Modellierung elektrochemischer Systeme – Von den Grundlagen zu Batterien

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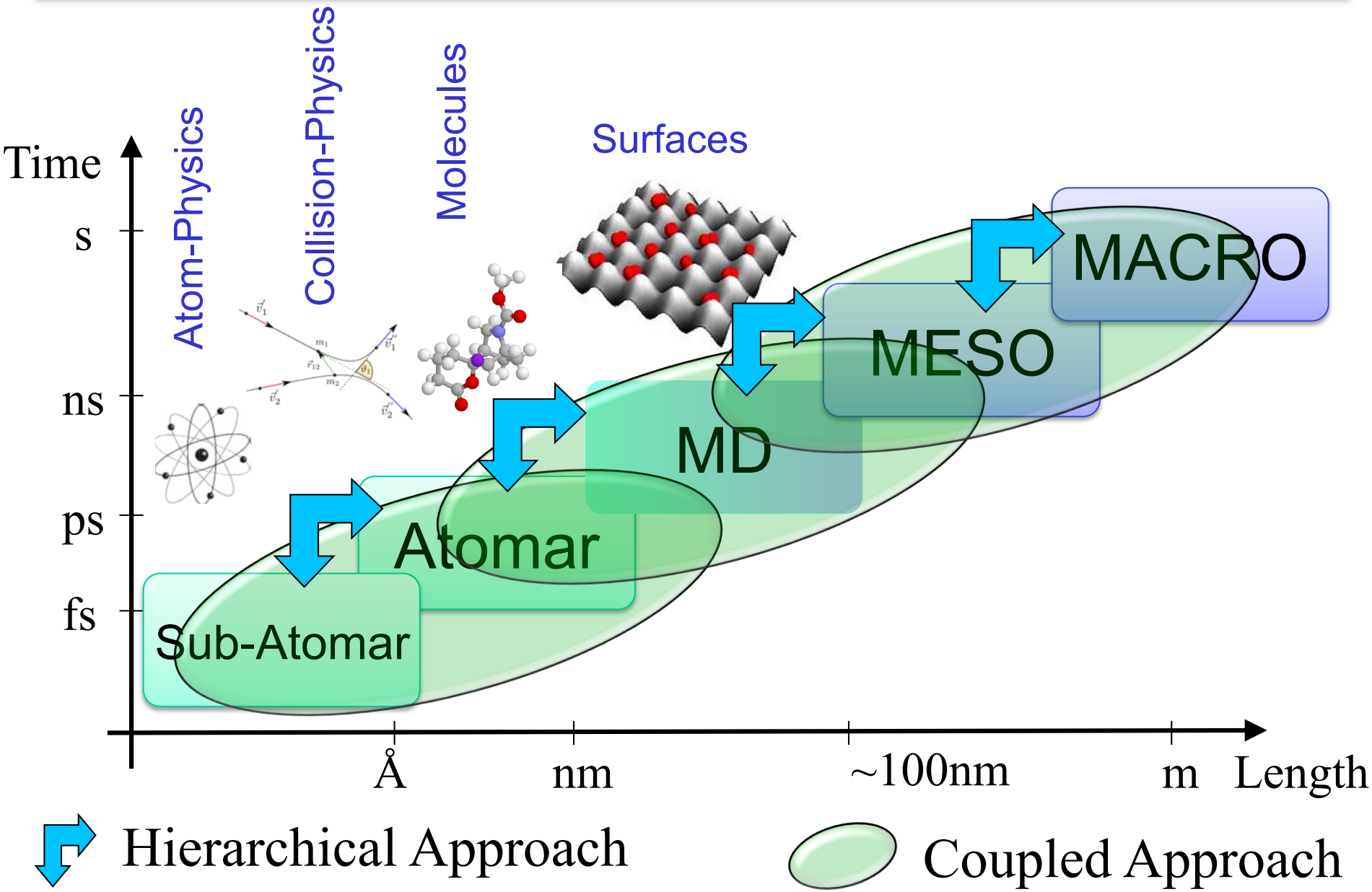
Helmholtz Institute Ulm
Electrochemical Energy Storage

Hierarchy of Modeling



Relativity → Batteries

PRL 106, 018301 (2011) PHYSICAL REVIEW LETTERS week ending 7 JANUARY 2011

Relativity and the Lead-Acid Battery

Rajeev Ahuja,[1,*] Andreas Blomqvist,[1] Peter Larsson,[1] Pekka Pyykkö,[2,†] and Patryk Zaleski-Ejgierd[2,‡]

[1]*Division of Materials Theory, Department of Physics and Astronomy, Uppsala University, Box 516, SE-751 20, Uppsala, Sweden*
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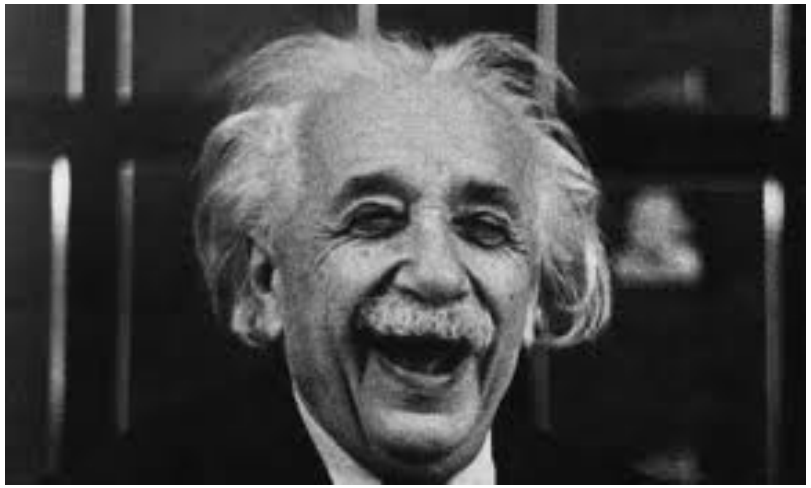
In conclusion, the lead-acid battery belongs to those phenomena whose characteristic features are due to the relativistic dynamics of fast electrons when they move near a heavy nucleus. In this case the main actors are the 6*s* electrons of lead, in the substances involved. This insight may not help one to improve the lead battery, but it might be useful in exploring alternatives. Finally, we note that cars start due to relativity.

Motivation



Ulm-Münster

$\longrightarrow$ **Relativity**

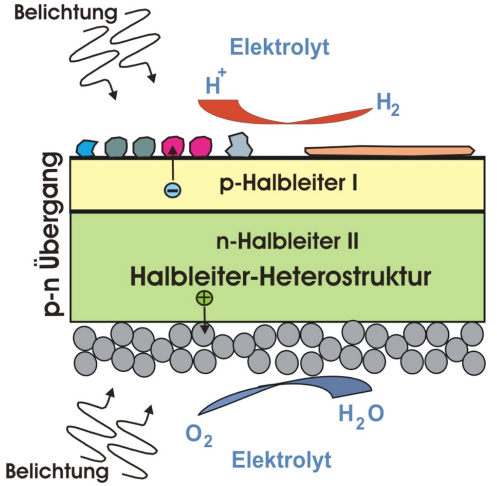
Overview

Applications

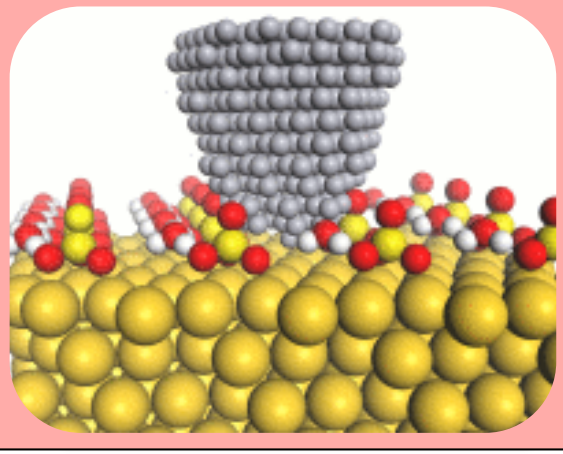
Fuel Cells

Li-Ion Batteries

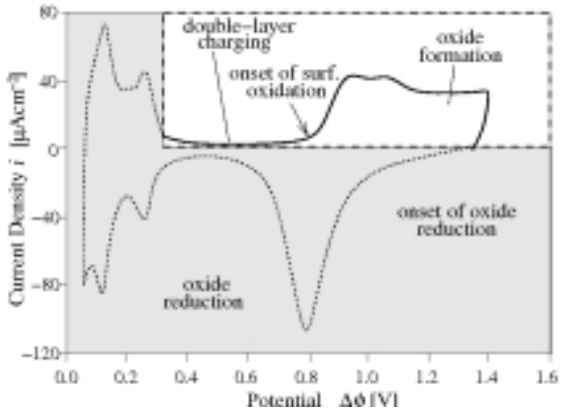
Photo-Electrocatalysis

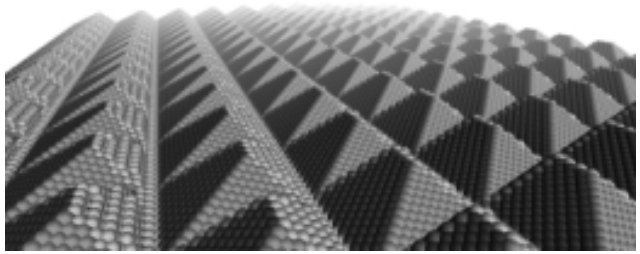


Fundamental Electrochemistry



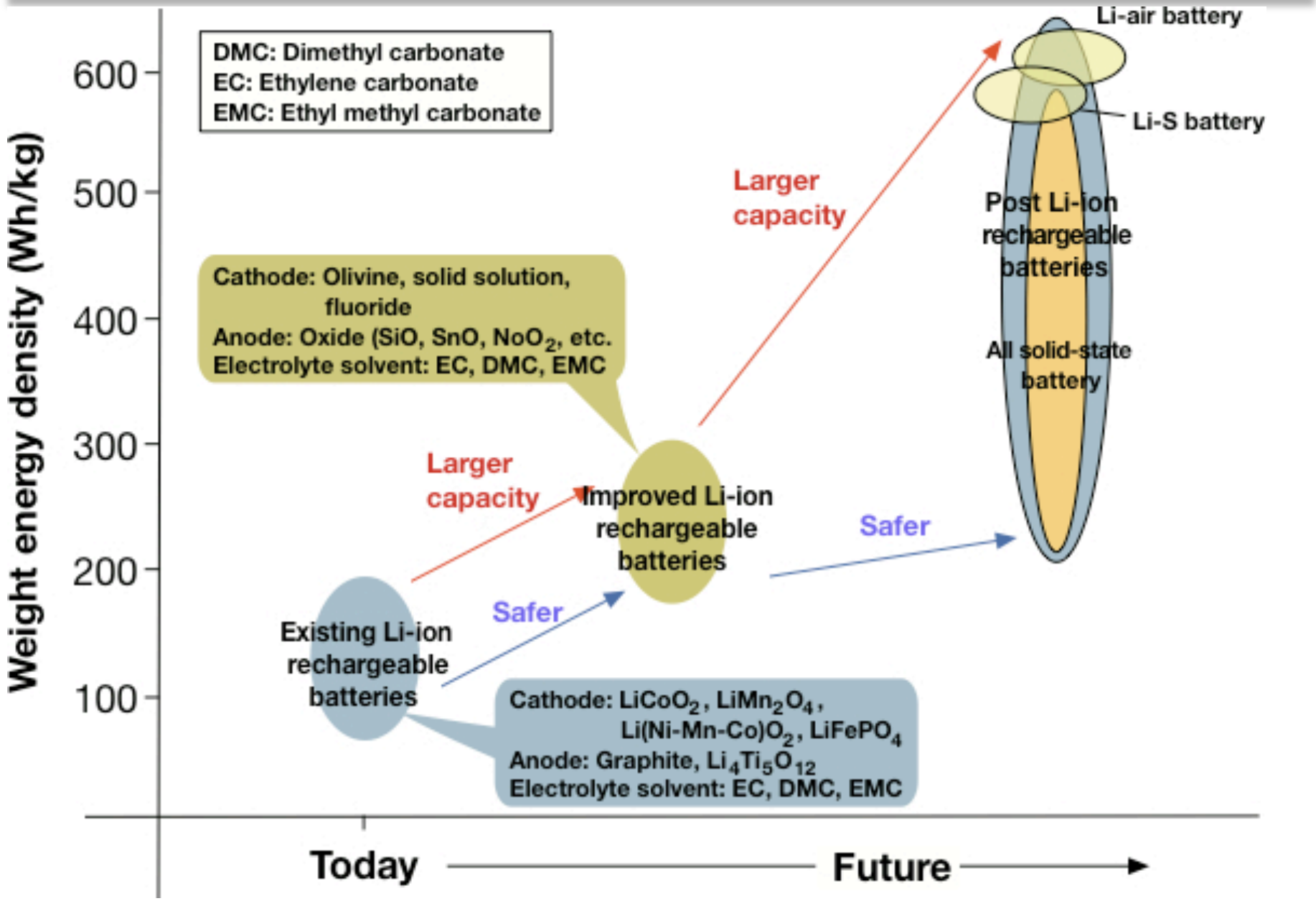
(Electro-)Catalysis





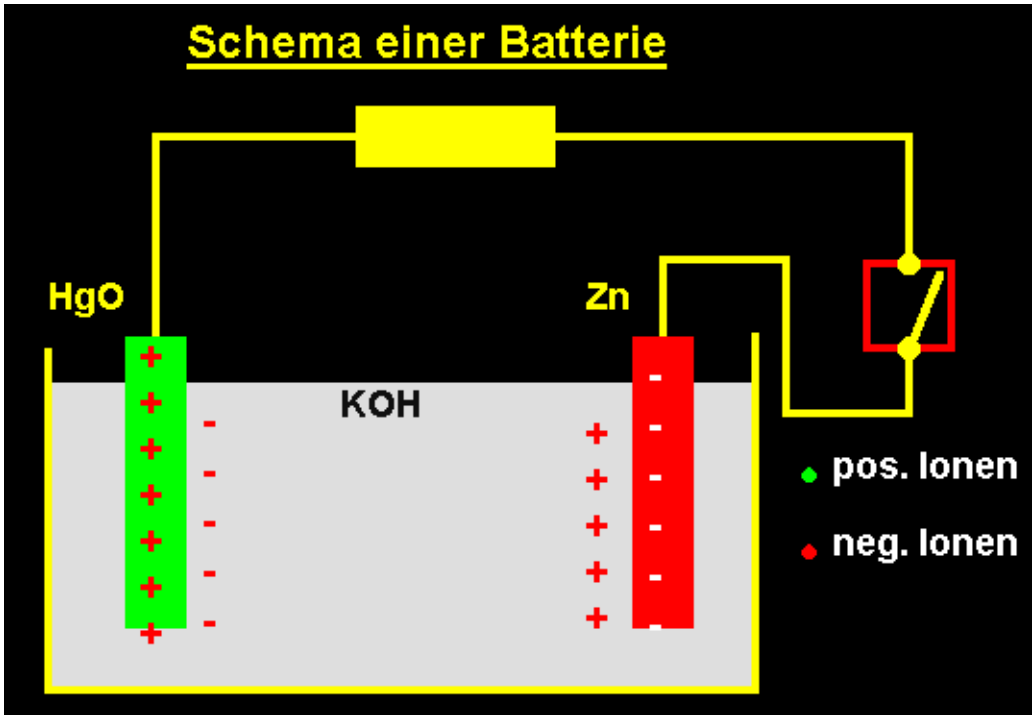
Methods

Battery-Types

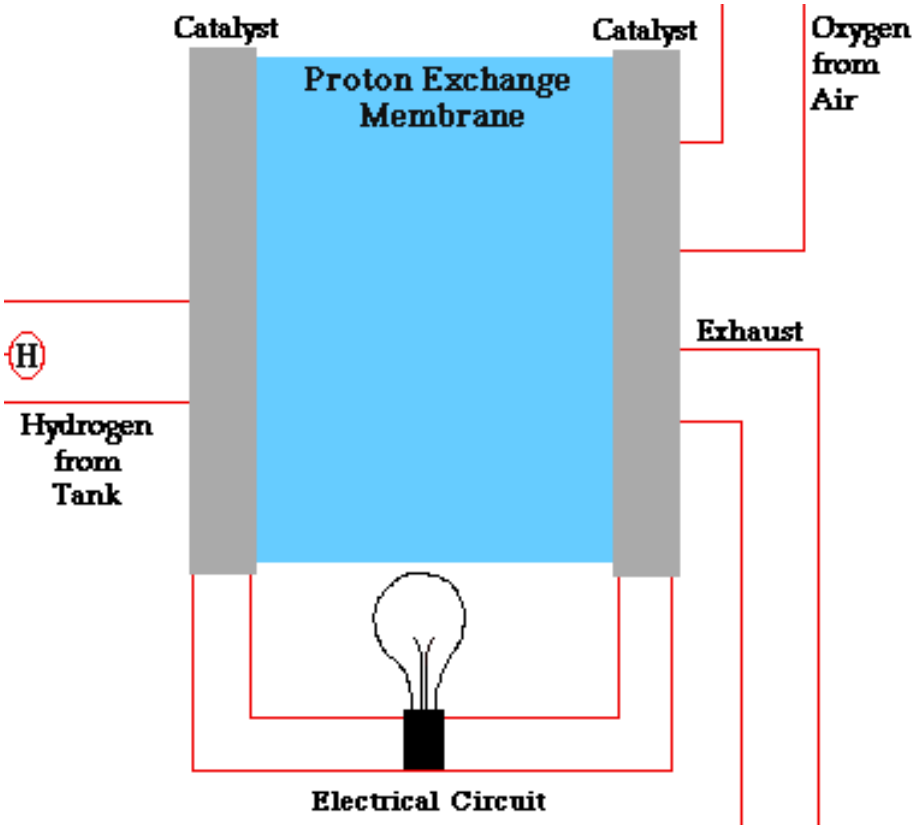


Motivation

Battery

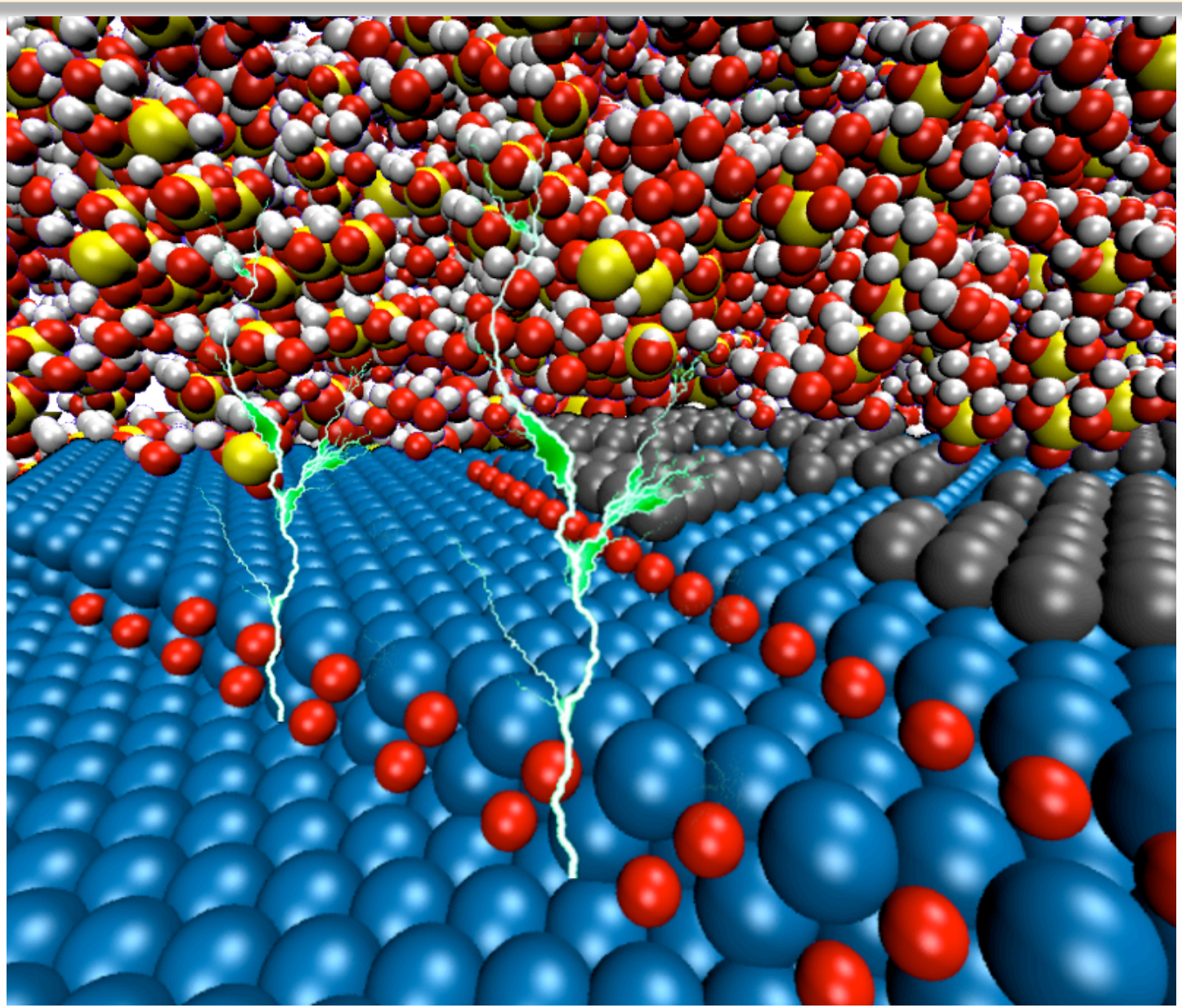


Fuel Cell

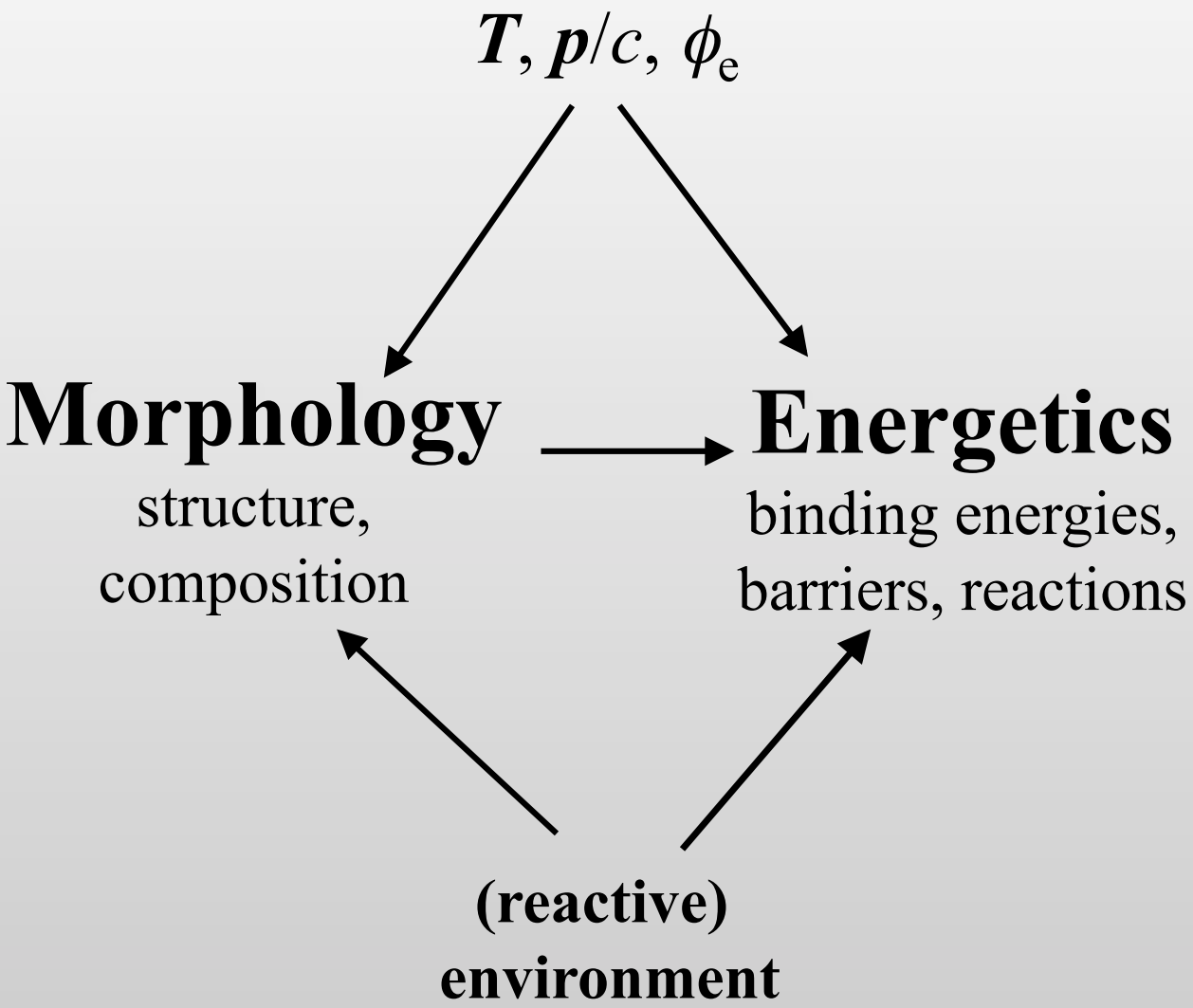


→ **Similar working principles**
(e.g. solid/liquid or solid/solid interfaces)

Electrochemistry

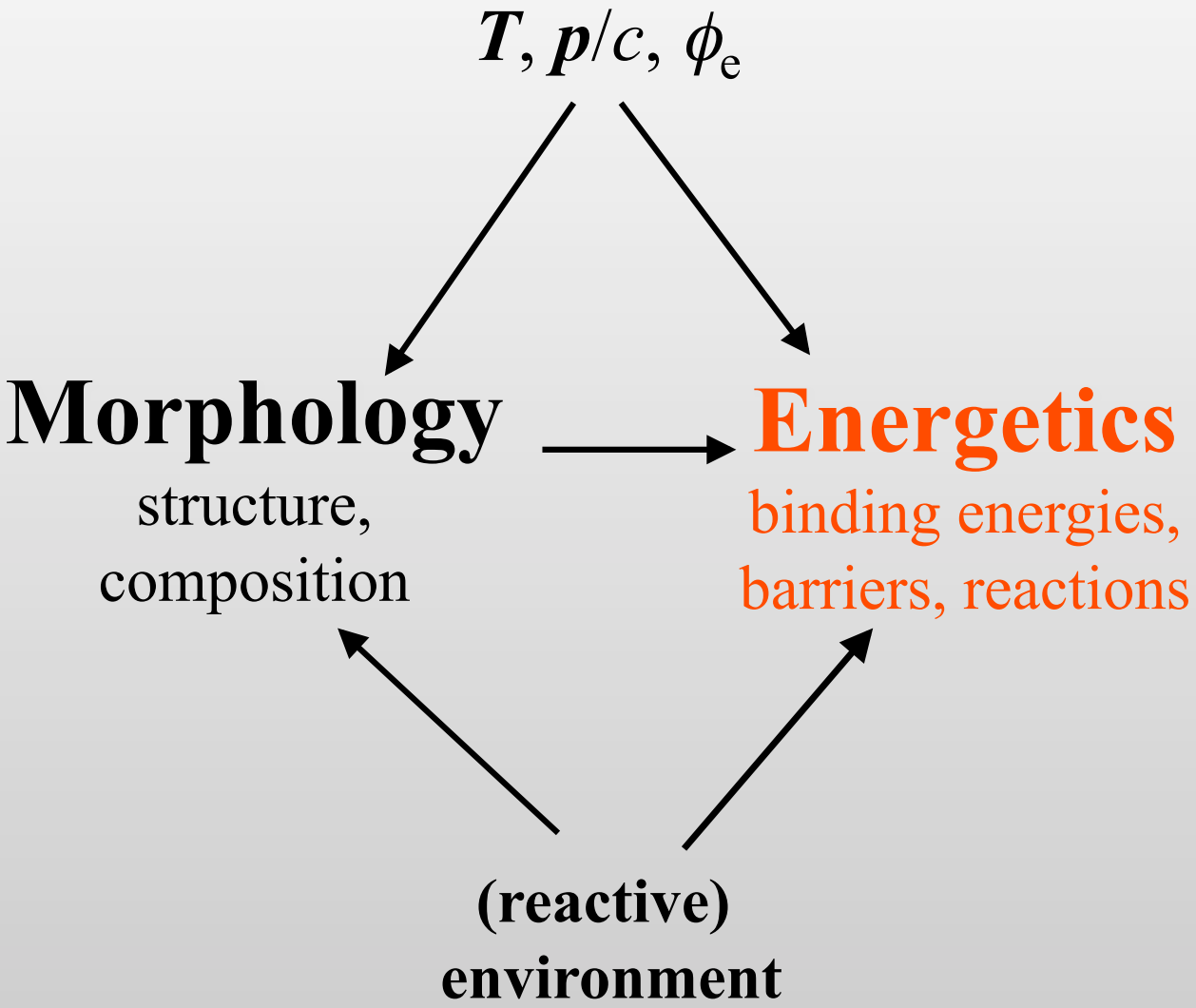


Multiple Effects in Electrochemistry



Cathode Reaction on pure Pt(111)

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



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

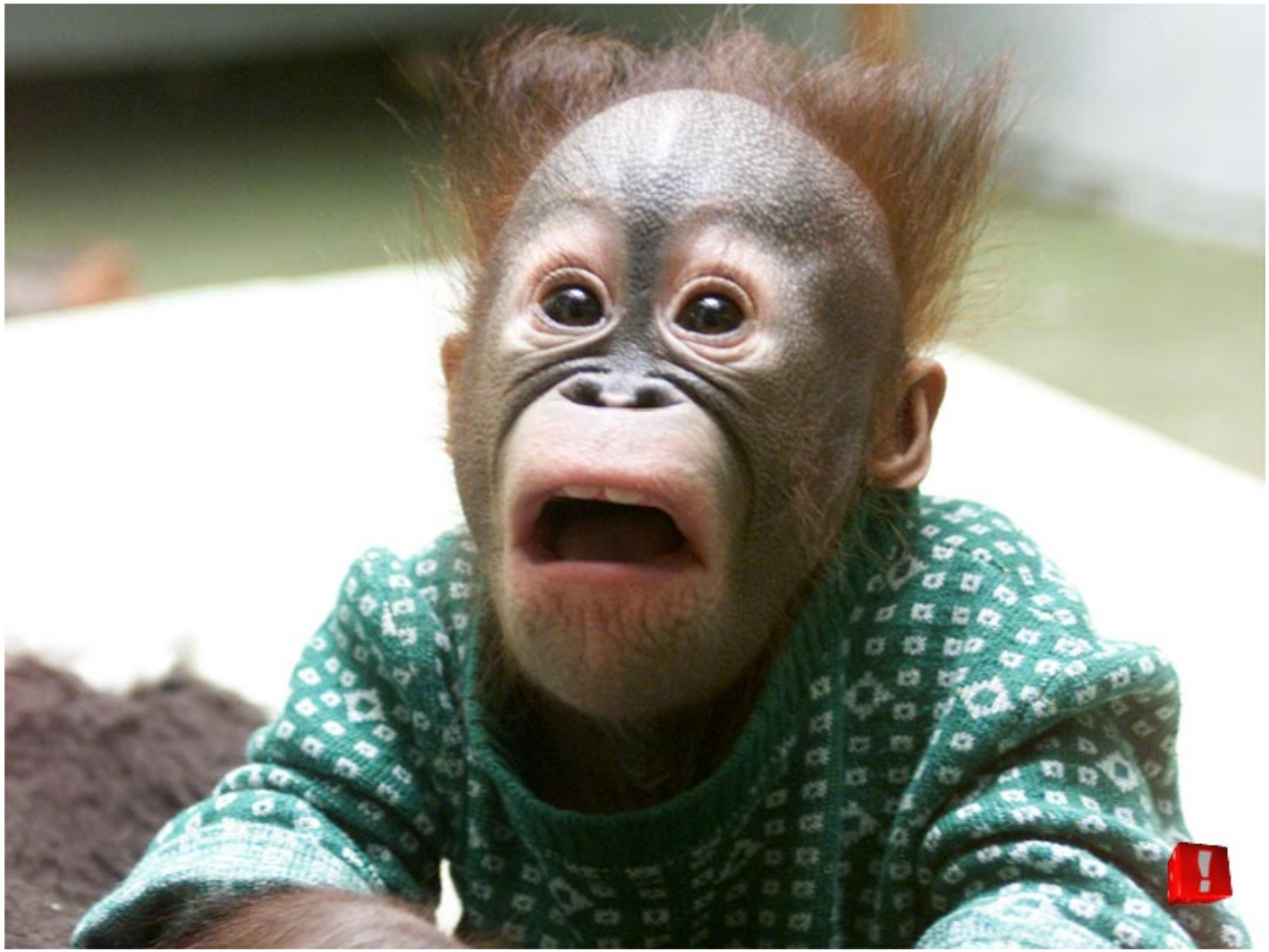
A. Damjanovic and V. Brusic,
***Electrochim. Acta* 1967, 12, 615**

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

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

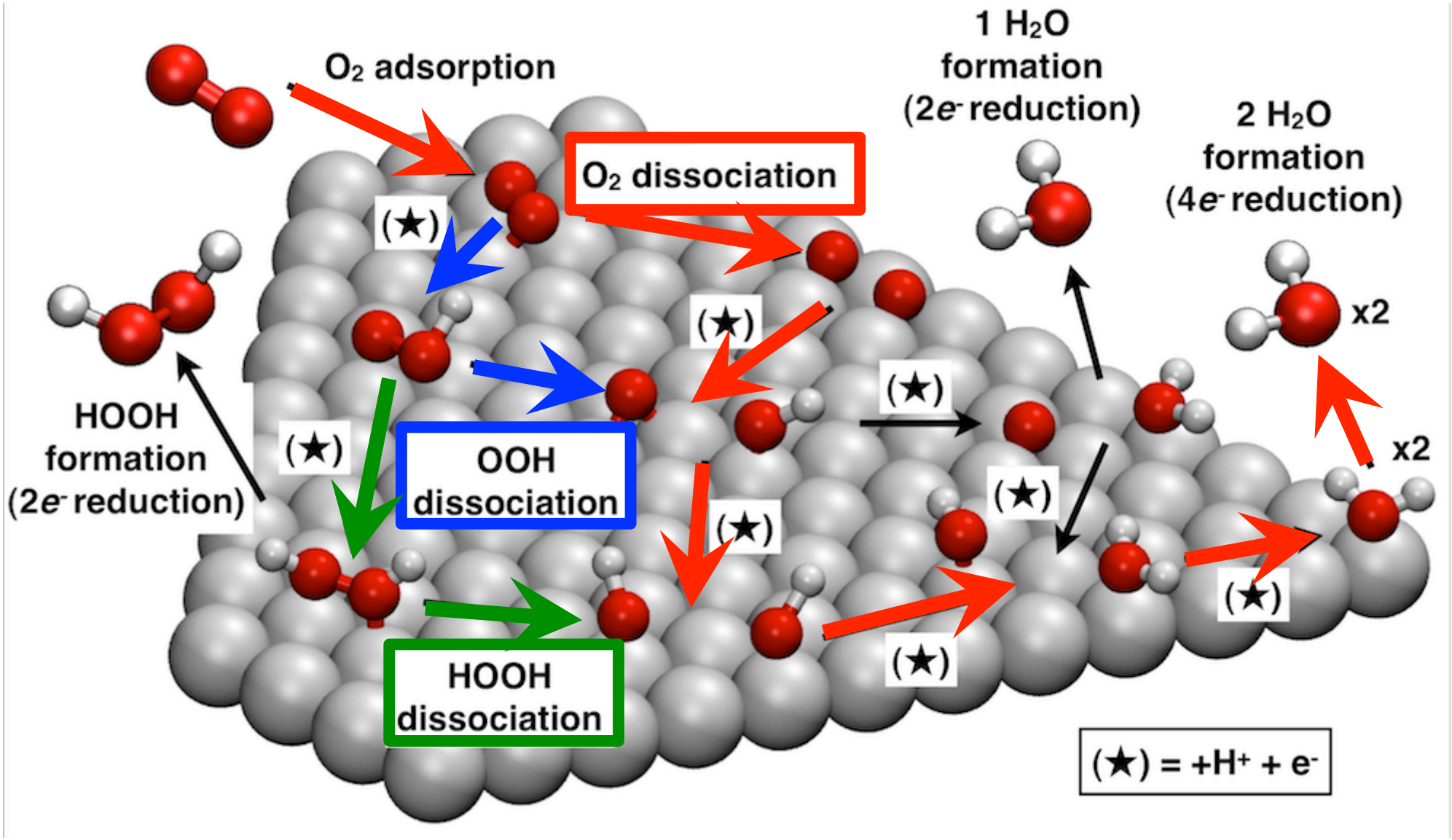
How does the ORR work?

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

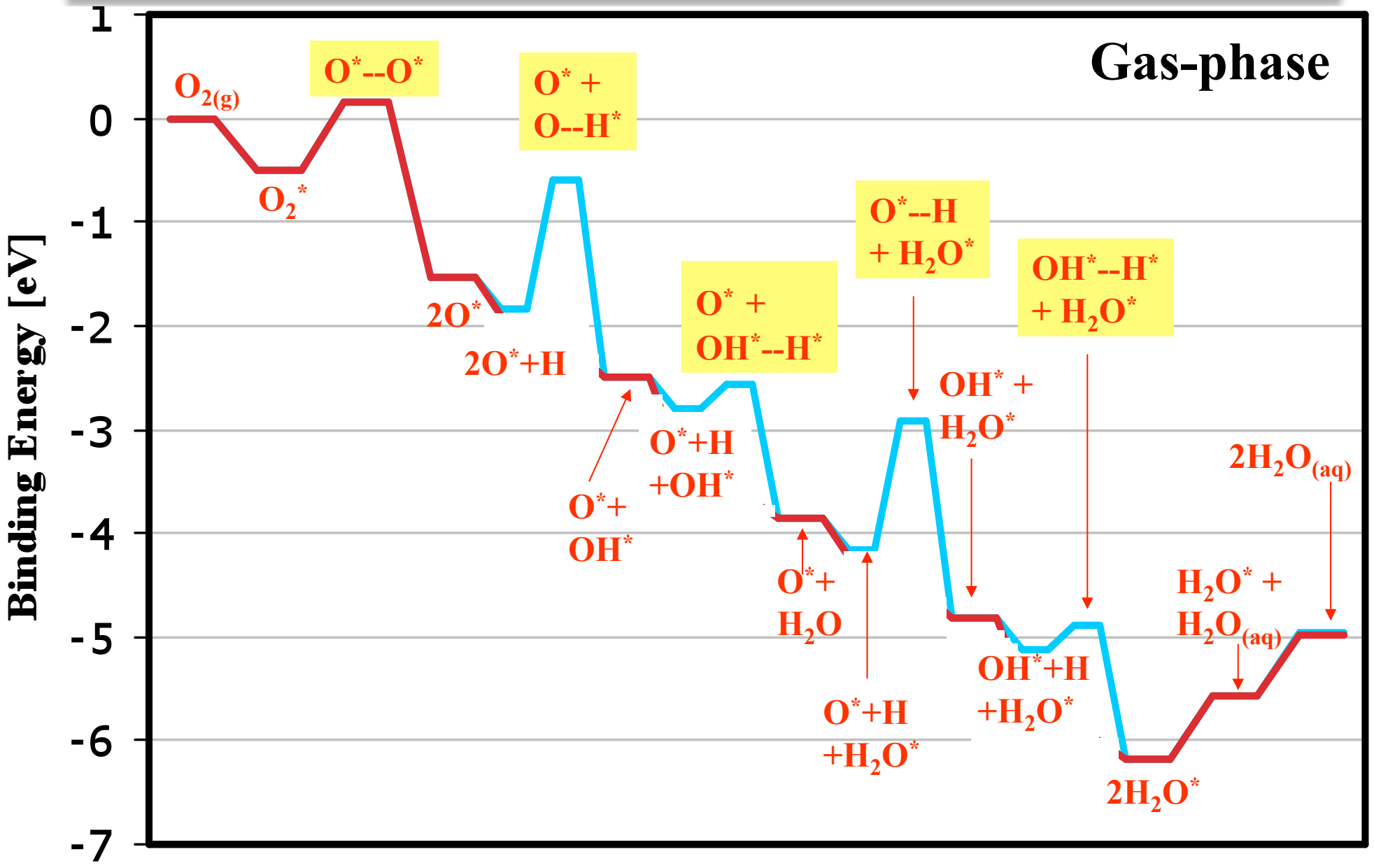


Considered pathways

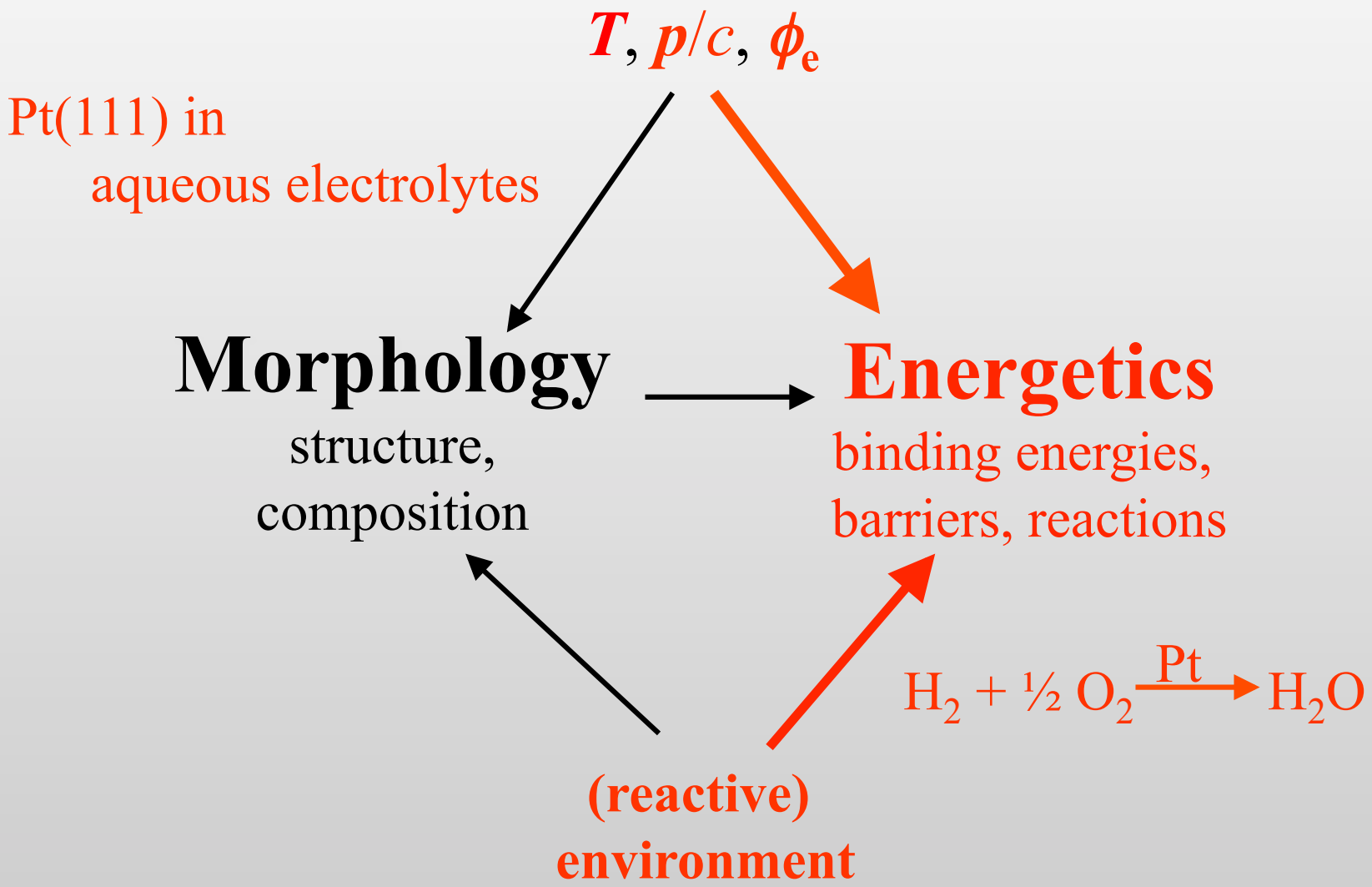
Determine the actual ORR mechanism dependent on *T*, *p*, *U*, and *pH*



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

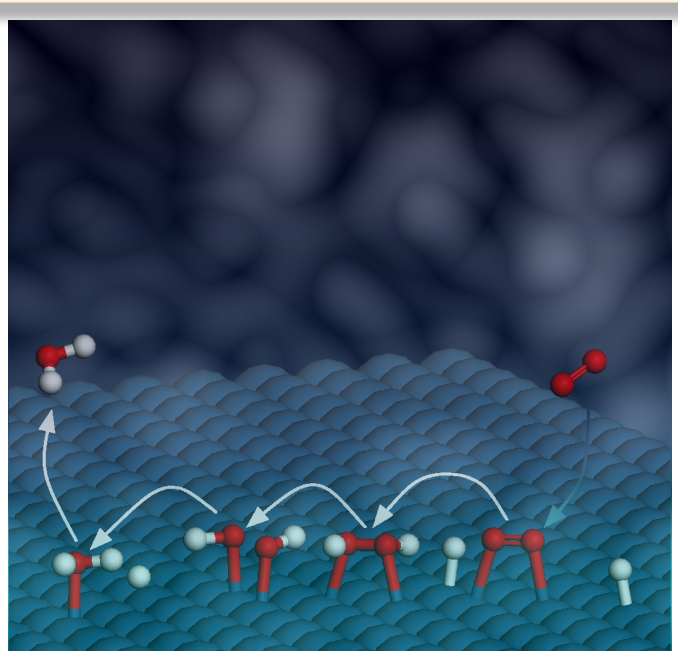


Influence of Environment on the ORR



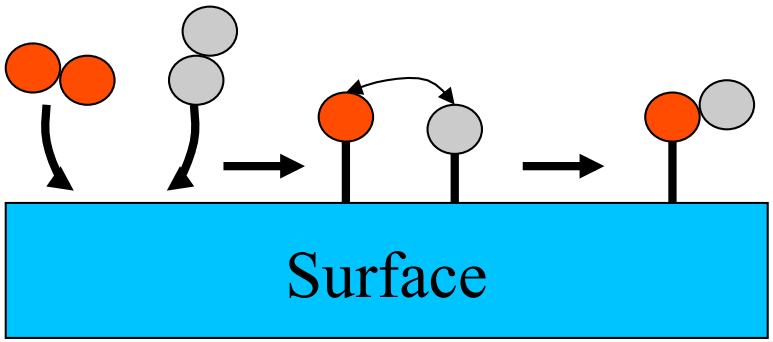
Influence of Environment

Water-Solvent:

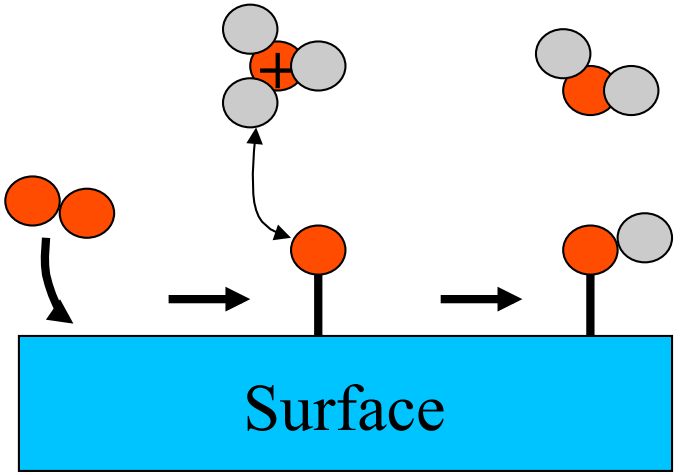


Reaction Mechanism:

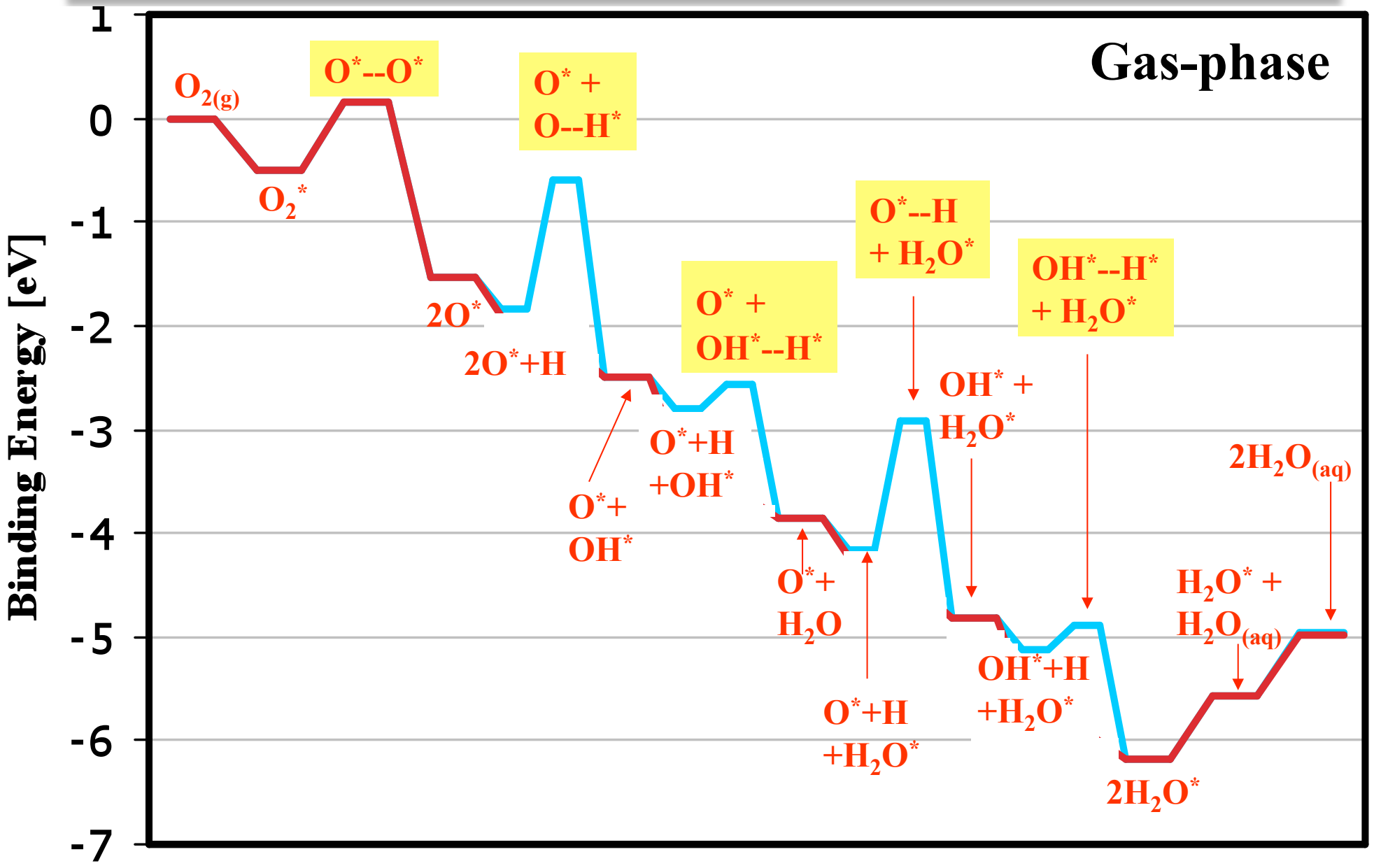
Langmuir–Hinshelwood-type



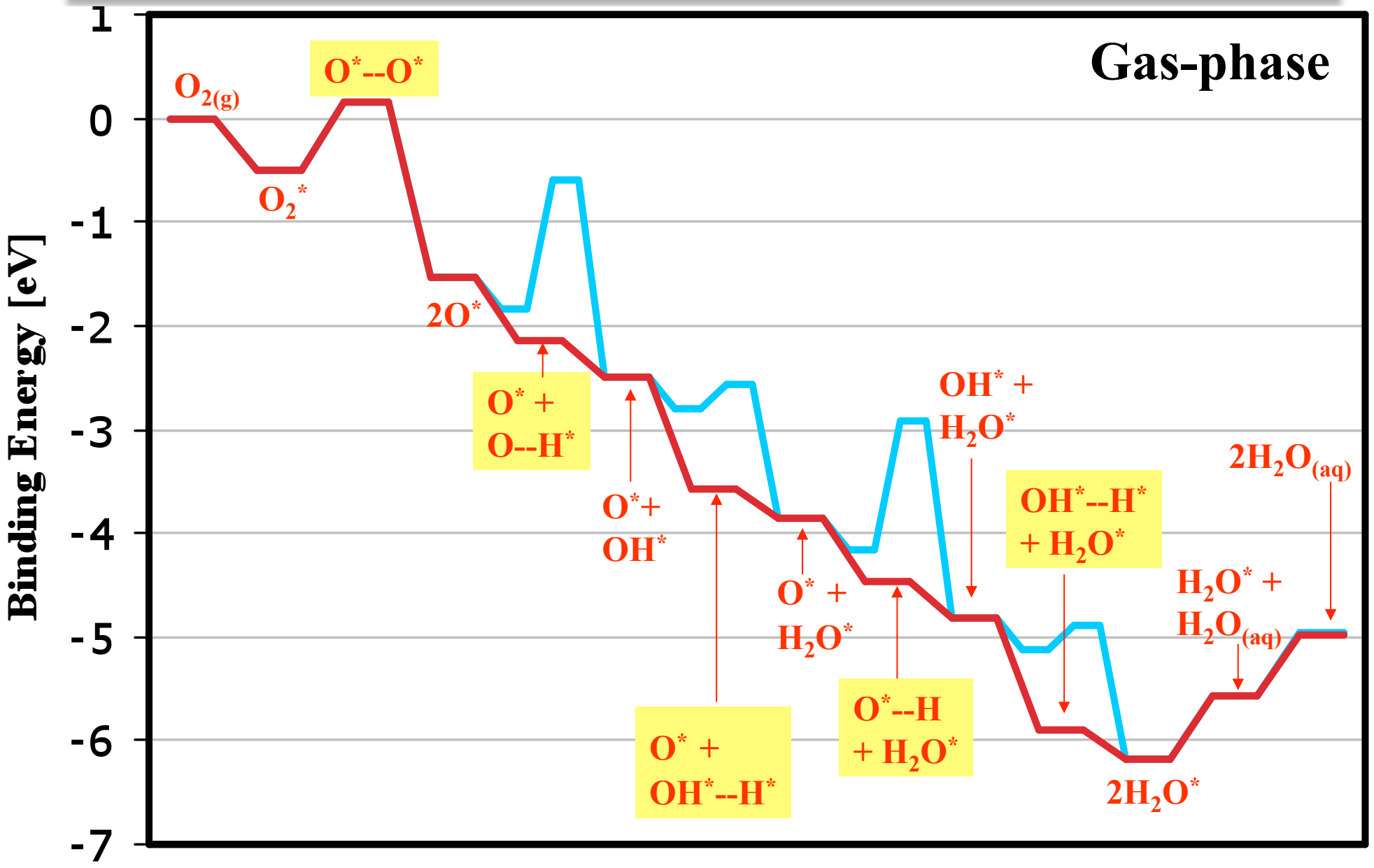
Eley–Rideal-type



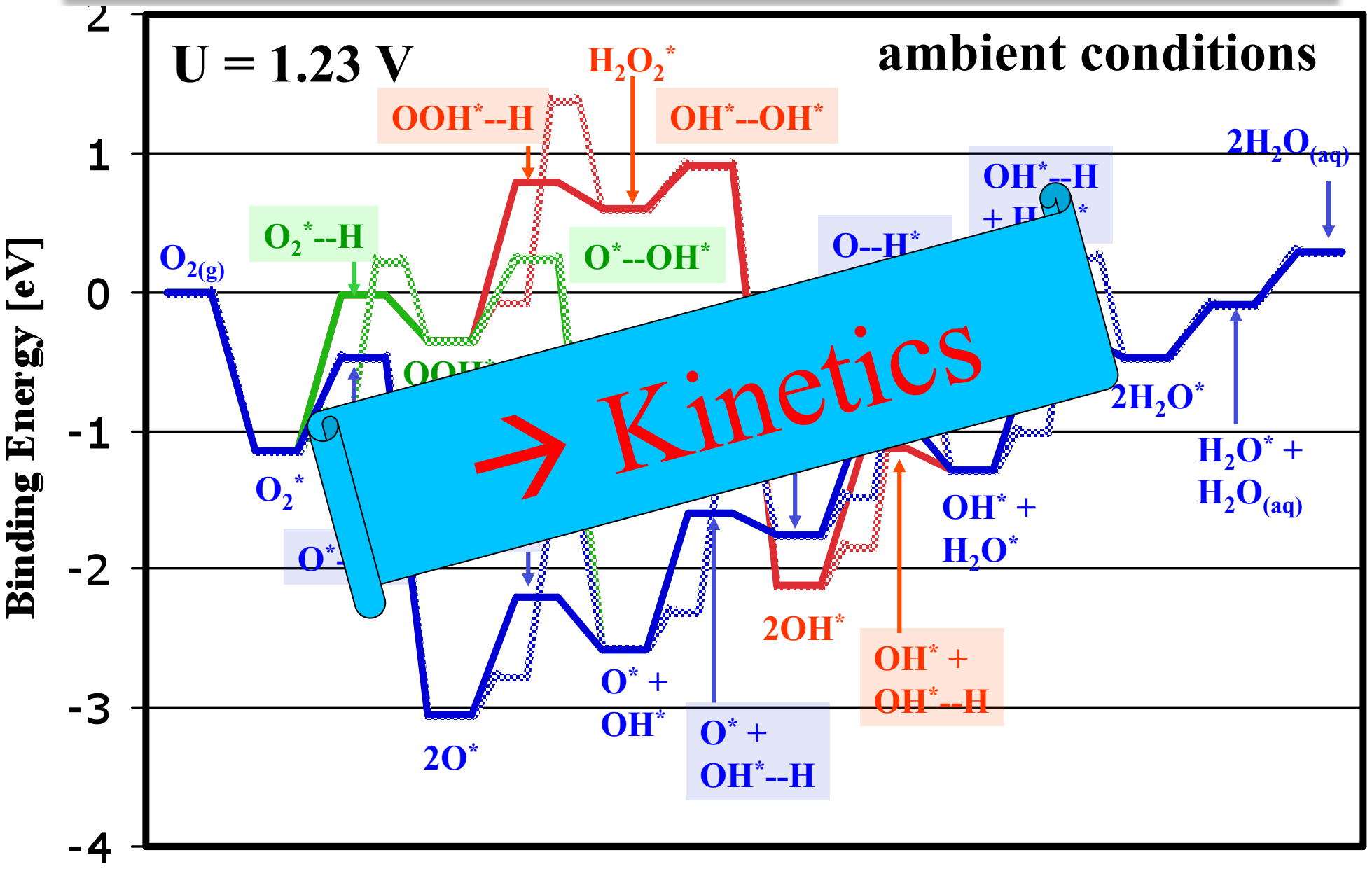
O_2-Dissociation Mechanism (Eley-Rideal + Langmuir Hinshelwood)



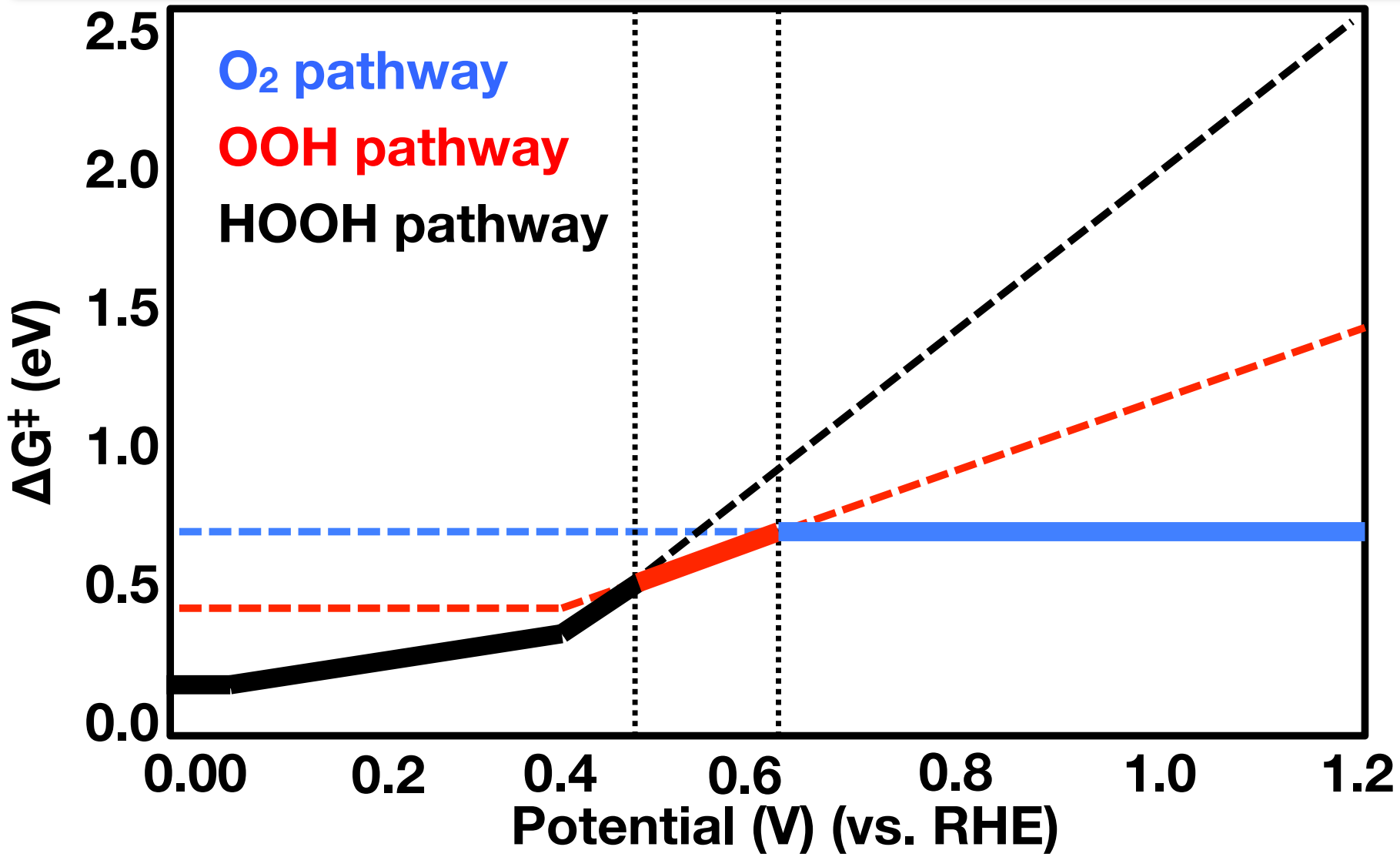
O_2-Dissociation Mechanism (Eley-Rideal + Langmuir Hinshelwood)



All Mechanisms
(Eley-Rideal + Langmuir-Hinshelwood)



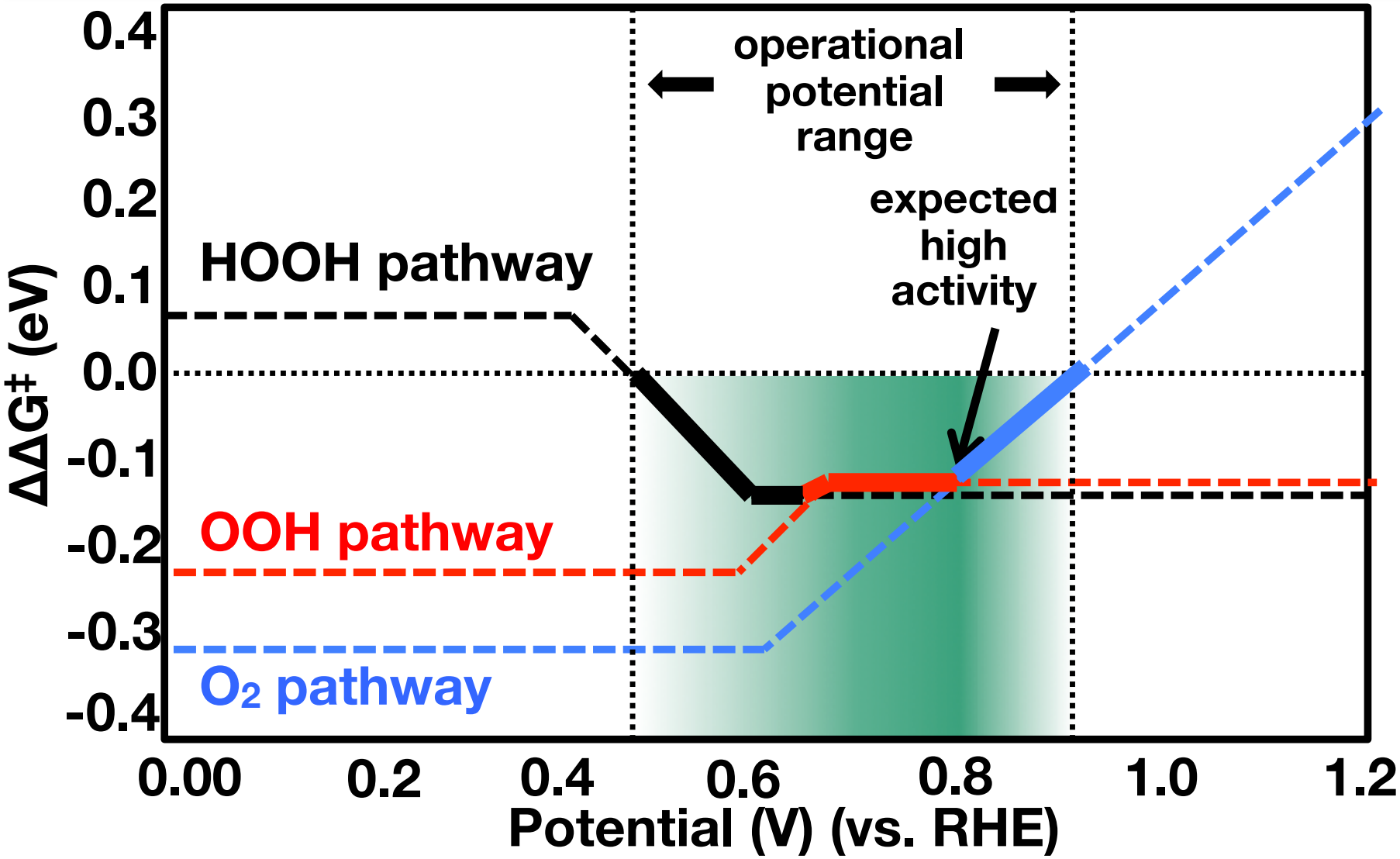
Barriers to form Intermediates



J. A. Keith, G. Jerkiewicz, T. Jacob, *Chem. Phys. Chem.* **11**, 2779 (2010)

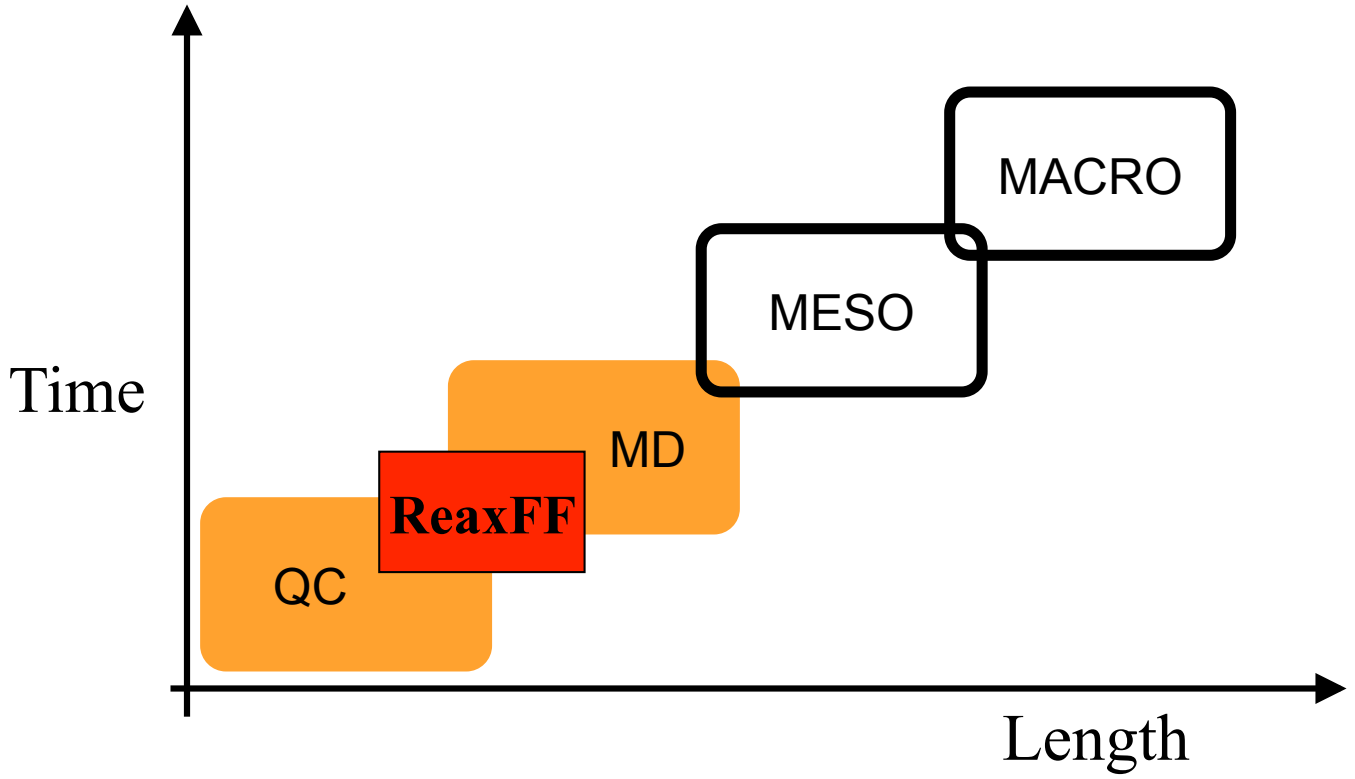
J. A. Keith, T. Jacob, *Angew. Chem. Int. Ed.* (hot article), **49**, 9521 (2010)

Differences in barrier (OUT) – barrier (IN)



J. A. Keith, G. Jerkiewicz, T. Jacob, *Chem. Phys. Chem.* **11**, 2779 (2010)
J. A. Keith, T. Jacob, *Angew. Chem. Int. Ed.* (hot article), **49**, 9521 (2010)

Cathode Reaction with ReaxFF (reactive forcefield)



ReaxFF

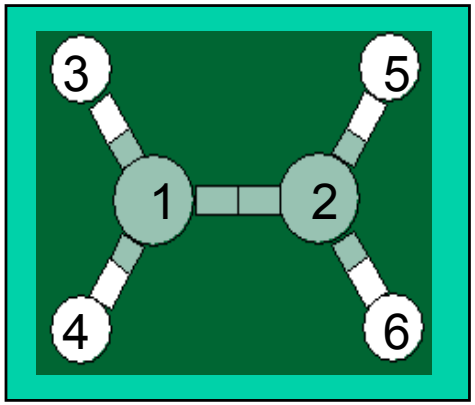
non-reactive forcefields
(only spheres and springs)

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



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

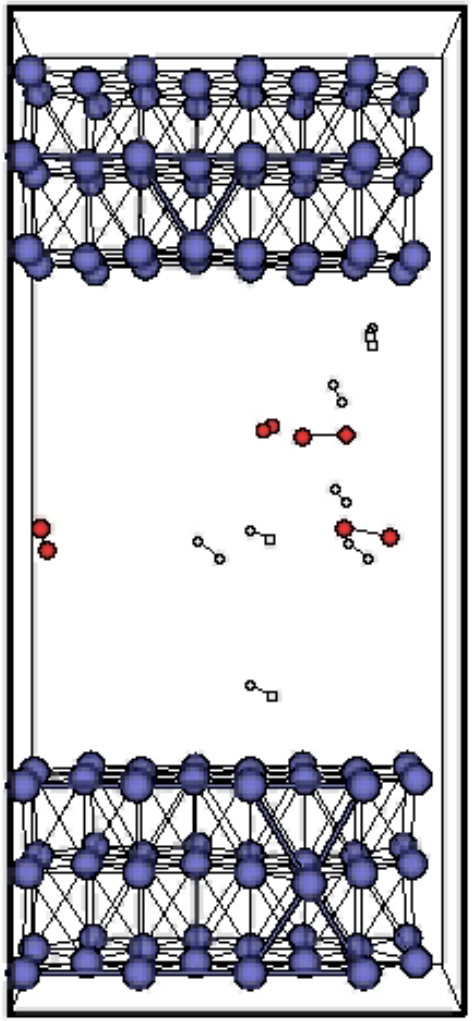
fixed

MD Routine

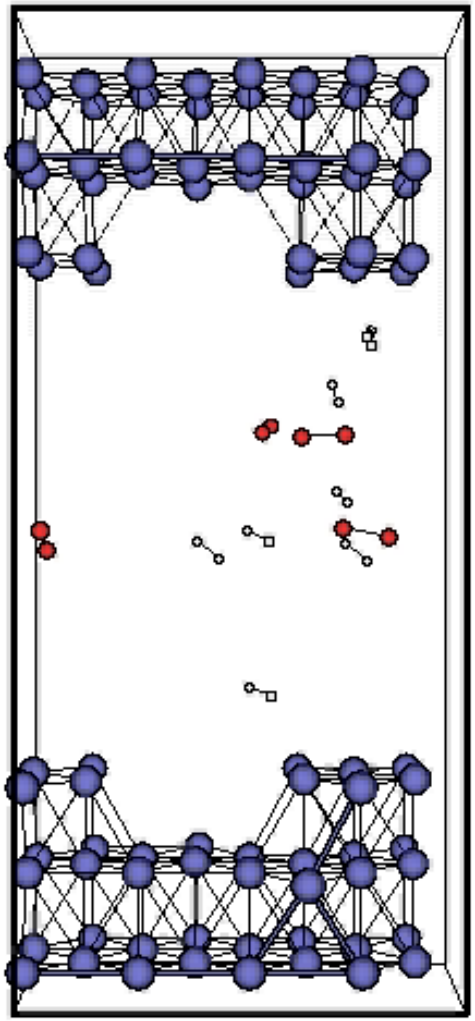
analyzing bonds

MD Routine

$H_2 + O_2$ reactions on Pt(111)

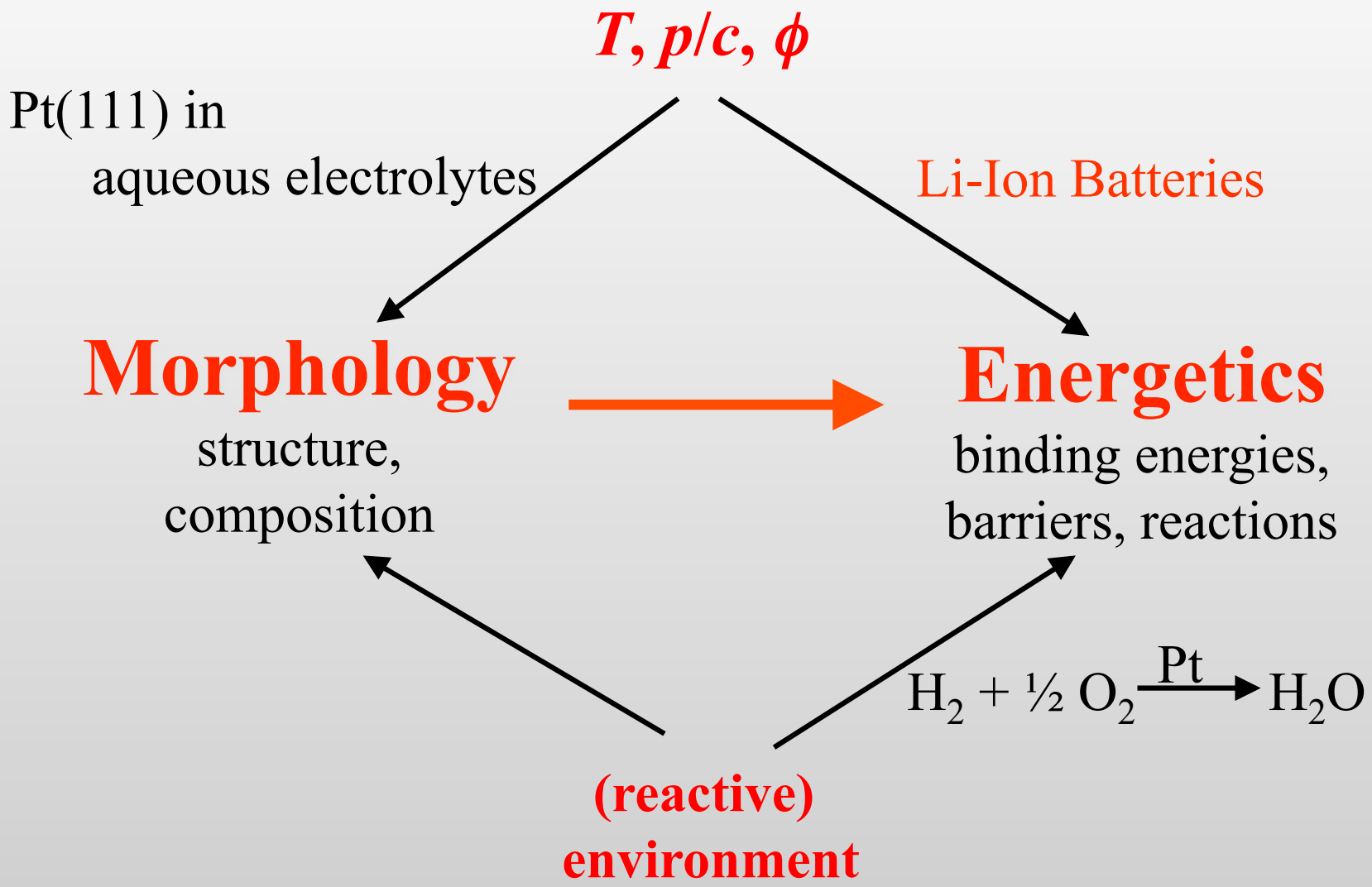


8 H_2+ 4 O_2 in contact with a perfect 96-atom (111) Pt-surface. T=1000K



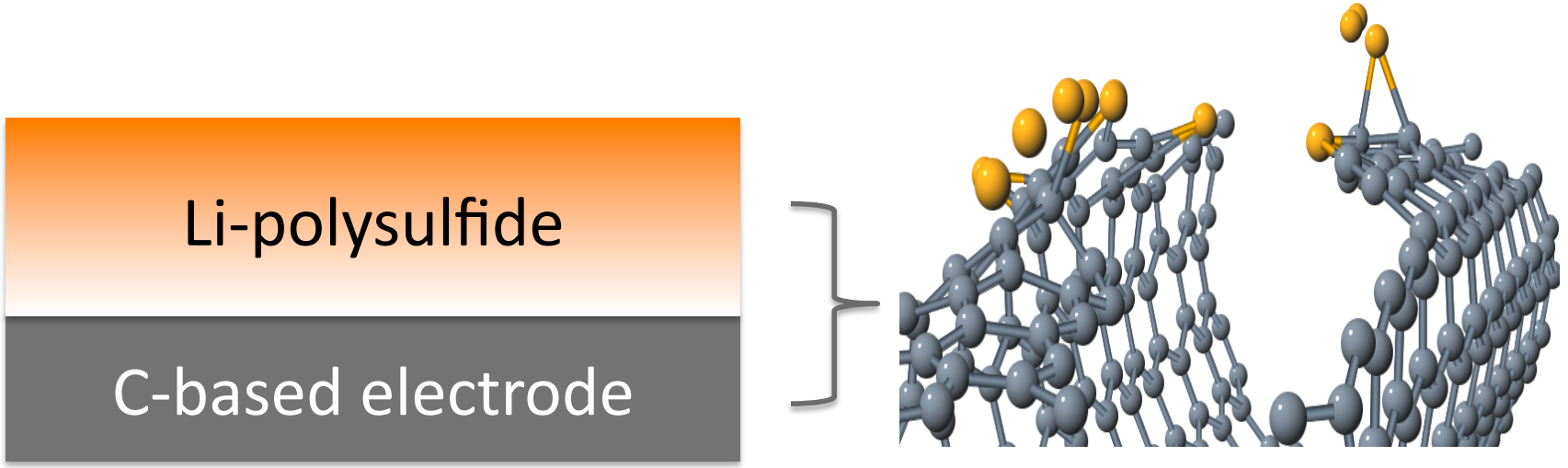
8 H_2 + 4 O_2 in contact with a stepped 84-atom (111) Pt-surface. T=1000K

Li-Sulfur Batteries



Li-Sulfur Batteries

- Density Functional Theory (DFT) calculations on Li-polysulfides in gas and in solution
- DFT of carbon-based electrodes
- DFT and Force field Simulations on the electrochemical interface

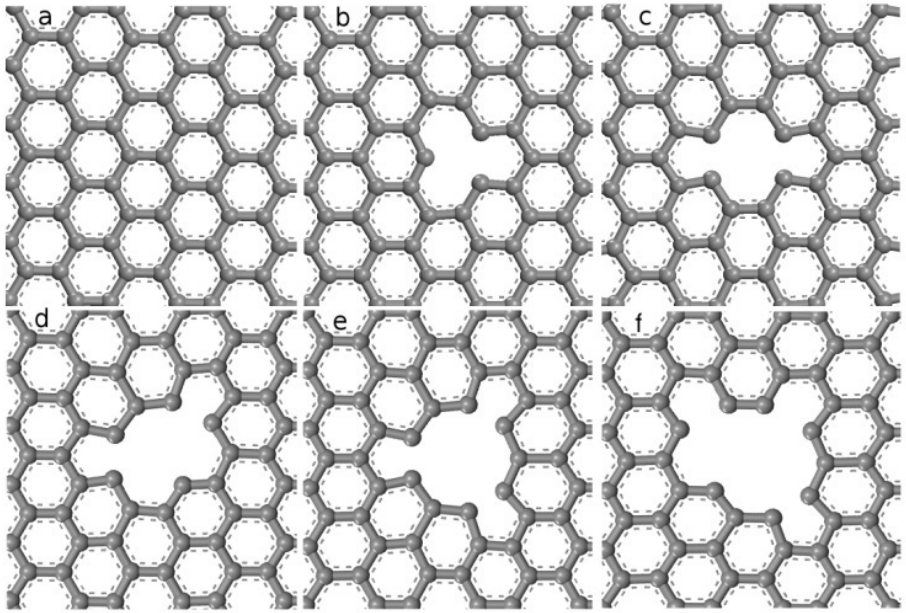


Li-Polysulfide Chemistry

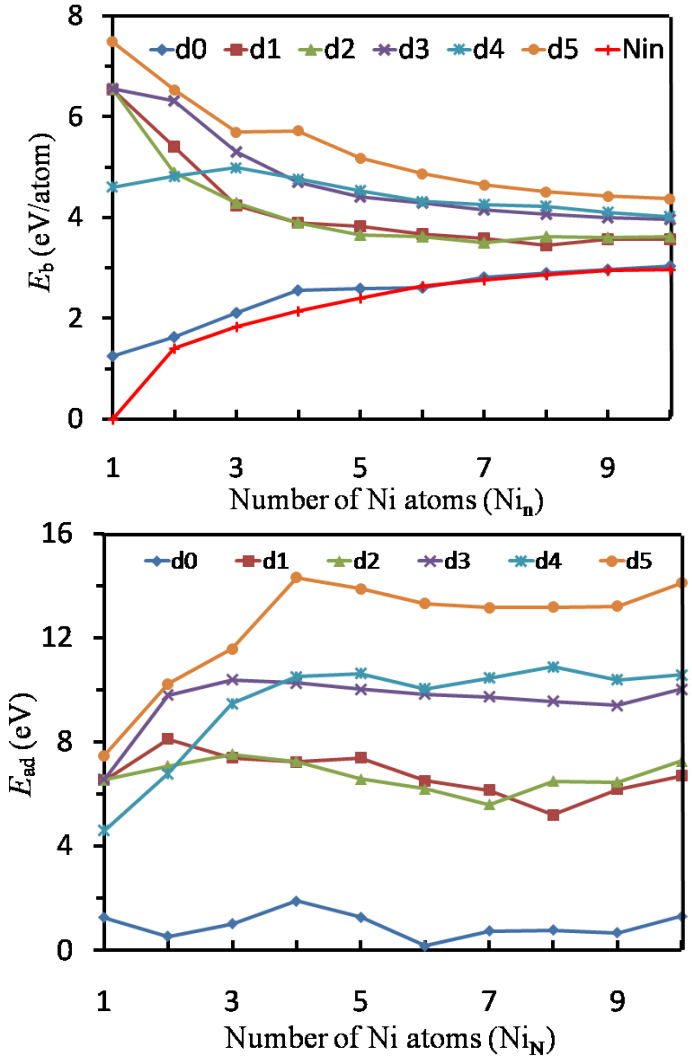
$$S_8 \longrightarrow Li_2S_8 \longrightarrow Li_2S_6 \longrightarrow Li_2S_4 \longrightarrow Li_2S_3 \longrightarrow Li_2S_2 \longrightarrow Li_2S$$

Ni cluster growth on graphene

Ni clusters were „grown“ one atom at a time on the illustrated graphene defects

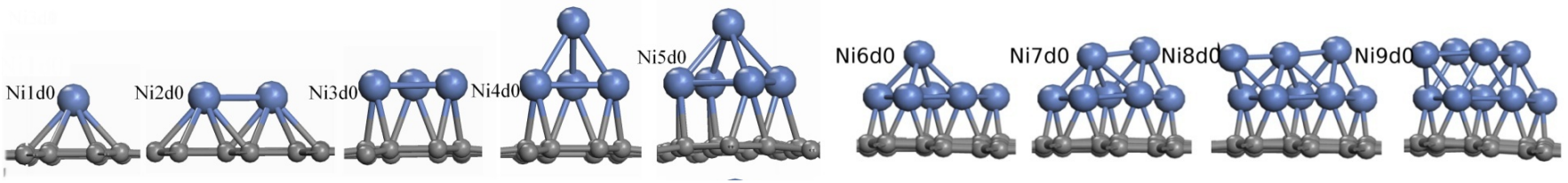


Atomization energies (E_b) and cluster adsorbtion energies (E_{ad}) were computed for each cluster.



Gao, W.; Mueller, J. E.; Anton, J.; Jiang, Q.; Jacob, T. *In preparation*.

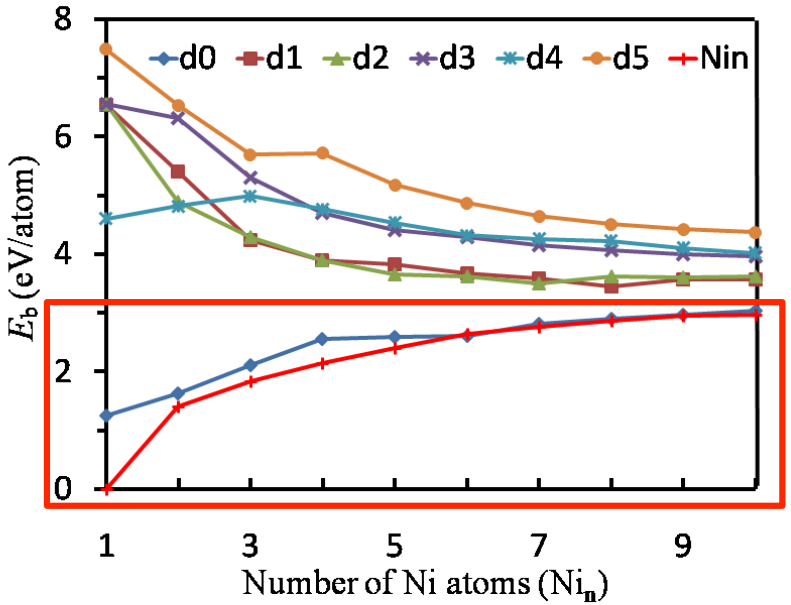
Bond types in Ni on graphene



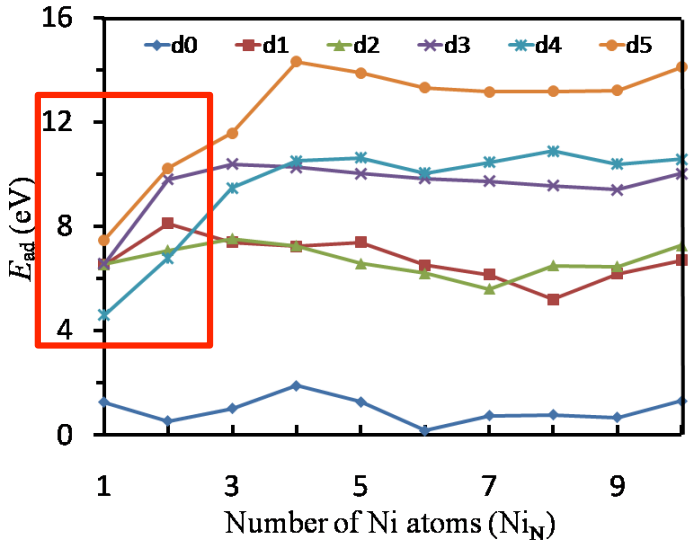
1.26	0.54	1.02	1.91	1.28	0.18	0.74	0.78	0.69	0.54

Adsorption Energies in eV

Ni-C-π bonding is worth **< 1 eV** per Ni



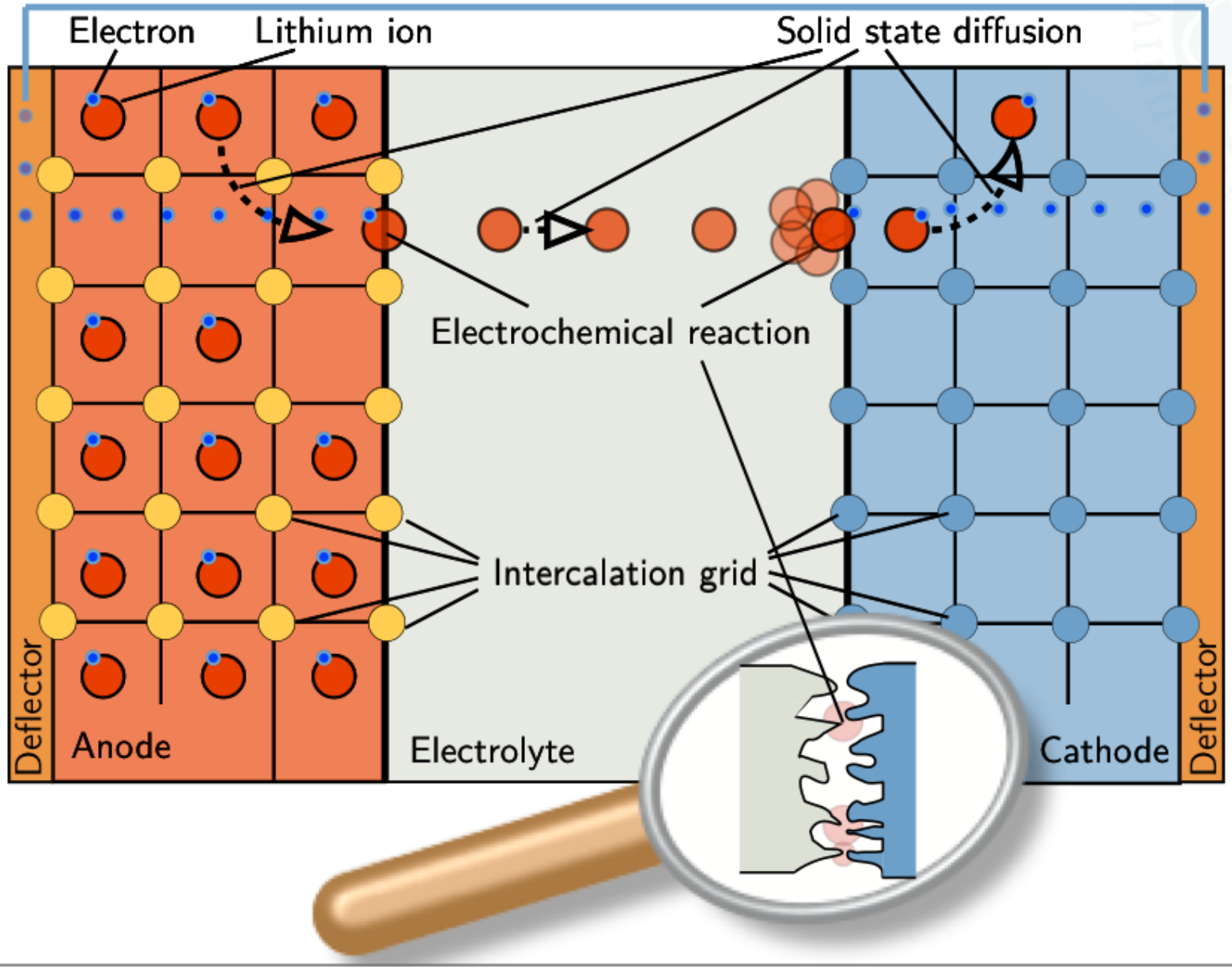
Ni-Ni bonding is worth **1.5 - 3 eV** per Ni



Ni-Cσ bonding is worth **> 4 eV** per Ni

Gao, W.; Mueller, J. E.; Anton, J.; Jiang, Q.; Jacob, T. *In preparation*.

Model for an **All-solid state battery**

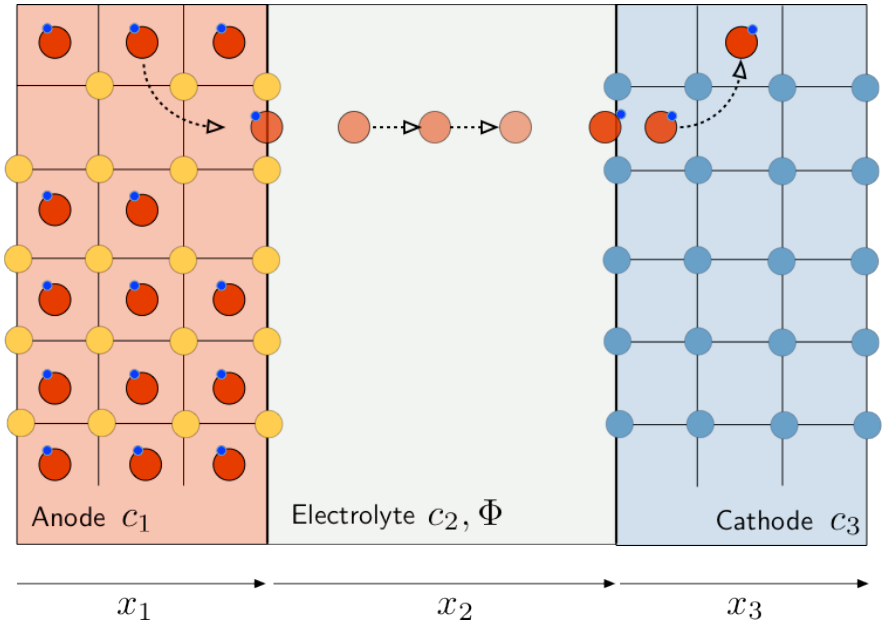


Battery Model

Transport equations:

- Lithium diffusion in anode/cathode
- Li^+ diffusion in solid-electrolyte

→ new system of equations



Double layer:

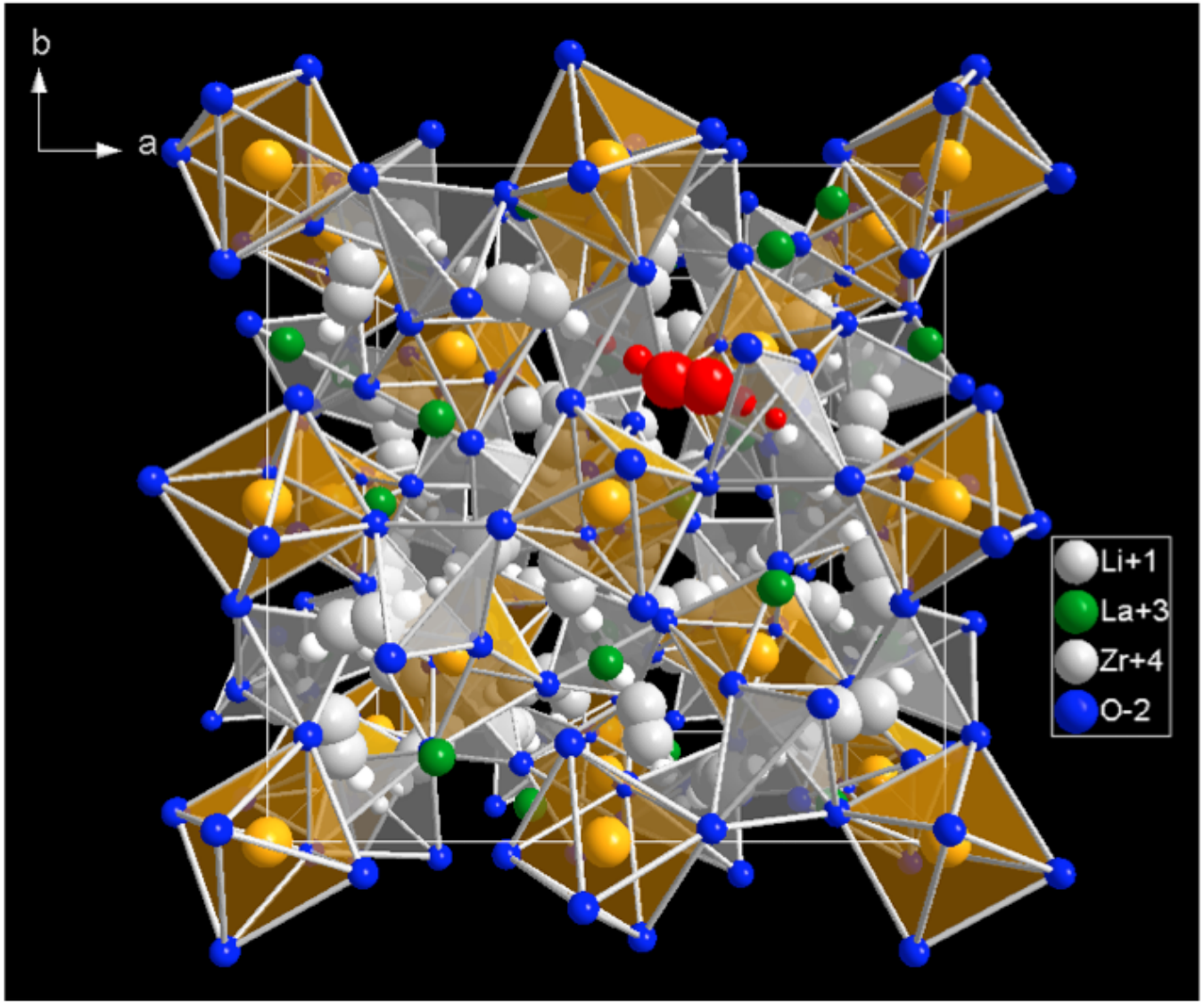
- Poisson equation

Boundary conditions:

- Potential-step at electrode/solid-electrolyte interface
- Electrochemical reactions
  - 1. order redoxreaction
  - Ion concentration at interface

→ 4 (non-linear) PDEs
8 Boundary conditions
} Numerical solution

Fest-Elektrolyt: $Li_7La_3Zr_2O_{12}$

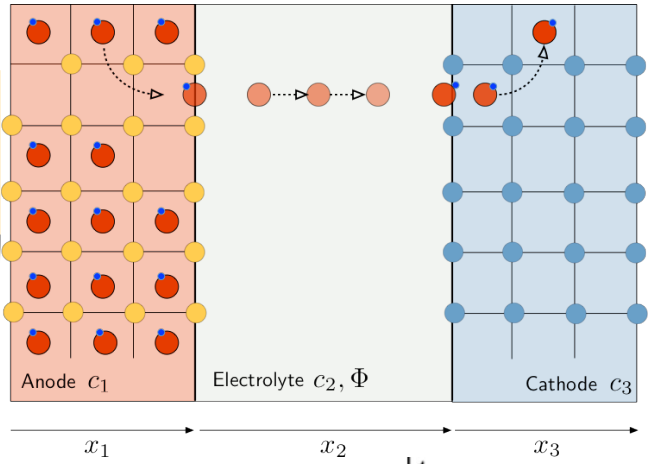


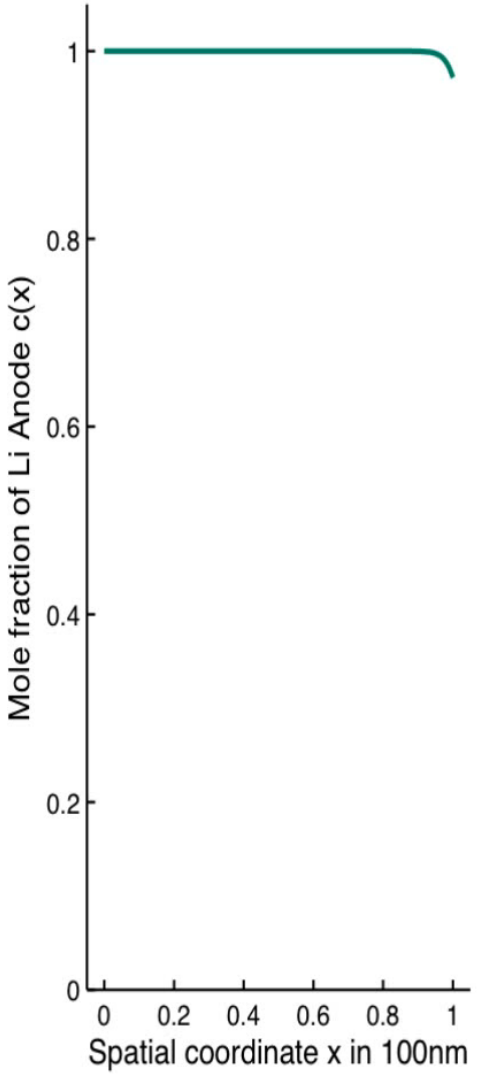
Weppner *et al.*, *Angew. Chem. Int. Ed.*, **46** (2007).

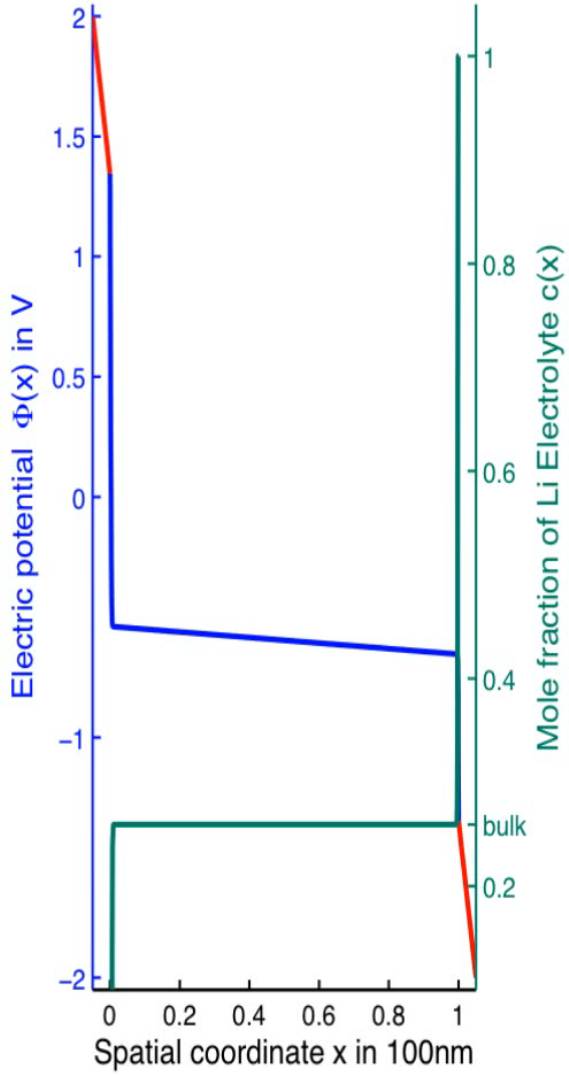
Discharge – Diffusion-limited

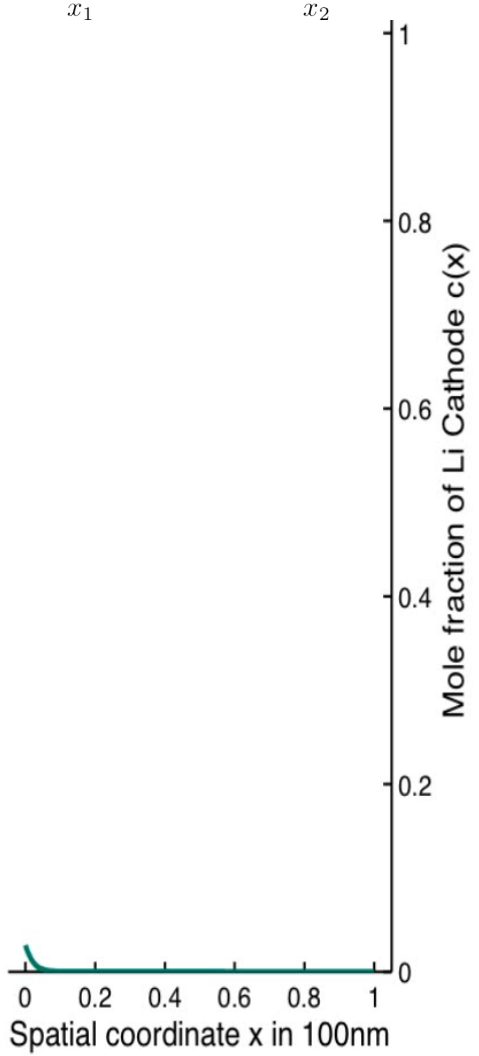
Solid-Electrolyte: $Li_7La_3Zr_2O_{12}$

Weppner *et al.*, *Angew. Chem. Int. Ed.*, **46** (2007).

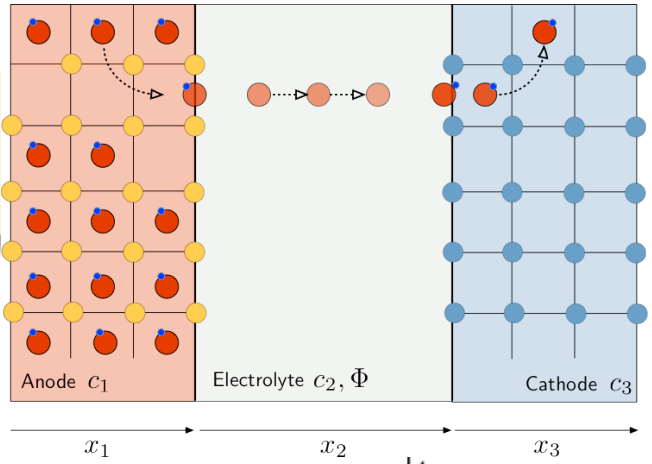


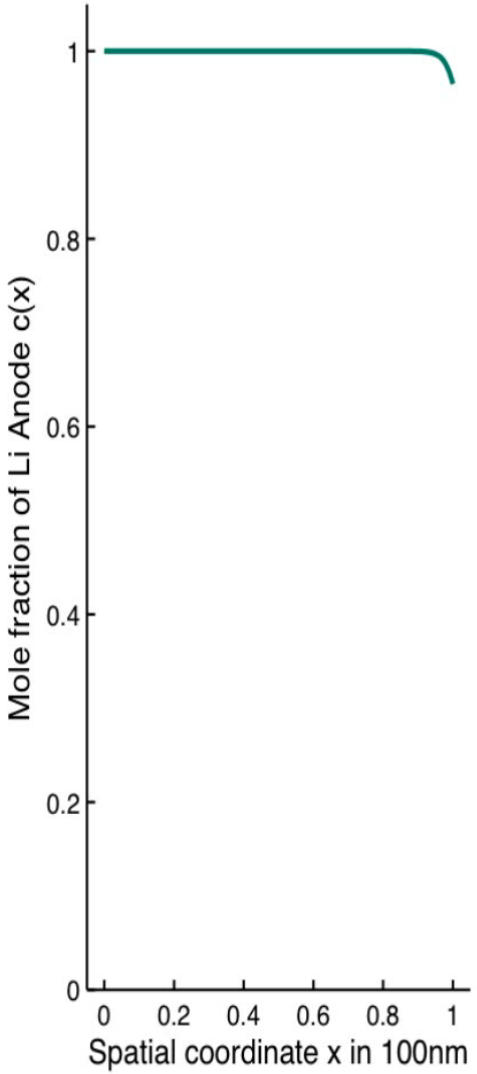


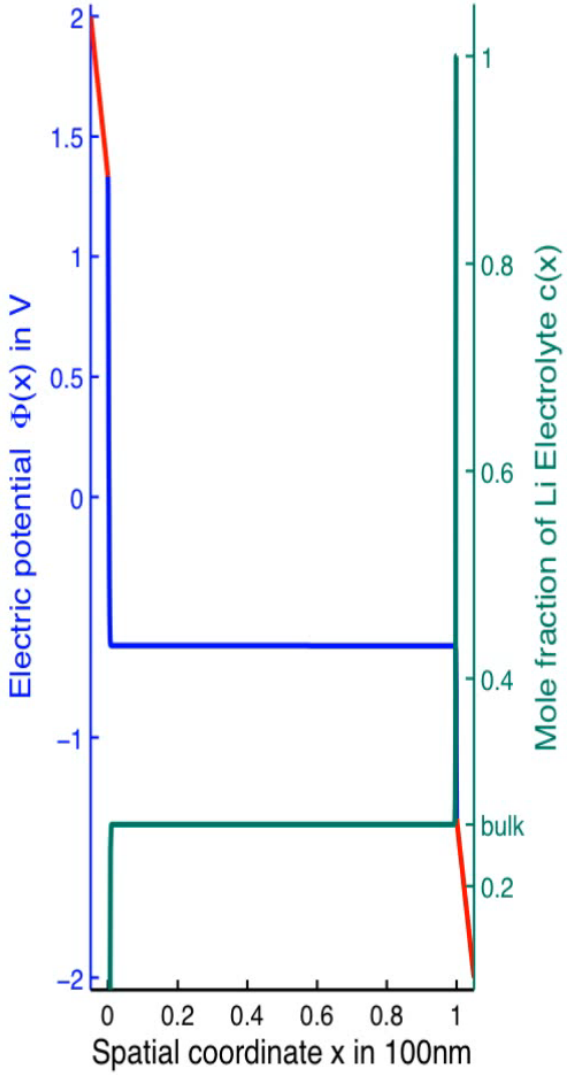


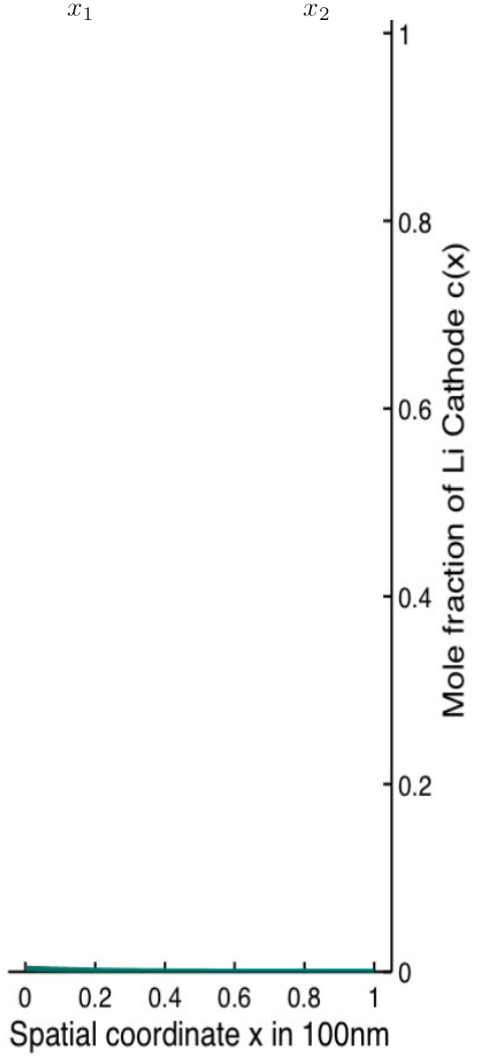


Discharge – Anode-limited

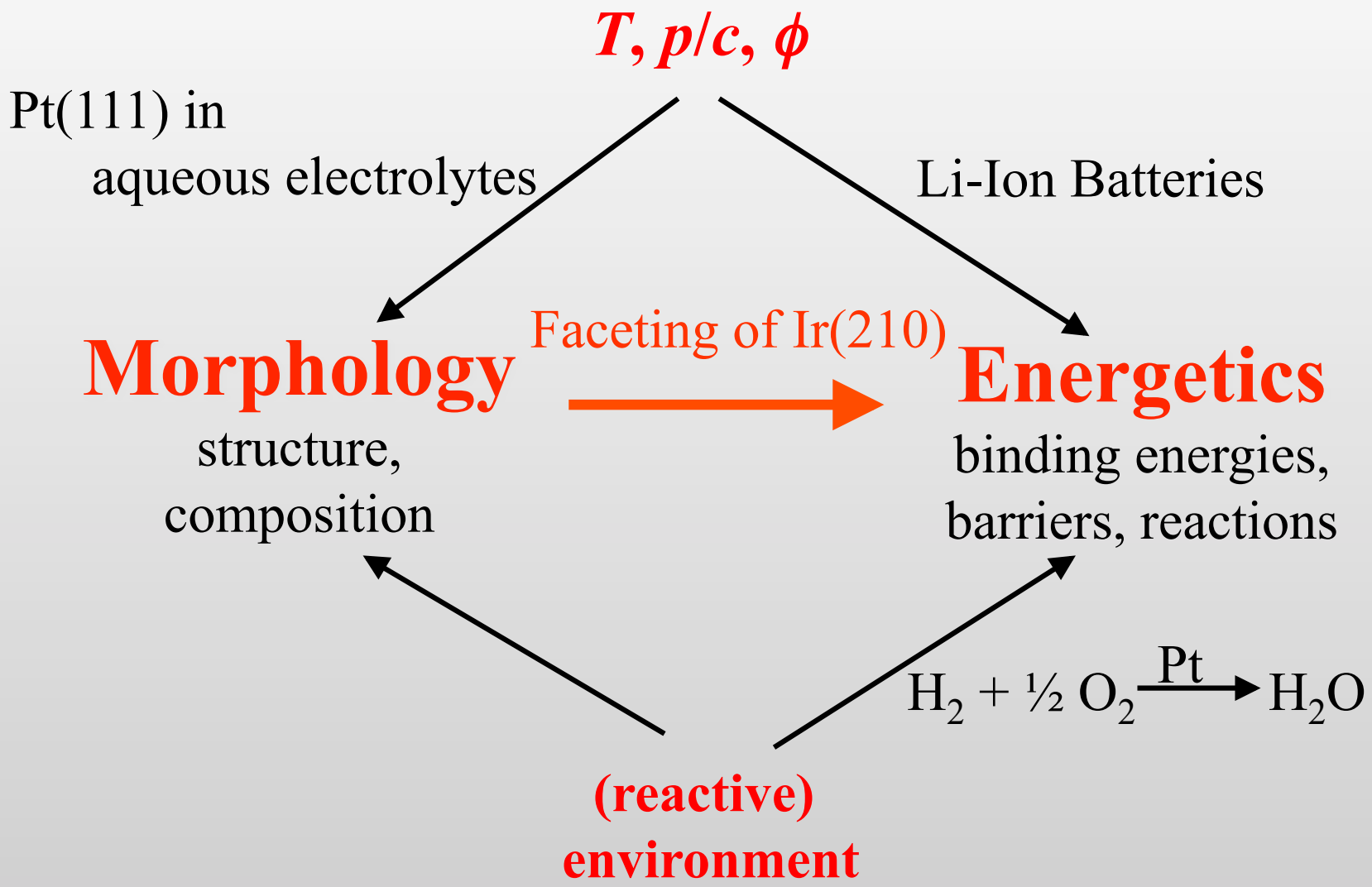




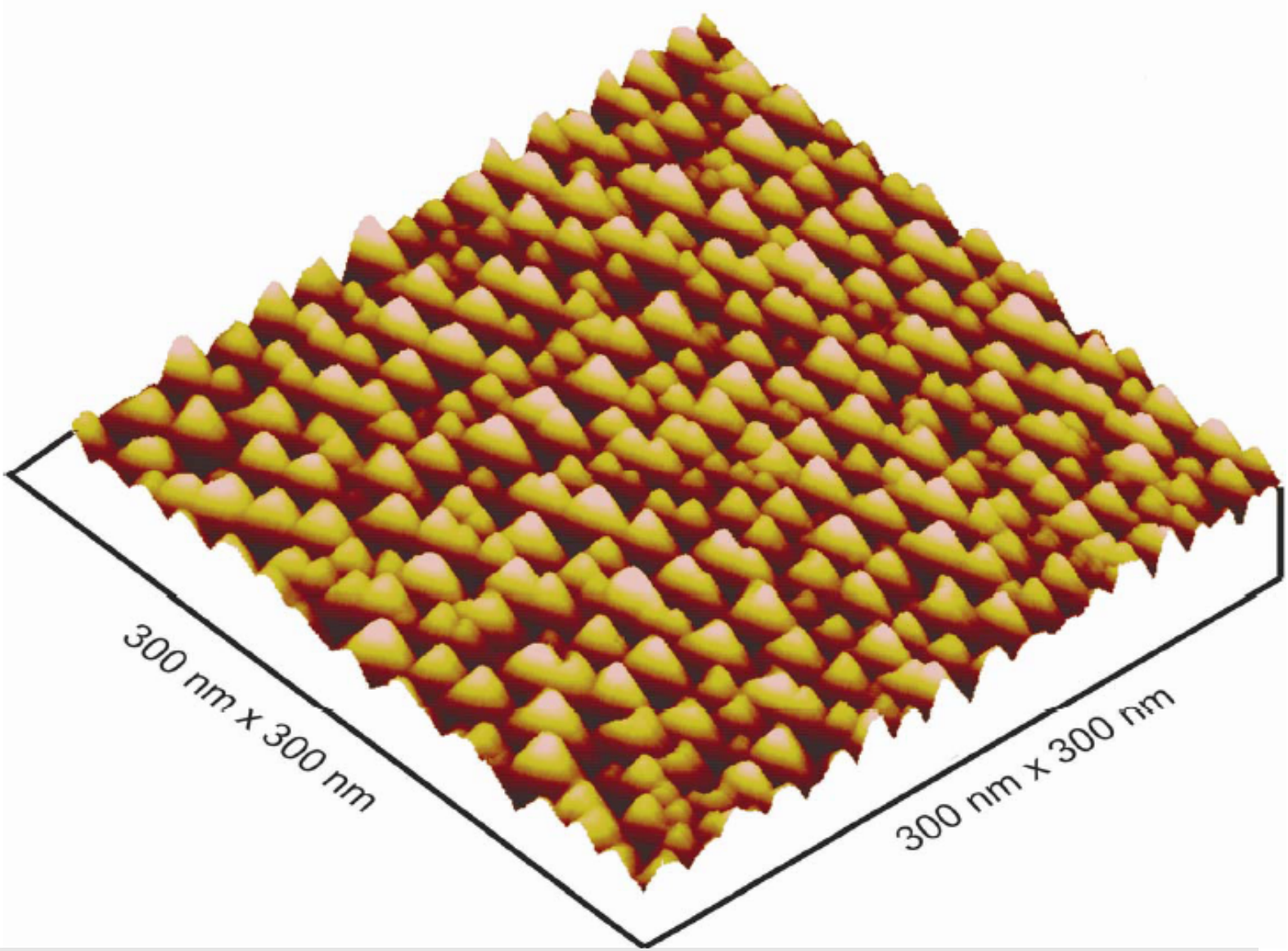




Potential-Induced Faceting of Ir(210)



Faceted Ir(210) in 0.1M H_2SO_4



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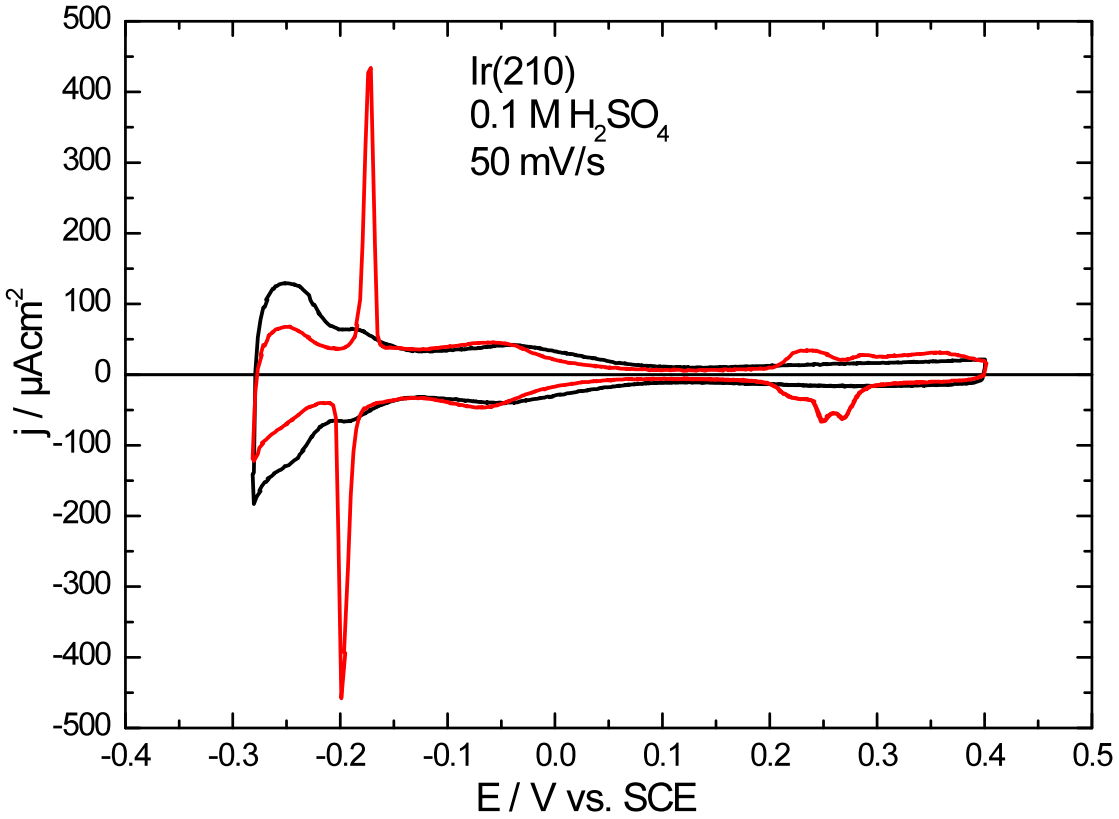
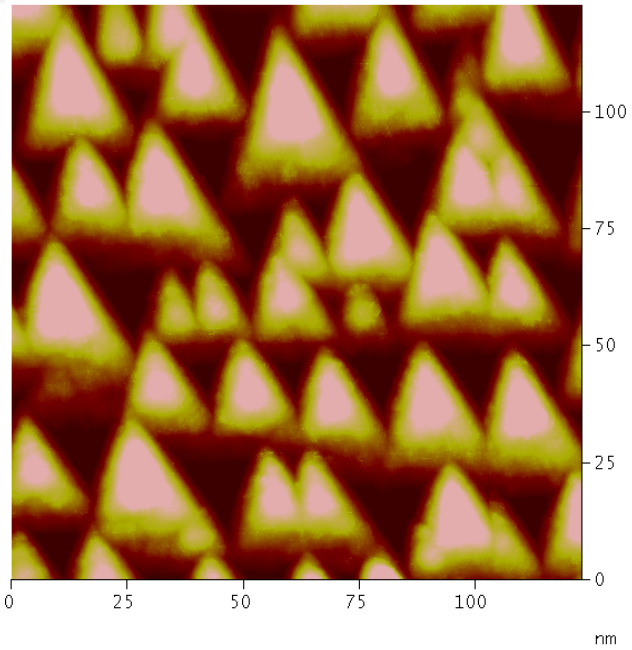
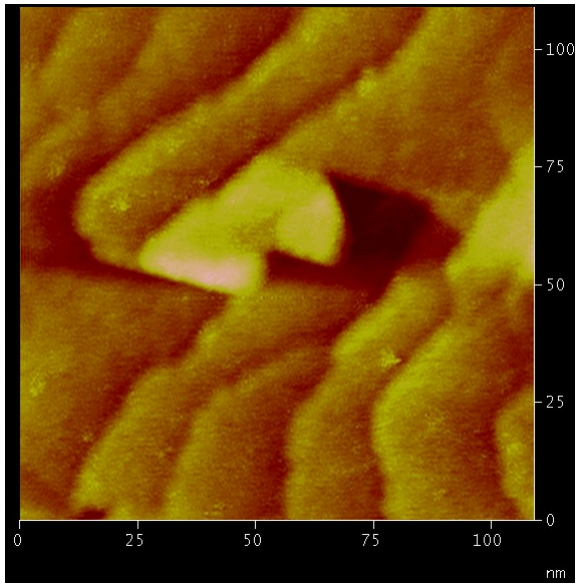
Characterization by *in-situ* STM

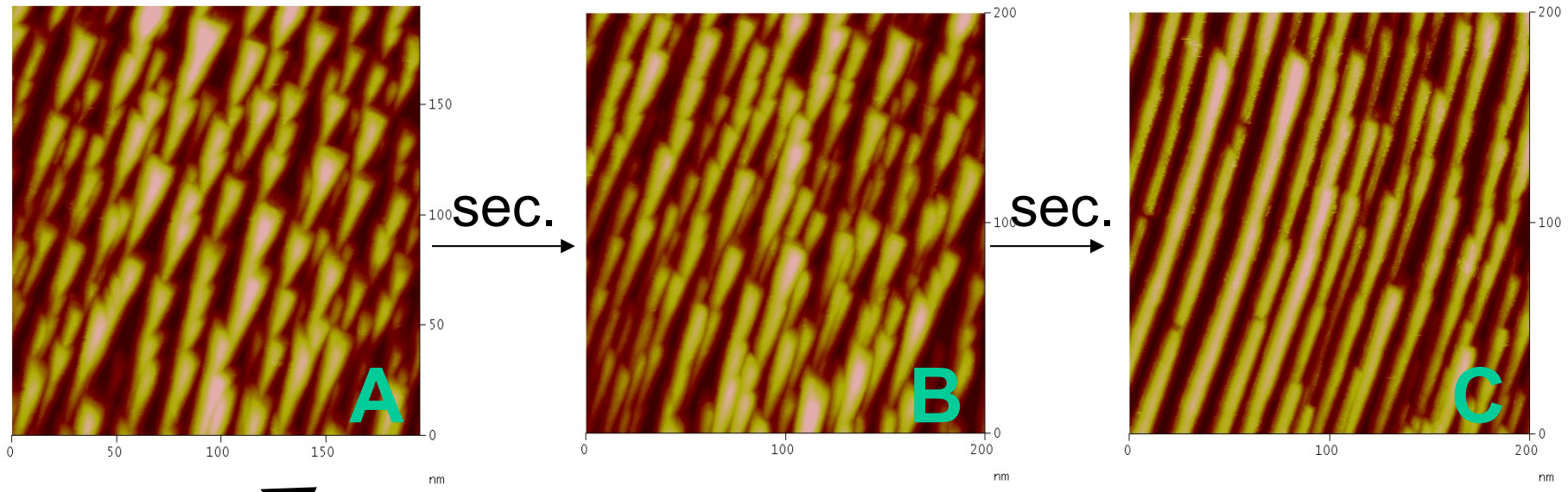






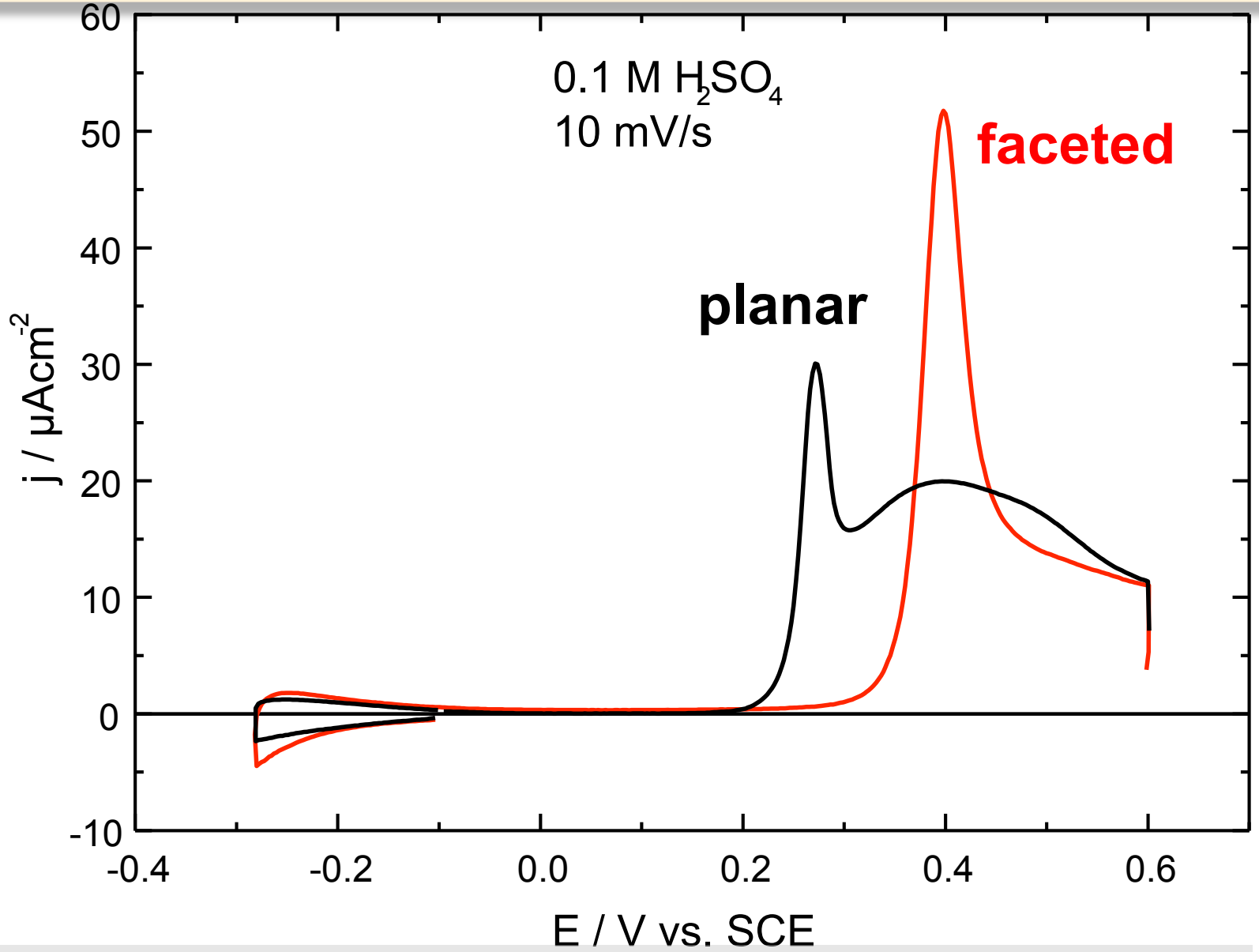
Structure Stability in $HClO_4$

Fixing potential at 0.2 V



Potential Cycling

CO adlayer oxidation (electrochemical)



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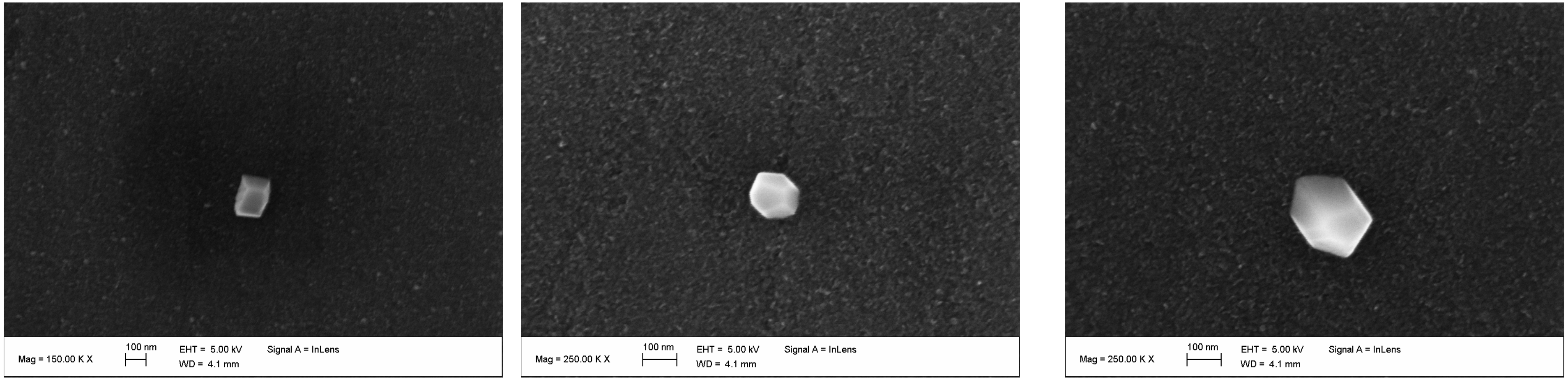
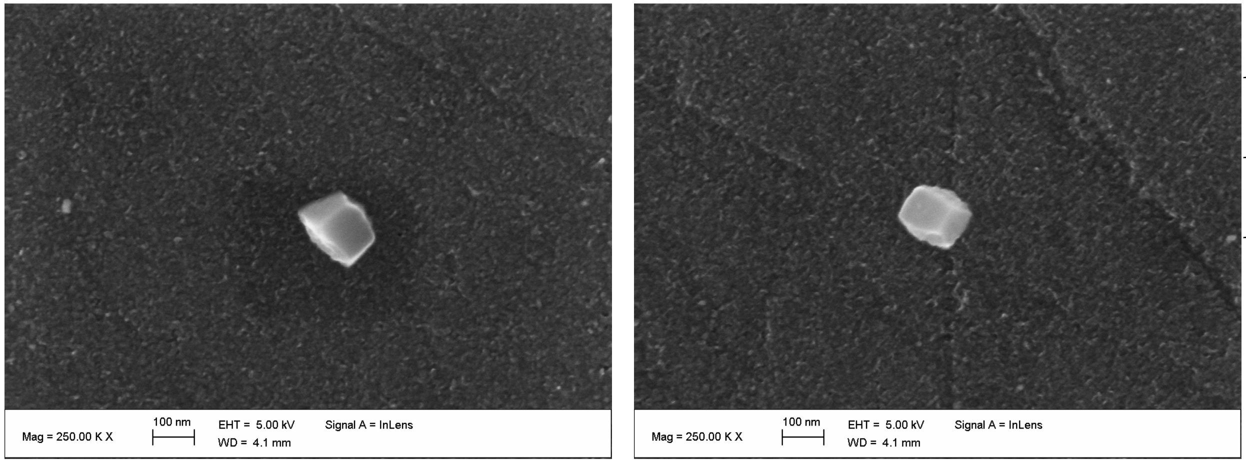
Ir-nanoparticles: Synthesis by square-wave pot.

SEM characterization





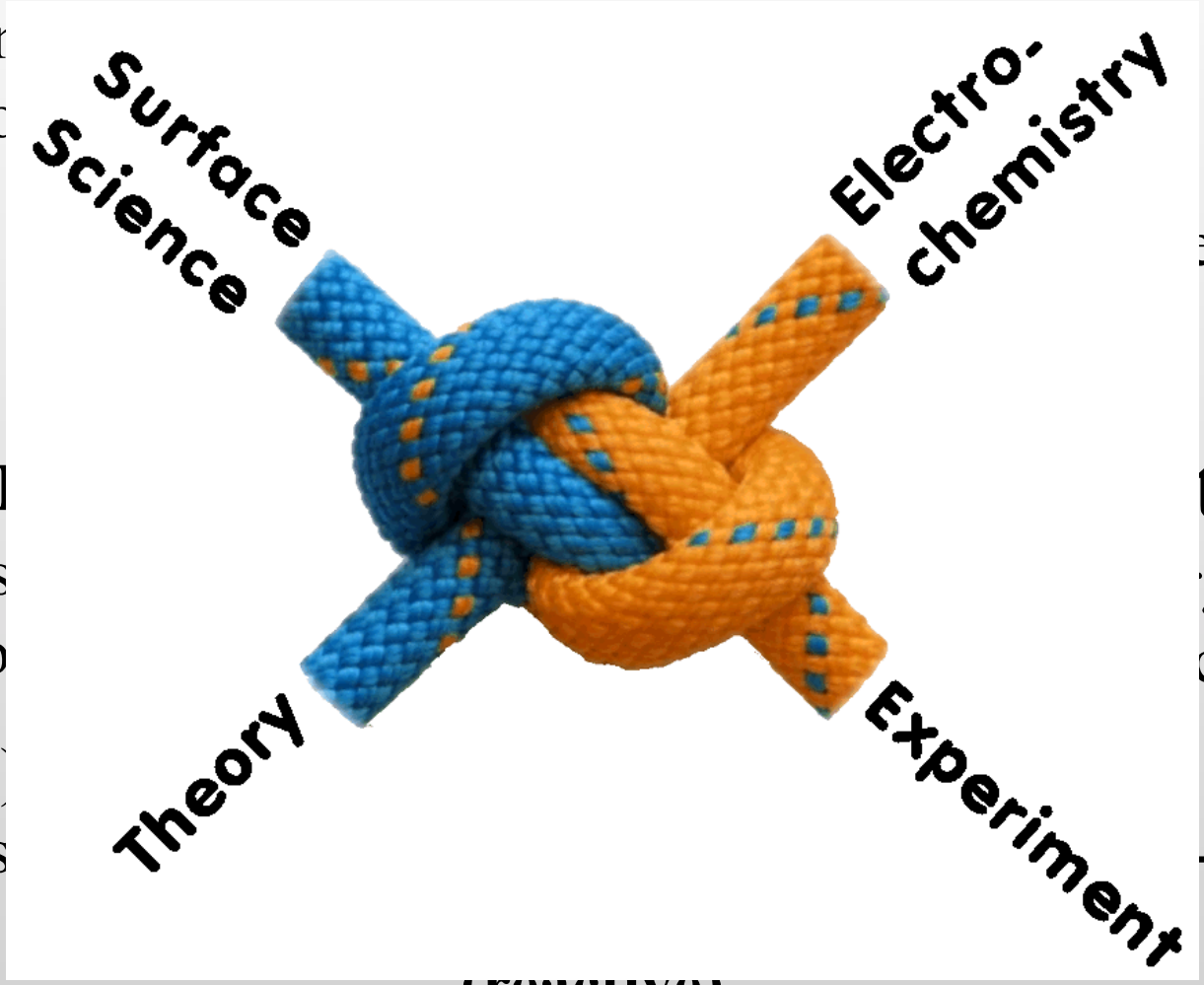
E_N = -0.90 V T_N =500 ms

E_L = -0.40 V T_L = 50 ms

E_U = 0.61 V T_U = 50 ms

Summary

Pt(111) ir
aquec



es

Mo **tics**

s gies,

co ctions

Pt(111)
O_2-atmos → H_2O

(reactive) environment

The Gang

Frühromantischer Kreis in Jena – Weimar

z.B. …, Novalis,
Gebrüder Schlegel,
Achim v. Arnim,
Schiller,
Herder,
Ritter,
Goethe,
Döbereiner, …

Verlässt man nie den herrlichen elektrochemischen Leitfaden, so kann uns das Übrige auch nicht entgehen.

Goethe in einem Brief an Döbereiner