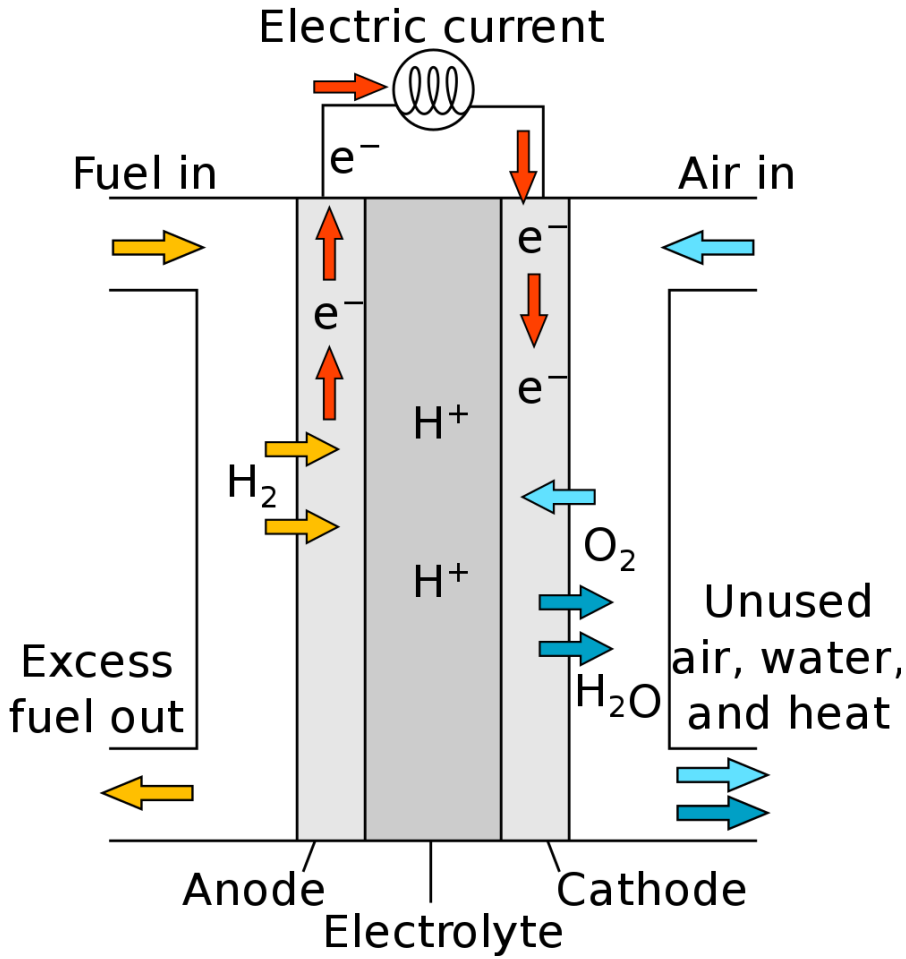
Karsten W. Jacobsen
Department of Physics
Technical University of Denmark

High Entropy Alloys for Catalysis

Outline

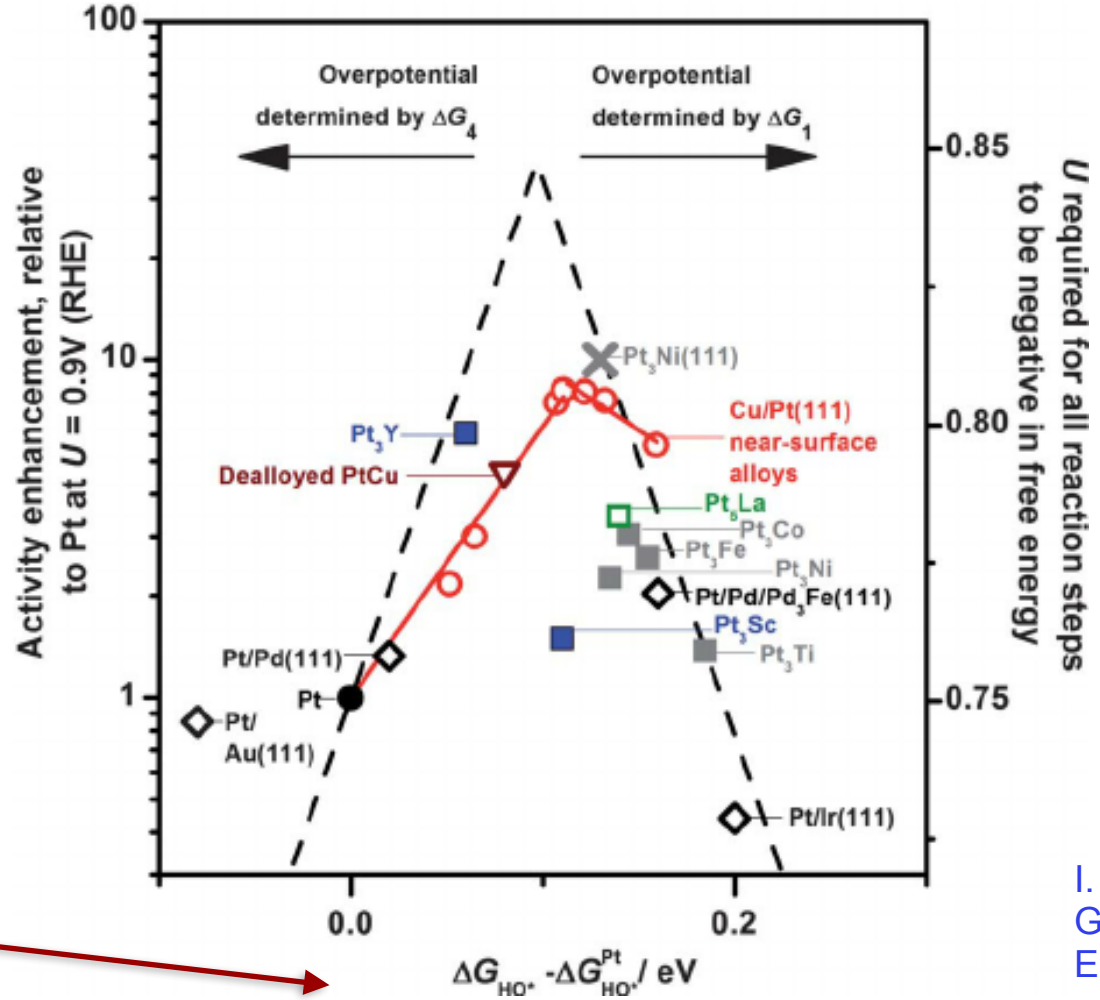
- Fuel cells and the oxygen reduction reaction
- Catalytic descriptor
- High entropy alloys - what are they?
- Linear bonding model for OH
- Optimization of catalysis through alloy composition

Proton exchange membrane (PEM) fuel cell



The difficult part: oxygen reduction reaction (ORR)

Oxygen reduction reaction - activity descriptor



Best material: OH binding should be 0.1 eV weaker than on Pt

”Descriptor”:
OH binding energy

I. E. L. Stephens, A. S. Bondarenko, U. Grønbjerg, J. Rossmeisl, and I. Chorkendorff, Energy Environ. Sci., 5, 6744 (2012)

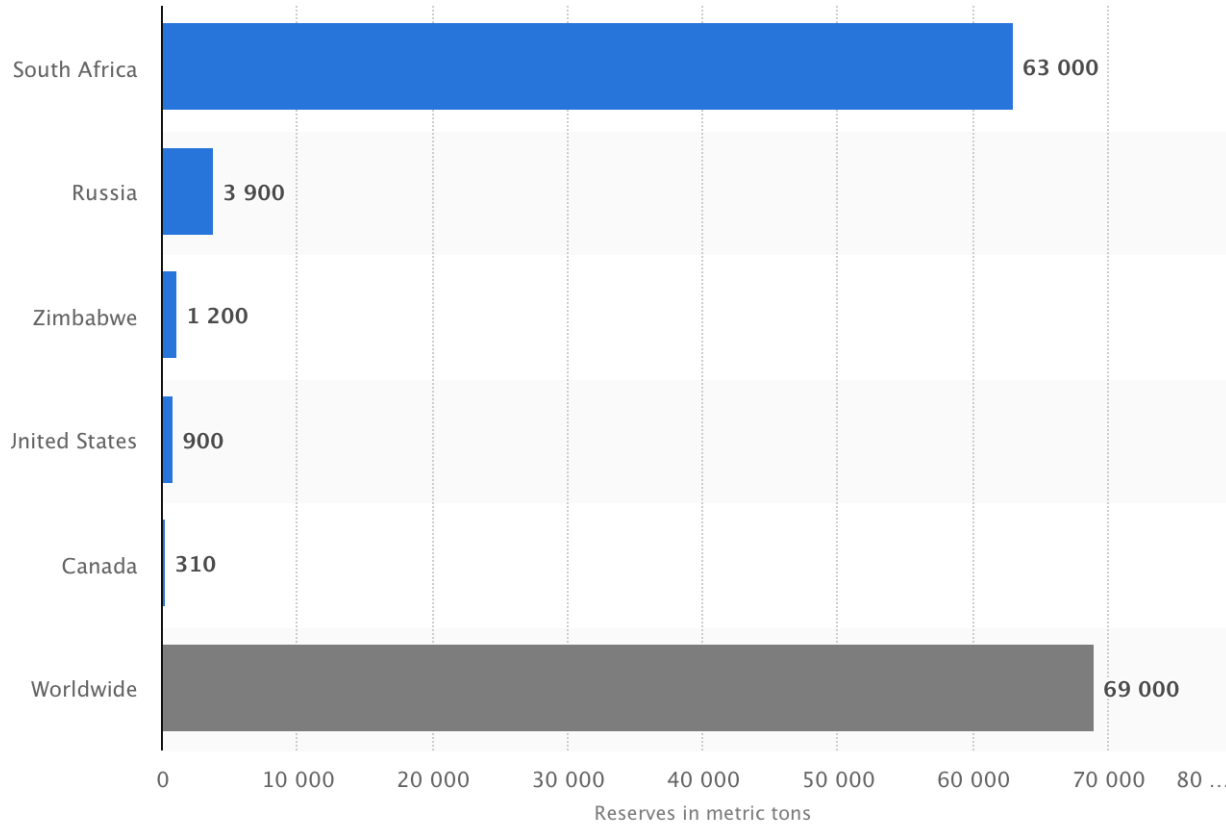
We need something different from platinum.

- **Platinum use in cars:**

- Used in a **catalytic converter**: 5g platinum per car
- Yearly production of cars: 80 million -> 400 tons of platinum

- More is needed for **fuel cells**!

Platinum reserves in the World ~69000 tons

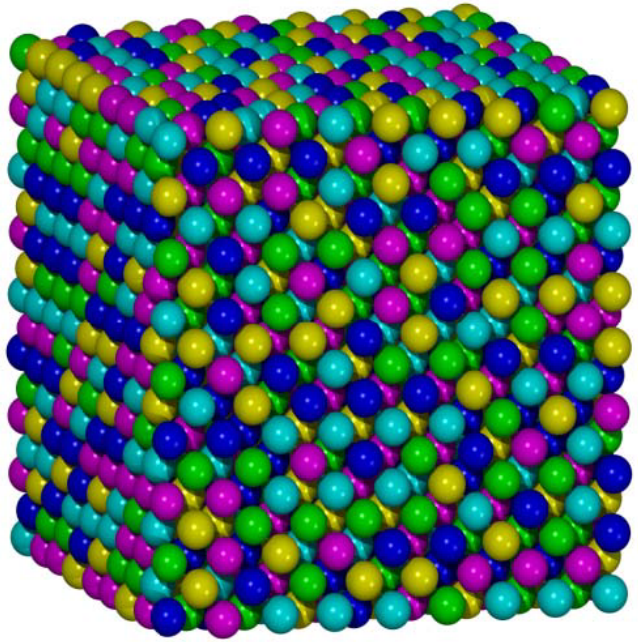


High-entropy alloys

Multi-element alloys dominated by entropy -> lattice disorder

Example: CoCrFeMnNi

Here: IrPdPtRhRu



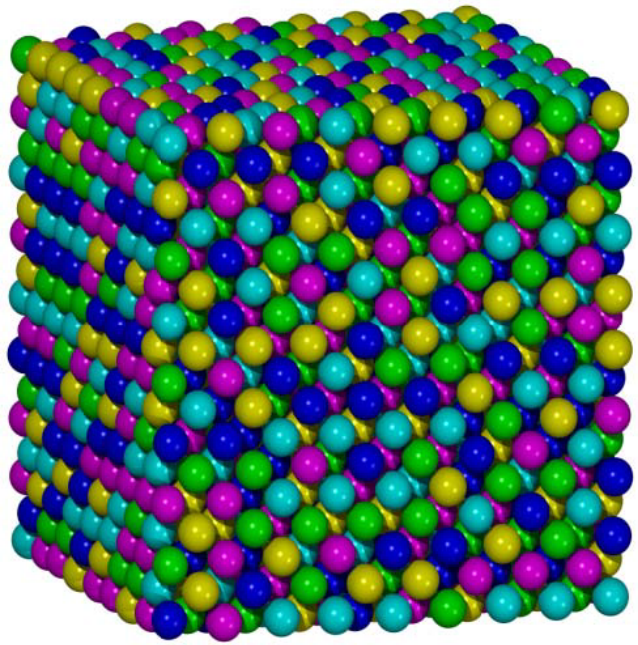
$$\Omega = \frac{T_m \Delta S_{mix}}{|\Delta H_{mix}|} \geq 1.1$$

Many different bonding configurations at the surface

High-entropy alloys

Multi-element alloys dominated by entropy -> lattice disorder

Example: CoCrFeMnNi

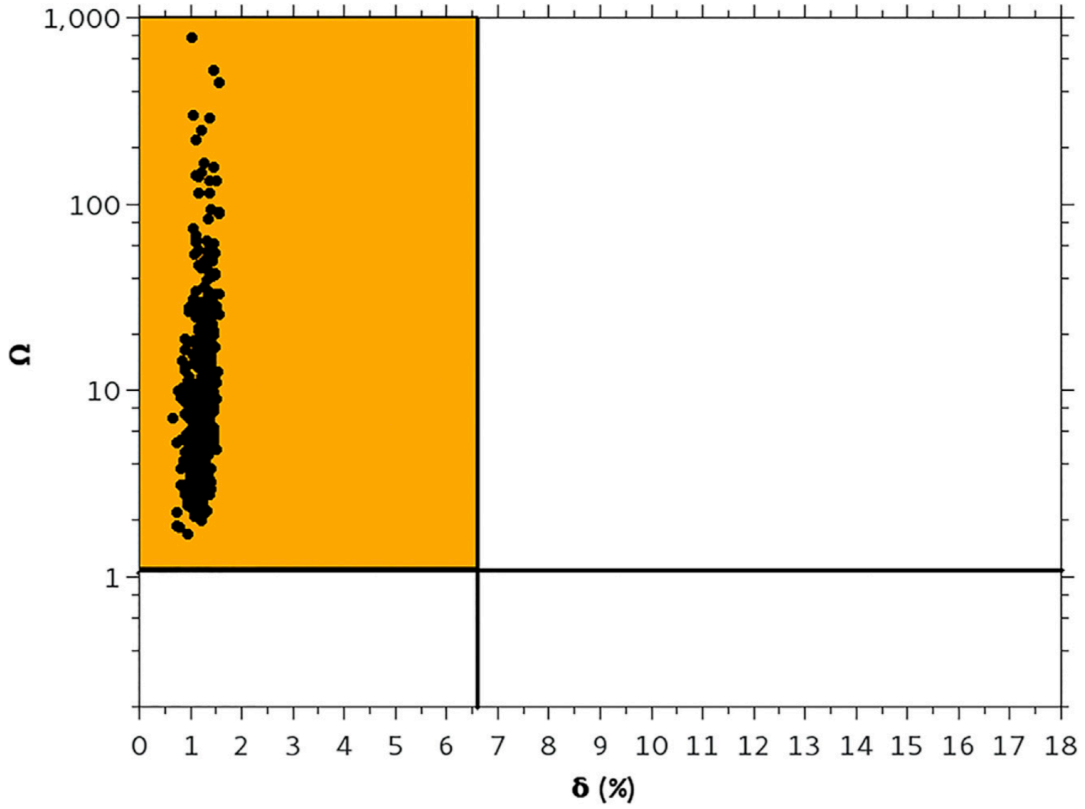


$$\Omega = \frac{T_m \Delta S_{mix}}{|\Delta H_{mix}|} \geq 1.1$$

$$\delta = \sqrt{\sum_{i=1}^{N} c_i (1 - r_i/\tilde{r})^2}.$$

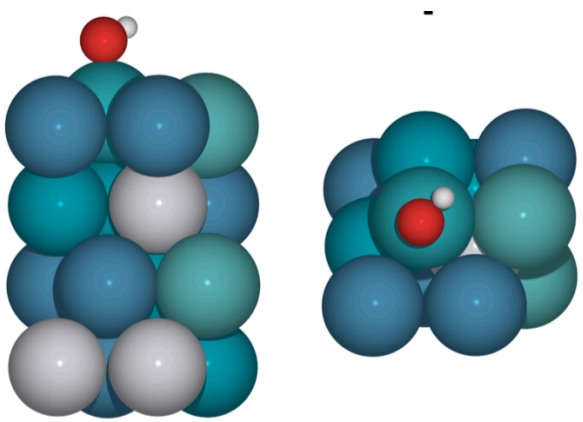
$$\delta \leq 6.6\%$$

IrPdPtRhRu
8-atom unit cells

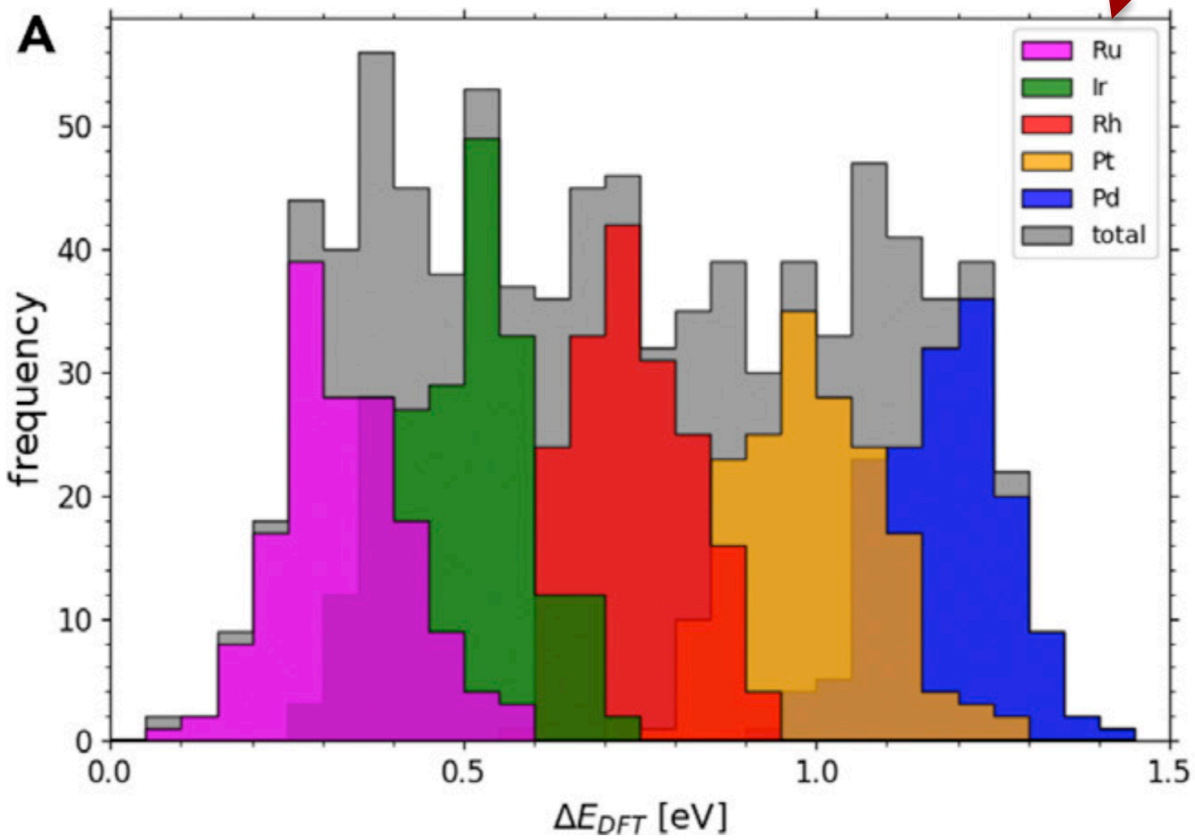


Binding energies of OH for small unit cells

871 2x2 periodic unit cells



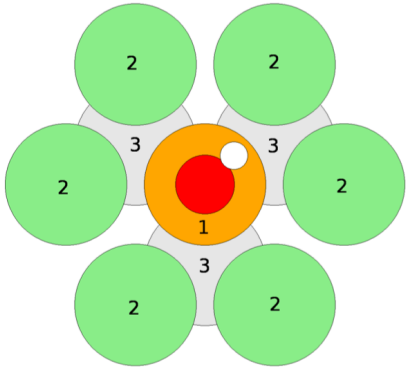
Nearest neighbor metal atom



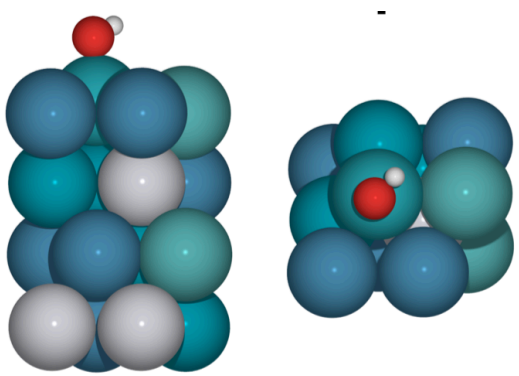
Batchelor, Pedersen, Winther, Castelli, Jacobsen, Rossmeisl, Joule,3, 834 (2019).

Linear model for OH binding energy

High Entropy Alloy: RuIrRhPtPd



Training: DFT on 871 small unit cells



Simple linear model of binding

$$\Delta E^i_{pred} = \sum_k^{metals} C_{1,k} N^i_{1,k} + \sum_k^{metals} C_{2,k} N^i_{2,k} + \sum_k^{metals} C_{3,k} N^i_{3,k}$$

15 parameters

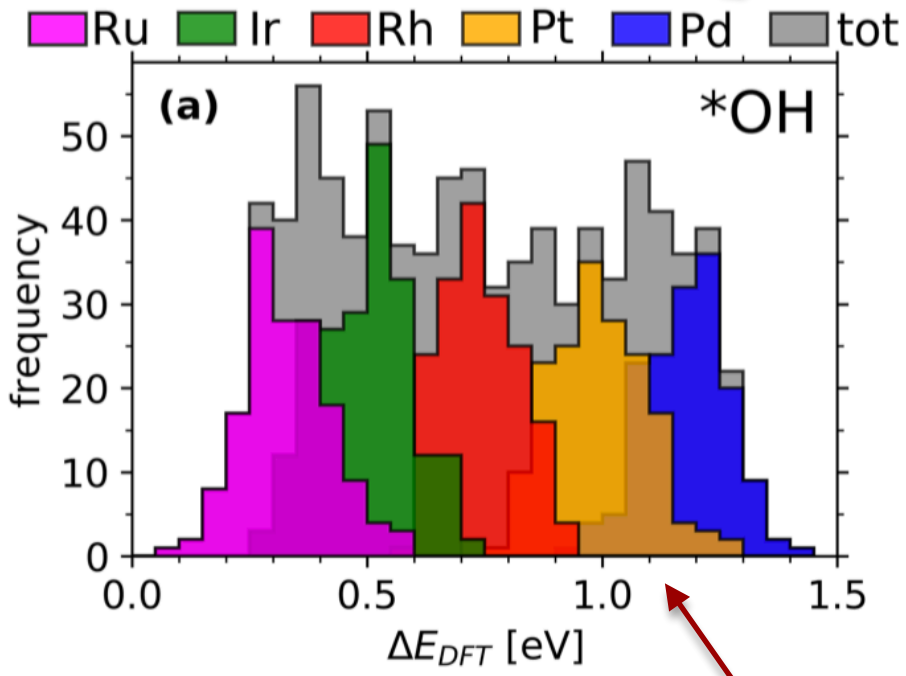
Batchelor, Pedersen, Winther, Castelli, Jacobsen, Rossmeisl, Joule,3, 834 (2019).

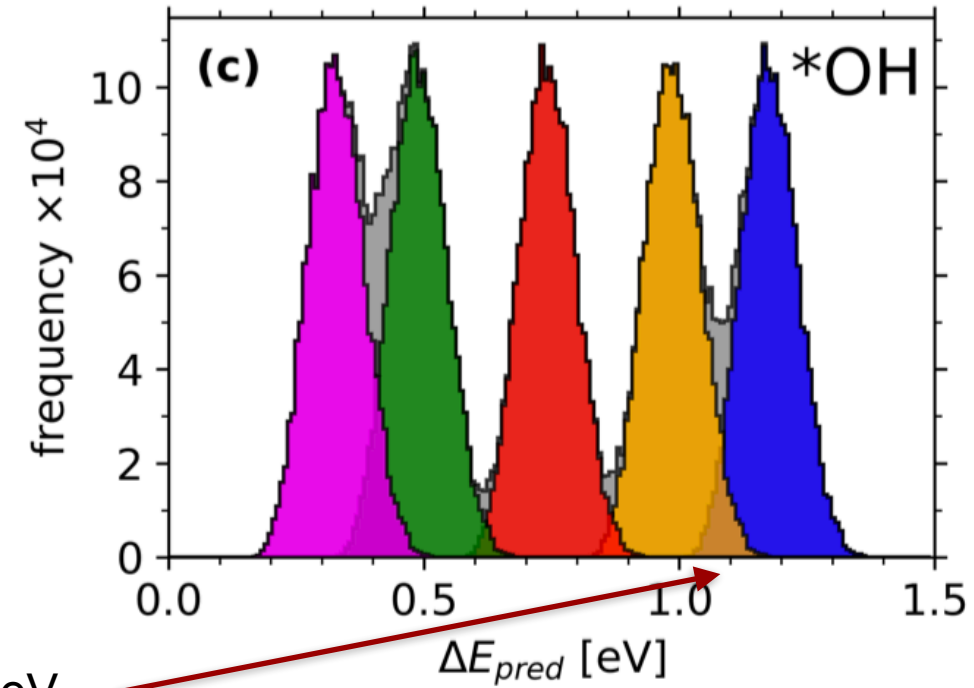
Linear model for OH binding energy

Training on 871 2x2 unit cells

Nearest neighbor metal atom

Predictions for all 2x2 unit cells

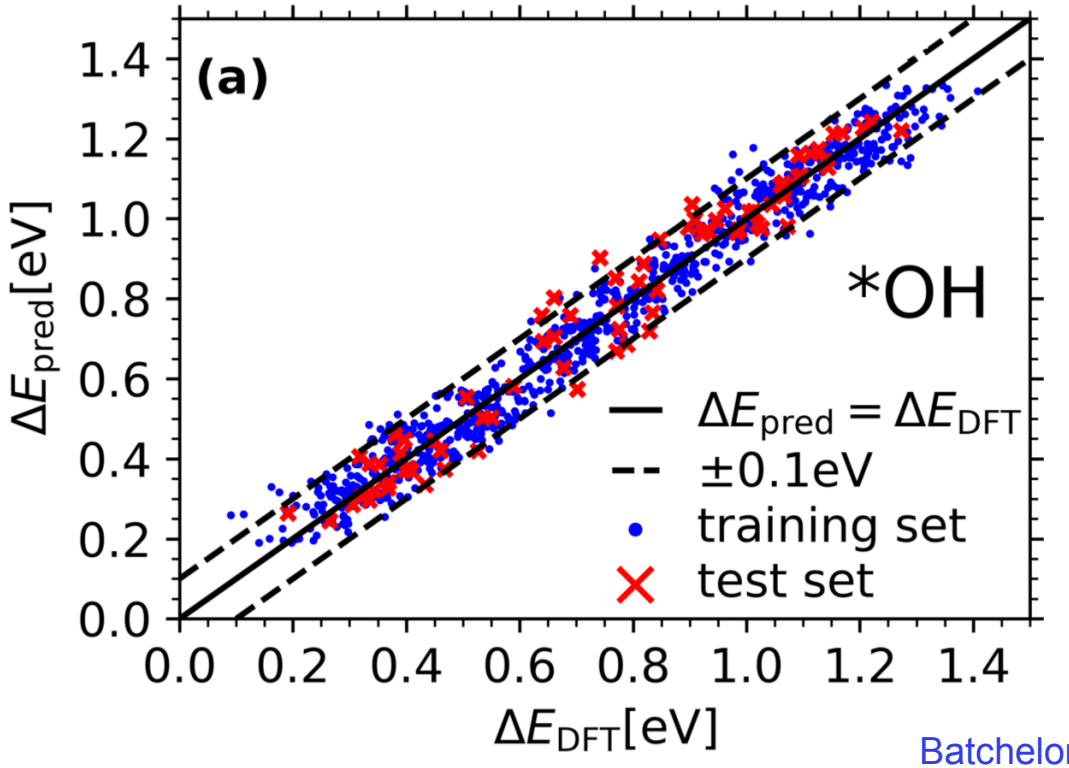


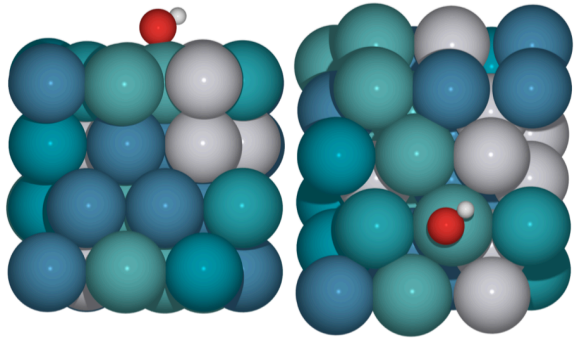


Optimal value ~1.1 eV

Test on larger unit cells

$$\Delta E^i_{pred} = \sum_k^{metals} C_{1,k} N^i_{1,k} + \sum_k^{metals} C_{2,k} N^i_{2,k} + \sum_k^{metals} C_{3,k} N^i_{3,k}$$





Training set RMSD ~ 0.05 eV
Test on 36 3x4 unit cells
RMSD ~ 0.06 eV

Batchelor, Pedersen, Winther, Castelli, Jacobsen, Rossmeisl, Joule,3, 834 (2019).

Model of catalytic activity

Frequency of binding configuration

$$A = \sum_{i=1}^{N} w_i \exp\left(-\frac{|\Delta E_i - \Delta E_{opt}|}{k_b T}\right)$$

$$A_{\mathrm{Pt}} = 0.021$$

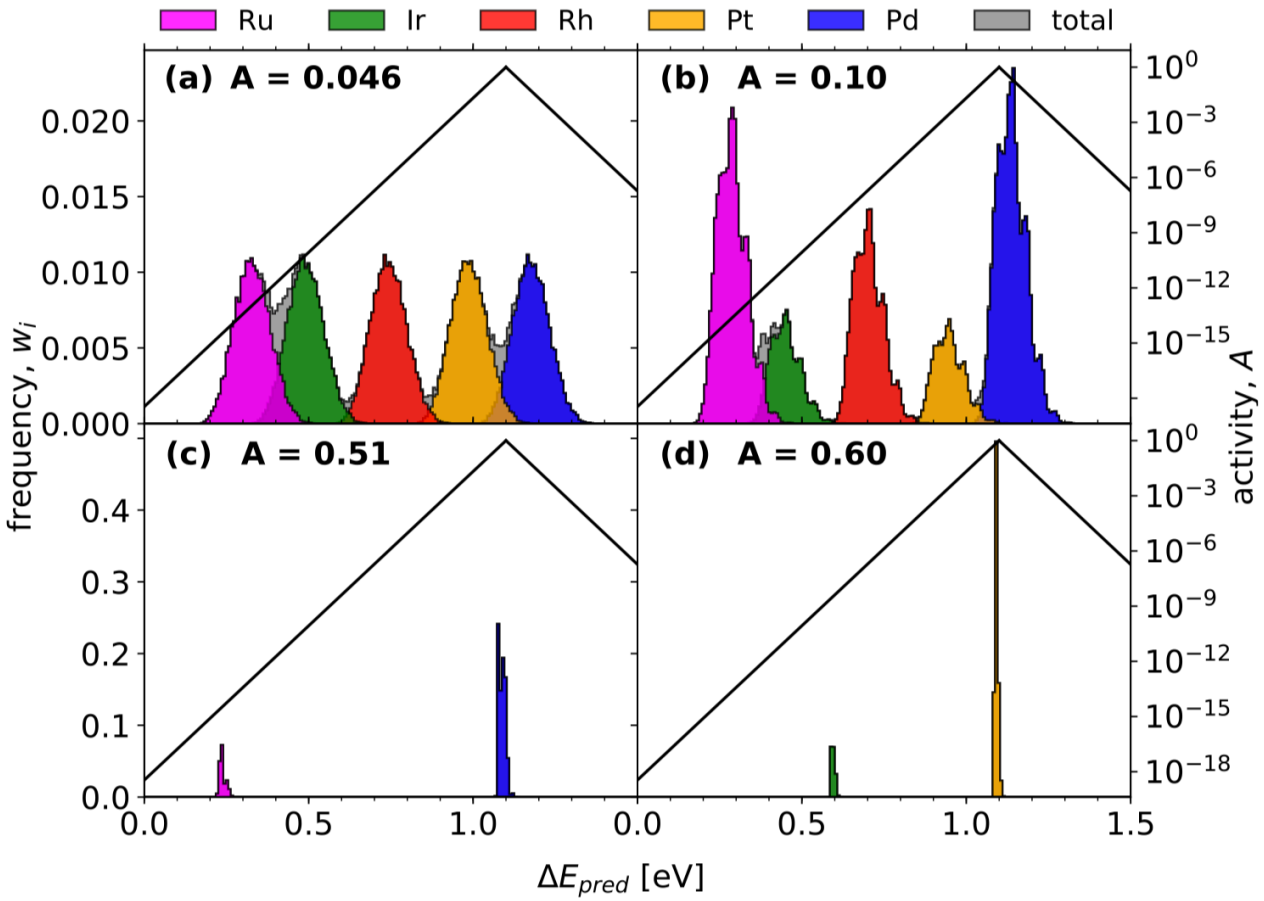
Optimization of activity

Model for activity:

$$A = \sum_{i=1}^{N} w_i \exp\left(-\frac{|\Delta E_i - \Delta E_{opt}|}{k_b T}\right)$$

A_{Pt} = 0.021

$Ru_{0.2}Ir_{0.2}Rh_{0.2}Pt_{0.2}Pd_{0.2}$



Best HEA:
(f_{Ru}, f_{Ir}, f_{Rh}, f_{Pt}, f_{Pd}) =
(0.29, 0.10, 0.20, 0.09, 0.32)

Local maximum
$Pd_{0.82}Ru_{0.18}$
but unstable alloy

Global maximum of activity
$Pt_{0.825}Ir_{0.175}$

Stable alloy with low surface segregation energy

High entropy alloys: a new playground for catalysis

- High entropy alloys disordered due to high entropy
- Large variety of bonding sites at surfaces
- Some of these sites could be optimal for the oxygen reduction reaction
- The frequency of sites can be controlled by bulk composition

- Question: How much does local order affect the properties?

Thanks to

University of Copenhagen:
Thomas A.A. Batchelor
Jack K. Pedersen
Simon H. Winther
Jan Rossmeisl

DTU:
Ivano E. Castelli

Batchelor, Pedersen, Winther, Castelli, Jacobsen, Rossmeisl, Joule,3, 834 (2019).