Development of new catalysts for water electrolysis

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Development of new catalysts for water electrolysis

Patricia Hernández-Fernández[1], **Elisa A. Paoli**[1], **Rasmus Frydendal**[1], **Ifan E.L. Stephens**[1], **Jan Rossmeisl**[2], **Ib Chorkendorff**[1]

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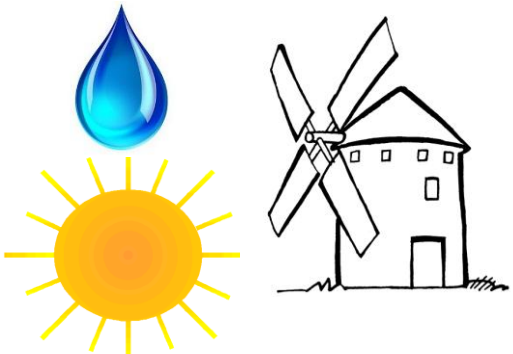
Symposium
Water electrolysis and hydrogen as part of the future Renewable Energy System

Outline

- ✓ Motivation
- ✓ Theoretical trends in oxygen evolution activity
- ✓ Corrosion protection mechanism
- ✓ Films preparation- Sputter deposition
- ✓ Nanoparticles- Cluster source
- ✓ Summary

Motivation



Renewable sources

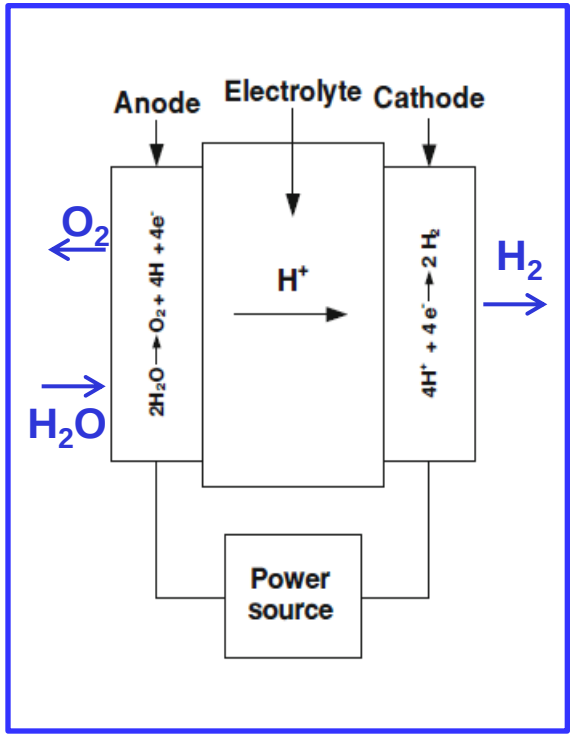
Electrical energy

Fuel Cells

Electrolysers

Chemical energy H_2

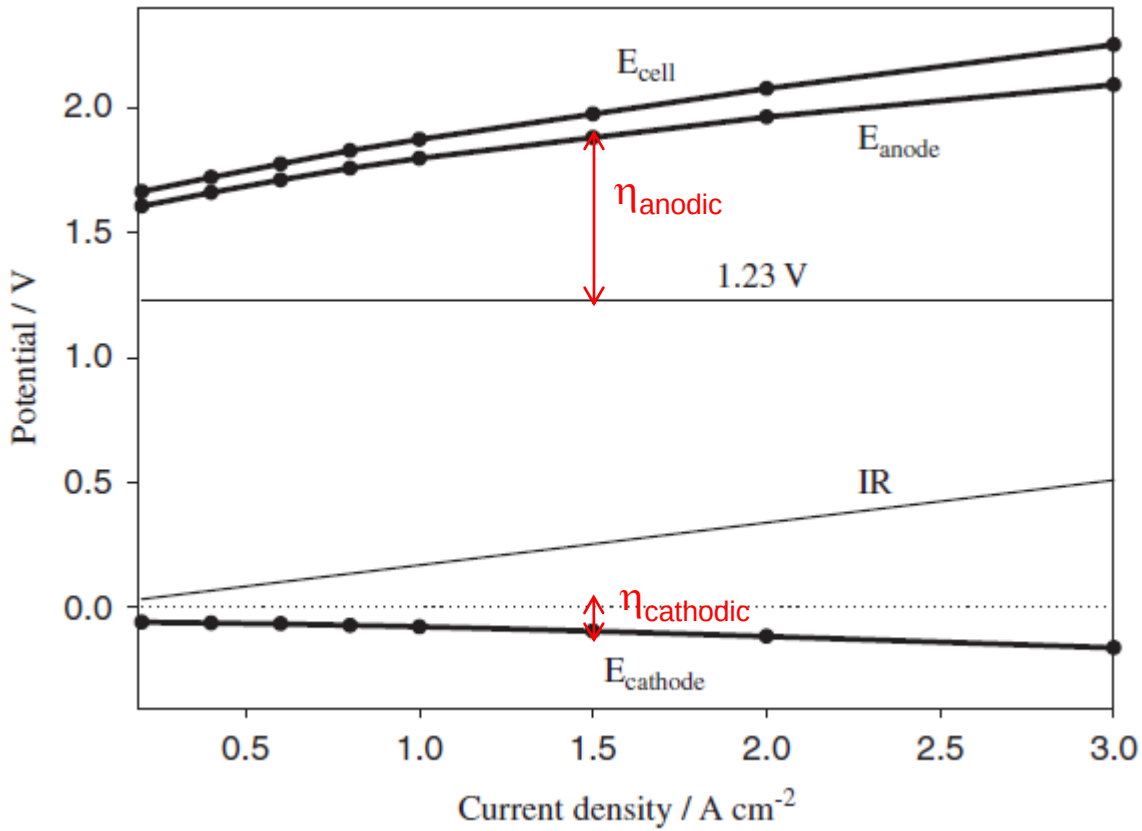
$$H_2O \leftrightarrow \frac{1}{2}O_2 + H_2$$



PEM

Motivation

Limitations of the efficiency of a PEM electrolyser

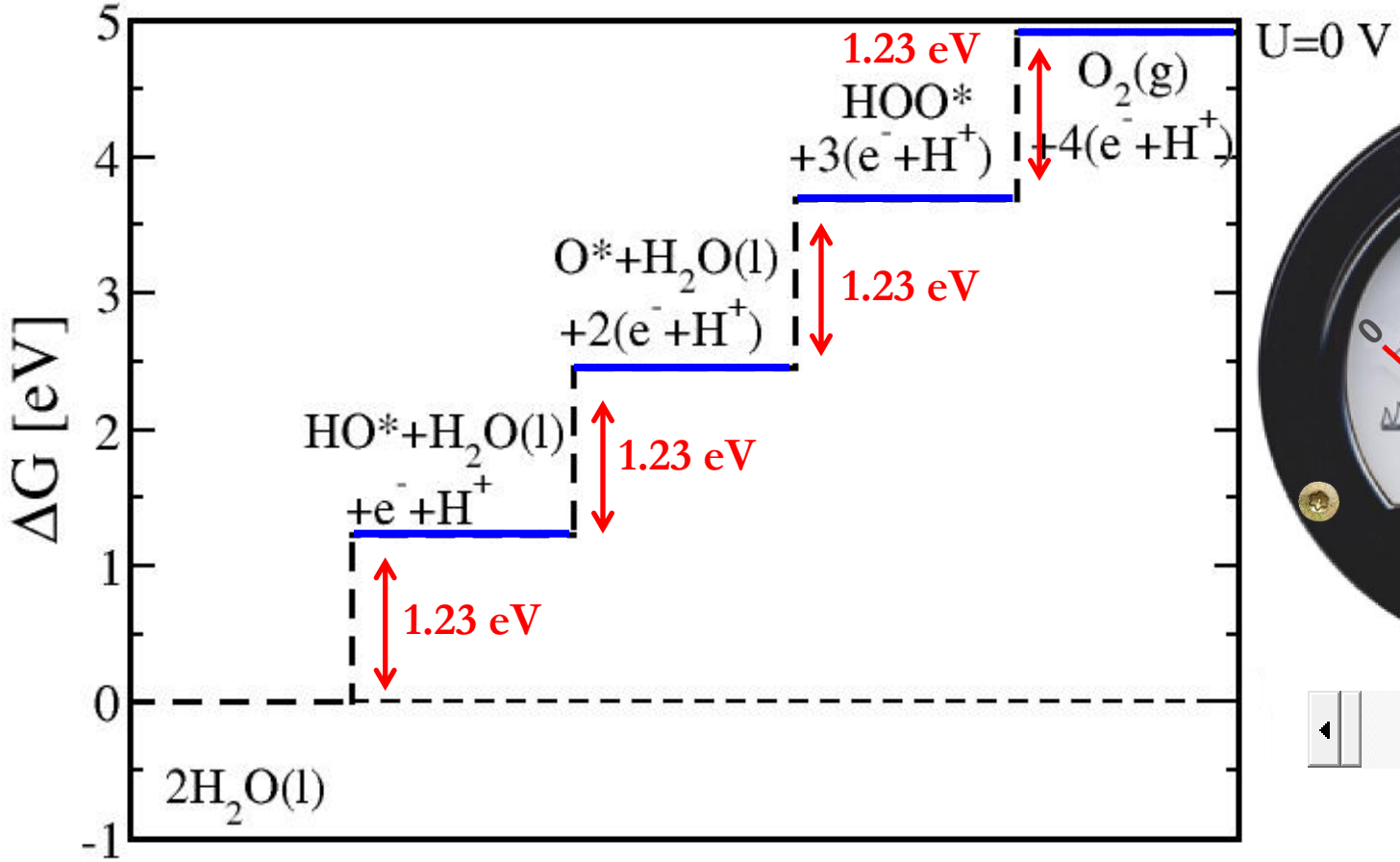


$$E_{cell} = E_0 + \eta_{anode} + \eta_{cathode} + IR$$

Marshall et al, Energy 32 (2007) 431

Theoretical trends in oxygen evolution activity

Ideal catalyst



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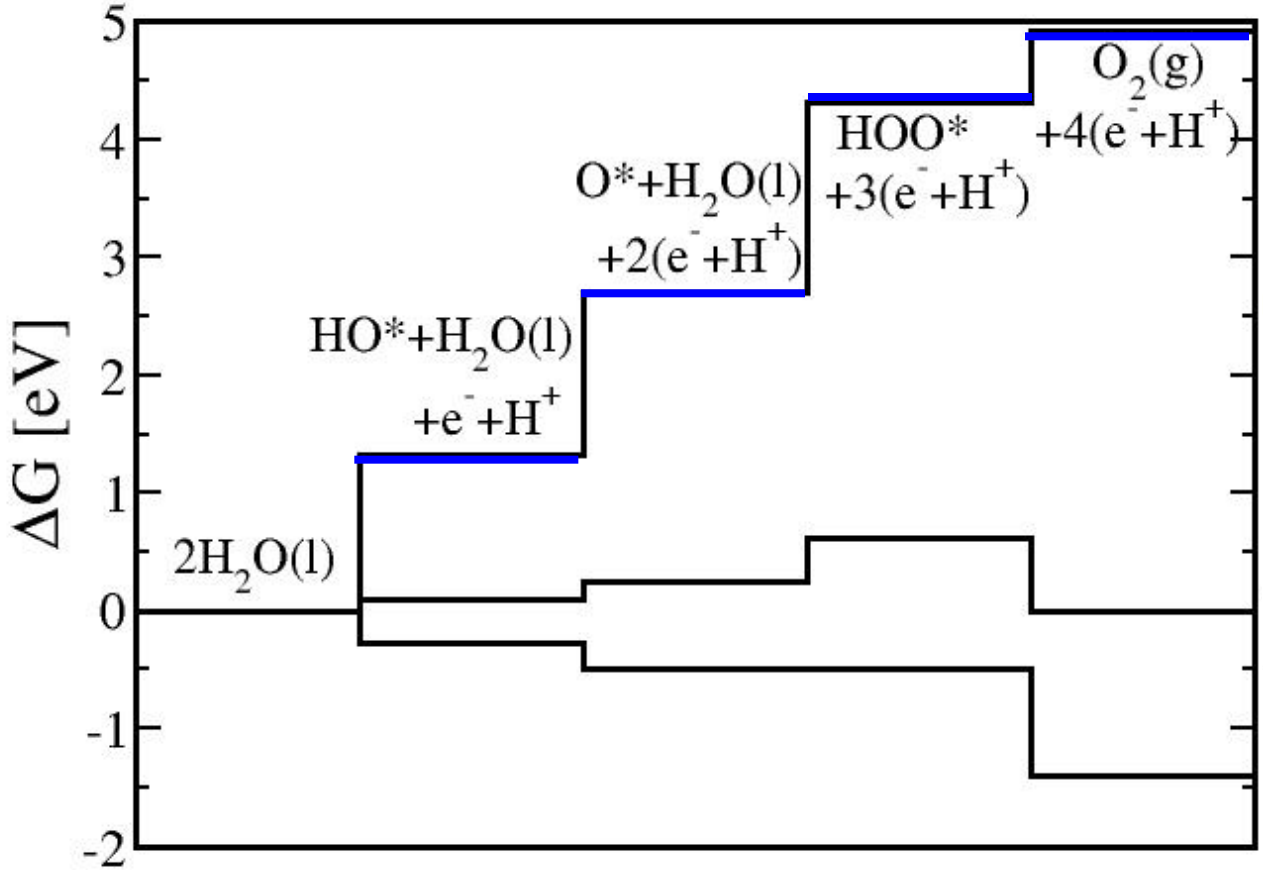
Theoretical trends in oxygen evolution activity

RuO_2 (110)



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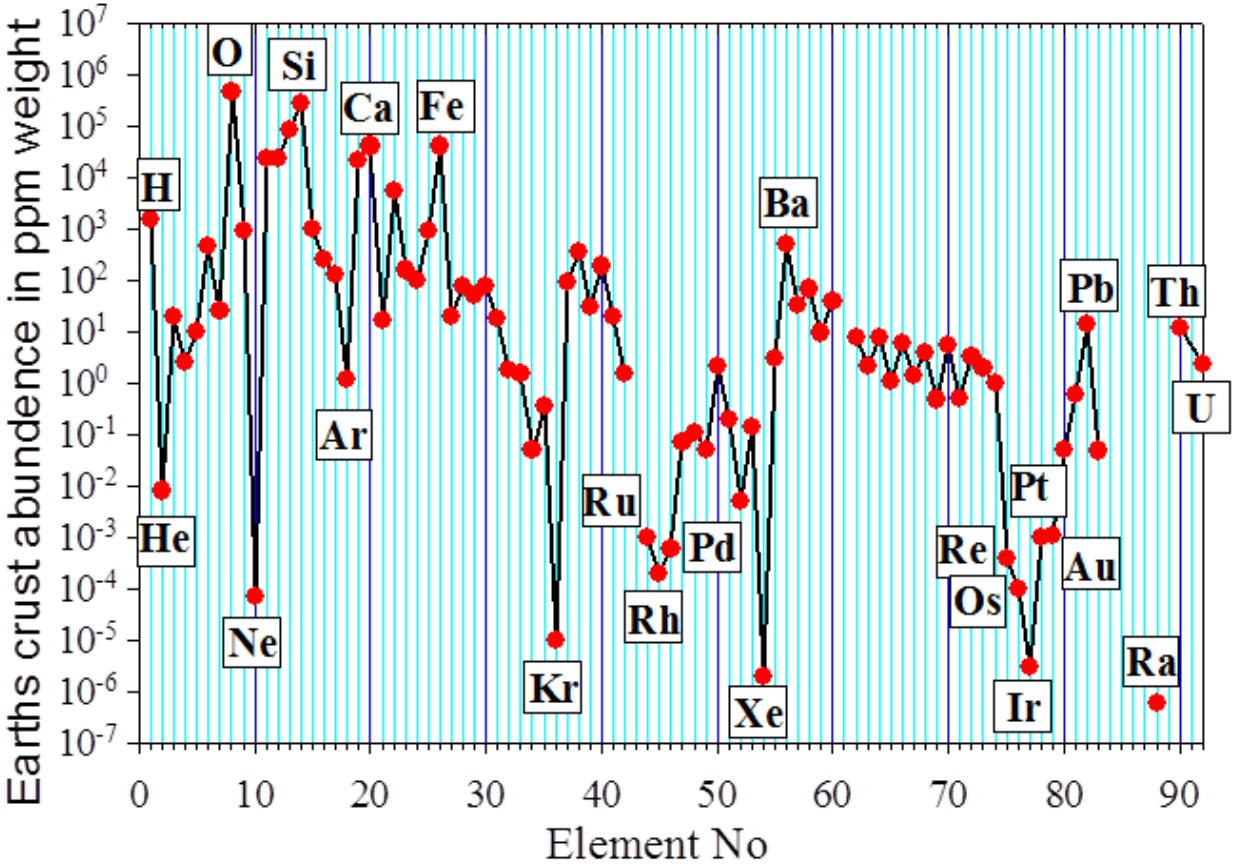
Theoretical trends in oxygen evolution activity

Composition of the earth crust



O, Si, Al, Fe, Ca, Na, Mg, K, Ti → 98.8%

Ru → 1E-7 %

Ir → 3E-8 %

Mn → 0.095%

Theoretical trends in oxygen evolution activity

$H_2O + * \rightarrow HO^* + H^+ + e^-$ ΔG_1

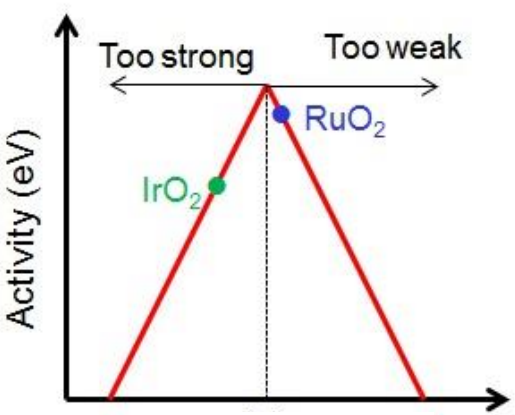
3.2 eV

$HO^* \rightarrow O^* + H^+ + e^-$ ΔG_2

$O^* + H_2O \rightarrow HOO^* + H^+ + e^-$ ΔG_3

$HOO^* \rightarrow O_2 + H^+ + e^-$ ΔG_4

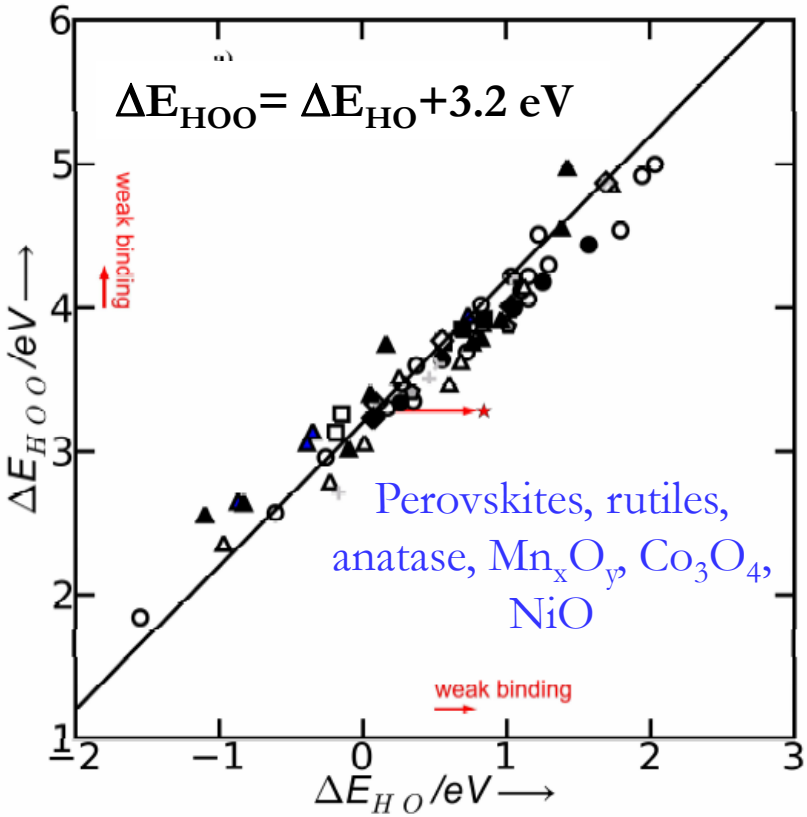
Descriptor of the oxygen evolving activity: $\Delta G_{O*}-\Delta G_{HO*}$



$\Delta G_{O*}-\Delta G_{HO*}$

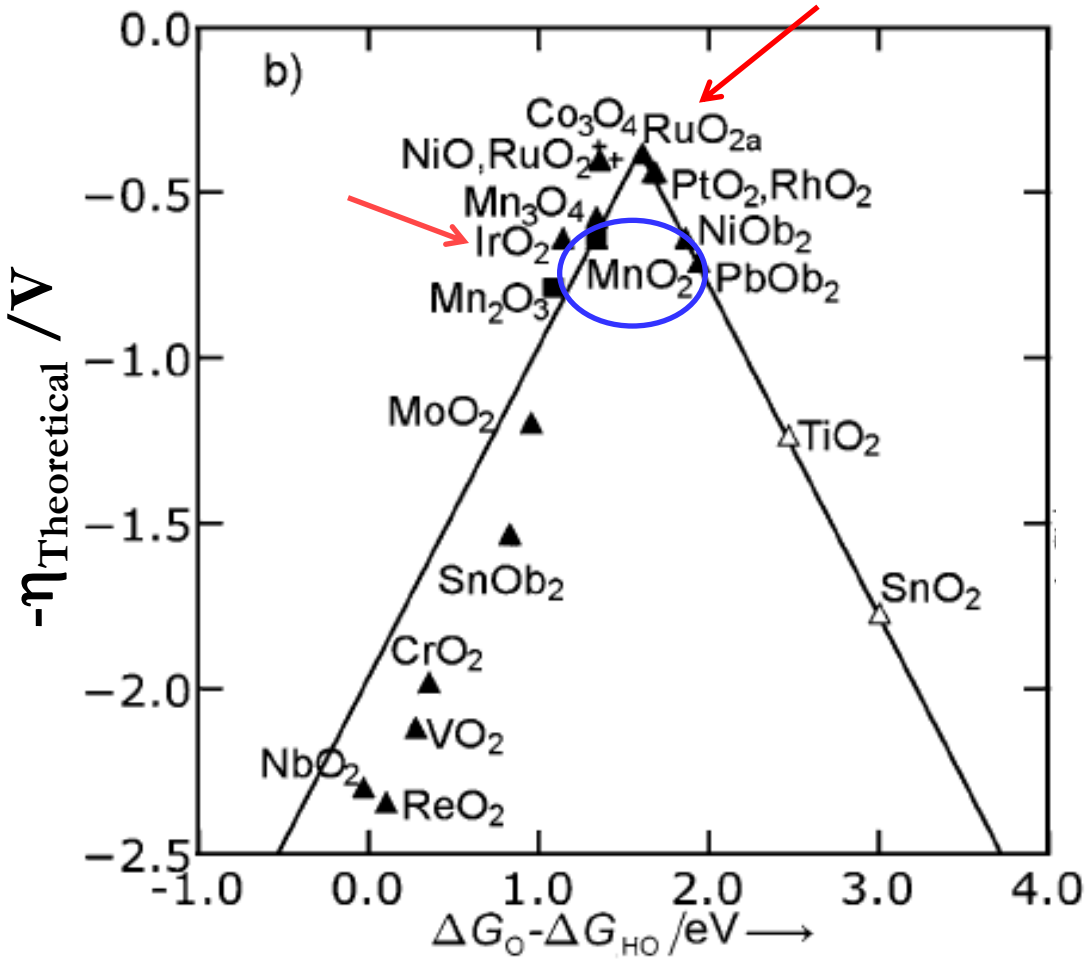
Volcano plots

Scaling relations:



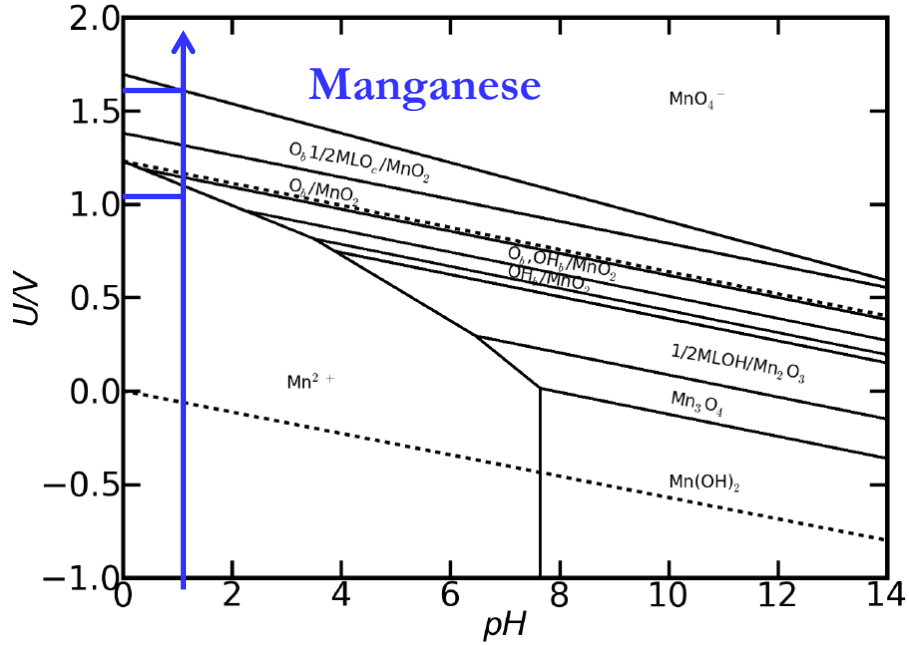
Theoretical trends in oxygen evolution activity

Volcano plots for oxides

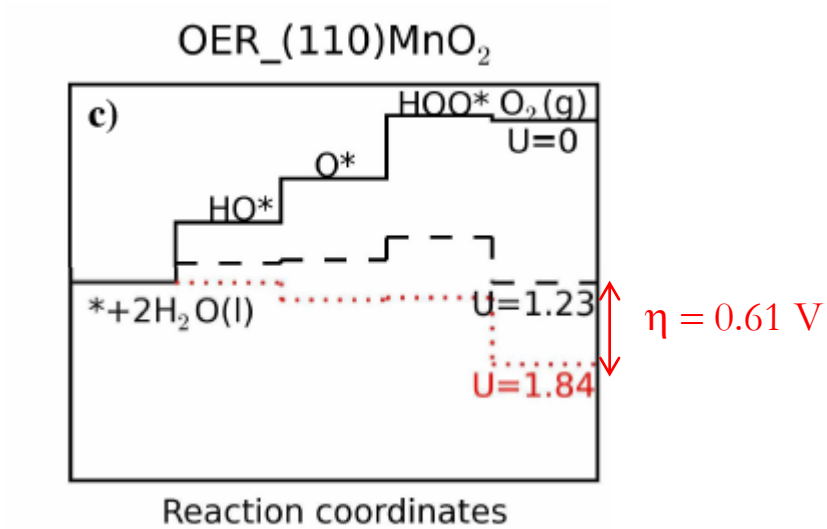


Garcia-Mota and col, Chem Cat Chem 3 (2011) 1159

Theoretical trends in oxygen evolution activity



MnO_2 →Stable from 1.1 to 1.7V at pH1



$\eta_{RuO2} \rightarrow$ **0.37 V**

$\eta_{IrO2} \rightarrow$ **0.57 V**

How to protect MnOx from corrosion

Mann I., Thesis, 2010, DTU Physics

Protection from corrosion

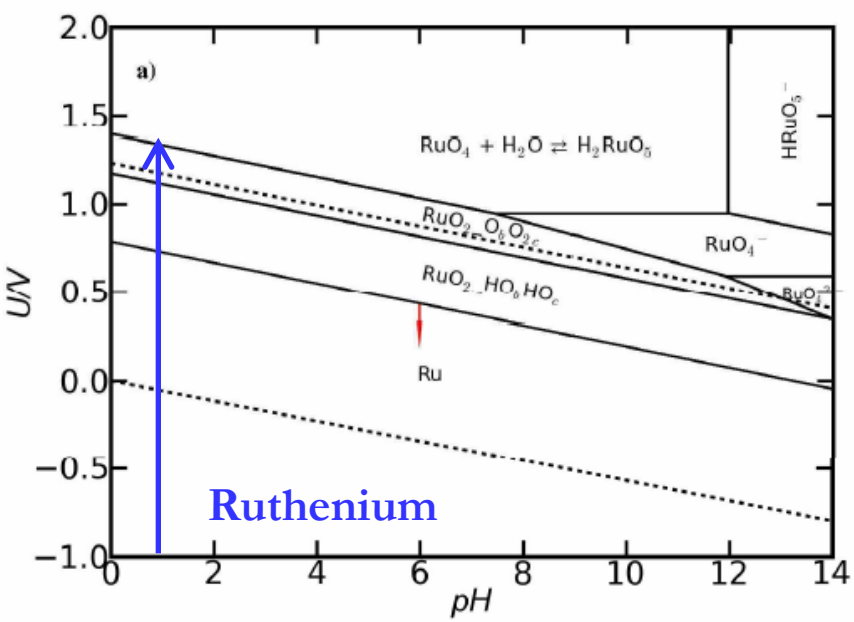
↑ activity (η = 0.42V @10mA/cm²)

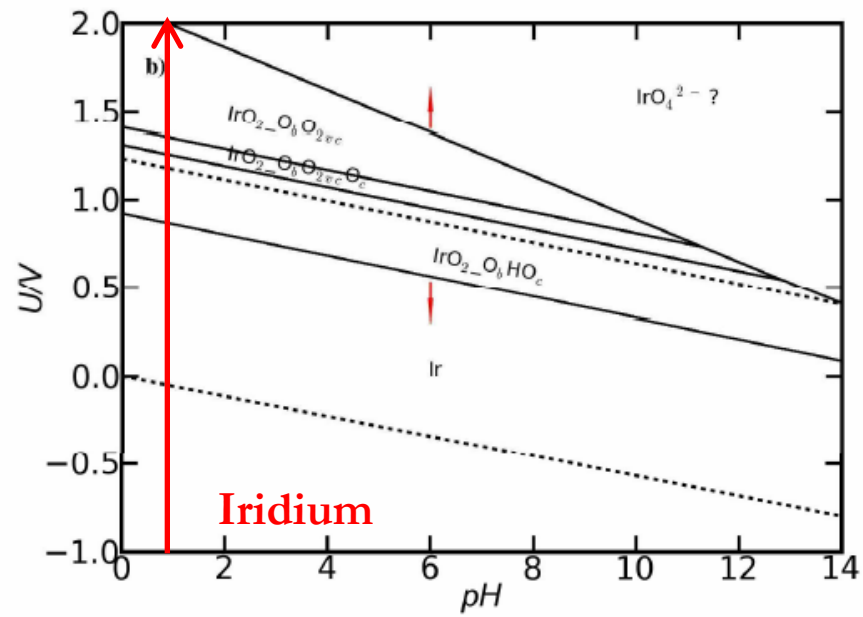
↓ corrosion resistance (1.4 V at pH1)

RuO_2-IrO_2

↓ activity (η = 0.58V @10mA/cm²)

↑ corrosion resistance (2.1 V at pH1)





Mann I., Thesis, 2010, DTU Physics

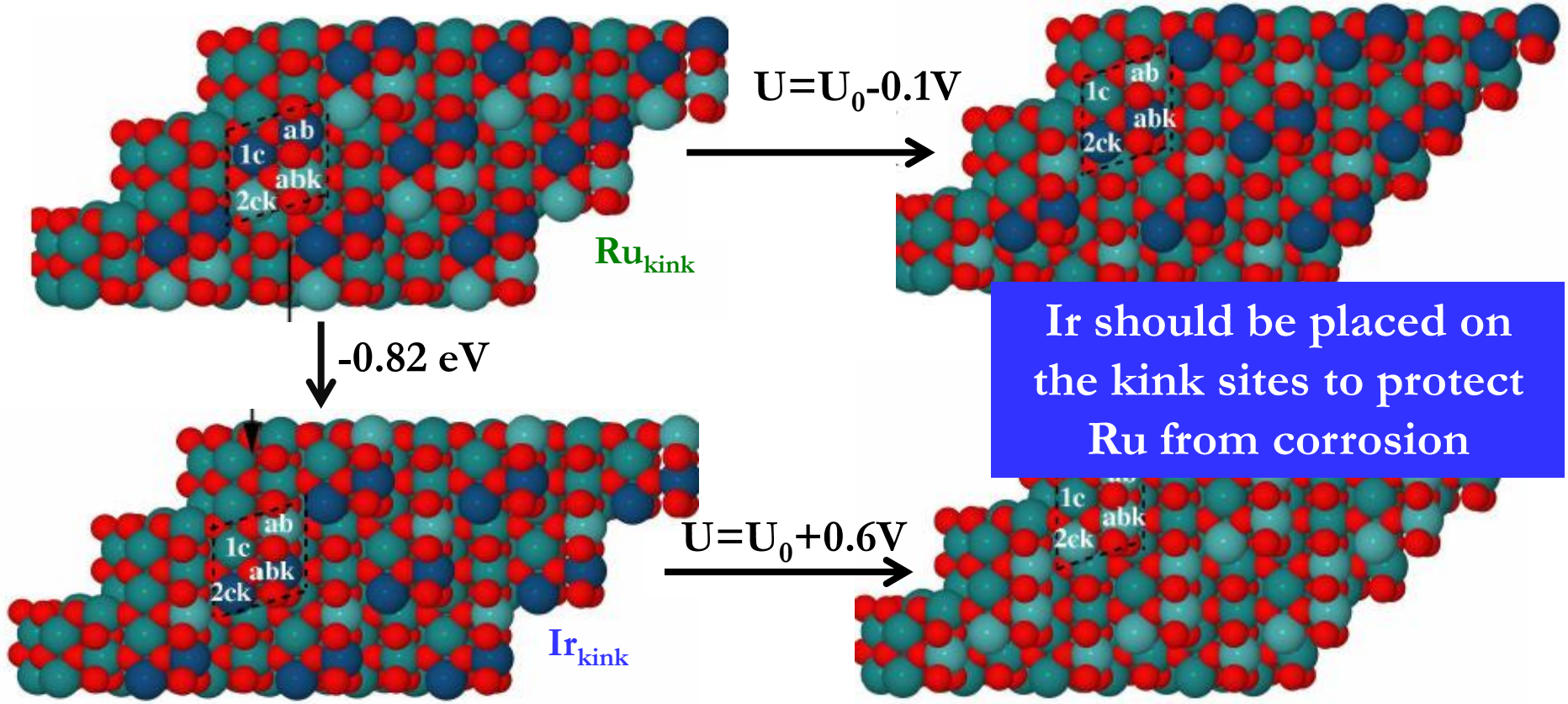
Trasatti et al, Materials Chem and Phys 22 (1989) 231

Protection from corrosion

$IrO_2 + 2H_2O \leftrightarrow IrO_4^{2-} + 4H^+ + 4e^-$ $U_0 = 2.057V$

$RuO_2 + 3H_2O \leftrightarrow H_2RuO_4 + 4H^+ + 4e^-$ $U_0 = 1.4V$

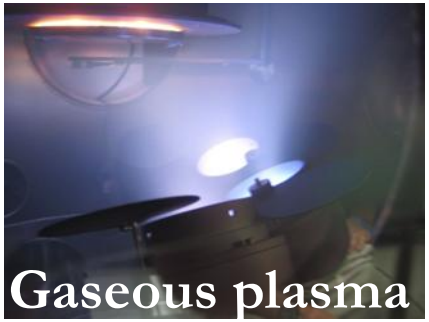
Ir segregates to the kink sites



Ir should be placed on the kink sites to protect Ru from corrosion

Mann, I. Thesis, 2011, DTU Physics

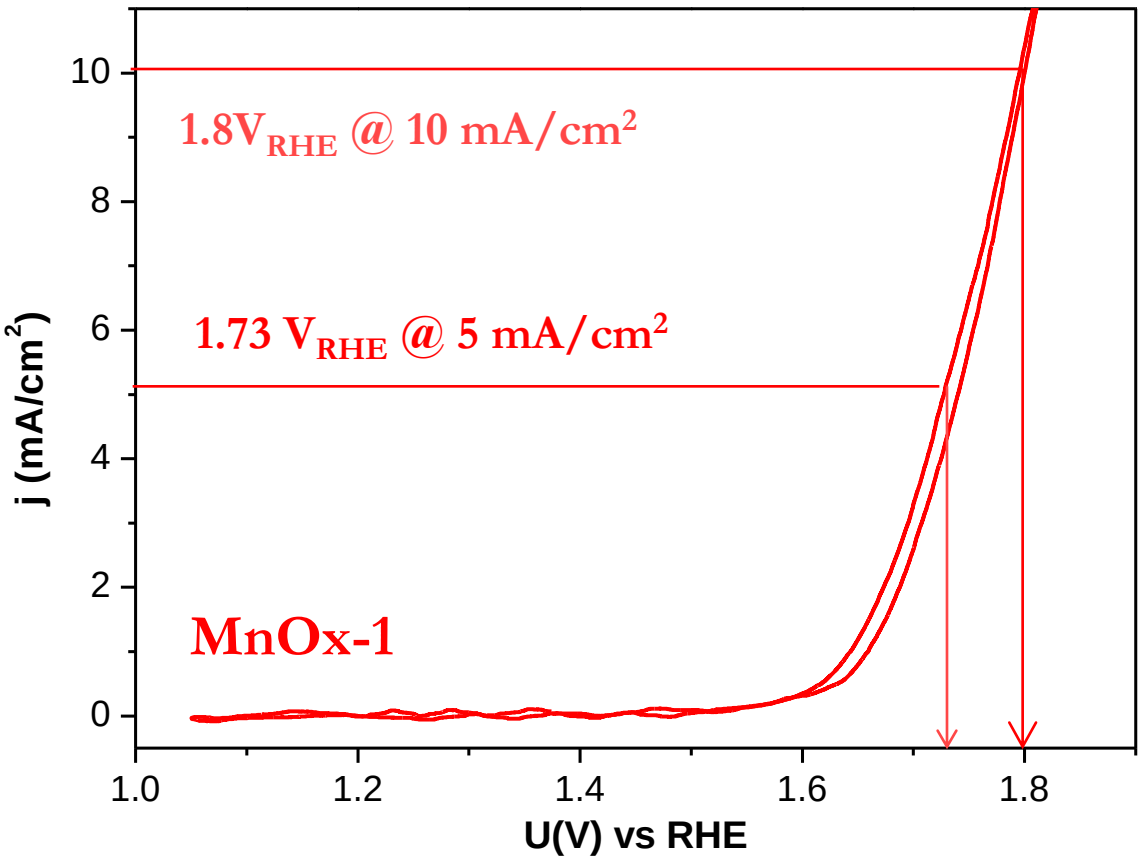
Film preparation- Sputter deposition



- **MnO_X-1**
  - **90 nm Mn** at 5 mTorr Ar and 480C
  - 100 W
  - Annealed in air at 480 C (Furnace)
- **MnO_X-2**
  - **1.5 nm Ti**
  - **90 nm MnO_X** at 3 mTorr Ar/O_2 (10sccm) and 150C
  - 100 W
  - Annealed in air at 480 C (Furnace)

Film preparation- Sputter deposition

OER activity in N_2 sat. 0.1M KOH
1600 rpm 5mV/s



Jaramillo et al., JACS 132 (2010) 13612

Table 1. Oxygen Electrode Activities

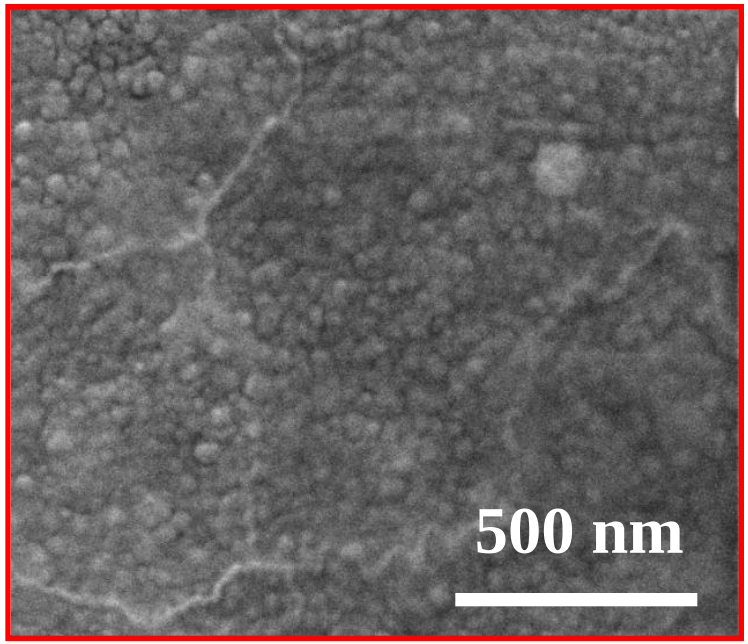
Catalyst Material	ORR: E(V) at $I = -3$ mA·cm^{-2}	OER: E(V) at $I = 10$ mA·cm^{-2}
20 wt % Ir/C	0.69	1.61
20 wt % Ru/C	0.61	1.62
20 wt % Pt/C	0.86	2.02 (1.88)[a]
Mn oxide	0.73	1.77

1.66 V$_{RHE}$ @ 5 mA/cm^2

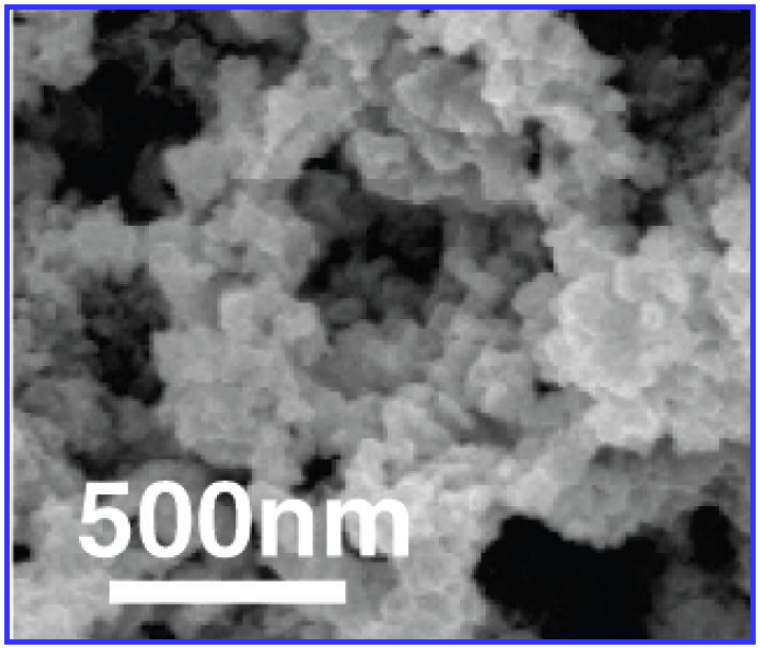
Film preparation- Sputter deposition

SEM

MnOx-1



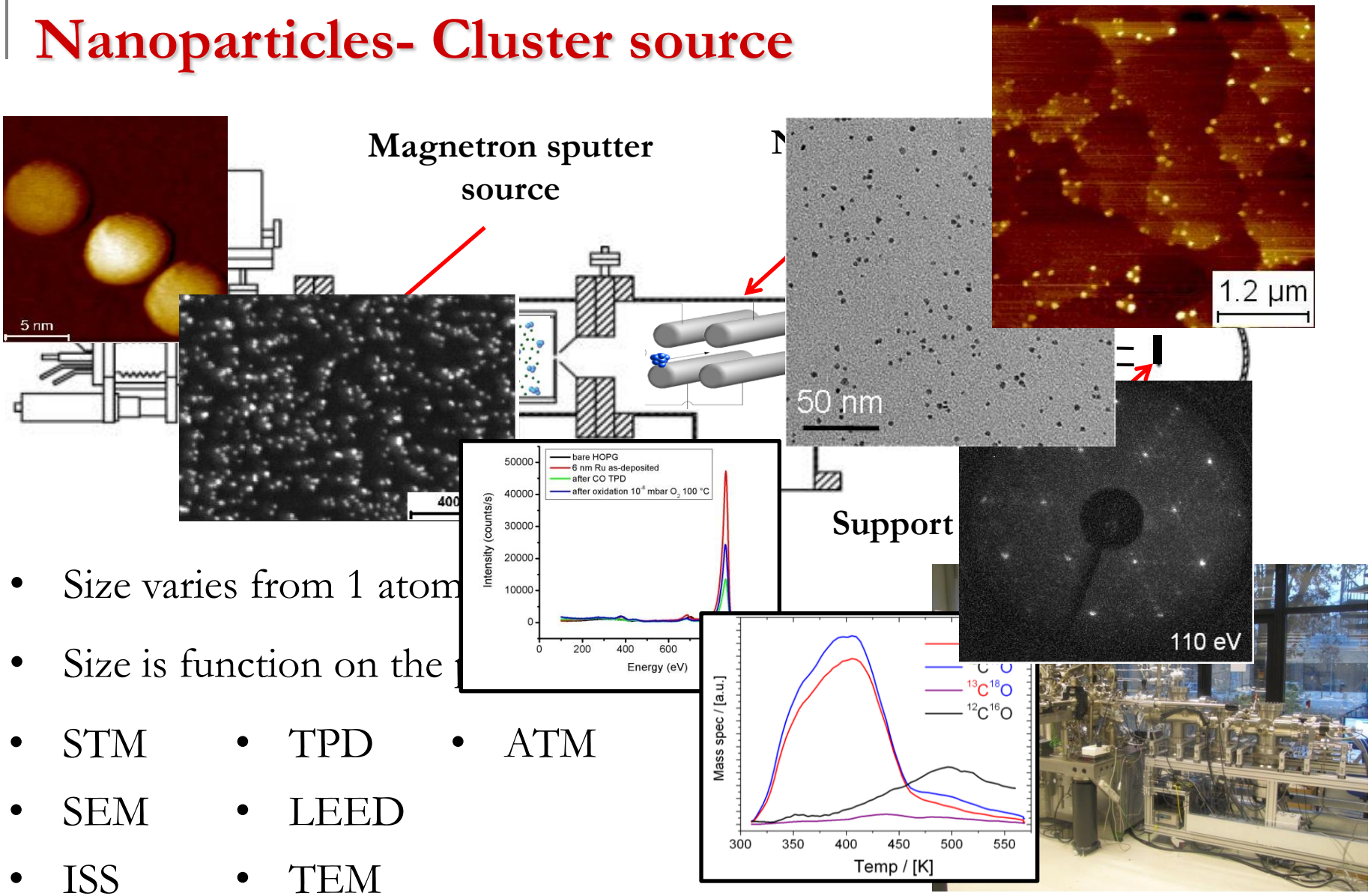
MnOx electrodeposited



Corrosion protection → Acidic media

Jaramillo et al, JACS 132 (2010) 13612

Nanoparticles- Cluster source

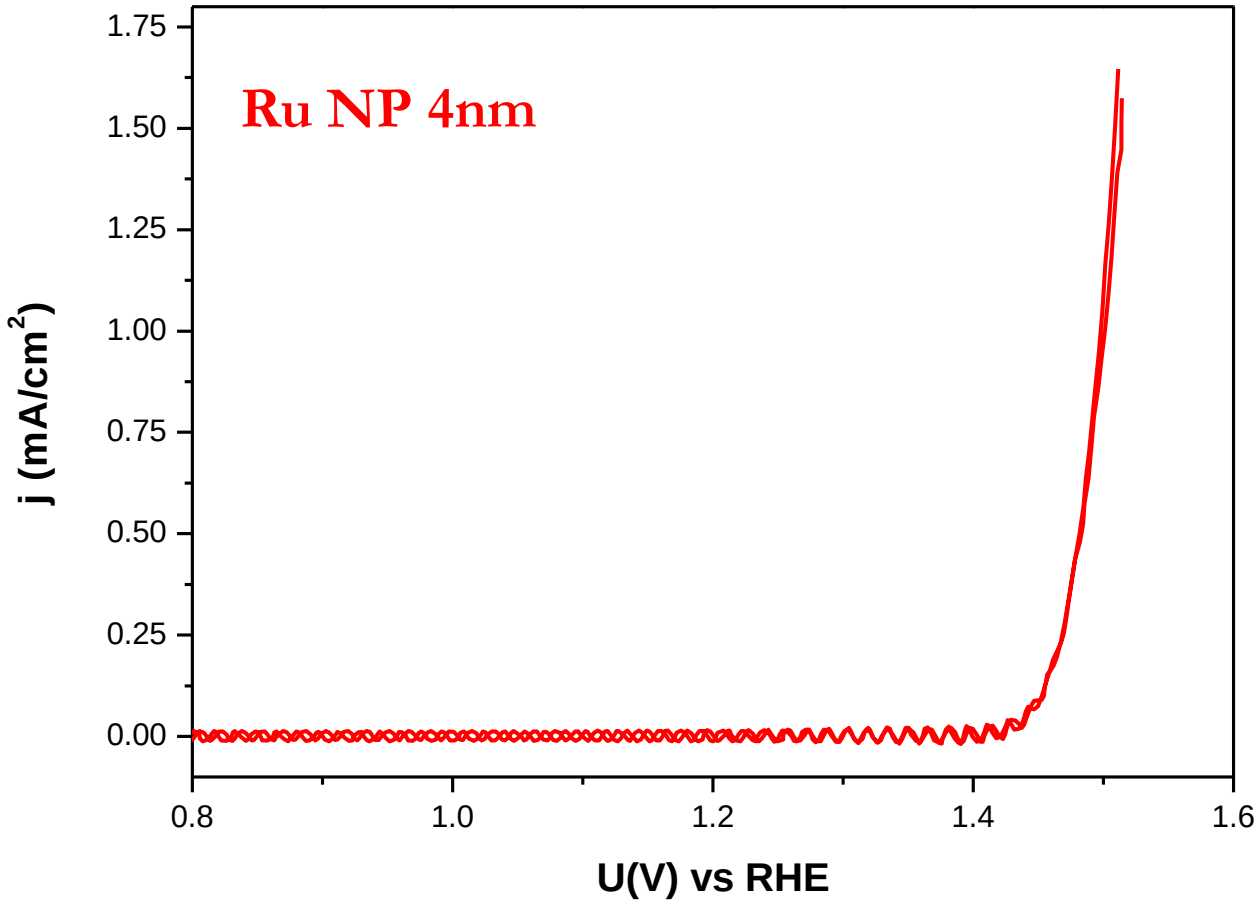


- Size varies from 1 atom
- Size is function on the

- STM
- SEM
- ISS
- TPD
- LEED
- TEM
- ATM

Nanoparticles- Cluster source

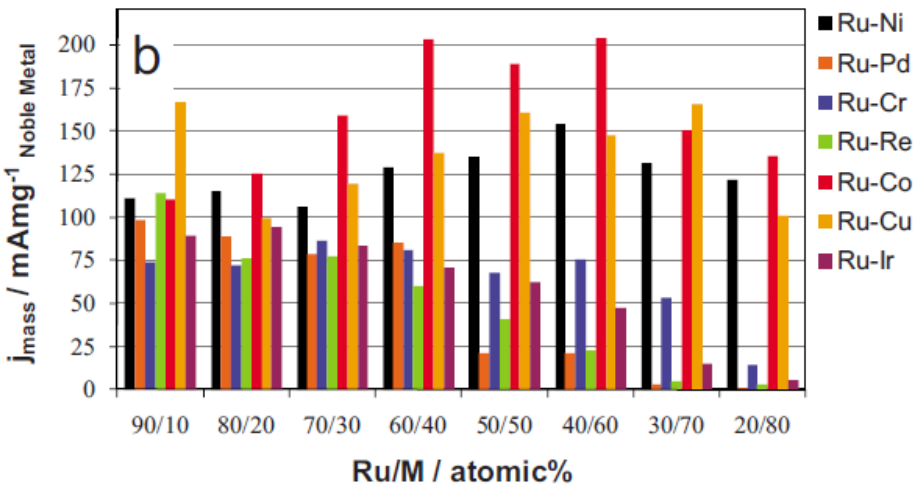
OER activity in N_2 sat. 0.1M $HClO_4$
1600 rpm 20mV/s



0.07 μg_{Ru}

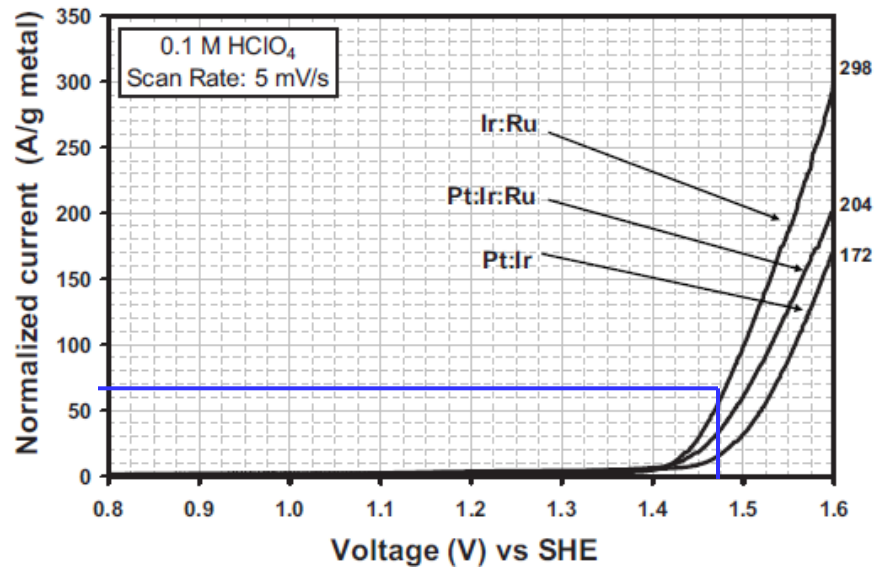
Nanoparticles- Cluster source

Strasser et al., Electrochem Solid St Lett 13 (2010) B36



Ru NP 4nm → 1344 mA/mg$_{Ru}$ @1.48V

Fuentes et al., Electrochem Solid St Lett 14 (2011) E5



Ru NP 4nm → 1344 A/g$_{Ru}$ @1.48V

Corrosion protection

Summary

- RuO_2 is the most active catalysts for OER, but we need to protect it from corrosion → Ir on the kink sites
- MnO_2 is a good candidate to replace RuO_2 because is active and abundant
- The catalytic activity of the MnO_2 films prepared by sputter deposition are comparable with the state of the art (alkaline)
- The mass activity of the Ru NP prepared in the cluster source is one order of magnitude higher than the state of the art

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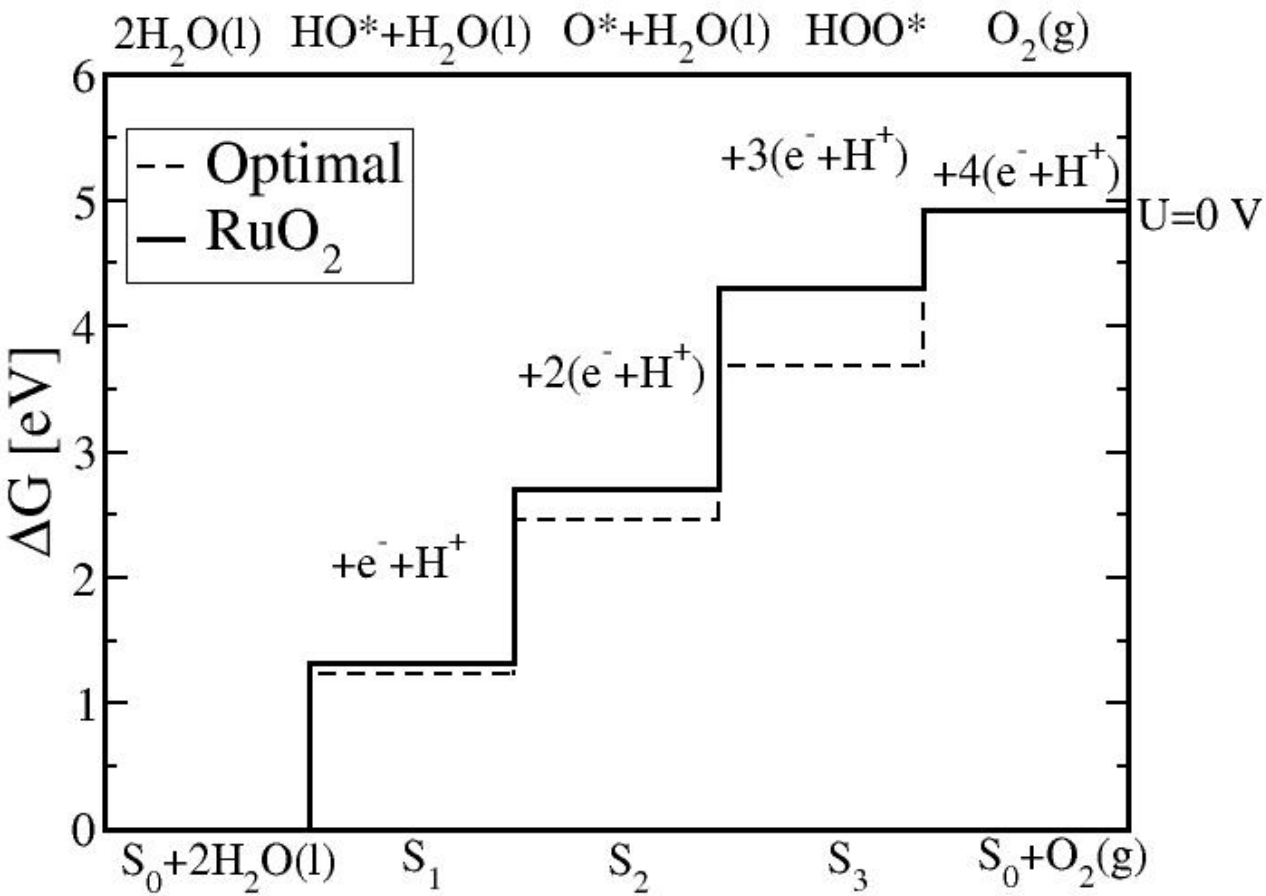
Theoretical trends in oxygen evolution activity

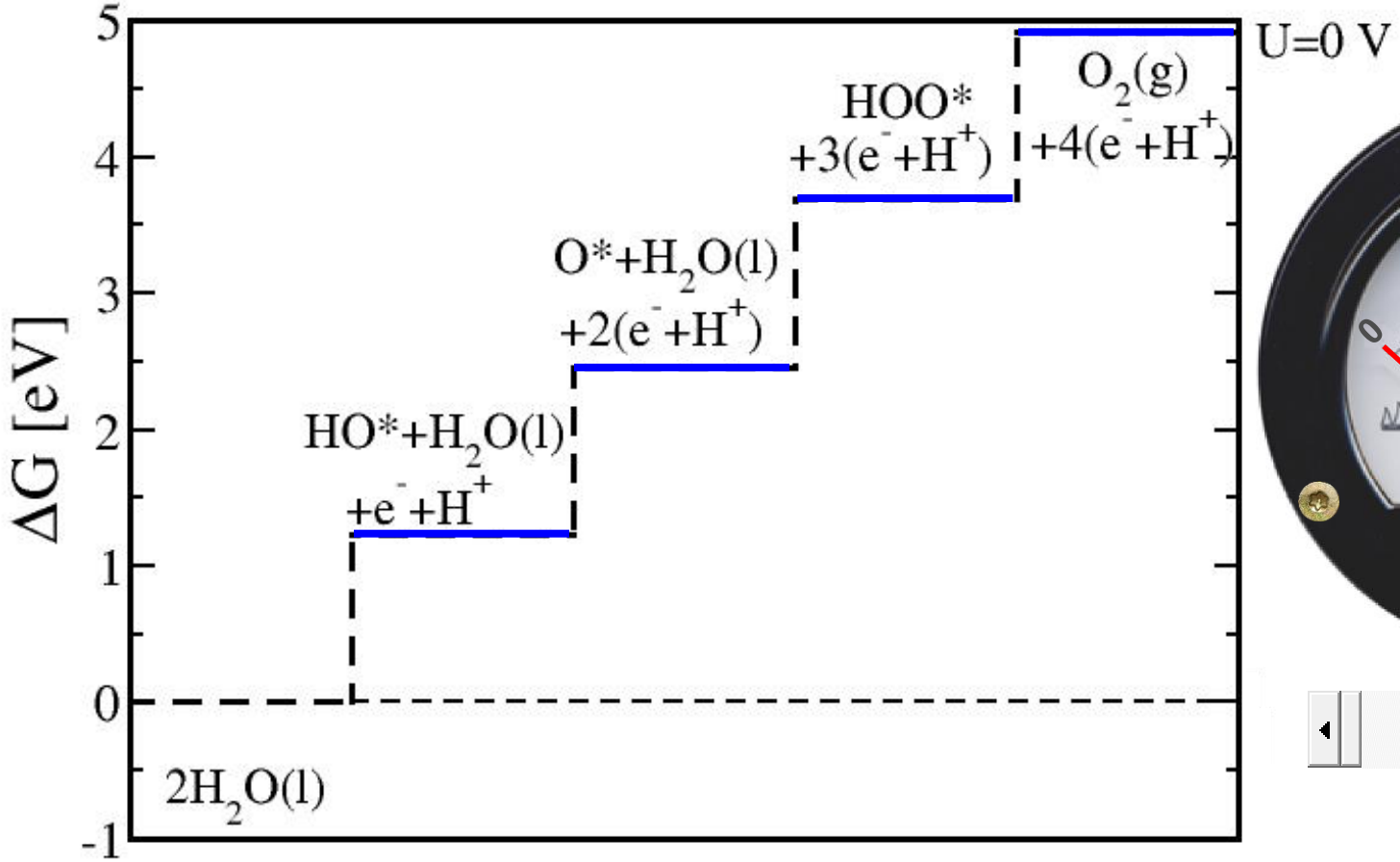
RuO_2 vs ideal catalyst



Rossmeisl et al, J Phys Chem C 111 (2007) 18821

Theoretical trends in oxygen evolution activity

Ideal catalyst



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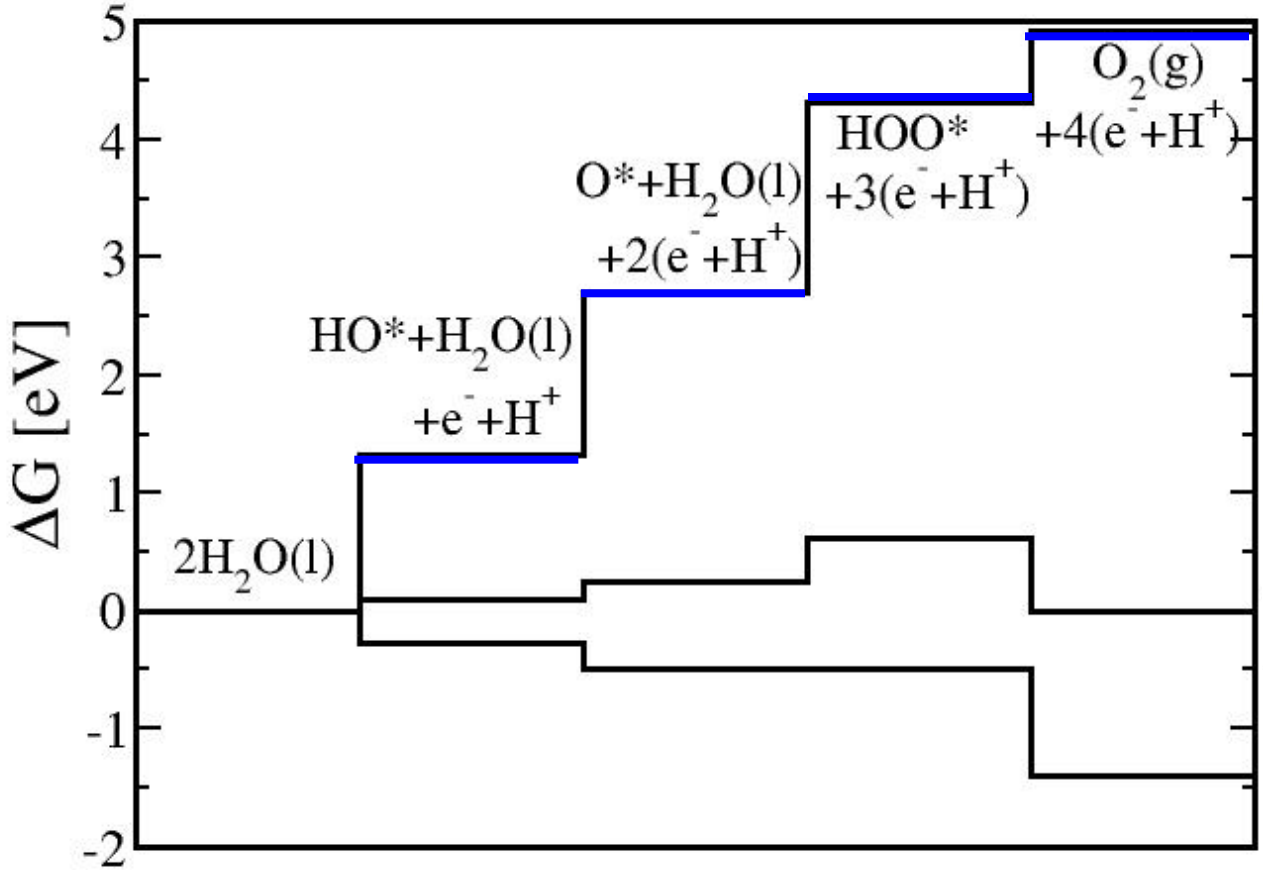
Theoretical trends in oxygen evolution activity

RuO_2 (110)



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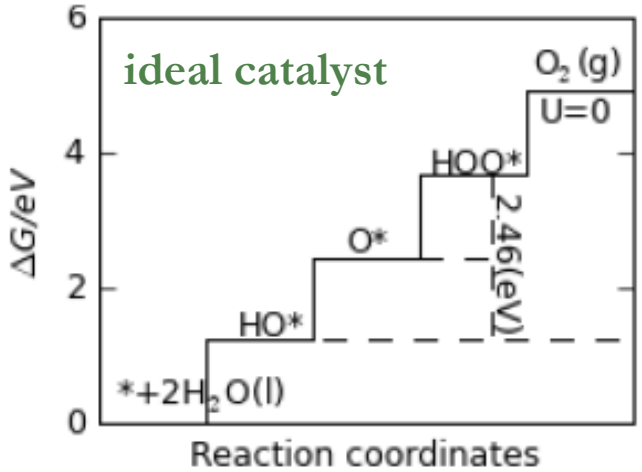
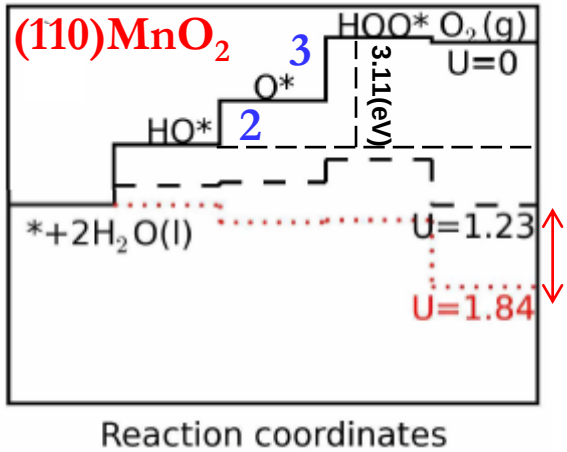
Theoretical trends in oxygen evolution activity

Free energy diagram:





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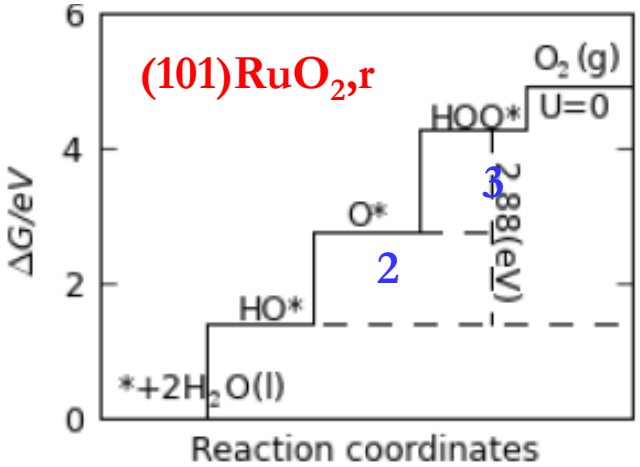

ΔG_3-ΔG_2 ~ 3 eV → O* position

$$HO^* \rightarrow O^* + H^+ + e^- \quad \Delta G_2$$

$$O^* + H_2O \rightarrow HOO^* + H^+ + e^- \quad \Delta G_3$$

Rossmeisl and col, Chem Cat Chem 3 (2011) 1159
Rossmeisl et al, J Electroanal Chem 607 (2007) 83