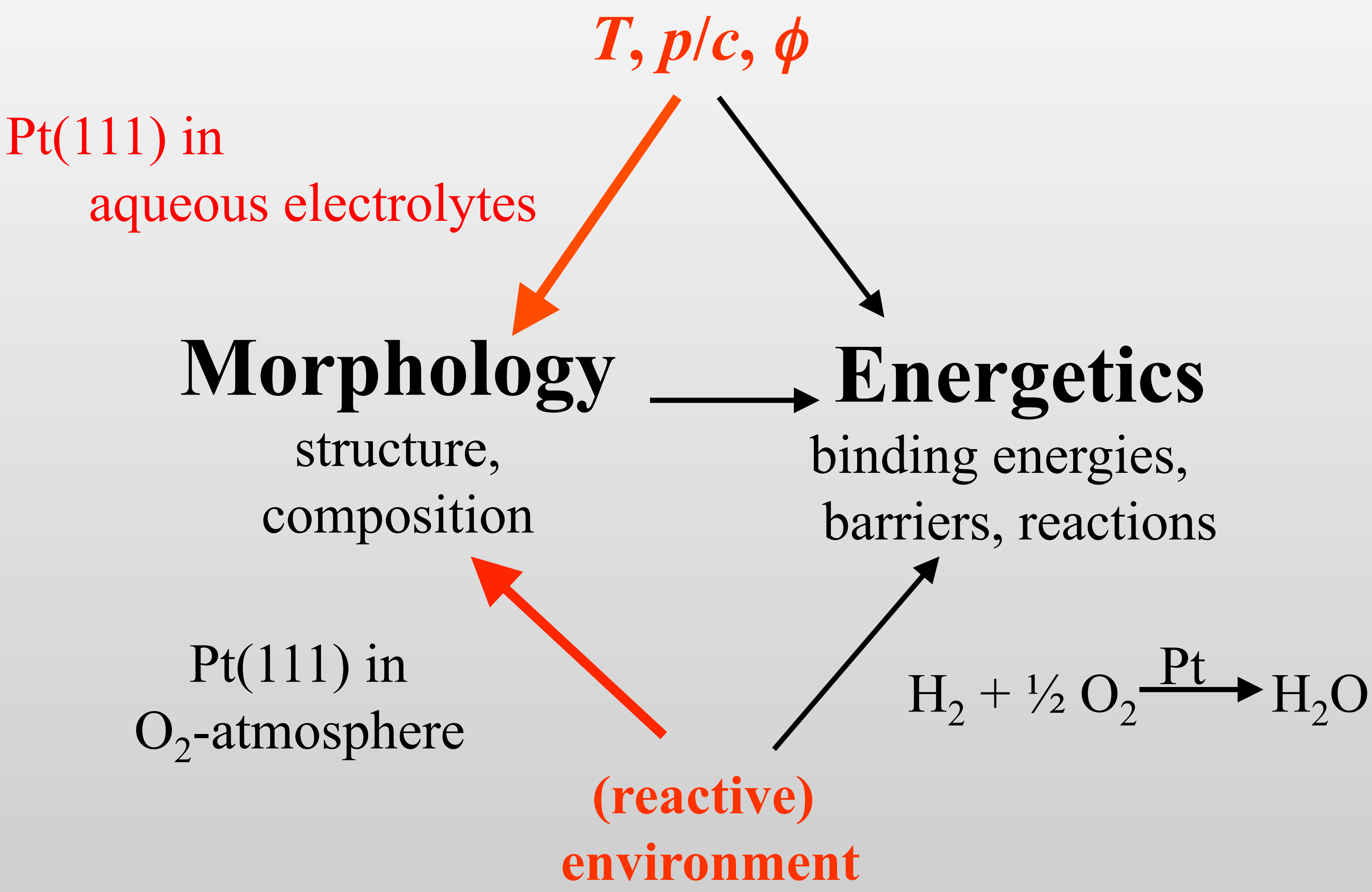
- CASTEP (and SeqQuest) periodic DFT-program
- 6-layer slabs (2 bottom layers fixed)
- ultrasoft pseudopotentials
- E-cutoff = 340eV
- 10×10 ***k***-grid (MP)
- PBE–GGA

D. H. Parker et al., *Surf. Sci.*, **217**, 489 (1989)
J. F. Weaver et al., *Surf. Sci.* **602**, 3116 (2008).

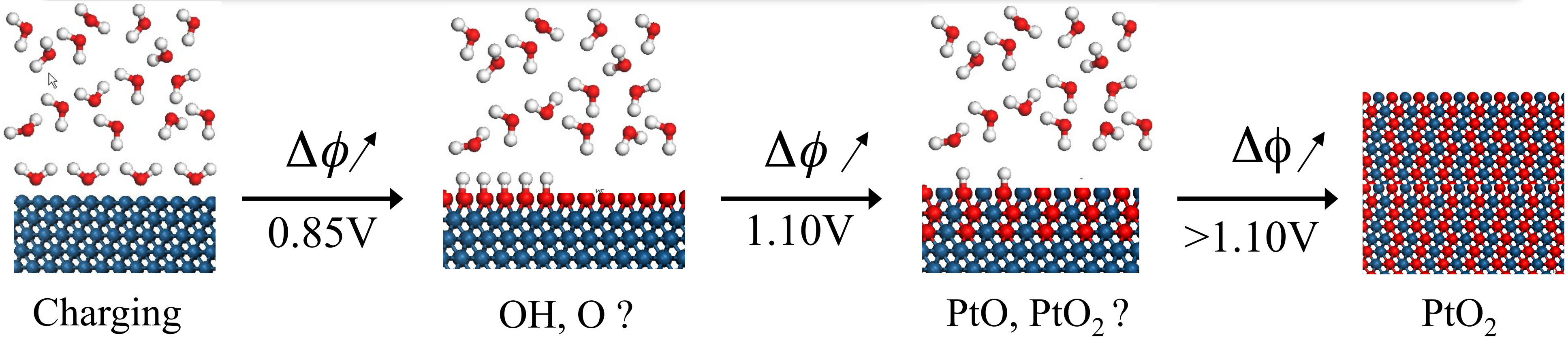
(*p*,*T*) — phase diagram

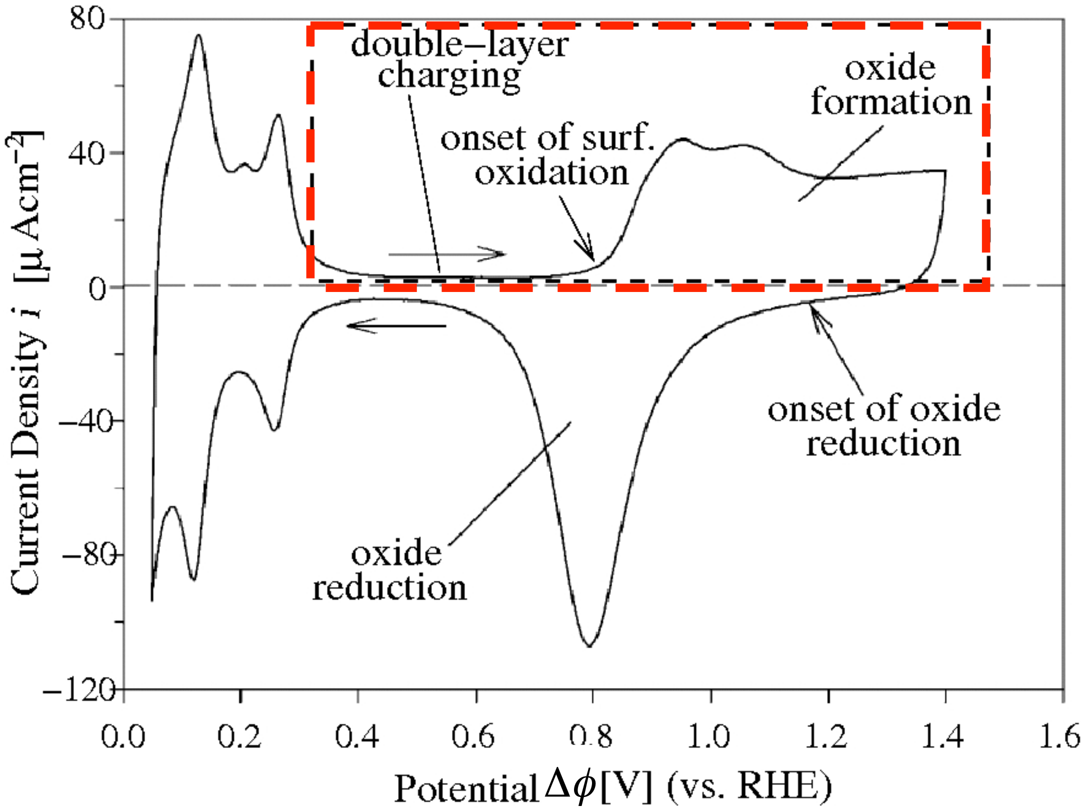


Electrode Potential
(Electro-Oxidation of Pt-electrodes)



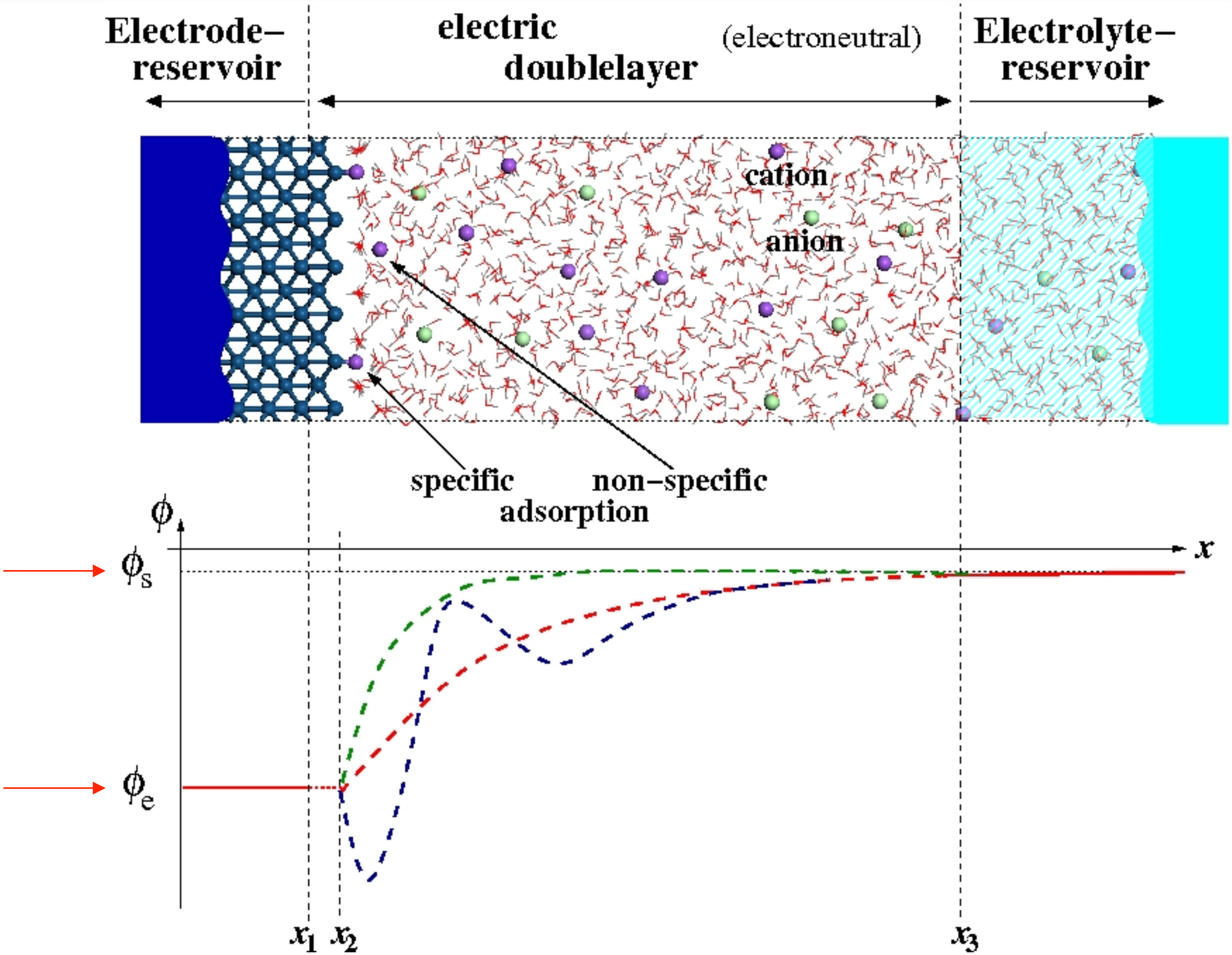
Pt_{poly} in 0.5M H_2SO_4





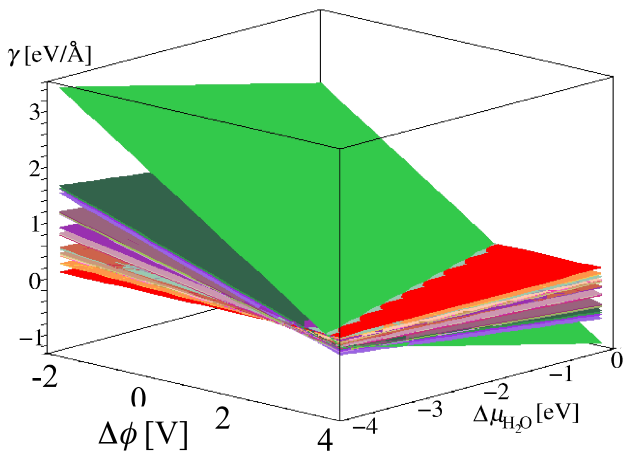
G. Jerkiewicz *et al.*, *Electrochim. Acta*, **49**, 1451 (2004)

Electrochemical Half-Cell



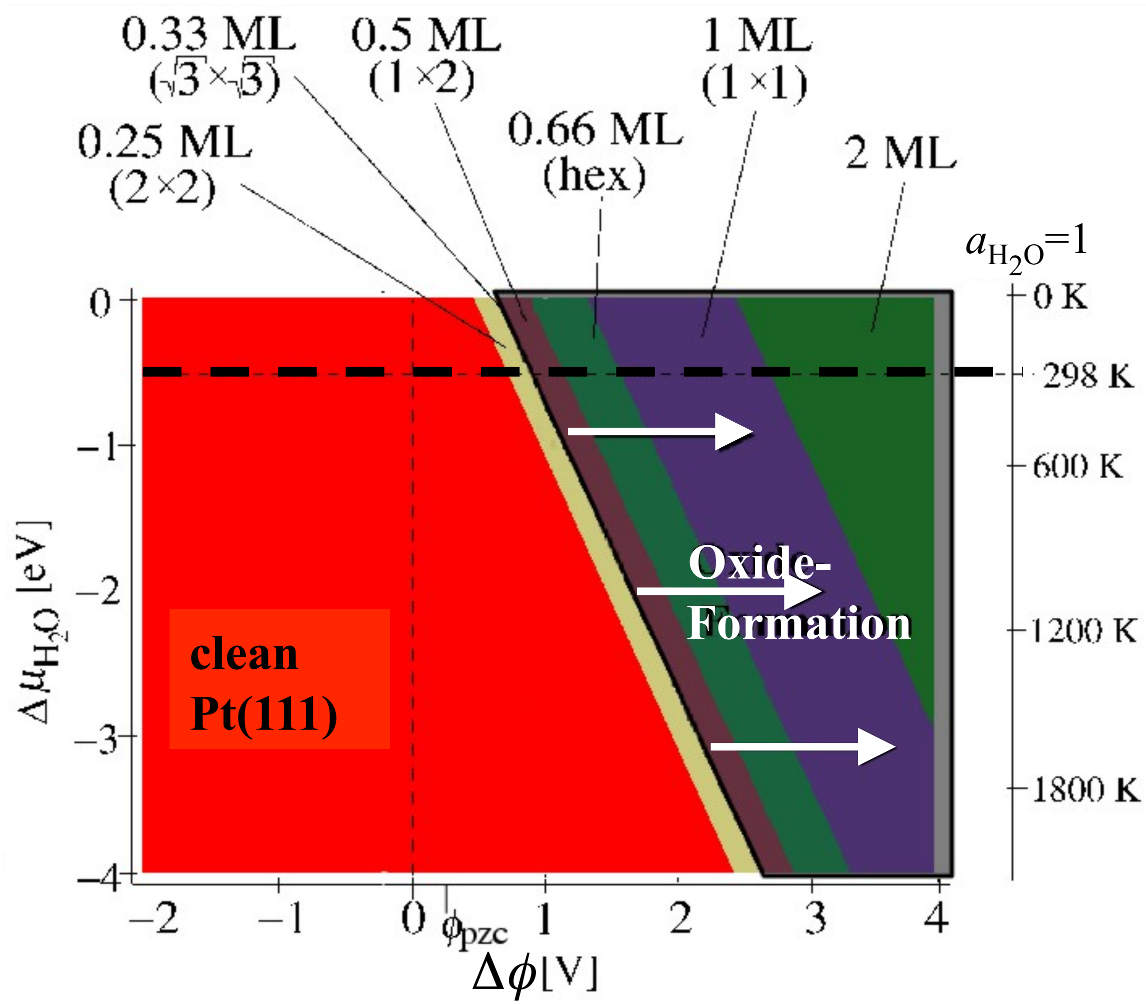
(p,T,ϕ) — Phase diagram

DFT-calc:
- SeqQuest
- Norm-conserving PP
- "double-ξ + pol."-basis set
- PBE–GGA



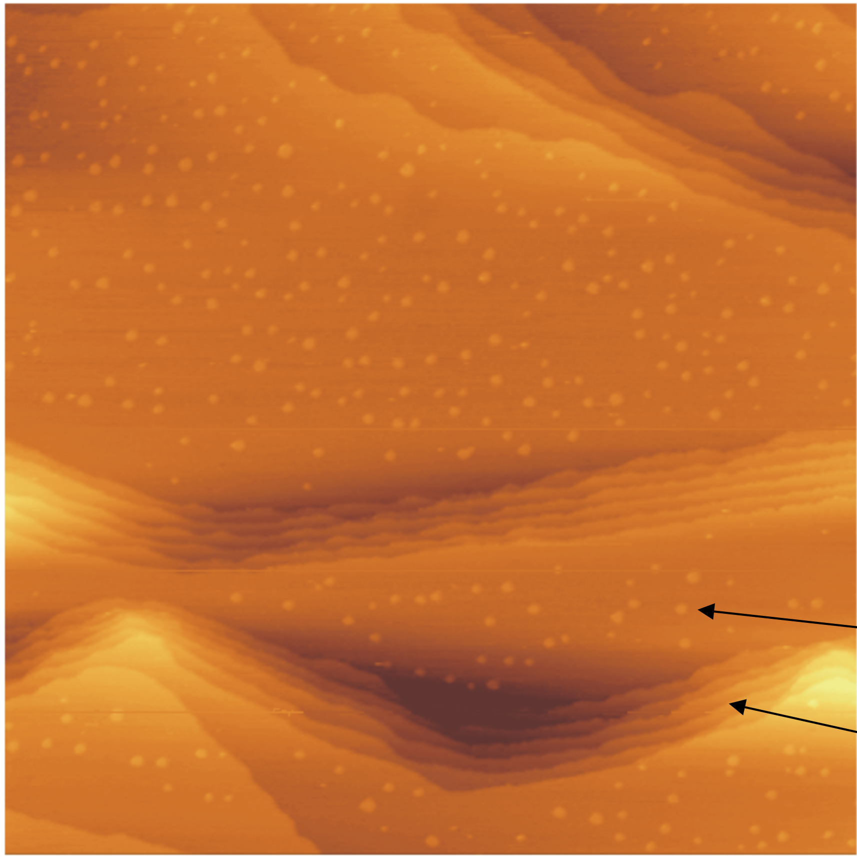
Results (T=298K, a_{H_2O}=1)

	Exp. [V]	Calc. [V]
no adsorption	**<0.85**	**<0.95**
O-adsorption	**$0.85<\phi_e$ $\phi_e<1.10$**	**$0.95<\phi_e$ $\phi_e<1.20$**
Oxide-formation	**$\phi_e>1.10$**	**$\phi_e>1.20$**



T. Jacob, *J. Electroanal. Chem*, 607, 158 (2007).

Real Surfaces are Terraced



STM image[1]: Au (111) surface, 500nm x 500nm, 550mV vs. SCE

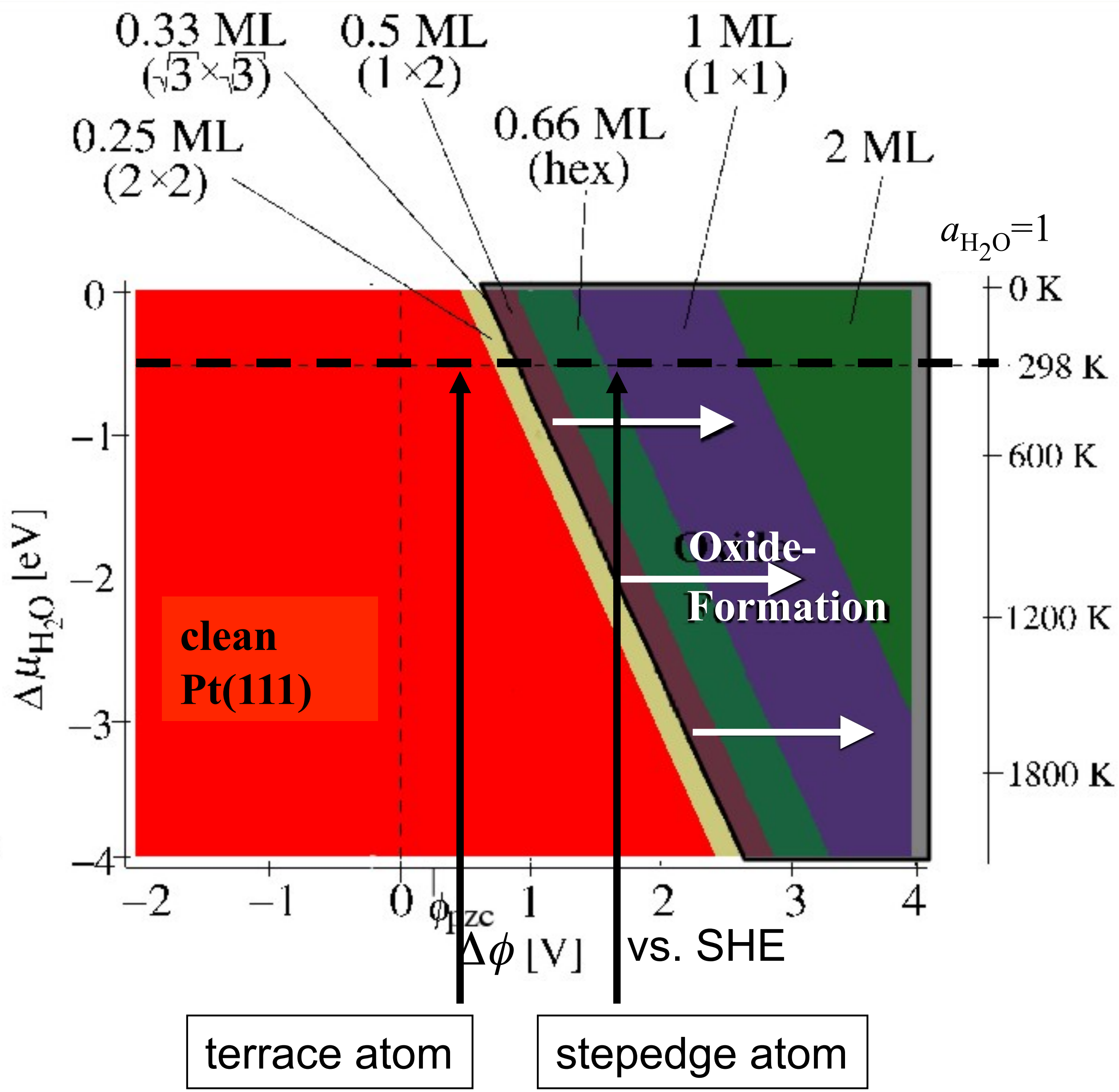
gold islands

stepedges

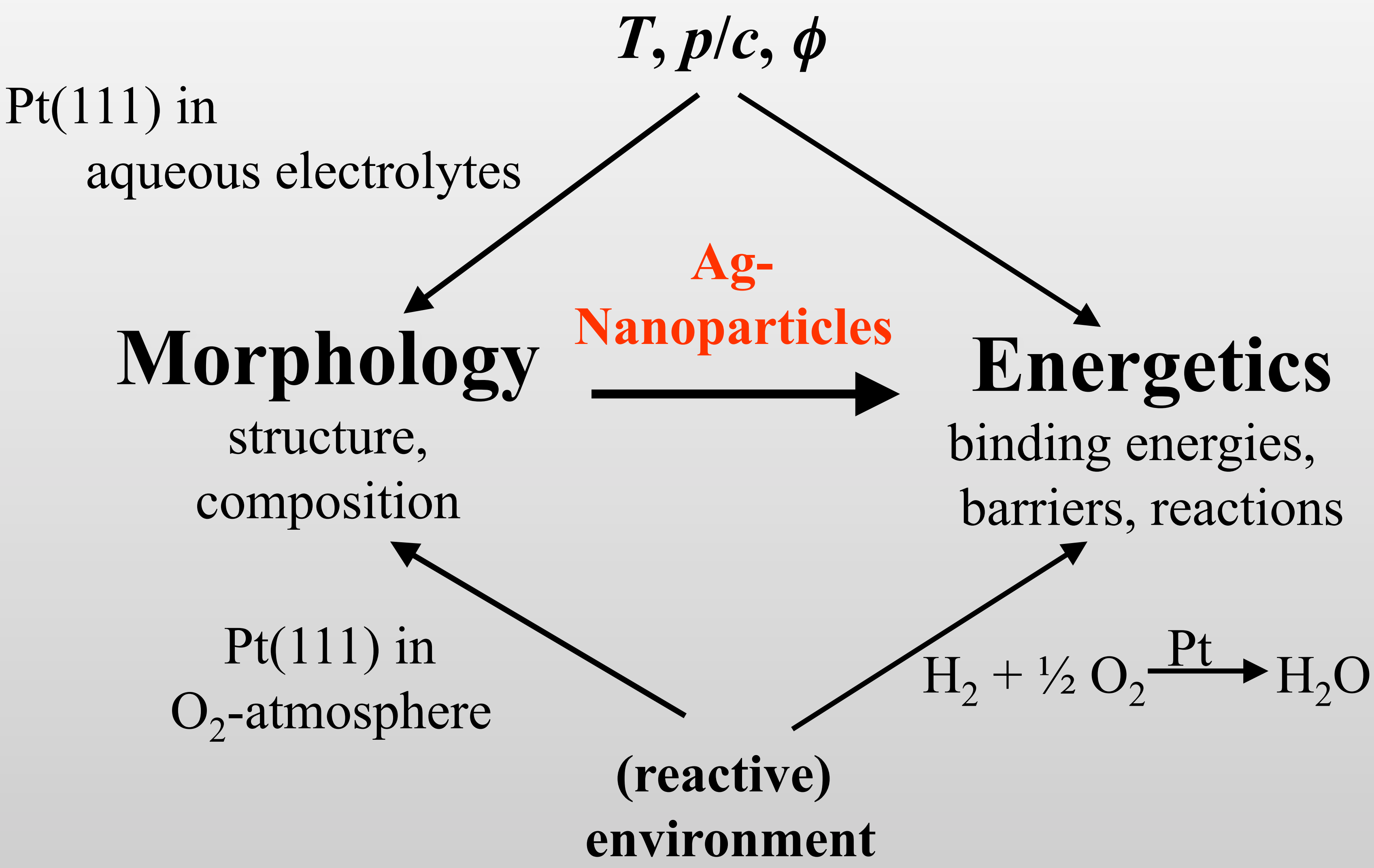
➡ Study Pt(322) and Pt(553) as examples for the stepped surface

C. Köntje, Uni Ulm, Diploma thesis (2007)

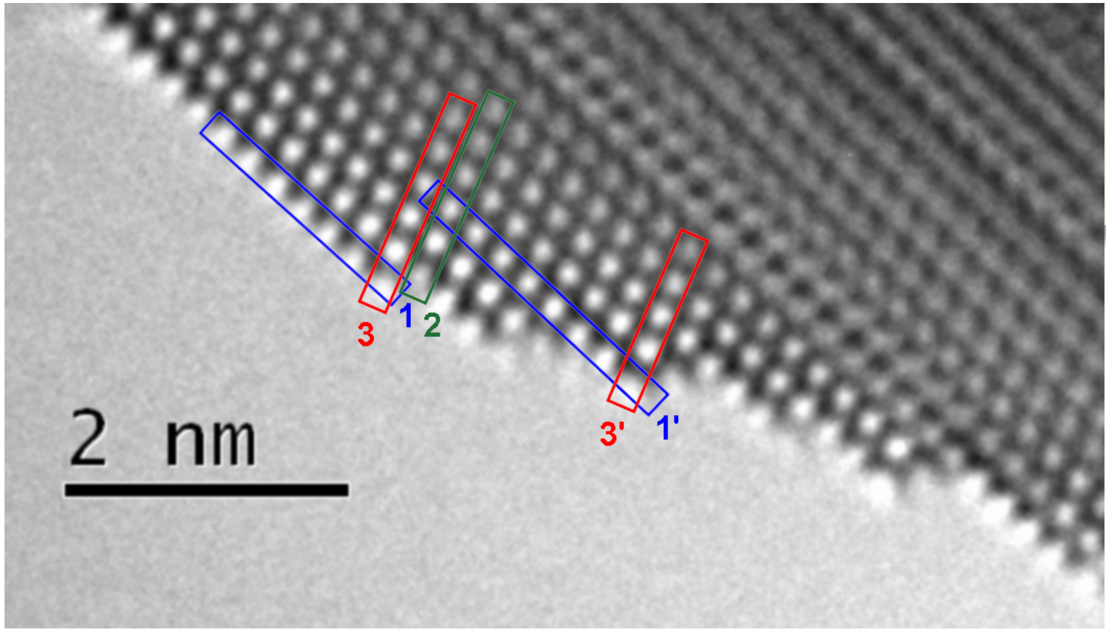
Oxidized Stepedges?

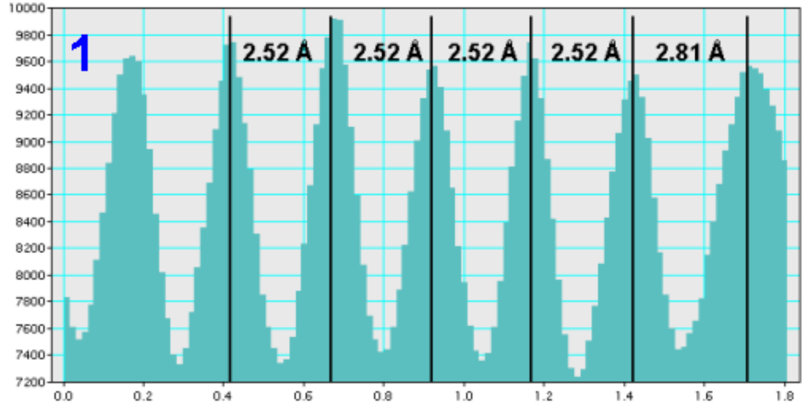


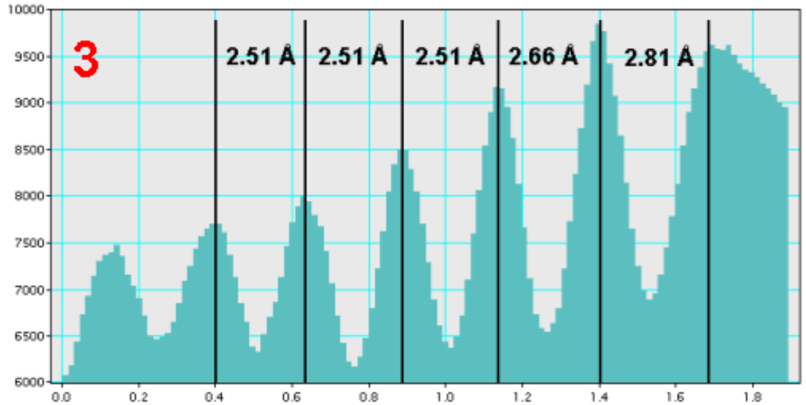
Nanoparticles



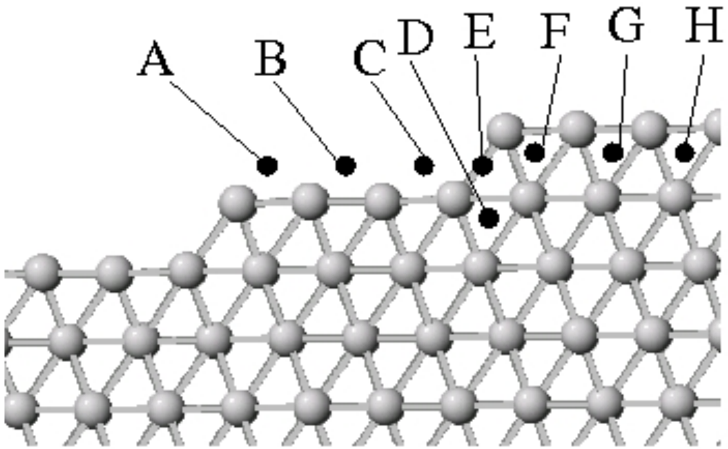
Ag on SiO_2

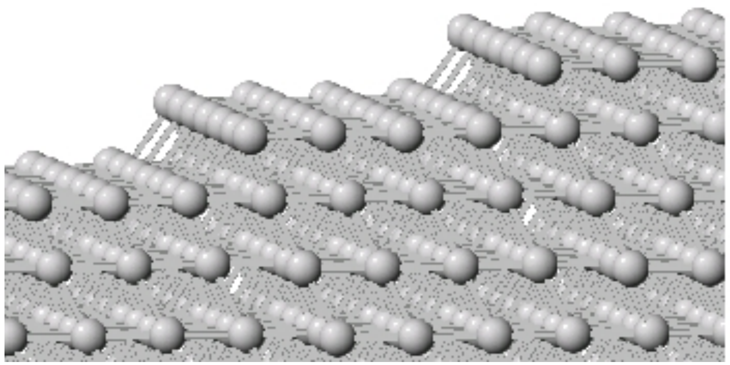


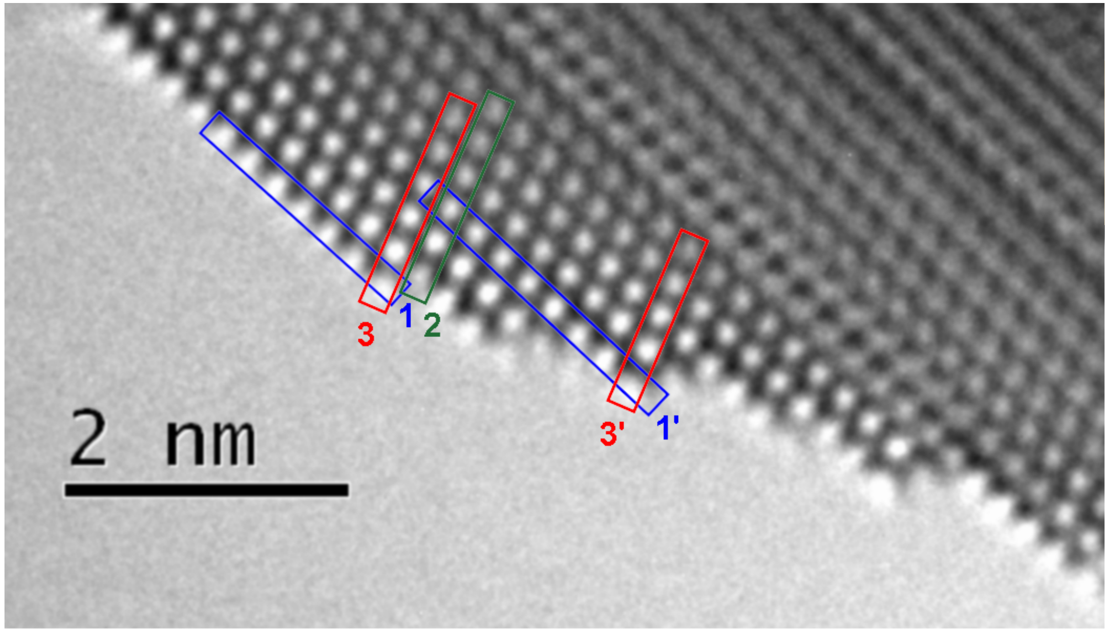




clean (100) step

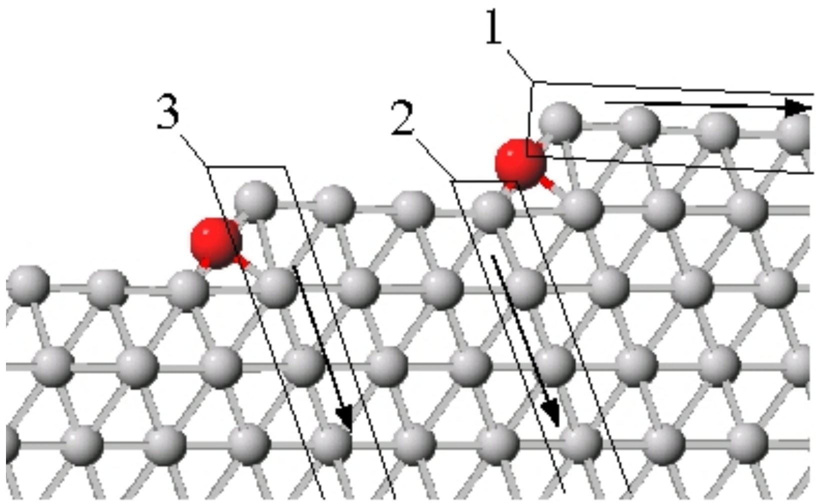


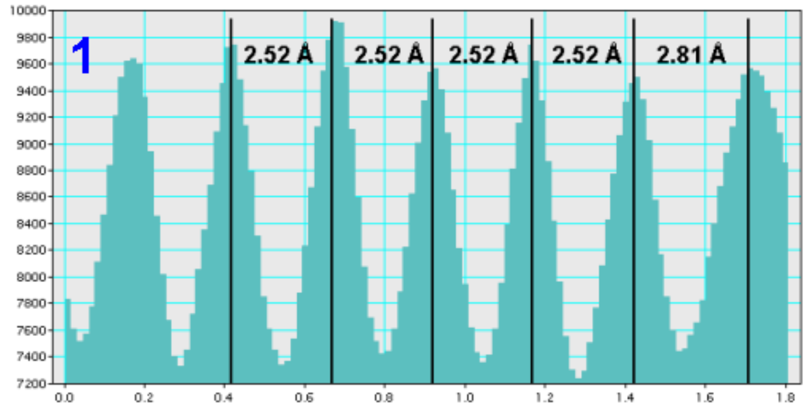


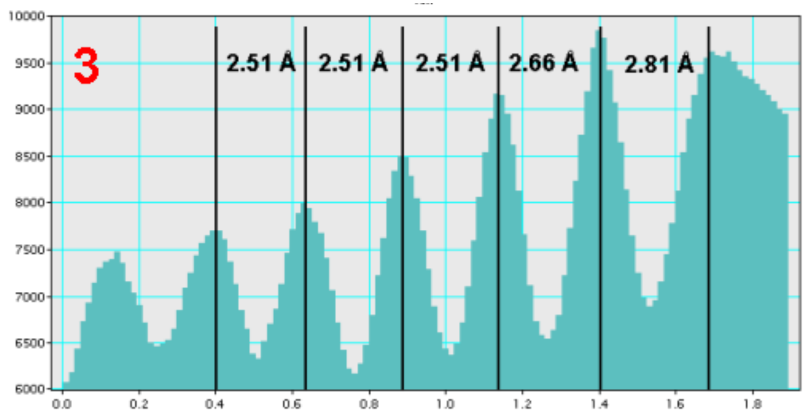


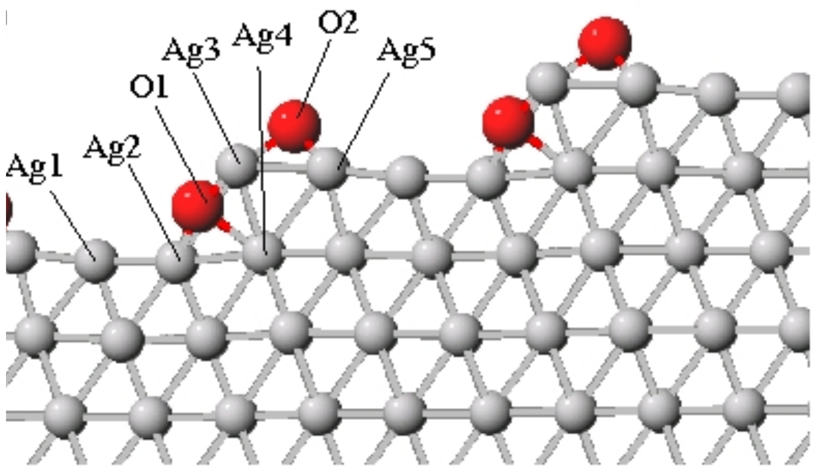
Ag on SiO_2

oxygen–adsorbed (100) step



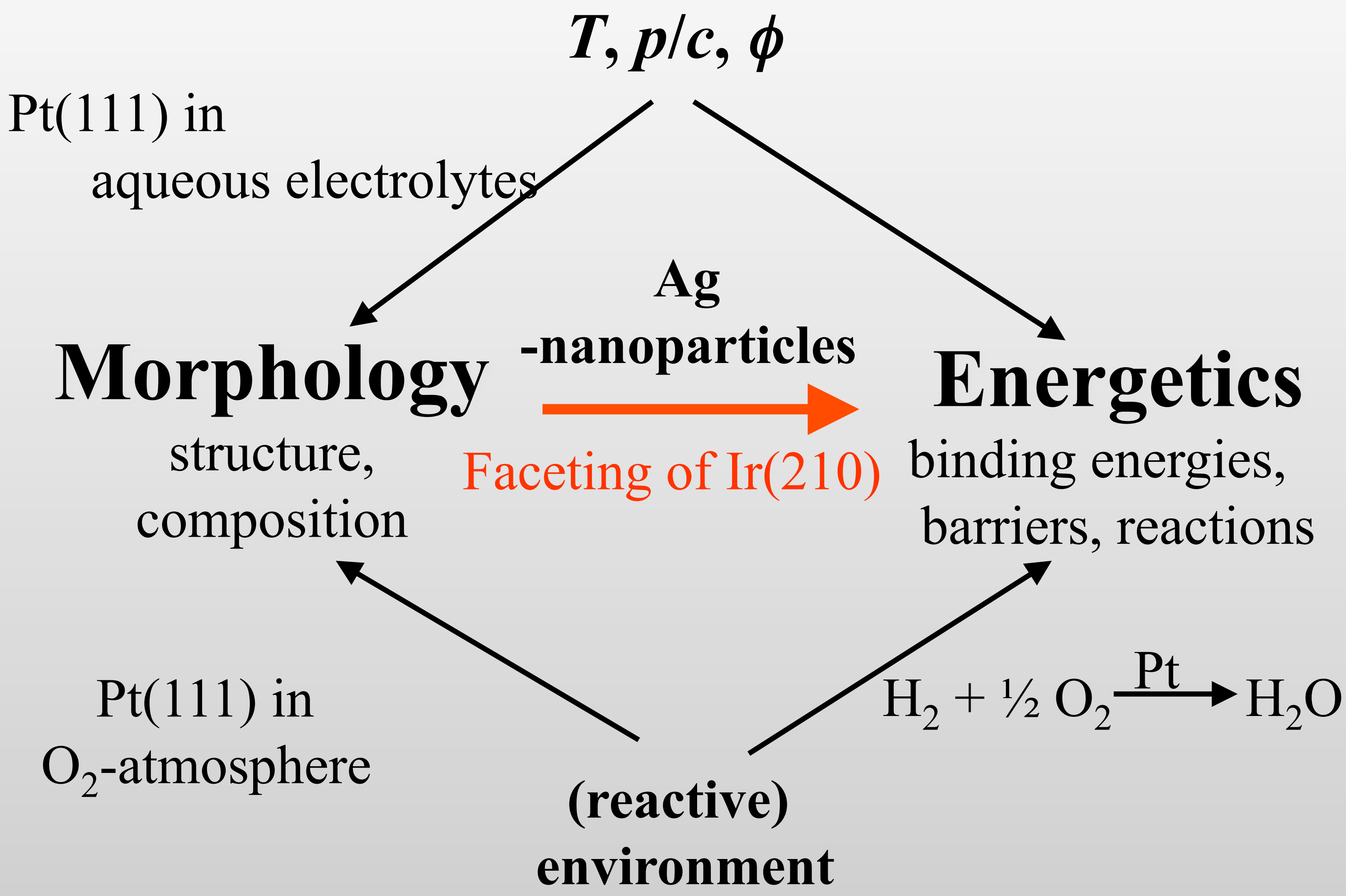




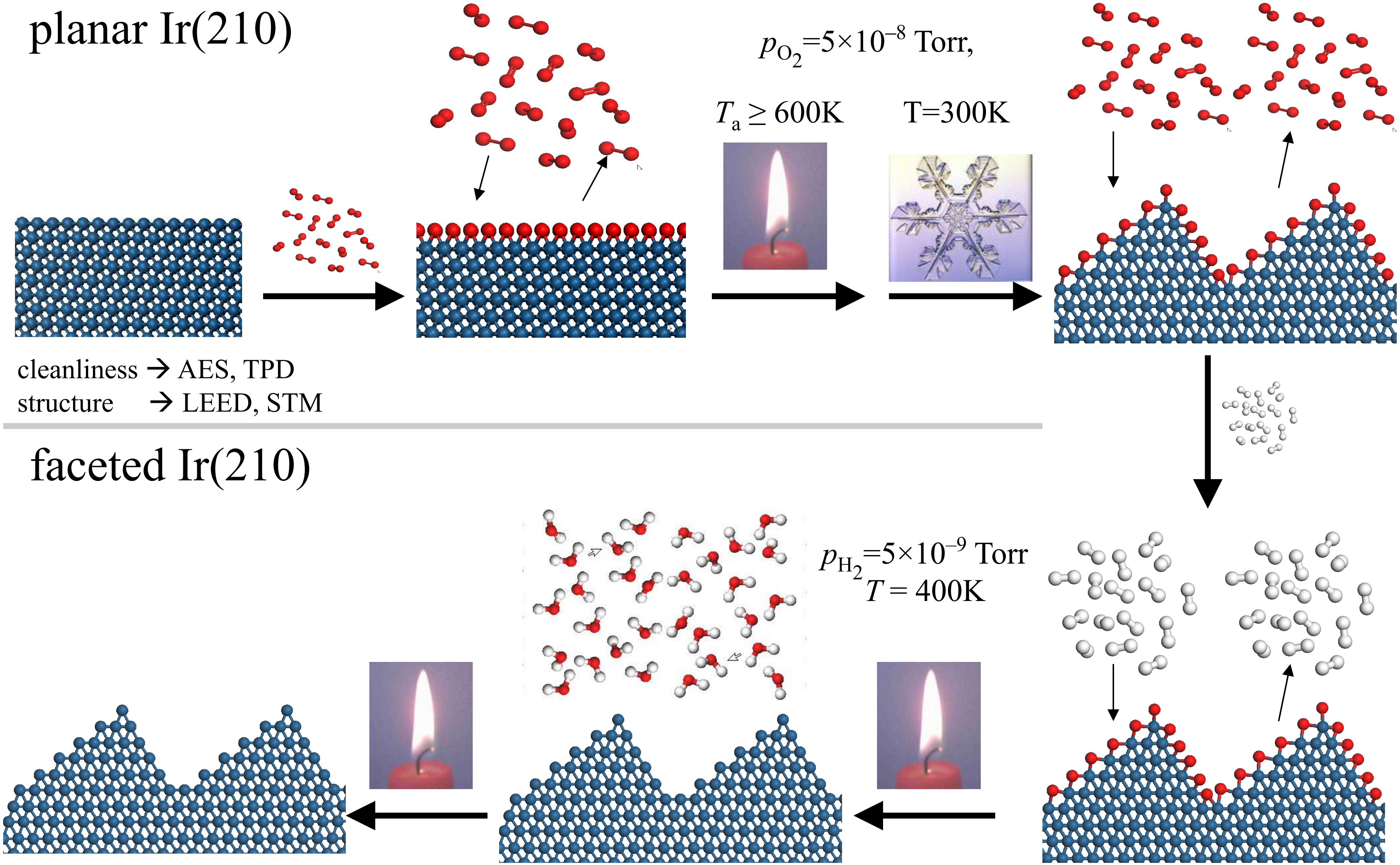


TJ *et al.*, *Angew. Chem. Int. Ed.*, **47**, 5005 (2008)

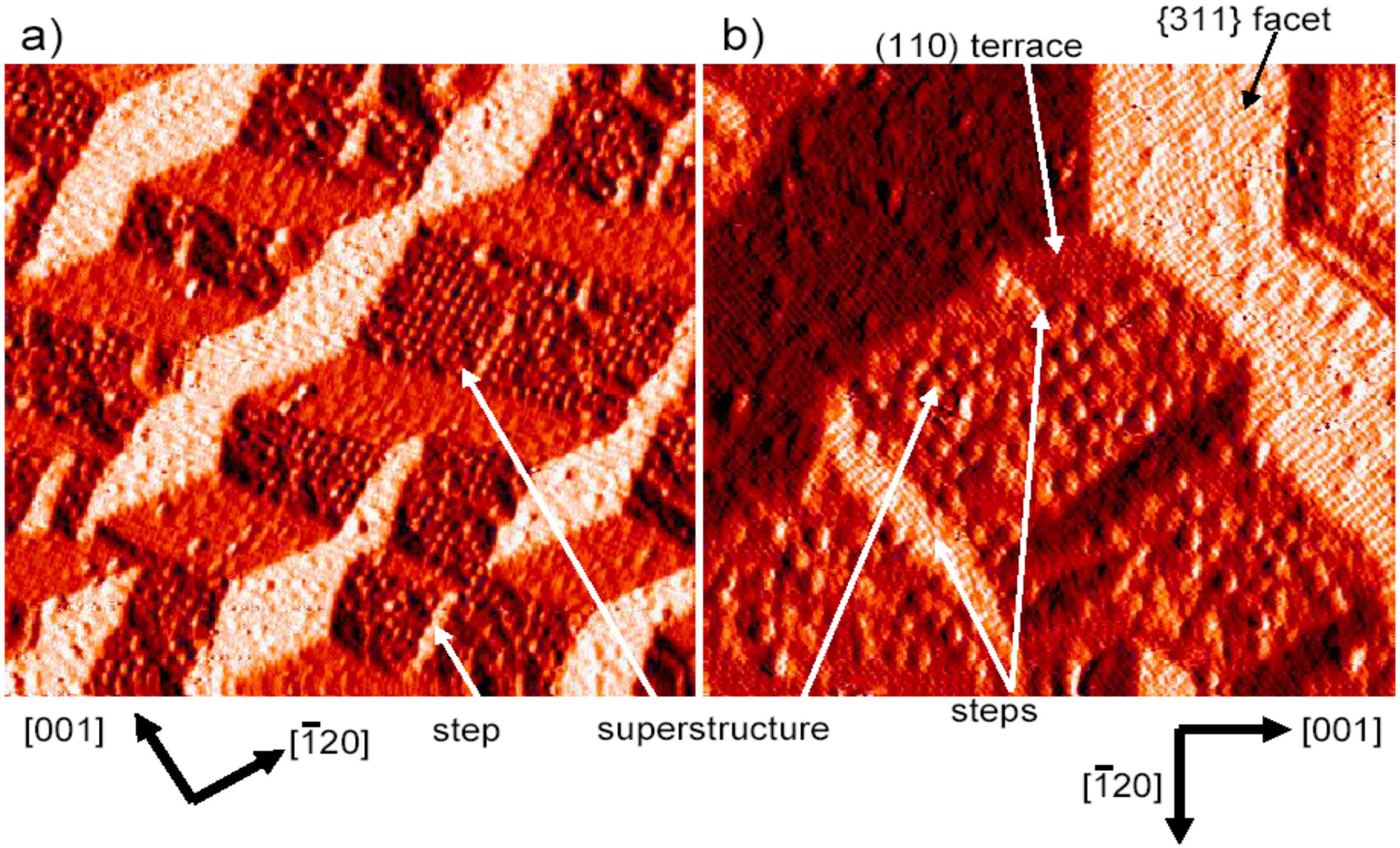
Potential-Induced Faceting of Ir(210)



Facet-Formation



Facet-Formation

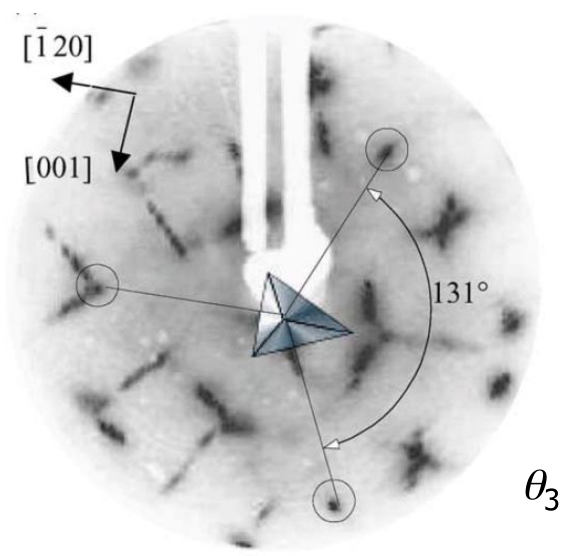


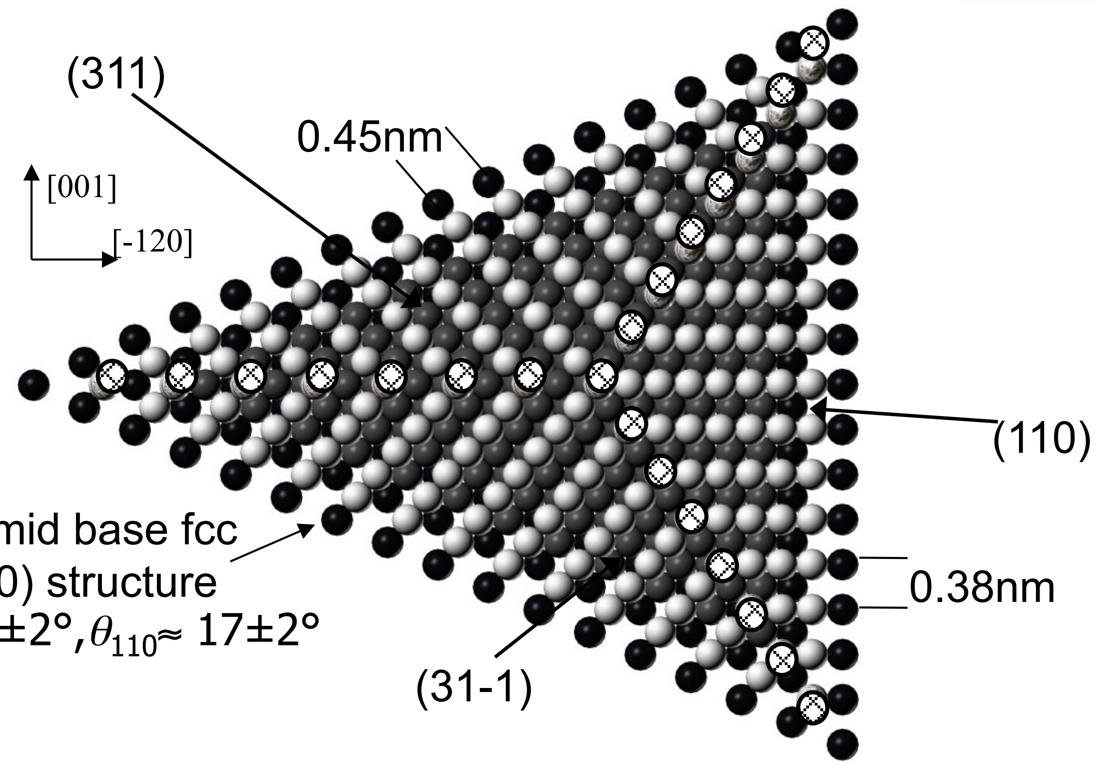
Facet-size: T_a=600K (5nm) < 950K (11nm) < 1700K (14nm)

Ref.: I. Ermanoski *et al. Surf. Sci.*, **549**, 1 (2004).

Structure of the nanoscale pyramids

LEED-Experiments:





Stability Condition:

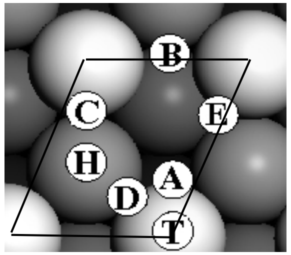
$$\frac{S_1}{\cos\theta_{311}} \cdot \gamma_{311}(T, p_O) + \frac{S_2}{\cos\theta_{110}} \cdot \gamma_{110}(T, p_O) < \gamma_{210}(T, p_O)$$

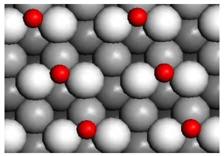
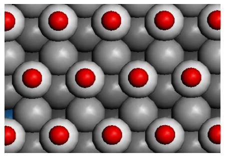
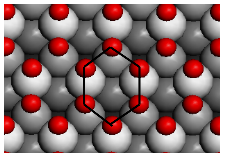
(S_i: normalized coefficients for the partial contribution to the faceted surface [S_1=0.7, S_2=0.3],
θ_i: facet tilt angles [geometrical considerations: $\theta_{311}\approx 19.29°$, $\theta_{110}\approx 18.44°$])

Oxygen Adsorption on Ir Surfaces

Ir(210)

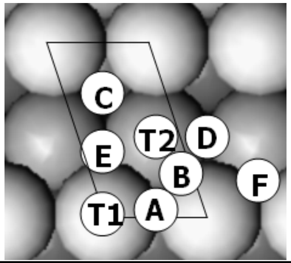
coverage [ML]	0.5	1	2
favorable site	B	T	C+A
E_{bind} [eV/O]	-2.10	-1.78	-1.00

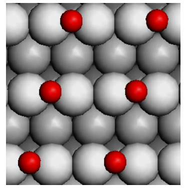
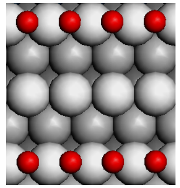
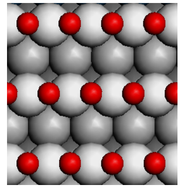


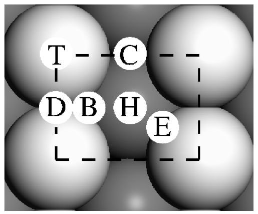
Ir(311)

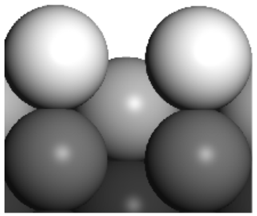
coverage [ML]	0.5	0.5	1
favorable site	A	A	A
E_{bind} [eV/O]	-2.15	-1.70	-1.71



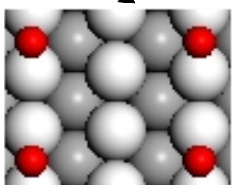
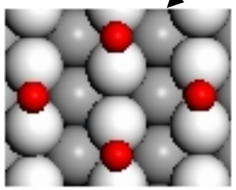
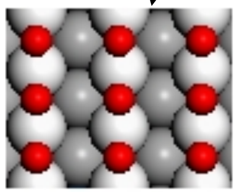




Ir(110)-regular



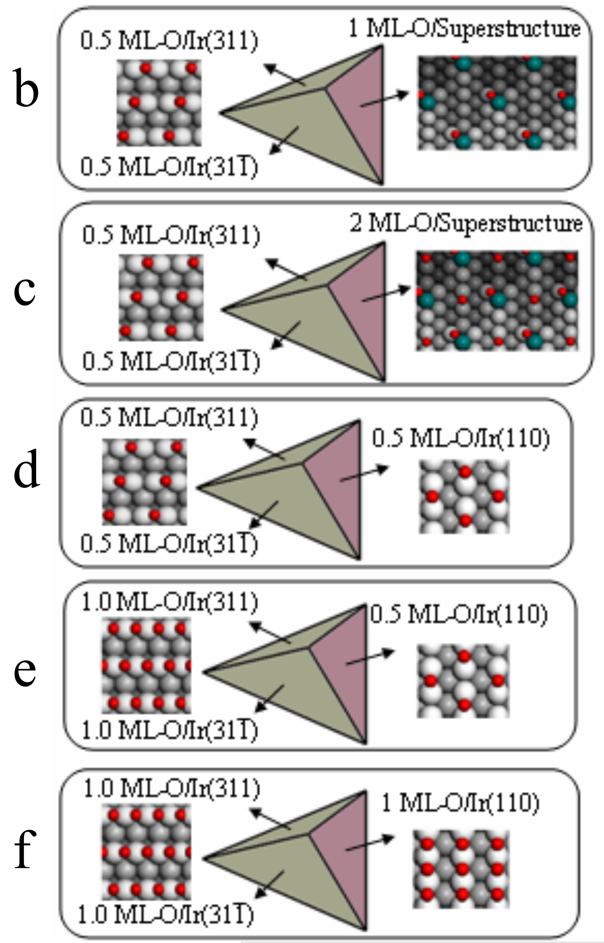


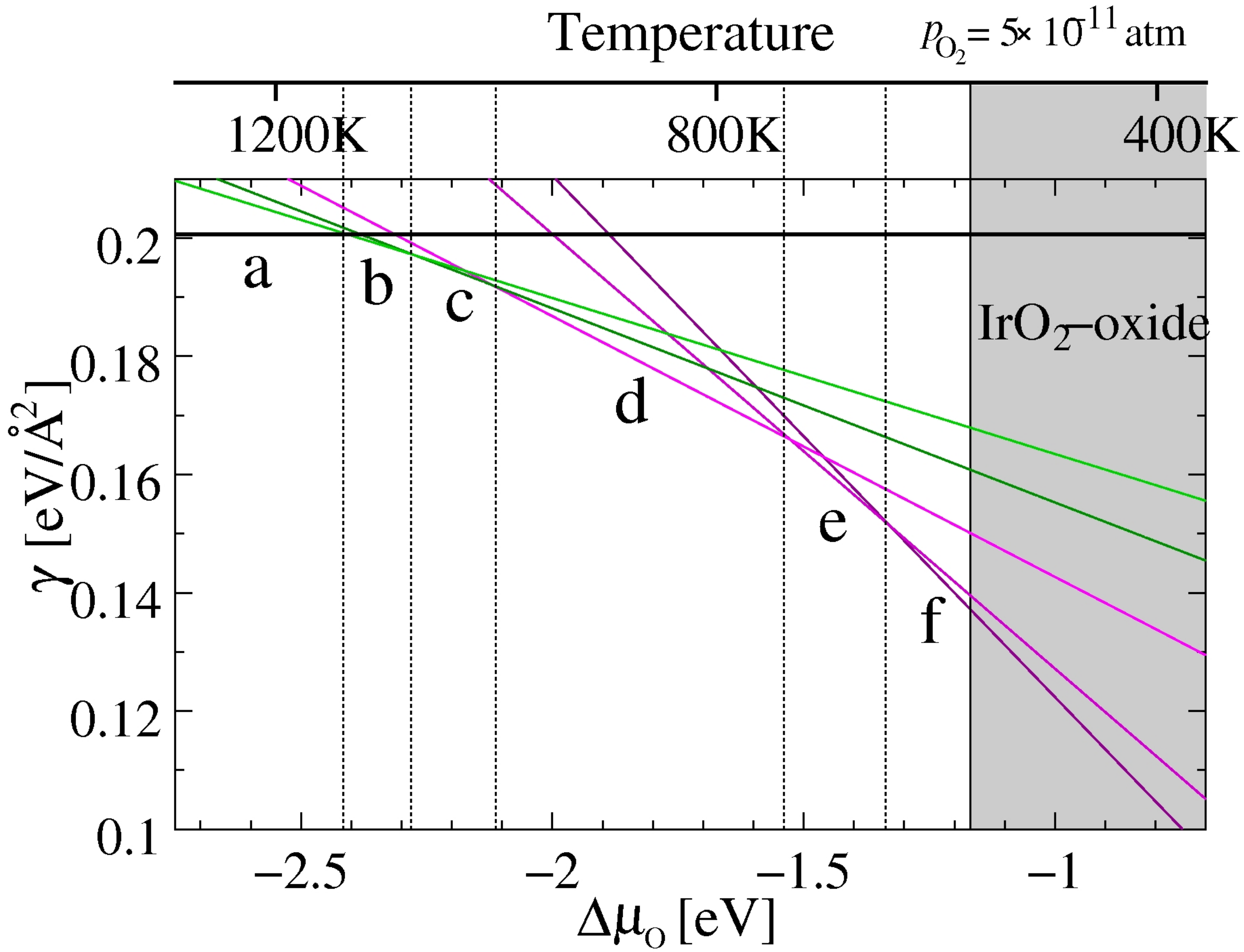
coverage [ML]	0.25	0.5	1
site	D	D	D
E_{bind} [eV/O]	-2.10	-1.78	-1.00

(p,T)-surface phase diagram

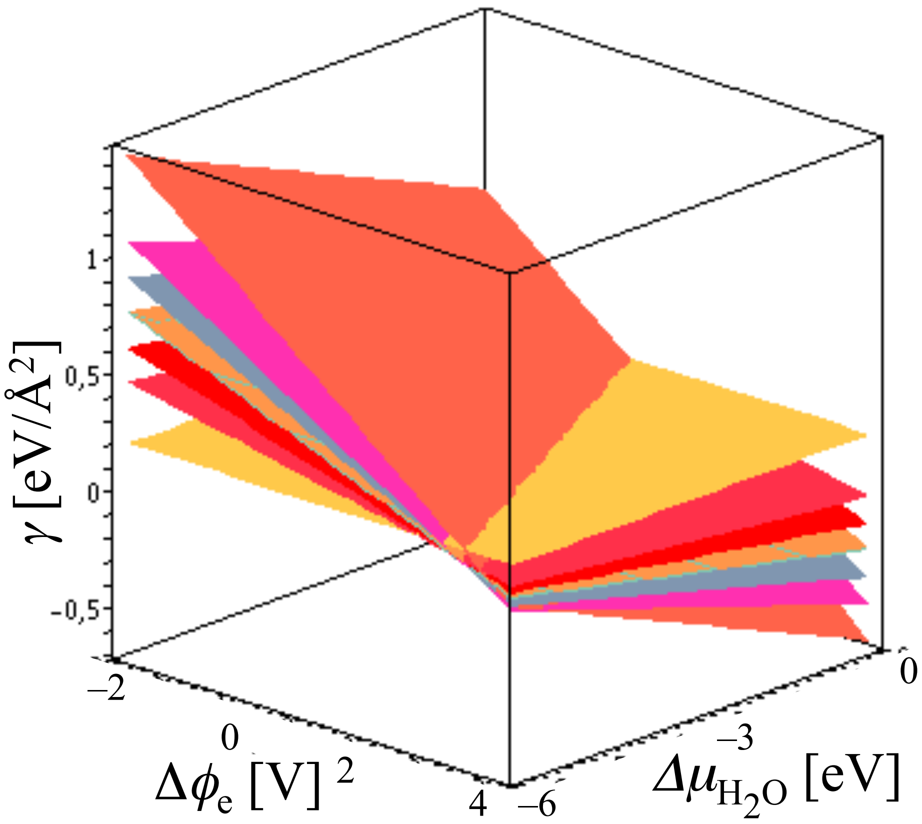
a planar Ir(210)

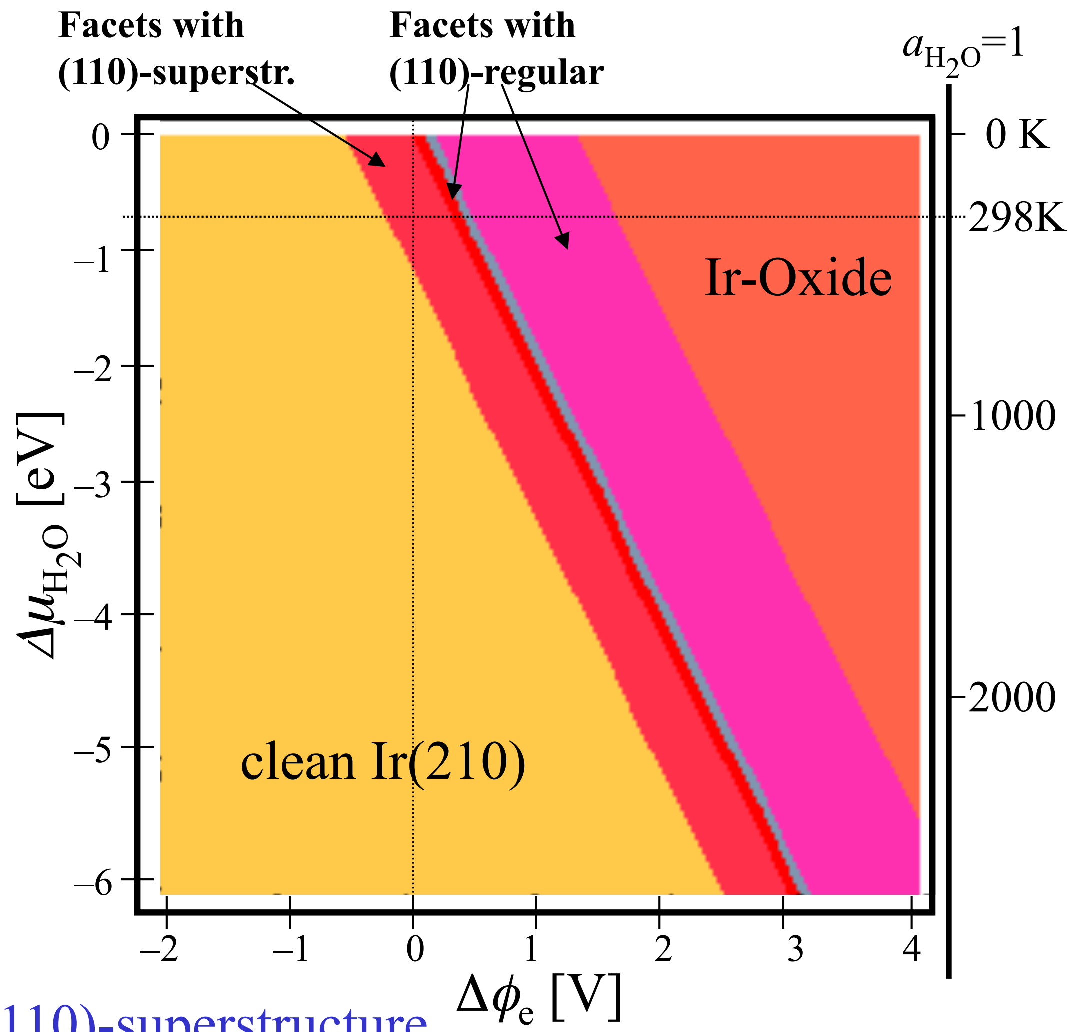




P. Kaghazchi, W. Chen, H. Wang, I. Ermanoski, T. E. Madey, TJ, *ACS Nano*, **2**, 1280 (2008)

Ir/O $(a,T,\Delta\phi_e)$ — Phase Diagram





- $\Delta\phi_e \leq -0.3$V: clean Ir(210)
- $-\,0.3$V $< \Delta\phi_e \leq 0.9$V: Facets with Ir(110)-superstructure
- $\Delta\phi_e < 0.95$V: Facets with Ir(110)-regular

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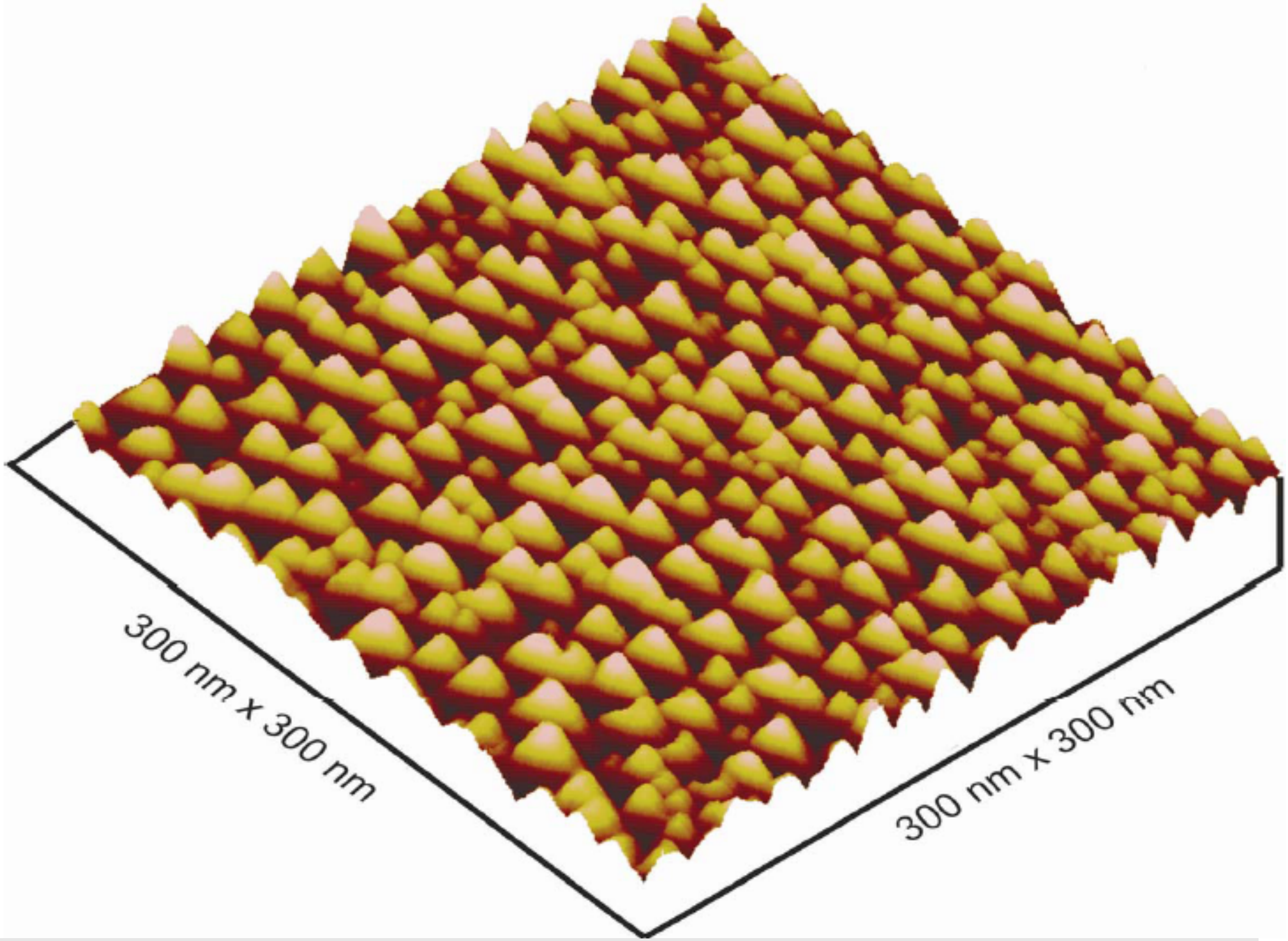
Faceted Ir(210) in 0.1M H_2SO_4



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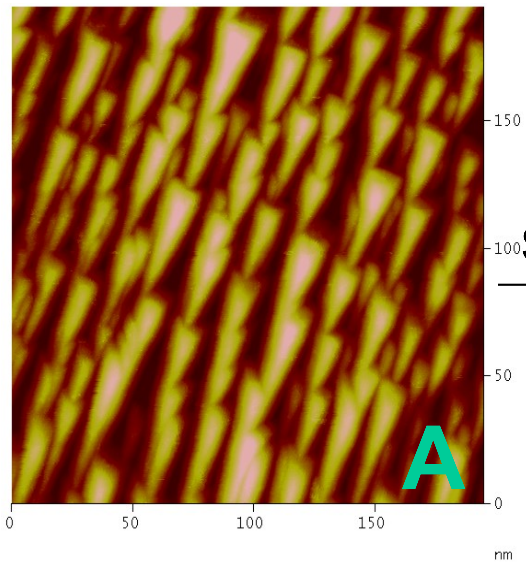
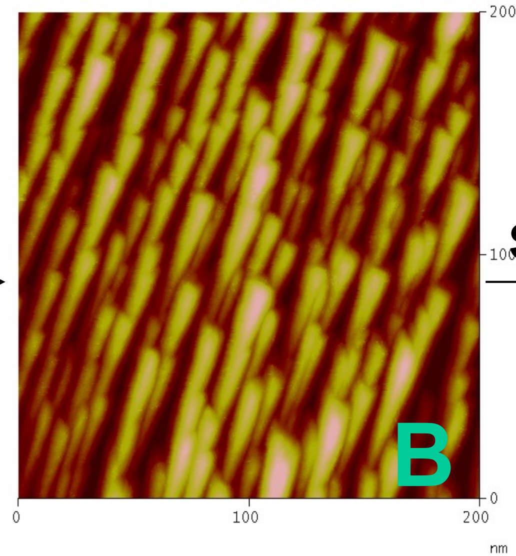
Structure Stability in $HClO_4$

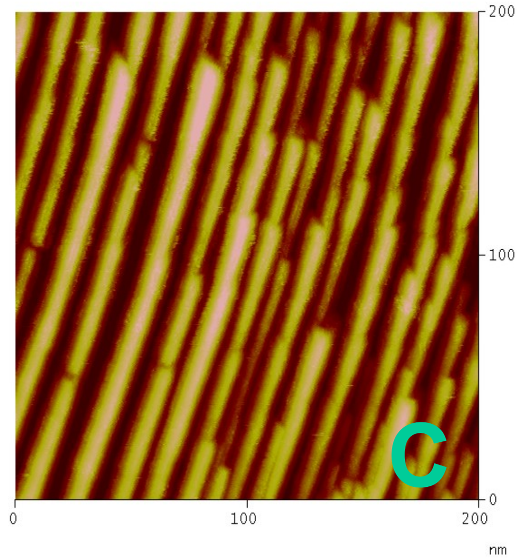
0.2 V



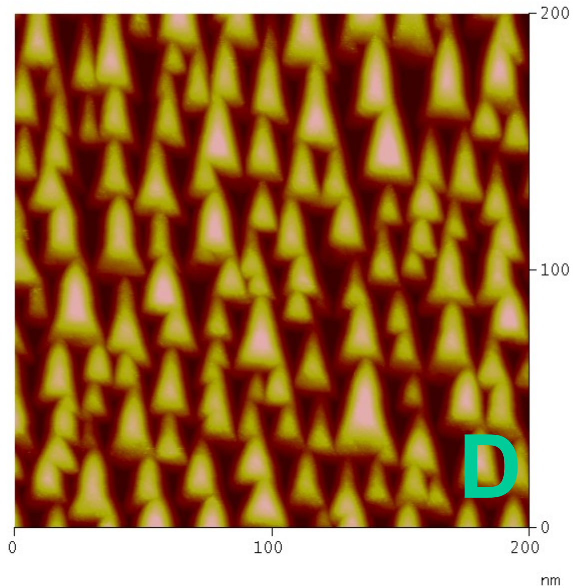
sec. →



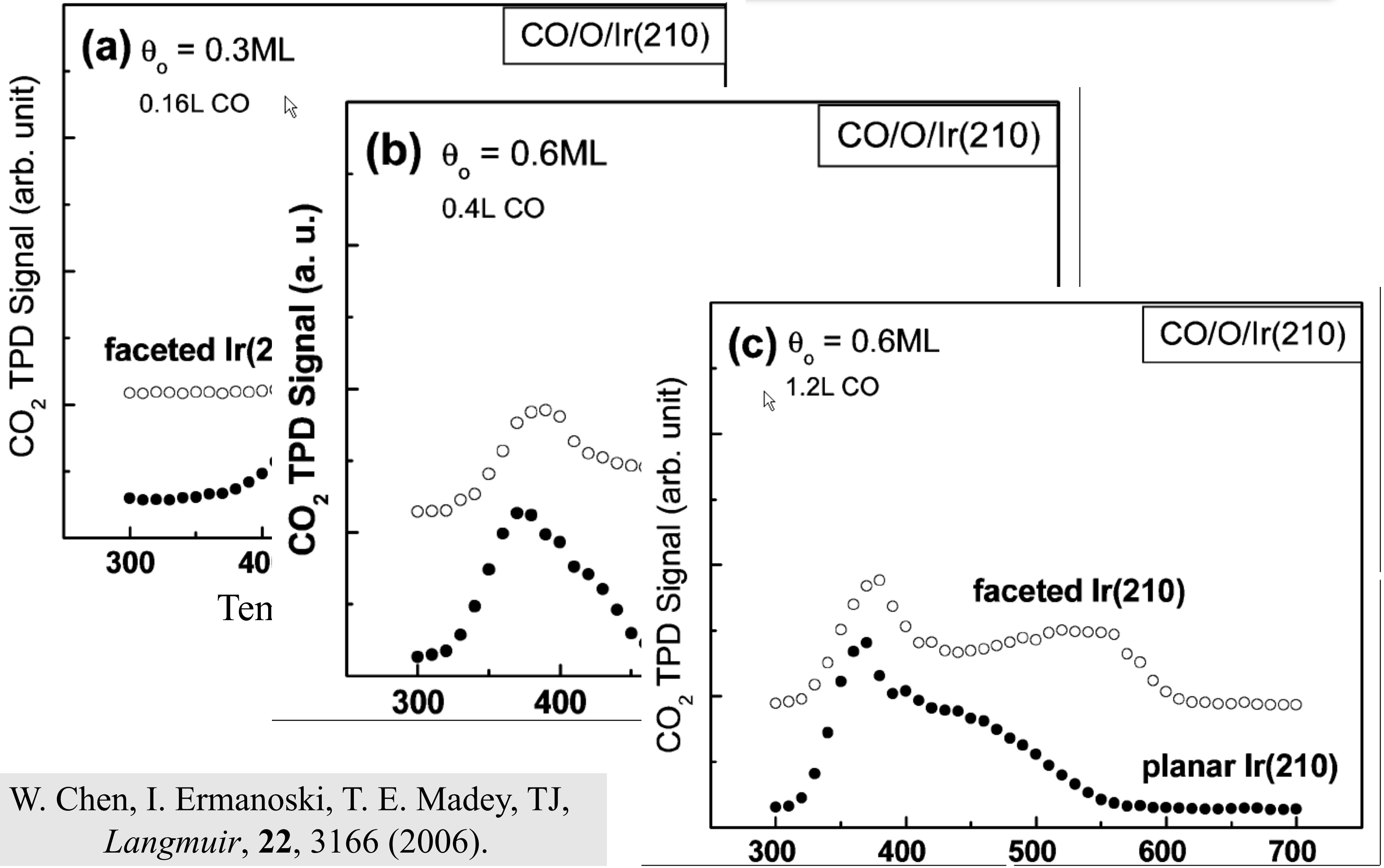
sec. →



by cycling

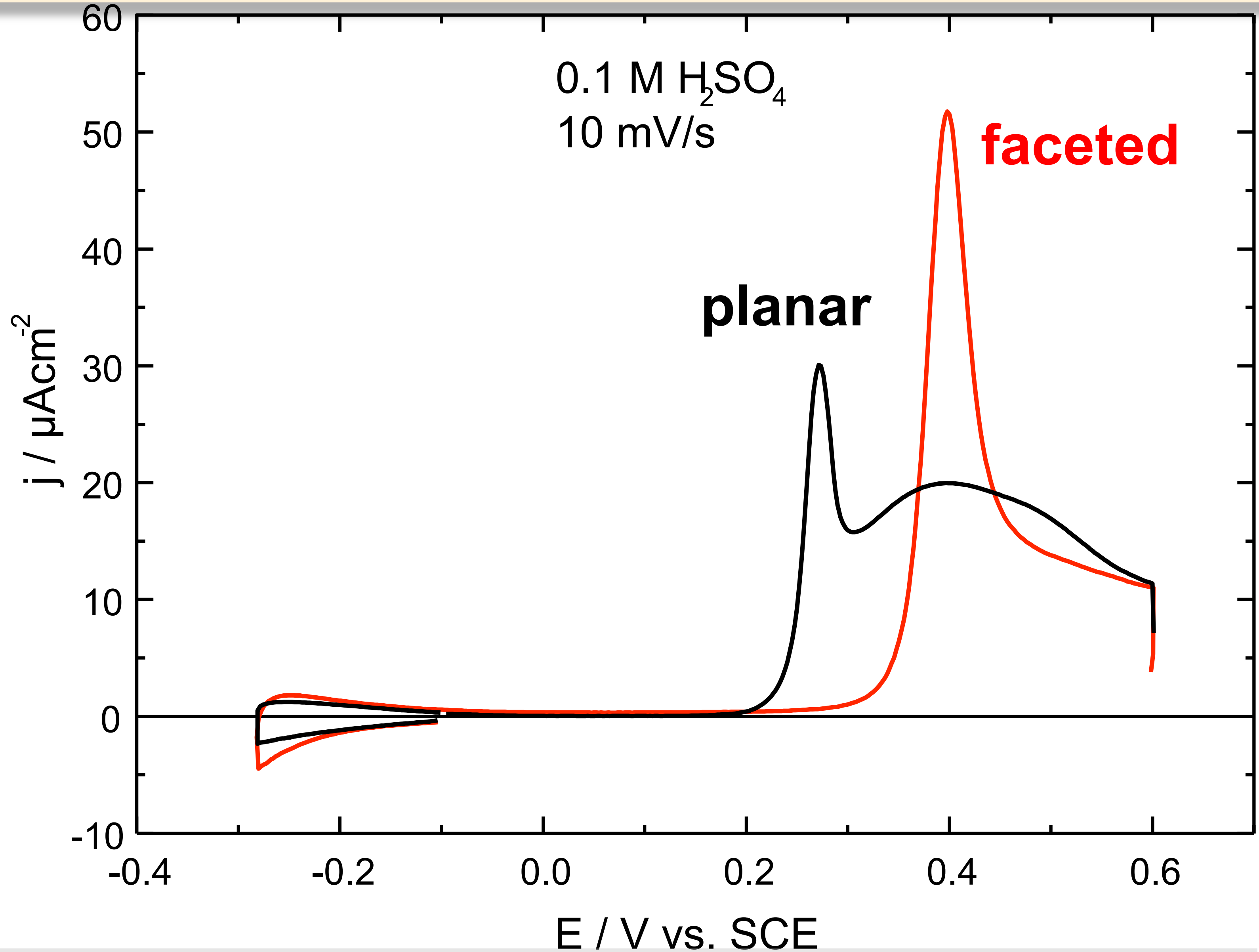


CO oxidation (UHV)



W. Chen, I. Ermanoski, T. E. Madey, TJ, *Langmuir*, **22**, 3166 (2006).

CO adlayer oxidation (electrochemical)



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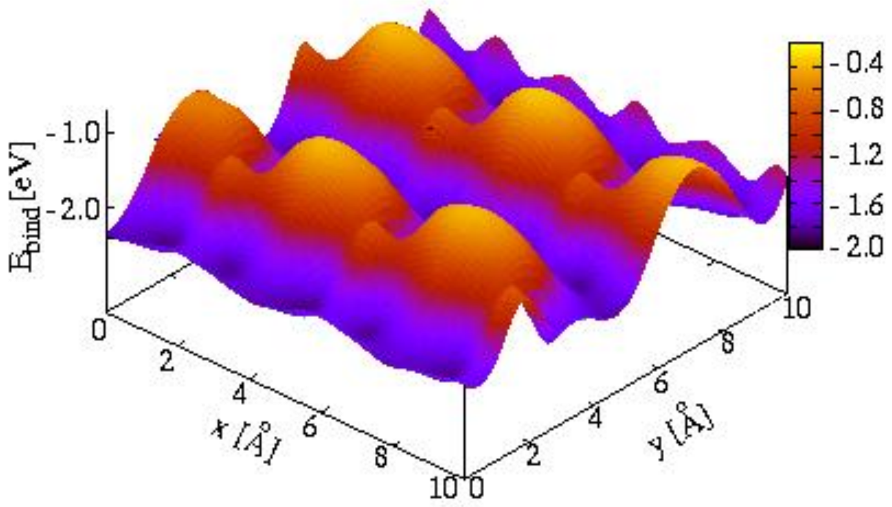
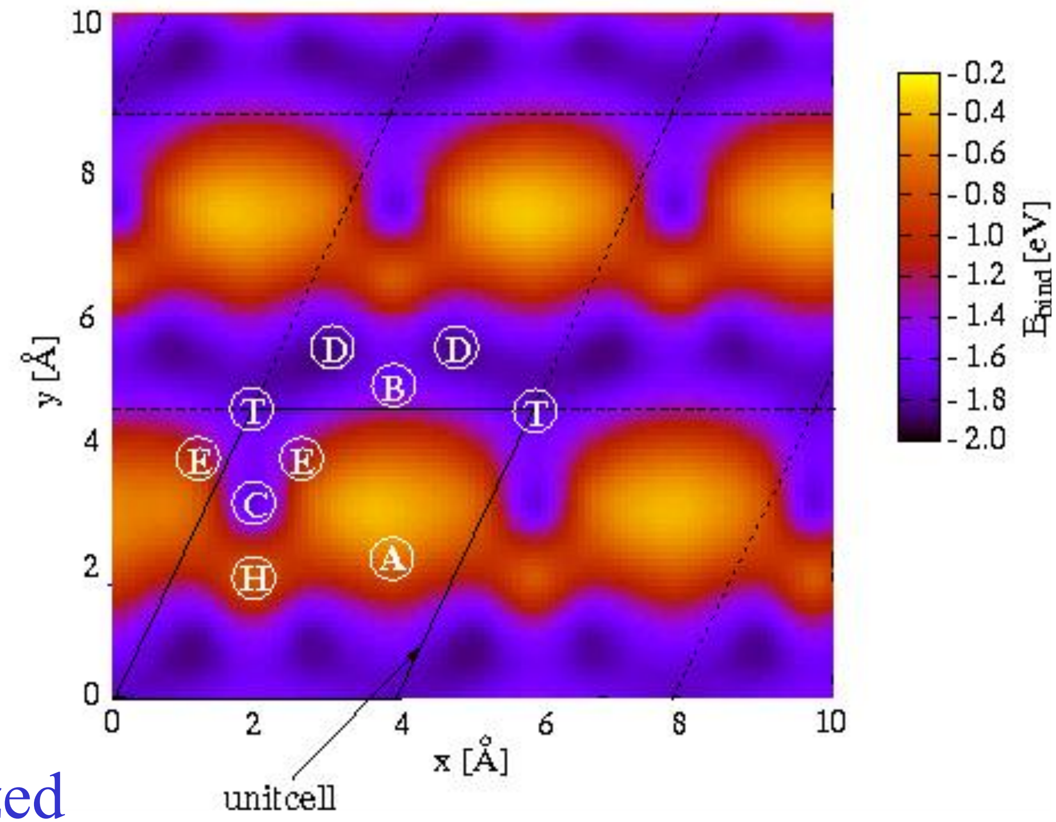
Oxygen on Ir(210) – 1ML

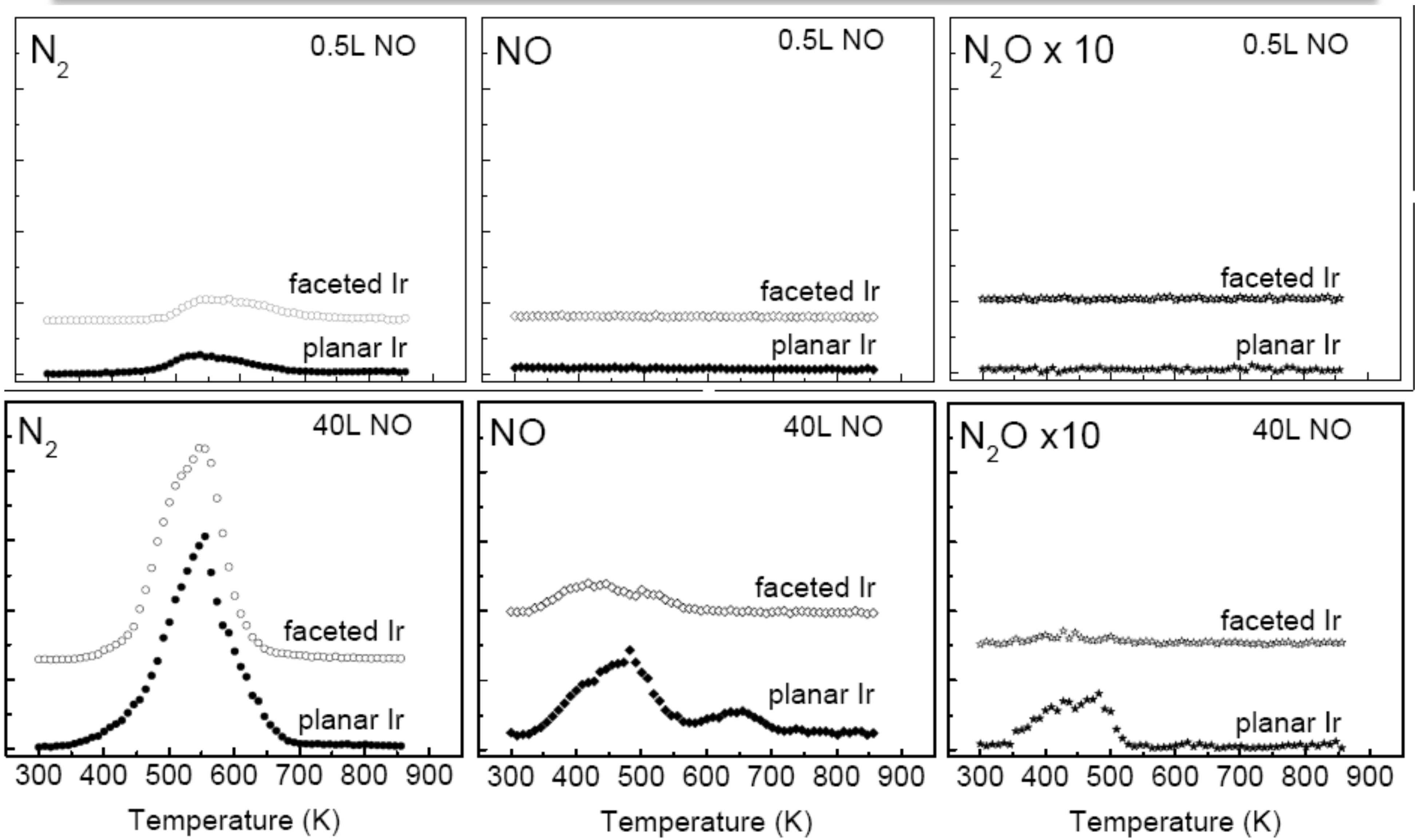




- Adsorption at C-site more localized
- Similar binding energies at T, D, C, B (±0.05 eV)
  → 1-D diffusion …T—D—B—D—T…
- Vibration frequencies: T≈1210 cm^{-1}
  C≈804 cm^{-1}

W. Chen, I. Ermanoski, T. E. Madey, T. Jacob, *Langmuir*, **22**, 3166 (2006).

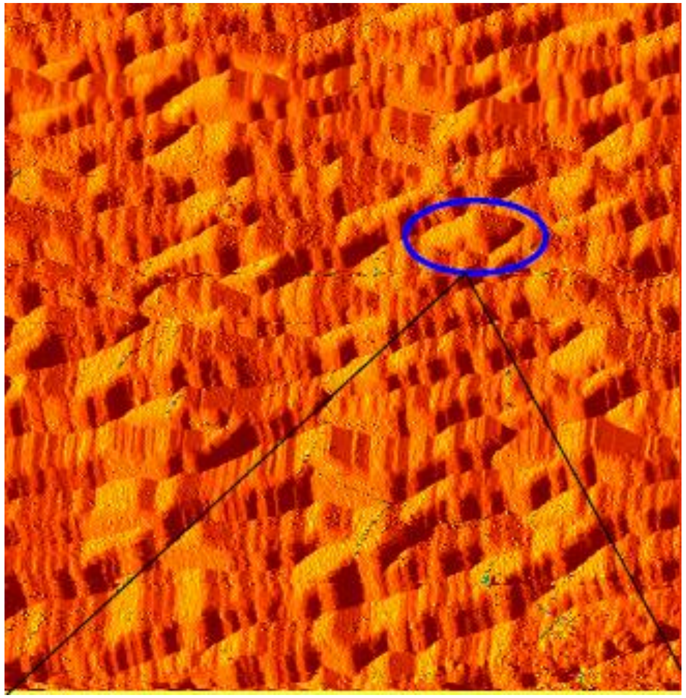
NO decomposition (UHV)

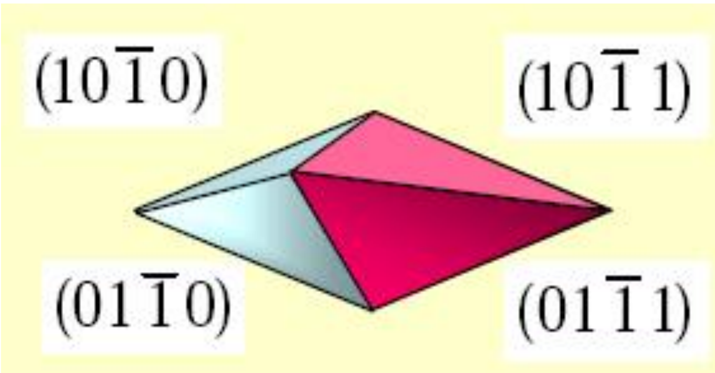


W. Chen, T. E. Madey, A. L. Stottlemyer, J. G. Chen, P. Kaghazchi, TJ, JPC-C, 112, 19113 (2008)

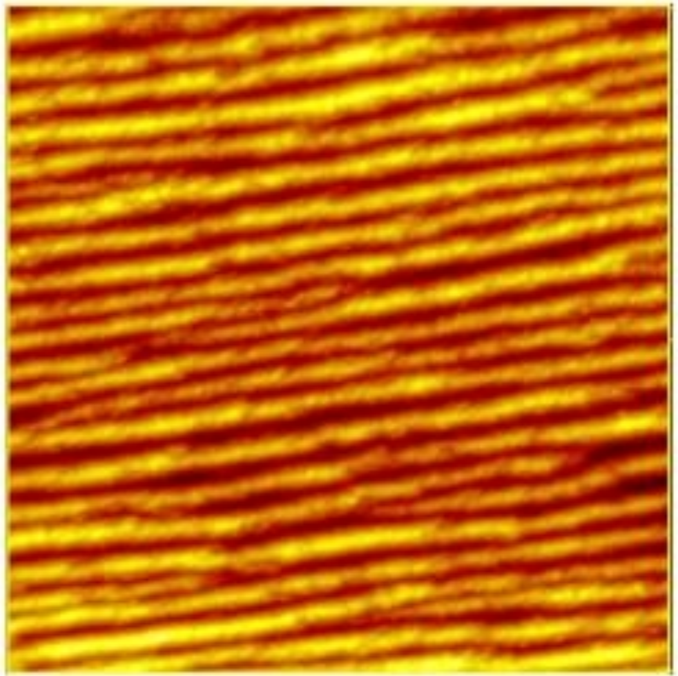
Re(11-21)-faceting

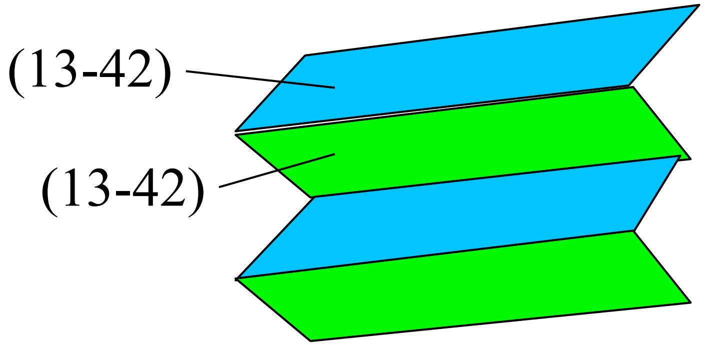
O-induced
x-slope STM image, 1000Å×1000Å



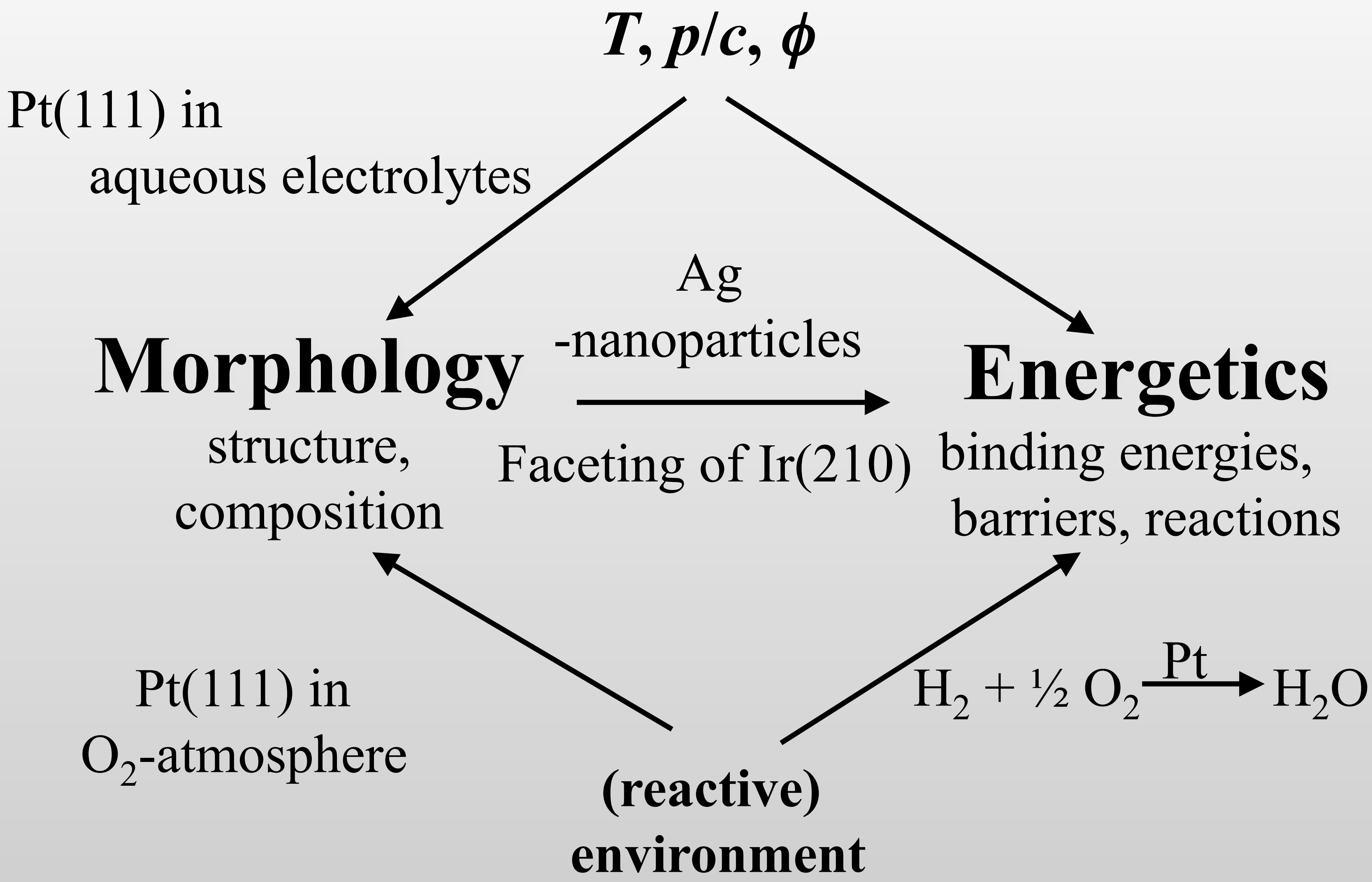


N-induced
STM image, 1000Å×1000Å





Summary



$T, p/c, \phi$
Pt(111) in aqueous electrolytes
Morphology
structure, composition
Ag -nanoparticles
Faceting of Ir(210)
Energetics
binding energies, barriers, reactions
Pt(111) in O_2-atmosphere
(reactive) environment
$H_2 + ½ O_2 \xrightarrow{Pt} H_2O$

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- Europäische Union (FP7)
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- Studienstiftung des dt. Volkes
- European Research Council (ERC)

AvH FCI FCI

DAAD

Bundesministerium für Bildung und Forschung

Emmy Noether-Programm
Deutsche Forschungsgemeinschaft DFG

erc

Studienstiftung des deutschen Volkes