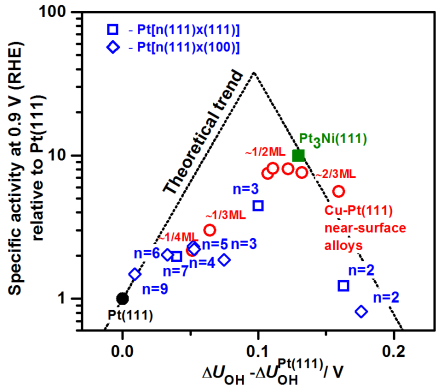
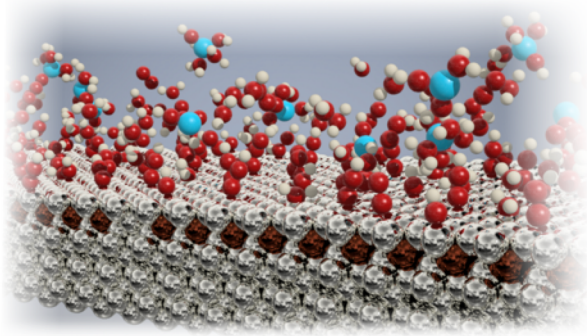
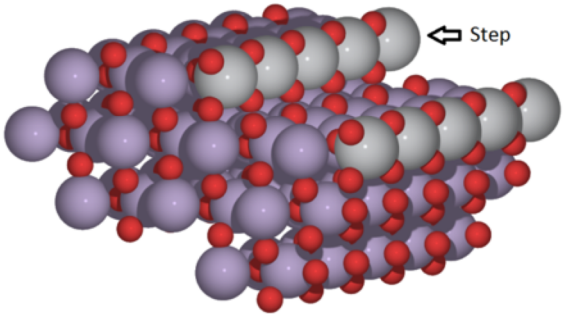
Collaborating with Theorists







Ifan E. L. Stephens

Department of Materials, Imperial College London

Food for thought

"It doesn't matter how beautiful your theory is, it doesn't matter how smart you are. If it doesn't agree with experiment, it's wrong."

Richard P Feynman
1918-1988
Nobel Laureate

Who said this?

Do you agree?

Food for thought

”Great data Ifan, but I am awfully confused. You mix experiment and theory, when in reality they are just fact and fiction.”

Can you relate this statement to your own research?

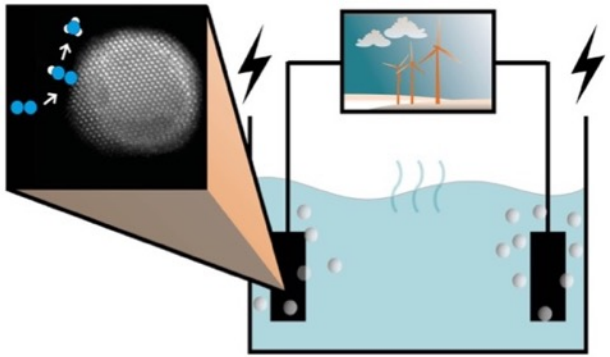
My own scientific background

Since July 2018

- *As of July 2017:* Senior Lecturer at Department of Materials, Imperial College London

Research focus:

- Fundamental electrochemistry investigations to drive forward energy conversion and chemical synthesis.

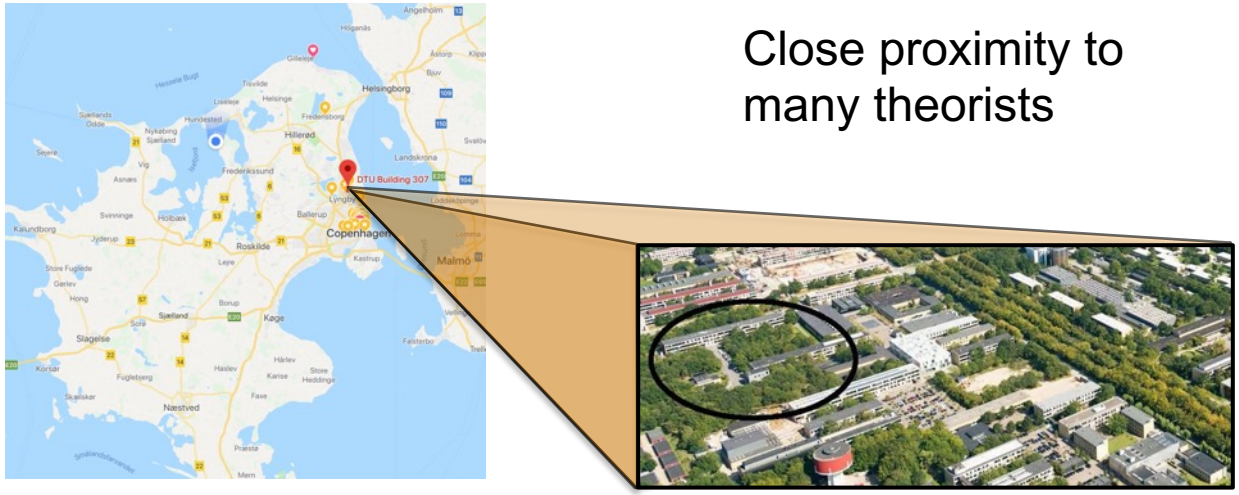


Reactions of interest:

A. O_2 reduction
B. O_2 evolution
C. CO_2 reduction
D. N_2 reduction to NH_3
E. Parasitic reactions in batteries

2008- 2017: Department of Physics Technical University of Denmark

- January 2008-December 2010: Postdoctoral researcher
- January 2011-March 2015: Assistant Professor
- March 2015-June 2017: Associate Professor
- ***Fundamental research applied towards the discovery of new catalyst materials for electrochemical devices***



Close proximity to many theorists

Theorists with whom I have collaborated (non-extensive)

Summary

1. O_2 reduction to H_2O for fuel cells
    a) Elucidating trends
    b) Alloys of Pt and rare earths
2. O_2 reduction to H_2O_2
3. O_2 evolution

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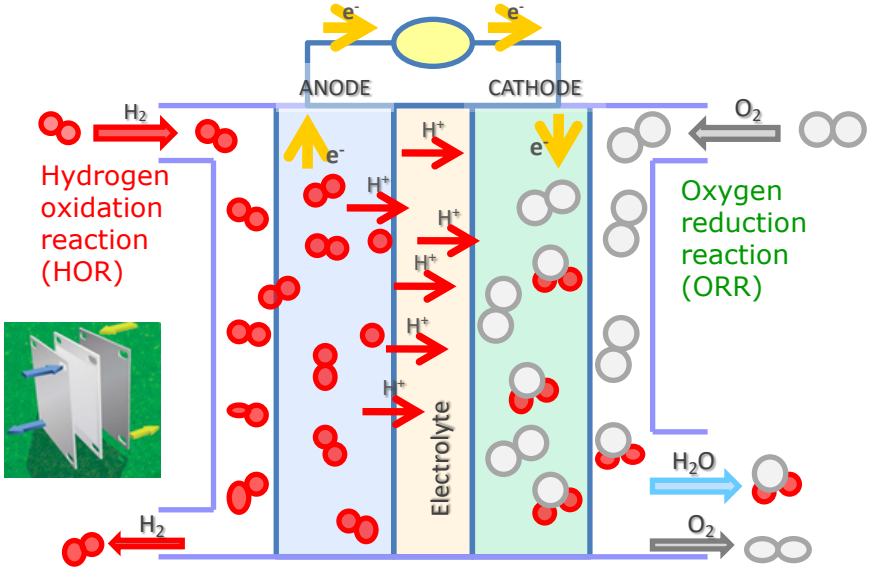
Oxygen reduction to H_2O for fuel cells

Ifan E. L. Stephens

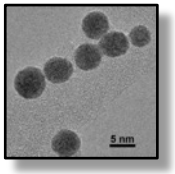
Polymer electrolyte membrane fuel cells (PEMFCs) for conversion of solar fuels to electricity



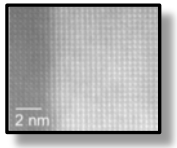
- Perfect for automotive vehicles
- 600 km driving range (Li batteries 200 km)
- Few minutes' refuelling time

Approach

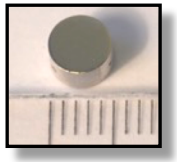
Nanoparticles



Thin films

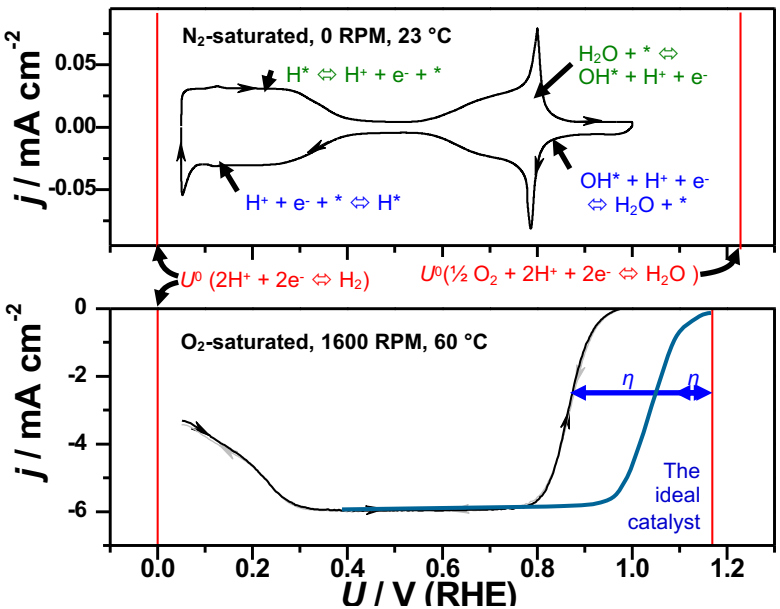


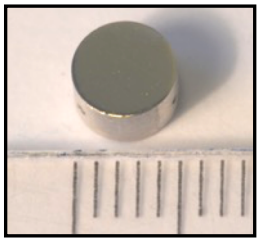
Single crystals

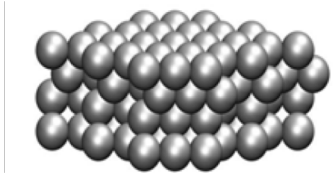


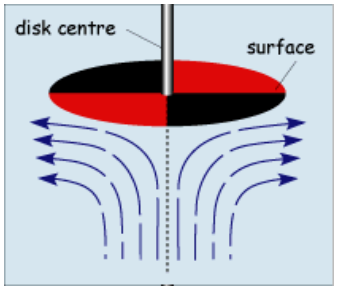
Three electrode cell with liquid electrolyte

Cyclic voltammetry (CV) of Pt(111) in 0.1 $HClO_4$ using rotating disk electrode









dU/dt = 50 mVs^{-1}

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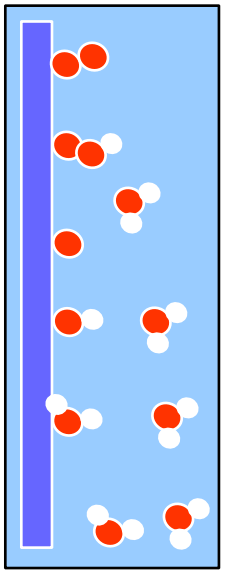
Elucidating trends in O_2 reduction activity

Ifan E. L. Stephens

The 4 electron pathway, according to density functional theory (DFT)



- Overall half cell reaction:

$$O_2 + 4\ H^+ + 4\ e^- \rightarrow 2\ H_2O$$

- Simplified reaction mechanism:
  Rossmeisl, Karlberg, Jaramillo, Nørskov, ***Faraday Disc***, 2008.

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

$*OOH + H^+ + e- + * \rightarrow *O + H_2O$ *or* $*OOH \rightarrow *OH + *O$

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

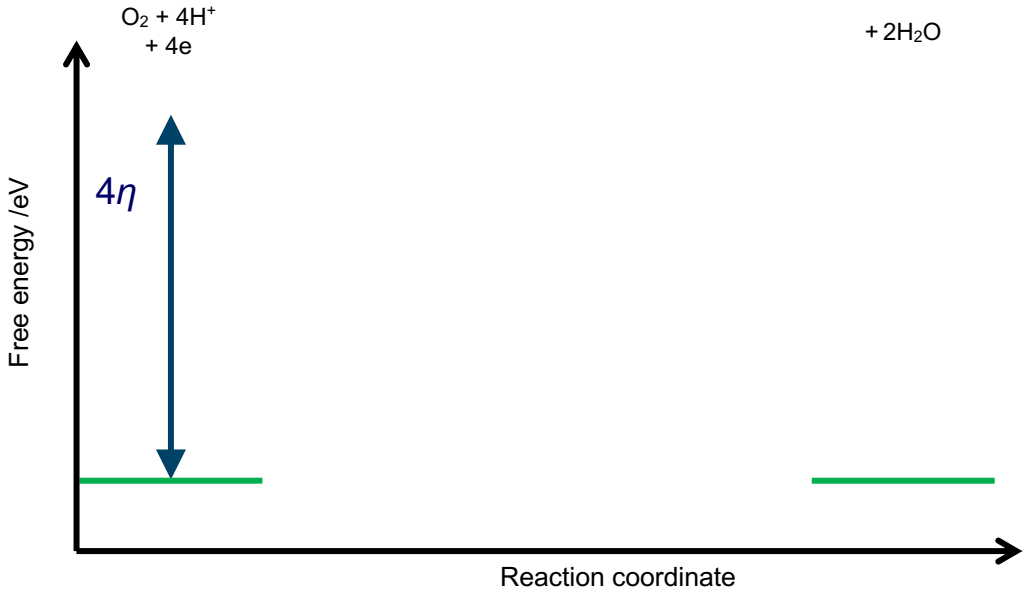
$*OH + H^+ + e^- + * \rightarrow * + H_2O$

* = catalytically active site on surface

More detailed mechanism in Tripkovic, Skúlason, Siahrostami, Nørskov, Rossmeisl, ***Electrochim. Acta***, 2010

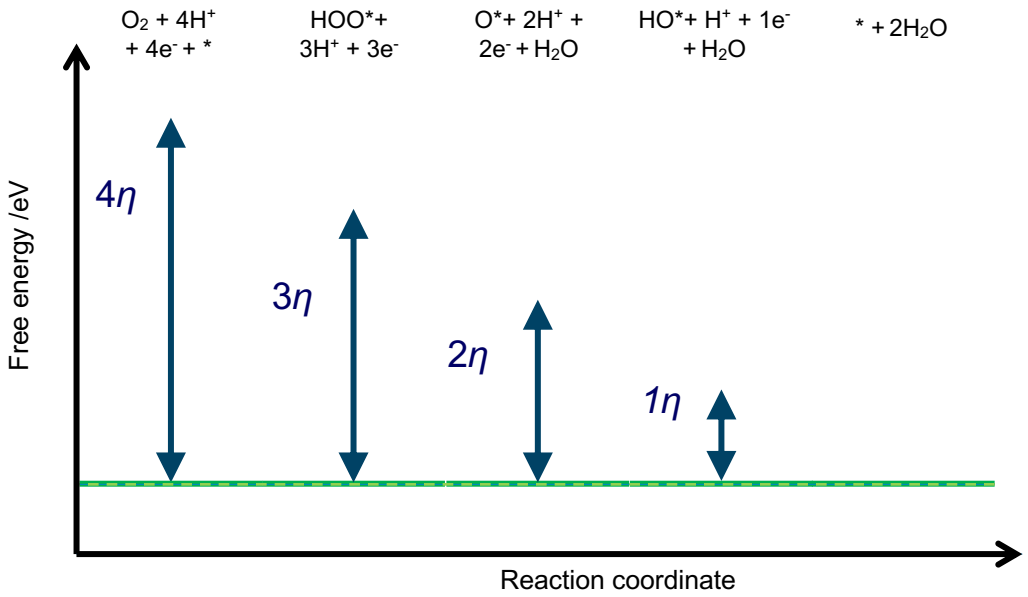
- Many different intermediates (*OOH, *OH, *O) = difficult to catalyse

Free energy diagam for O_2 reduction



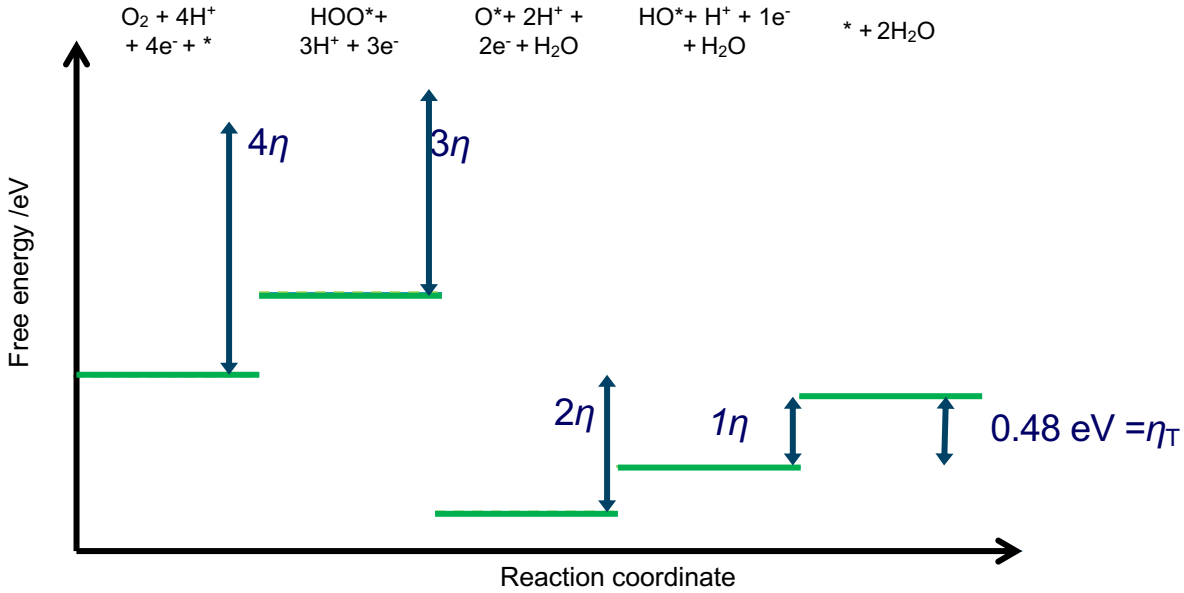
$U = \eta$

The ”ideal” catalyst

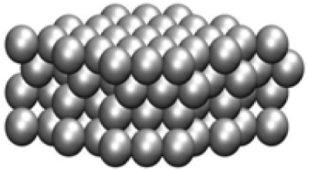


$U = \eta$

Pt(111)



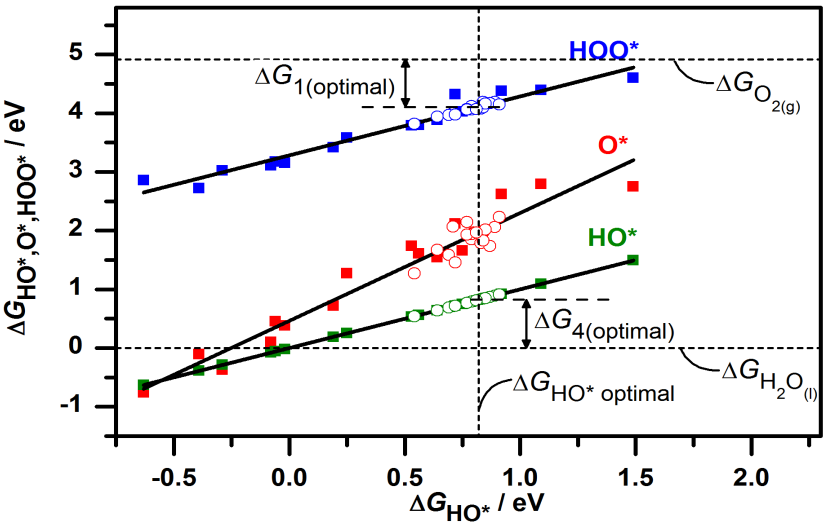
U = 1.23-0.48 = 0.75 V



Calculations from Greeley, Stephens, Bondarenko, Johanneson, Hansen, Jaramillo, Rossmeisl, Chorkendorff, Nørskov, *Nature Chemistry*, 2009.

Linear scaling relations for metal surfaces

Figure from: Stephens, Bondarenko, Grønbjerg, Rossmeisl, Chorkendorff, ***Energy Environ. Sci.*** 2012

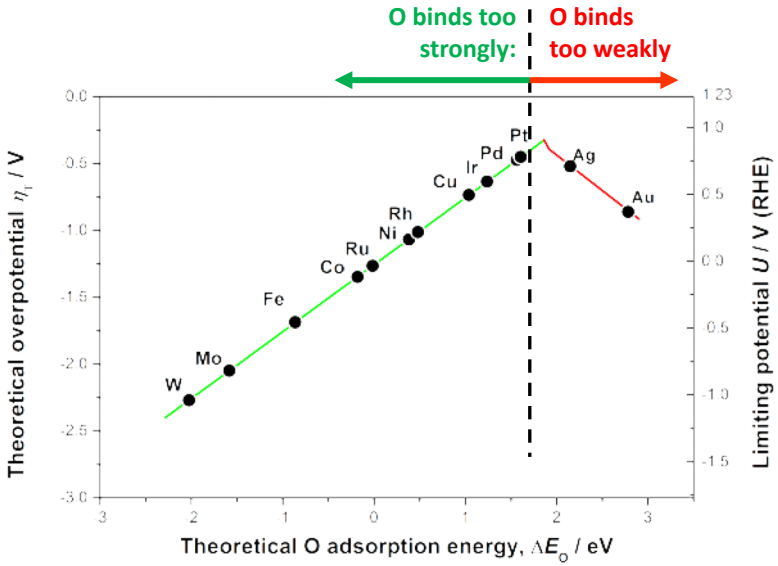


- Binding energies of O*, HOO* and HO* scale linearly

Data from: Rossmeisl, Logadottir, Nørksov, ***Chem. Phys.***, 2005; Abild-Pedersen, Greeley, Studt, Rossmeisl, Munter, Moses, Skulason, Bligaard, Nørskov, ***PRL*** 2007; Nørskov, Rossmeisl, Logadottir, Lindqvist, Kitchin, Bligaard **JPCB**, 2004; Greeley, Rossmeisl, Hellman, Nørskov, ***Z. Phys. Chem***. 2006.; Hansen, ***PhD thesis, DTU Physics*** 2009.

Theoretical trends for oxygen reduction: ΔE_O as a 'descriptor' for (111) surfaces of pure metals

Nørskov, Rossmeisl, Logadottir, Lindqvist, Kitchin, Bligaard ***J. Phys. Chem. B***, 2004 Karlberg, Rossmeisl, Nørskov, ***PCCP***, 2007.



Optimum catalyst

- binds *O ~0.2 eV weaker than Pt(111)
- binds *OH ~0.1 eV weaker than Pt(111)

The most optimal catalyst should exhibit moderate binding to the reaction intermediates (neither too strong nor too weak)

Sabatier, ***Berichte Der Deutschen Chemischen Gesellschaft*** 1911.

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Experimental proof of Sabatier volcano?

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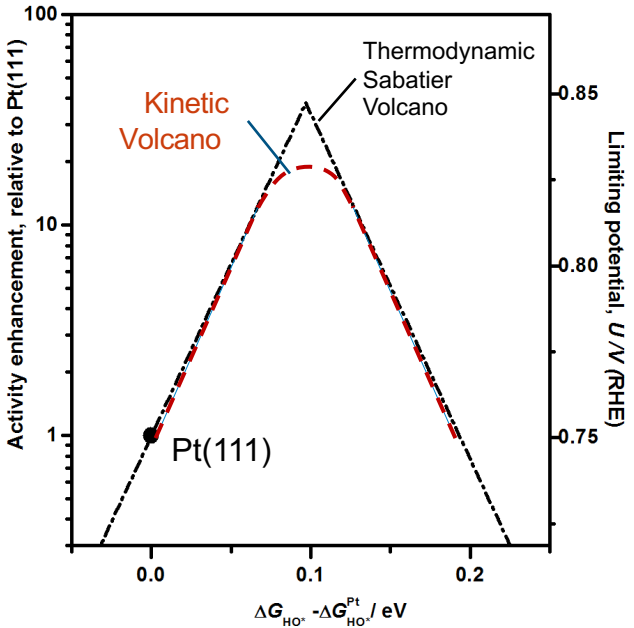
Theoretical enhancement in oxygen reduction activity over Pt(111)



- Thermodynamic Sabatier volcano quantifies:
  - maximum enhancement
  - position of optimum ΔG_{HO^*}

  Nørskov, Rossmeisl, Logadottir, Lindqvist, Kitchin, Bligaard ***JPCB***, 2004

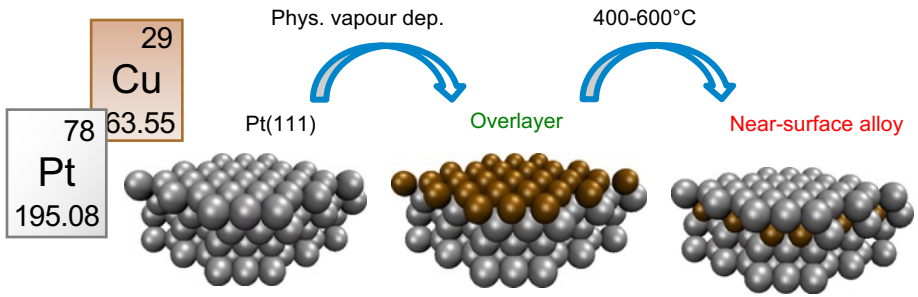
- Kinetic volcano
  - Enhacement smaller than thermodynamic Sabatier volcano

  Karlberg, Rossmeisl, Nørskov, Faraday Discuss., 2007
  Hansen, Viswanathan, Nørskov, *JPCC* 2014

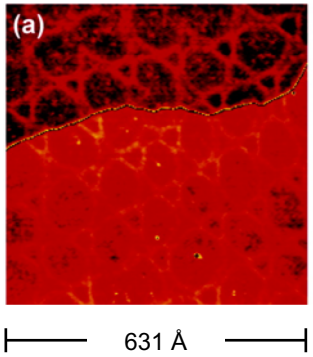
Cu/Pt near surface alloys (NSA) under ultra high vacuum (UHV)

Knudsen, Nilekar, Vang, Schnadt, Kunkes, Dumesic, Mavrikakis, Besenbacher, ***JACS*** 2007

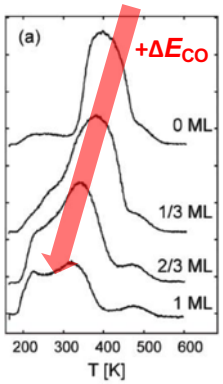
Andersson, Calle-Vallejo, Rossmeisl, Chorkendorff, ***JACS***., 131 (2009)



STM image



CO-TPD

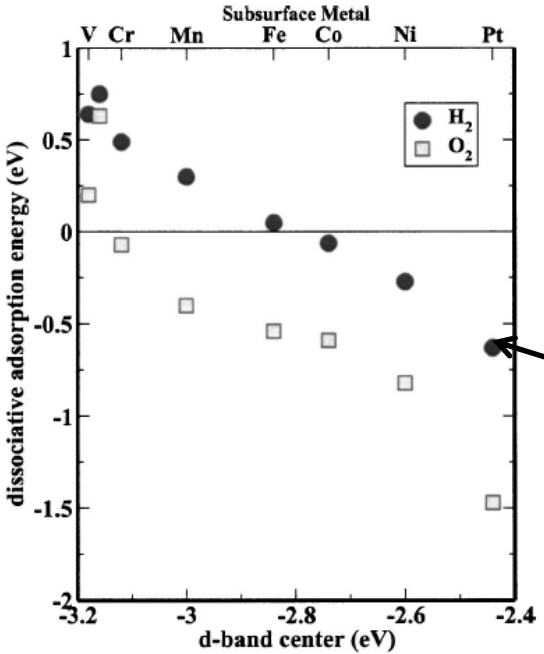


- Scanning Tunnelling Microscopy
- Low Energy Electron Diffraction
- X-ray photoelectron spectroscopy
- Ion Scattering Spectroscopy

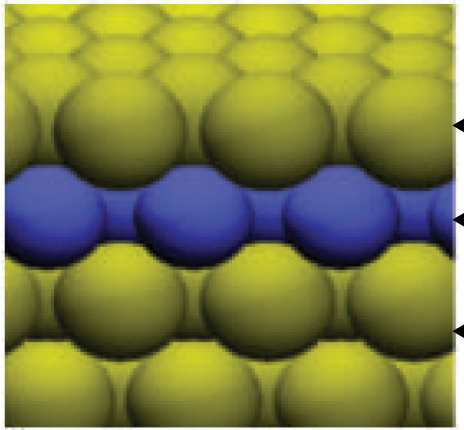
- Temperature programmed desorption of CO (CO-TPD)
- Density Functional theory
- Ligand effect/subsurface alloying controls reactivity of Pt terrace atoms

DFT: The ligand effect

Kitchin, Nørskov, Barteau & Chen. ***J. Chem. Phys.*** 2004



ΔE_O for Pt (111)



Pt Surface

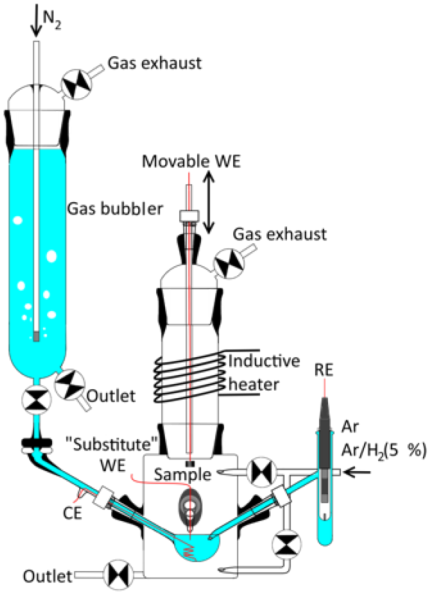
Solute only in 2nd layer

Pt Bulk

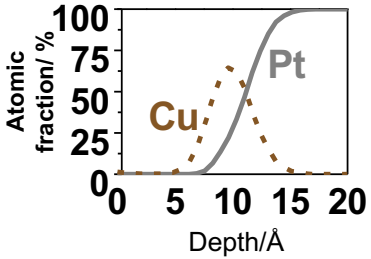
- Subsurface metal weakens ΔE_O
- Where is the experimental evidence???

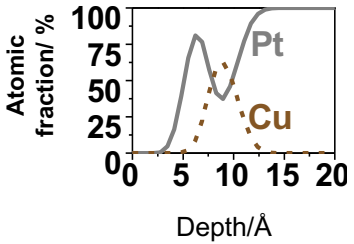
Preparation of the Cu/Pt(111) in an electrochemical cell

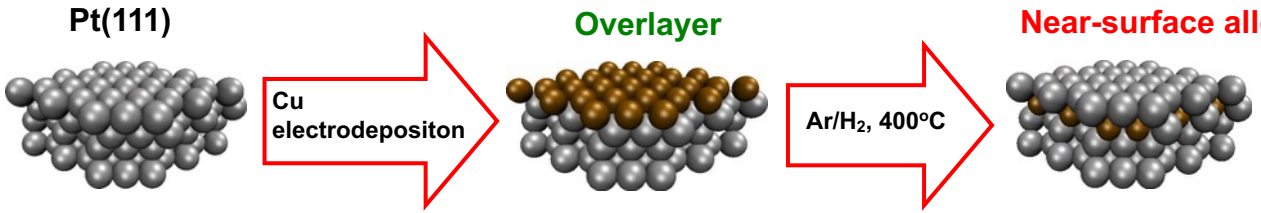
Bondarenko, Stephens, Chorkendorff. ***Electrochem. Comm.*** 2012 ,



Depth profiles from angle resolved X-ray photoelectron spectroscopy

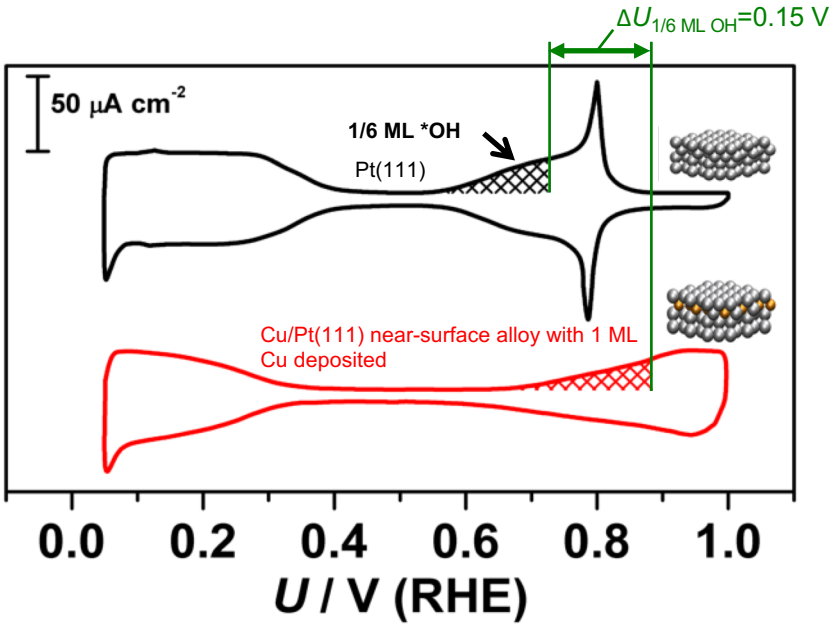






Measuring shift in OH binding energy through $\Delta U_{1/6\ ML\ OH}$

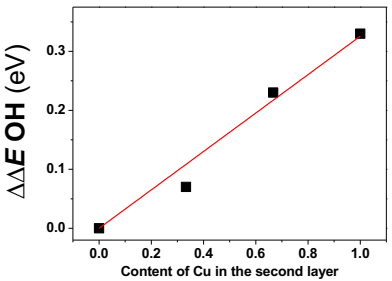
Stephens, Bondarenko, Pérez-Alonso, Calle-Vallejo, Bech, Johansson, Jepsen, Frydendal, Knudsen, Rossmeisl, Chorkendorff, ***JACS***. 2011



- On a homogeneous surface:

  $\Delta U_{1/6\ ML\ OH} = \Delta\Delta E_{\ OH}$

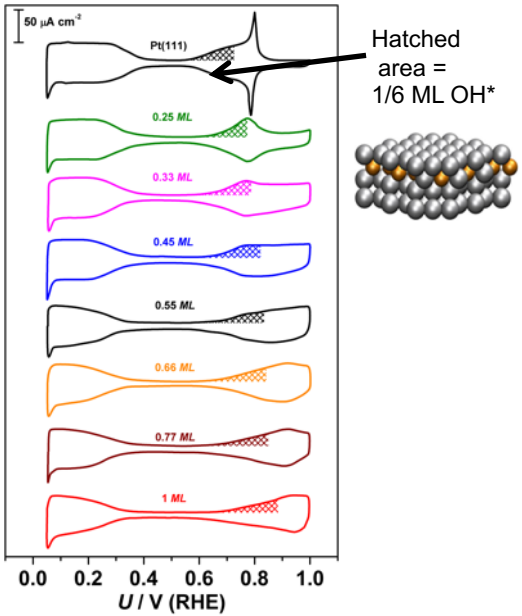
  Rossmeisl , Karlberg, Jaramillo, Nørskov, ***Faraday Discuss.*** 2008.
  Stamenkovic, Fowler, Mun, Wang, Ross, Lucas, Markovic, ***Science***, 2007.
  Hoster, Alves, Koper, ***ChemPhysChem*** 2010.



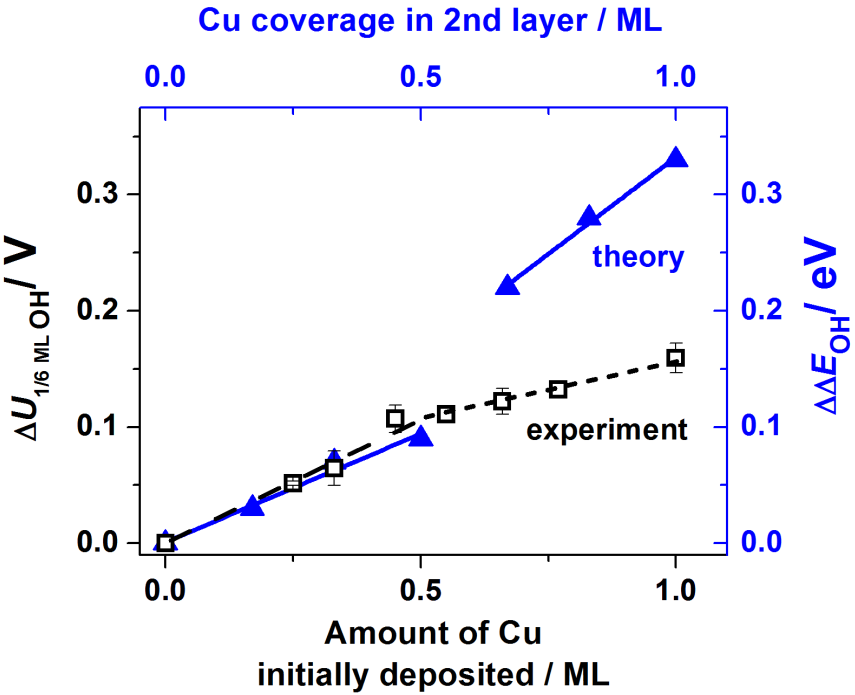
- $\Delta\Delta E_{\ OH}$ is not as destablised as we expect from DFT
- We can reach optimal activity with the surface with $\Delta U_{1/6\ ML\ OH} = \Delta\Delta E_{\ OH}$

Monitoring ΔE_{OH} through $\Delta U_{1/6\ ML\ OH}$

Stephens, Bondarenko, Pérez-Alonso, Calle-Vallejo, Bech, Johansson, Jepsen, Frydendal, Knudsen, Rossmeisl, Chorkendorff, ***JACS***. 2011

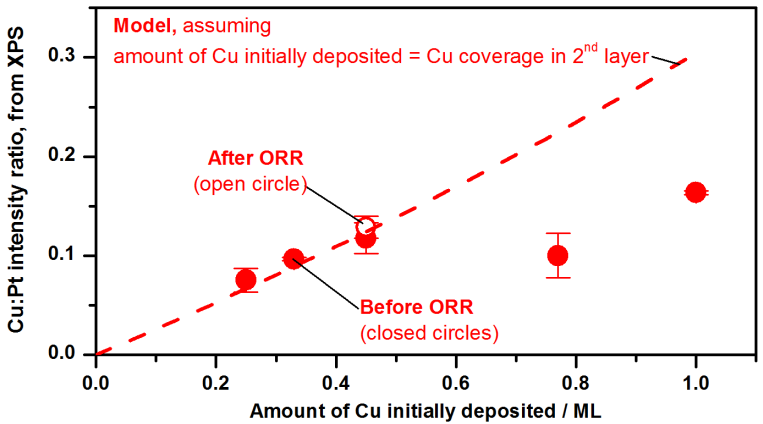


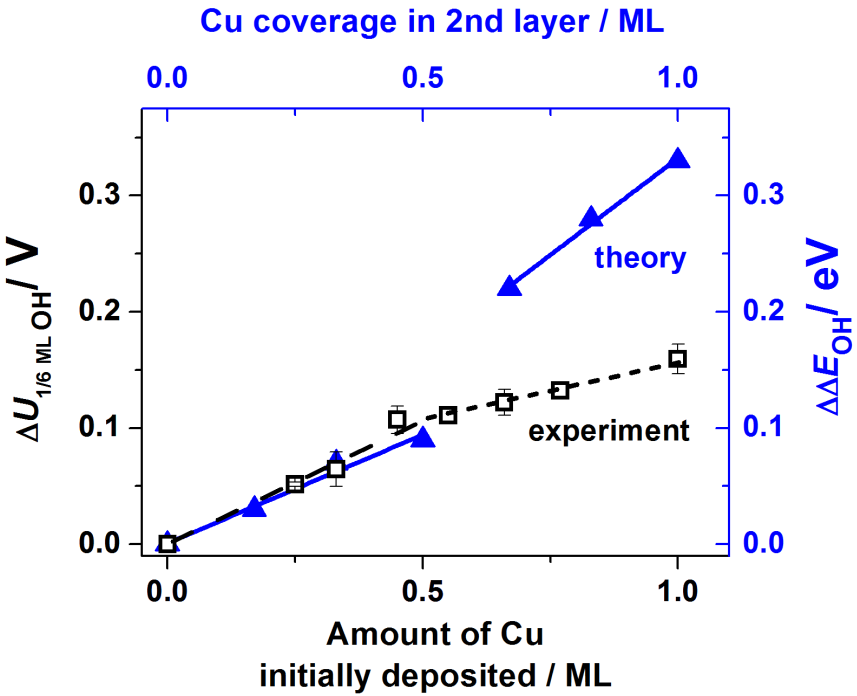
Hatched area = 1/6 ML OH*



Monitoring ΔE_{OH} through $\Delta U_{1/6\ ML\ OH}$

Stephens, Bondarenko, Pérez-Alonso, Calle-Vallejo, Bech, Johansson, Jepsen, Frydendal, Knudsen, Rossmeisl, Chorkendorff, ***JACS***. 2011

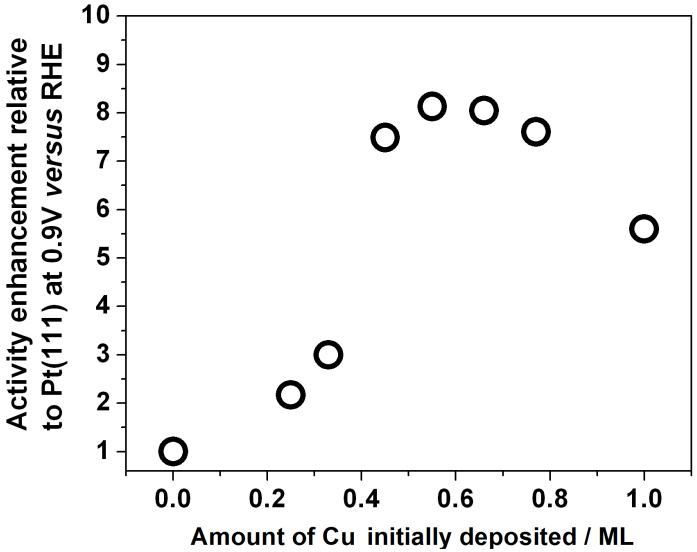




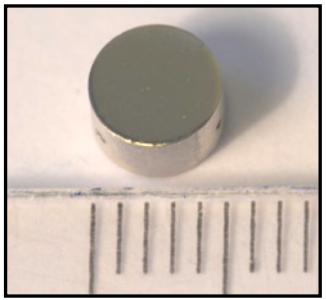
- XPS and $\Delta\Delta E_{OH}$ /$\Delta U_{1/6\ ML\ OH}$ show the same trend
- At high coverages, Cu is lost to the bulk.

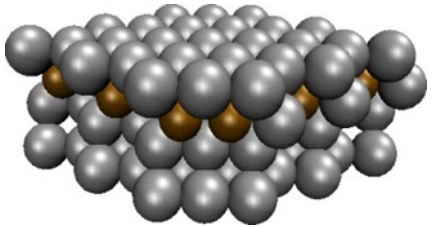
O_2 reduction activity of Cu/Pt(111) near-surface alloy

Stephens, Bondarenko, Pérez-Alonso, Calle-Vallejo, Bech, Johansson, Jepsen, Frydendal, Knudsen, Rossmeisl, Chorkendorff, ***JACS***. 2011

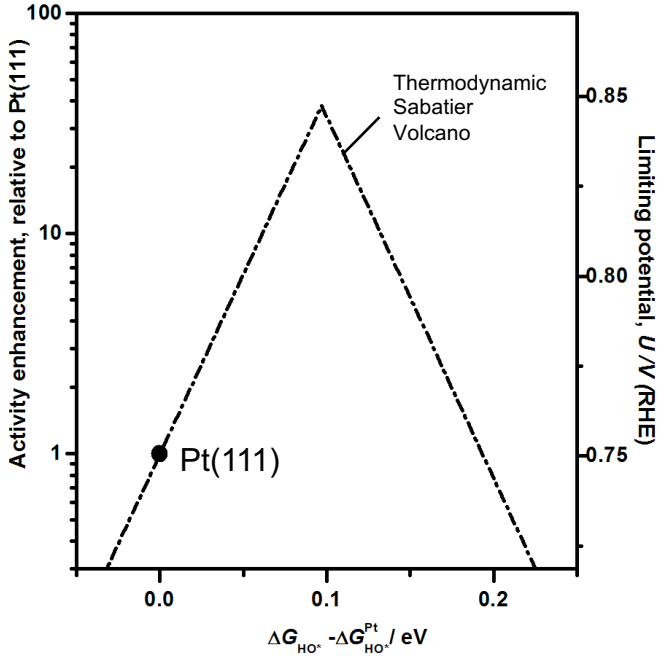


U = 0.9 V, 50 mV/s, 1600 RPM in O2-saturated 0.1 M $HClO_4$



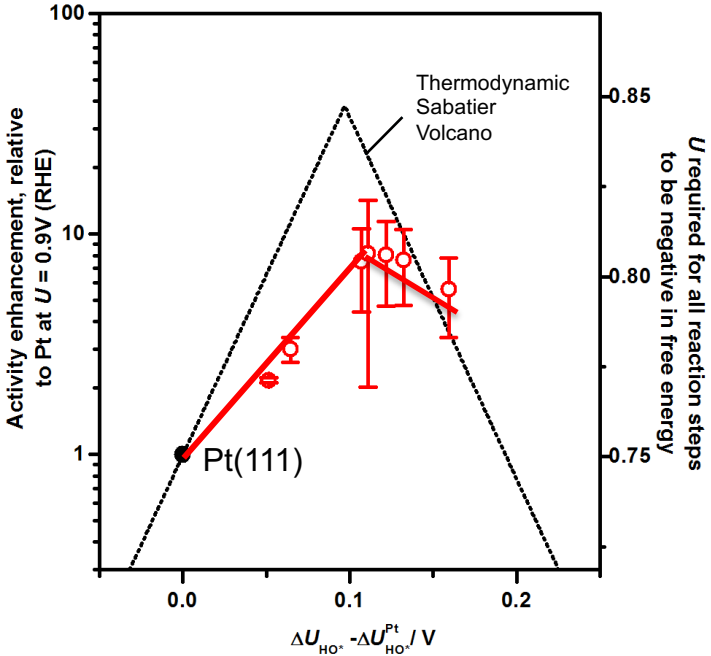


Volcano: theory versus experiment



- Theory: *Nørskov, Rossmeisl, Logadottir, Lindqvist, Kitchin, Bligaard, Jonsson, JPCB 2004*
  Rossmeisl , Karlberg, Jaramillo, Nørskov, Faraday Discuss. 2008

Volcano: theory versus experiment

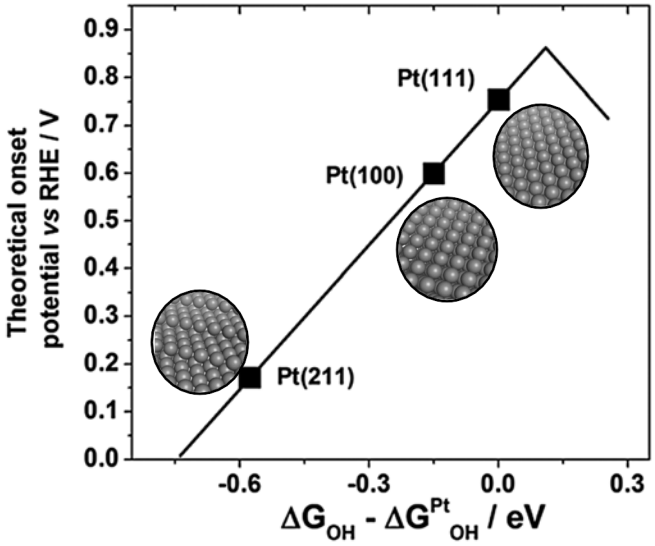


- **Theory**: Nørskov, Rossmeisl, Logadottir, Lindqvist, Kitchin, Bligaard, Jonsson, ***JPCB*** 2004
  Rossmeisl , Karlberg, Jaramillo, Nørskov, ***Faraday Discuss***. 2008

- **Cu/Pt(111) Near-surface alloy**
  Stephens, Bondarenko, Pérez-Alonso, Calle-Vallejo, Bech, Johansson, Jepsen, Frydendal, Knudsen, Rossmeisl, Chorkendorff, ***JACS***. 2011.

What about other Pt single crystal surfaces?

Bandarenka, Rossmeisl, Hansen, Stephens ***PCCP*** 2014 with DFT data from Greeley, Rossmeisl, Hellman & Nørskov**. *Z. Phys. Chem.*** 2007.

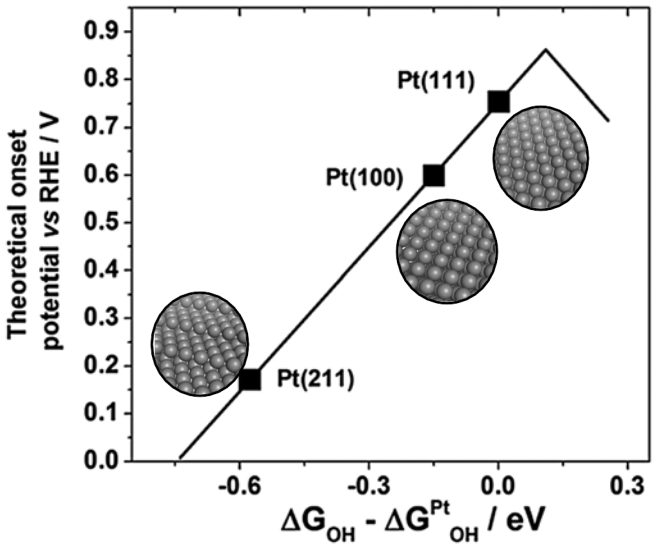


- Terrace sites most active
- Step sites bind oxygen reduction intermediates too strongly

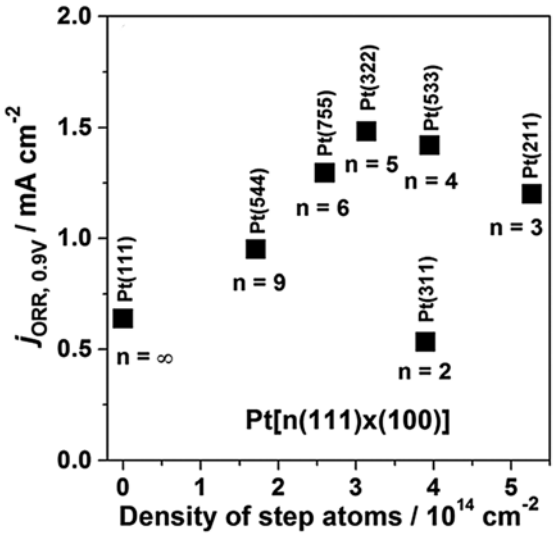
What about other Pt single crystal surfaces?

Bandarenka, Rossmeisl, Hansen, Stephens ***PCCP*** 2014,
with DFT from Greeley, Rossmeisl, Hellman & Nørskov. ***Z. Phys. Chem.*** 2007

DFT

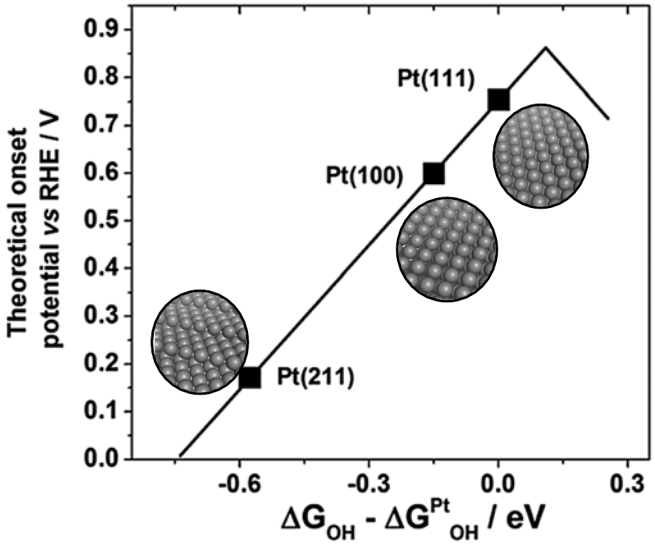


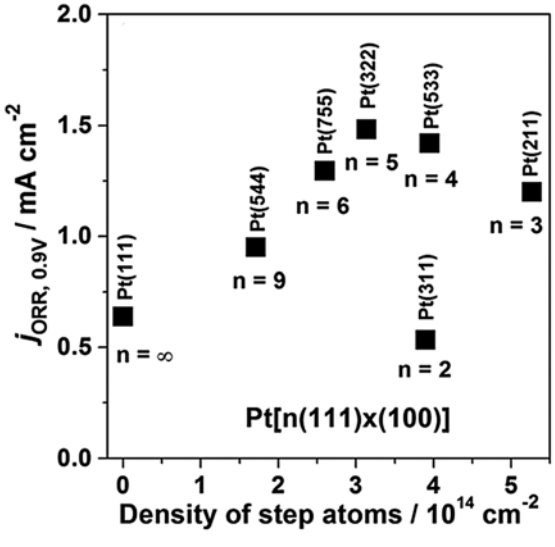
Experiment



What about other Pt single crystal surfaces?

Bandarenka, Rossmeisl, Hansen, Stephens ***PCCP*** 2014 with DFT data from Greeley, Rossmeisl, Hellman & Nørskov**.** ***Z. Phys. Chem.*** 2007. Experiments from Clavilier, Rodes, Elachi, ***J.Chim. Phys. Phys.-Chim. Biol***. 1991;Kuzume, Herrero, Feliu, ***JEAC*** 2007; Hitotsuyanagi, Nakamura, Hoshi, ***Electrochim. Acta,*** 2012.

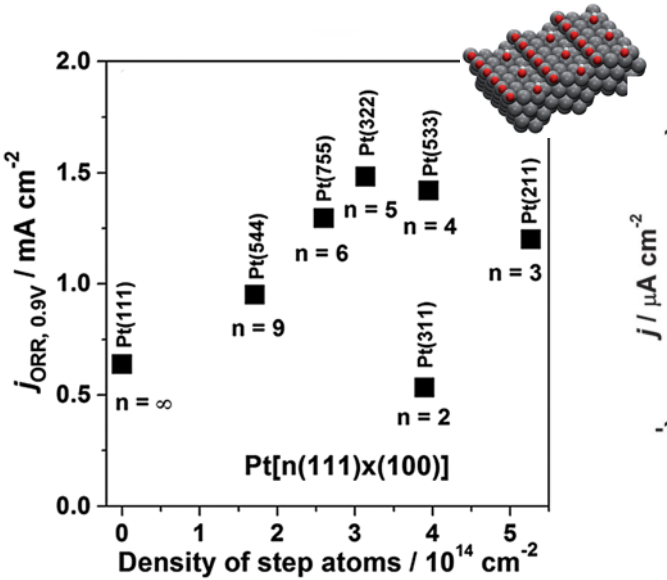


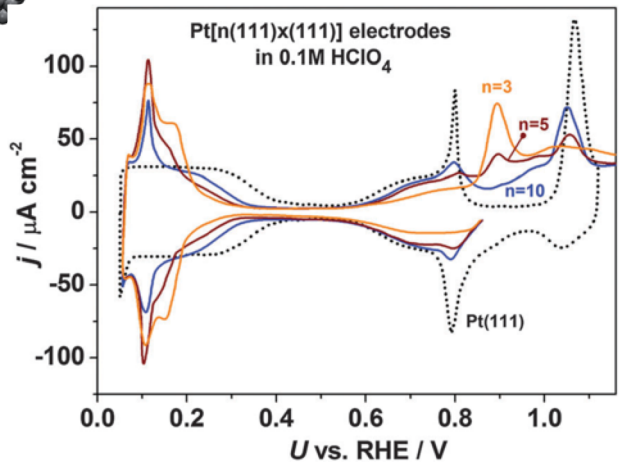


Theory ≠ Experiment

What about other Pt single crystal surfaces?

Bandarenka, Rossmeisl, Hansen, Stephens **PCCP** 2014 with data from Clavilier, Rodes, Elachi, ***J.Chim. Phys. Phys.-Chim. Biol***. 1991;Kuzume, Herrero, Feliu, ***JEAC*** 2007; Hitotsuyanagi, Nakamura, Hoshi, ***Electrochim. Acta,*** 2012.





Destablisation of *OH on concave terrace sites, adjacent to step

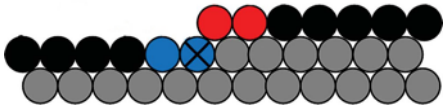
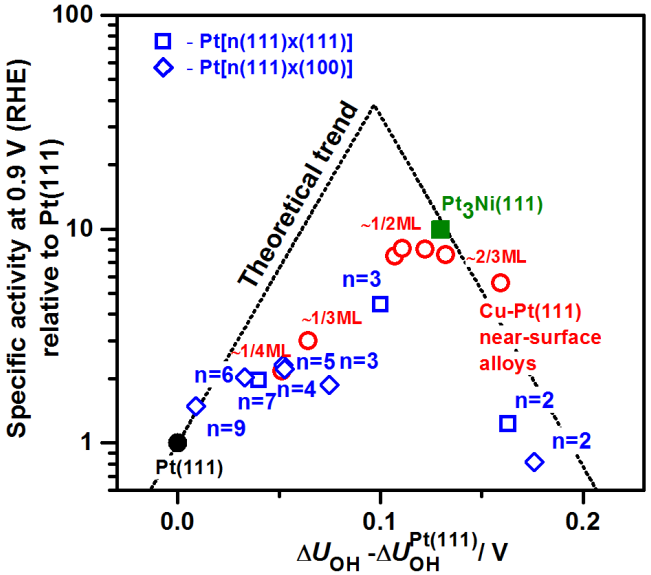


Figure adapted from Calle-Vallejo, Pohl, Reinisch, Loffreda, Sautet, Bandarenka, ***Chem. Sci.*** 2017

Experimental volcano can be extended to other Pt-based single crystals

Bandarenka, Hansen, Rossmeisl, Stephens, ***PCCP*** 2014.



- **Cu/Pt(111) Near-surface alloy**
  Stephens, Bondarenko, Pérez-Alonso, Calle-Vallejo, Bech, Johansson, Jepsen, Frydendal, Knudsen, Rossmeisl, Chorkendorff, ***JACS***. 2011.

- **Stepped Pt:**
  Clavilier, Rodes, Elachi, *J.Chim. **Phys. Phys.-Chim. Biol***. 1991; Kuzume, Herrero, Feliu, ***JEAC*** 2007; Hitotsuyanagi, Nakamura, Hoshi, ***Electrochim. Acta***, 2012.

- **$Pt_3Ni(111)$:**
  Stamenkovic, Fowler, Mun, Wang, Ross, Lucas, Markovic, ***Science***, 2007.

- **Theory:**
  Nørskov, Rossmeisl, Logadottir, Lindqvist, Kitchin, Bligaard, Jonsson, ***JPCB*** 2004;
  Rossmeisl , Karlberg, Jaramillo, Nørskov, ***Faraday Discuss***. 2008.

In 0.1 M $HClO_4$ (pH 1), Sabatier volcano exists

Imperial College London

ECLOREL Workshop

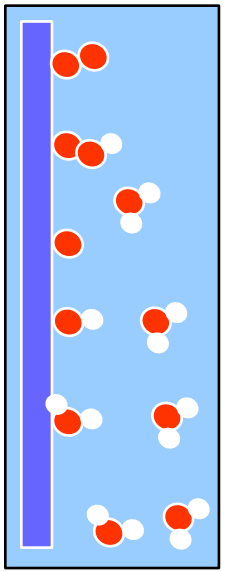
24 September 2018

What are the trends in alkaline media?

Ifan E. L. Stephens

The 4 electron pathway, according to density functional theory (DFT)

Rossmeisl, Karlberg, Jaramillo, Nørskov, ***Faraday Disc***, 2008.



- **Overall reaction in acid:**

$$O_2 + 4\,H^+ + 4\,e^- \rightarrow 2\,H_2O$$

- Reaction mechanism:

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

$*OOH + H^+ + e- \rightarrow *O + H_2O$

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

$*OH + H^+ + e^- \rightarrow * + H_2O$

* = catalytically active site on surface

- **Overall reaction in base:**

$$O_2 + 2\,H_2O + 4\,e^- \rightarrow 4\,OH^-$$

- Reaction mechanism:

Rossmeisl, Karlberg, Jaramillo, Nørskov, ***Faraday Disc***, 2008.

$O_2 + H_2O + e^- + * \rightarrow *OOH + OH^-$

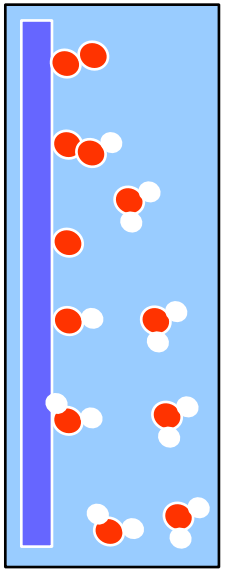
$*OOH + e^- \rightarrow *O + OH^-$

$*O + H_2O + e^- \rightarrow *OH + OH^-$

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

The 4 electron pathway, according to density functional theory (DFT)

Rossmeisl, Karlberg, Jaramillo, Nørskov, ***Faraday Disc***, 2008.



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$*OOH + e^- \rightarrow *O + OH^-$

$*O + H_2O + e^- \rightarrow *OH + OH^-$

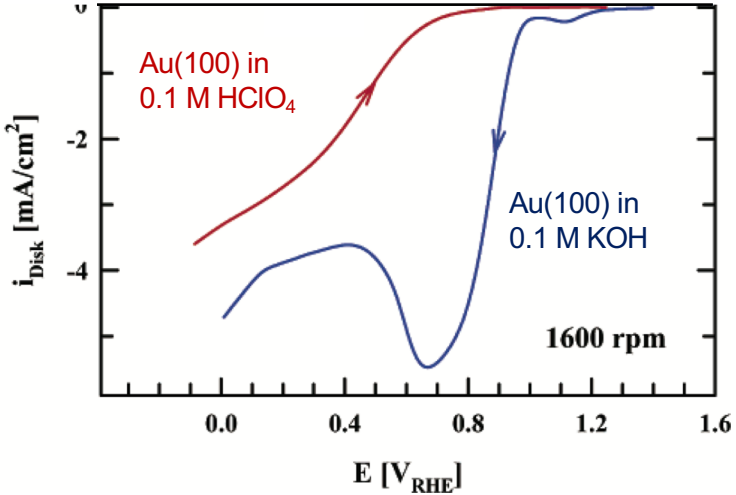
$*OH + e^- \rightarrow * + OH^-$

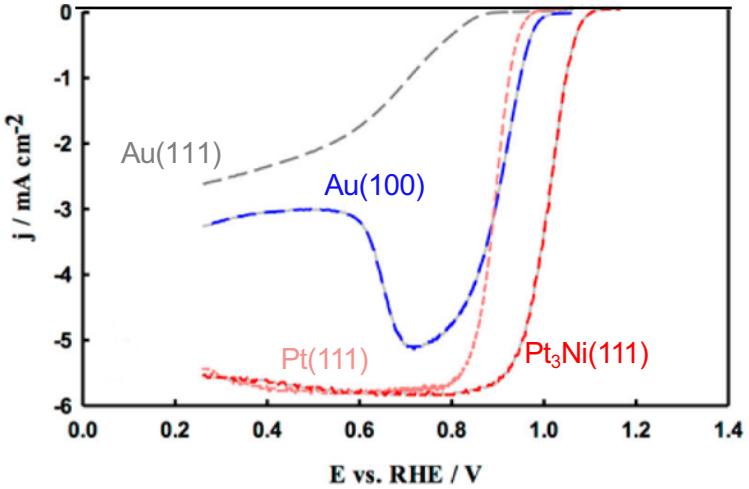
Driving force for all reaction steps equal on reversible hydrogen electrode scale (proton coupled electron transfer)

Trends for oxygen reduction in alkaline media?

Blizanac, Lucas, Gallagher, Arenz, Ross, Markovic´ ***JPCB*** 2004

Staszak-Jirkovský, Subbaraman, Strmcnik, Harrison, Diesendruck, Assary, Frank, Kobr, Wiberg, Genorio, Connell, Lopes, Stamenkovic, Curtiss, Moore, Zavadil & Markovic. ***ACS Catalysis*** 2015





- Activity of Au(100) ≈ Pt(111)
- At 0.9 V, activity of $Pt_3Ni(111)$ ~300 mA/cm^2 !!!

Trends for oxygen reduction in alkaline media?

- **Only proton coupled electron transfer**.

  $O_2 + H_2O + e^- + * \rightarrow *OOH + OH^-$

  $*OOH + e^- \rightarrow *O + OH^-$

  $*O + H_2O + e^- \rightarrow *OH + OH^-$

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

- **Proton decoupled electron transfer in first step**

  Quaino, Luque, Nazmutdinov, Santos & Schmickler. ***Angew. Chem.-Int. Edit.*** 2012

  Koper ***Chem. Sci***. 2013

  $O_2 + e^- \rightarrow O_2^-$ (U_0=0.401 versus standard hydrogen electrode)

  $O_2^- + H_2O + e^- + * \rightarrow *O + 2OH^-$

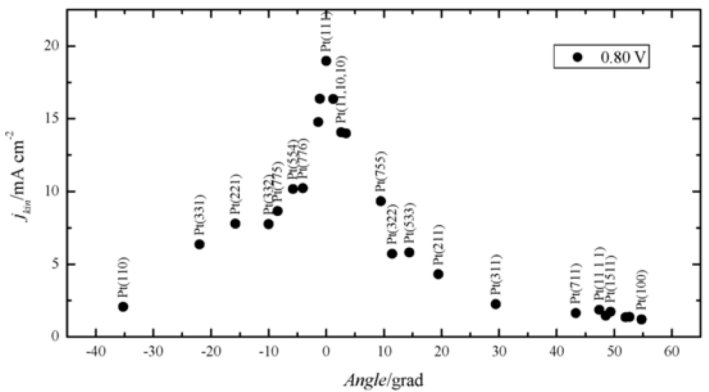
  $*O + H_2O + e^- \rightarrow *OH + OH^-$

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

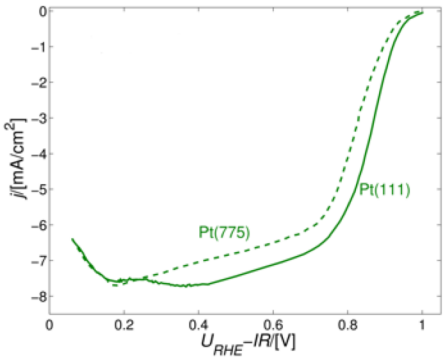
Effect of pH on reaction rates (barriers) is challenging to calculate

Stepped Pt surfaces in alkaline media?

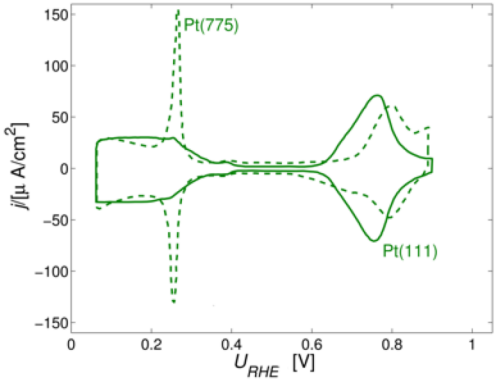
Rizo, Herrero & Feliu. ***PCCP*** 2013



- Activity of Pt(111) >> Stepped surfaces



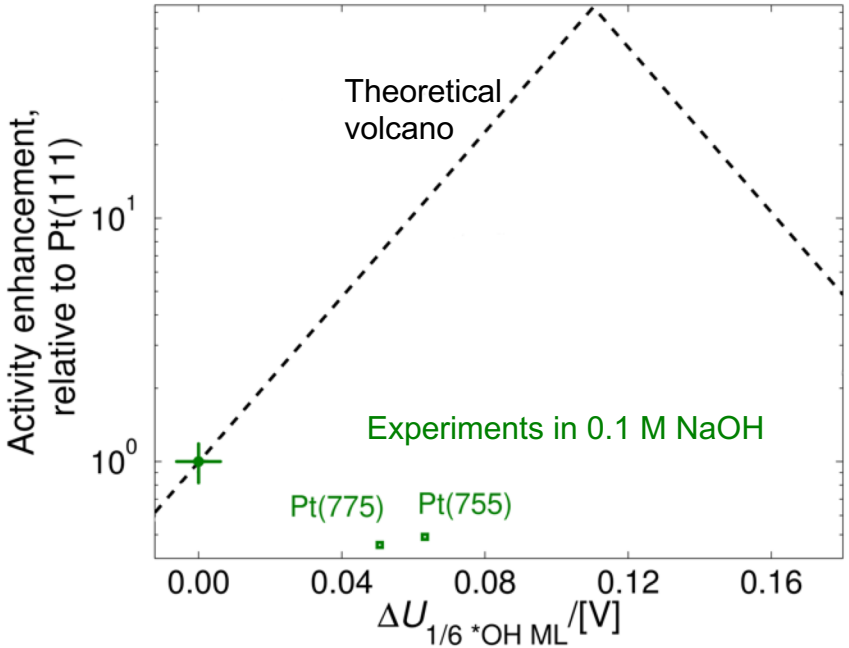
O_2-saturated 0.1 M NaOH, 2500 RPM



N_2-saturated 0.1 M NaOH

Trends for oxygen reduction in alkaline media?

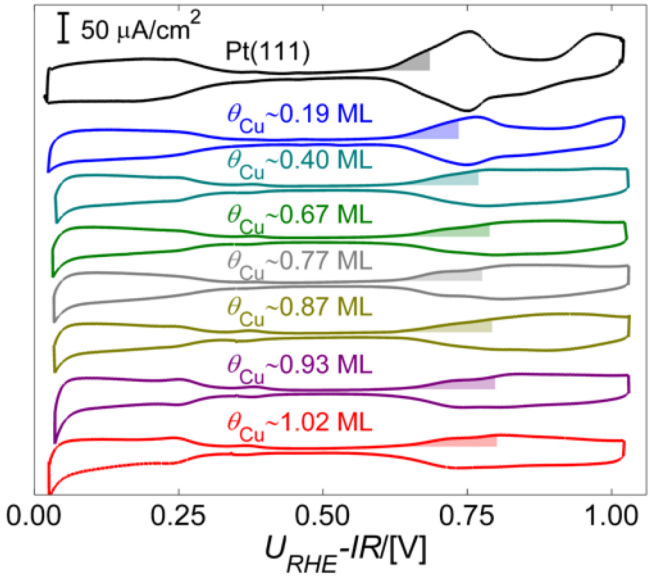
Adapted from izo, Herrero & Feliu. *PCCP* 2013

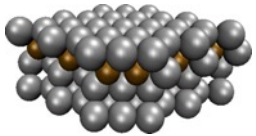


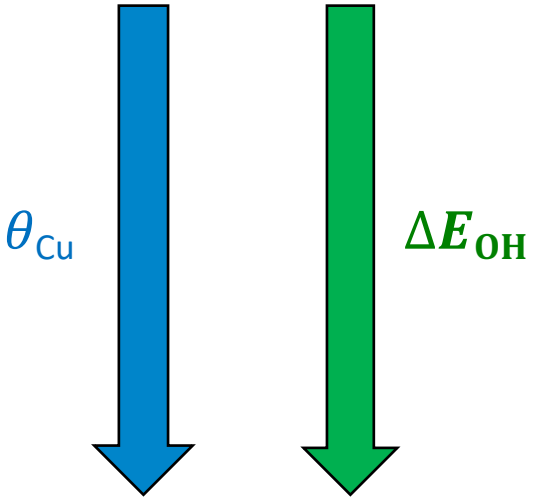
Does the Sabatier volcano model apply in alkaline media?

Cu/Pt(111) Near Surface Alloys in 0.1 M KOH

Jensen, Tymoczko, Bandarenka, Chorkendorff, Rossmeisl, Escudero- Escribano, Stephens ***Angew. Chem. Int. Ed****.2018*

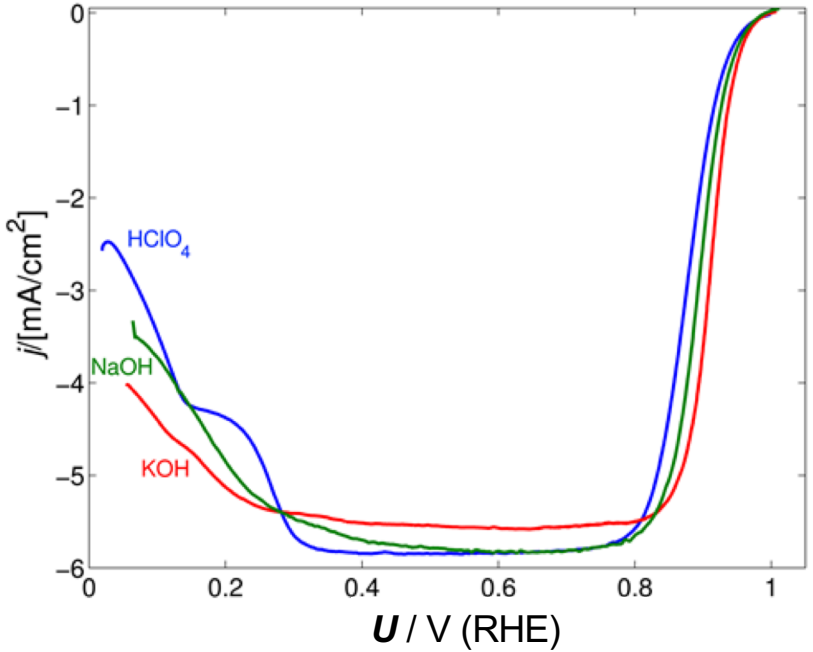






Pt(111) in acid versus base

Jensen, Tymoczko, Bandarenka, Chorkendorff, Rossmeisl, Escudero- Escribano, Stephens ***Angew. Chem. Int. Ed.*** 2018

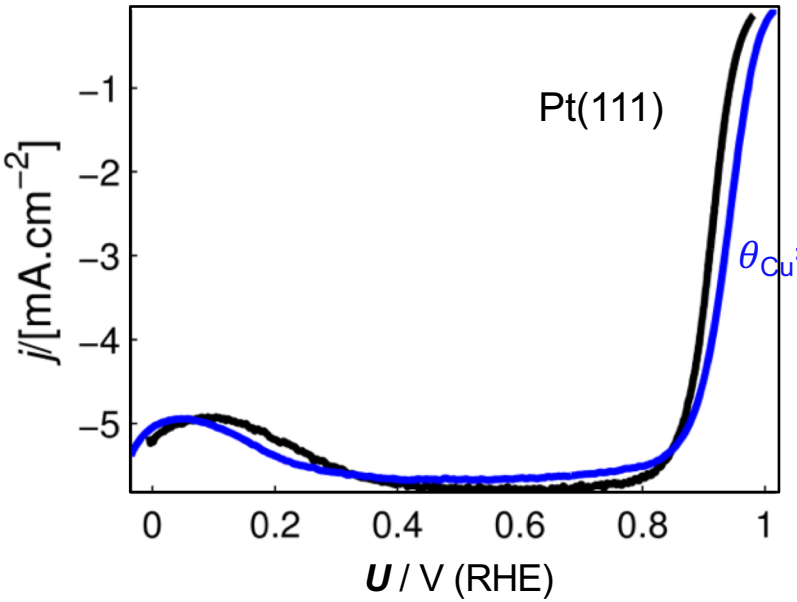


50 mV/s in O_2-saturated electrolyte, 1600 RPM

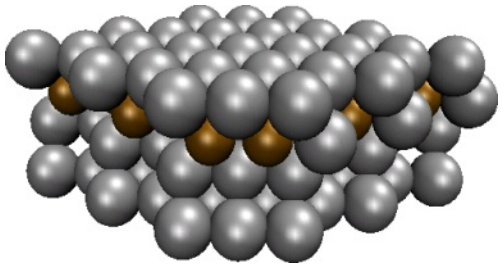
- ~4 fold improvement in actvity between 0.1 M $HClO_4$ to 0.1 M KOH
- ~ 2 fold improvement between 0.1 M NaOH and 0.1 M KOH

Pt(111) vs Cu/Pt(111) Near Surface Alloys in alkaline media

Jensen, Tymoczko, Bandarenka, Chorkendorff, Rossmeisl Escudero- Escribano, Stephens ***Angew. Chem. Int. Ed.*** 2018



50 mV/s in O_2-saturated 0.1 M KOH, 1600 RPM



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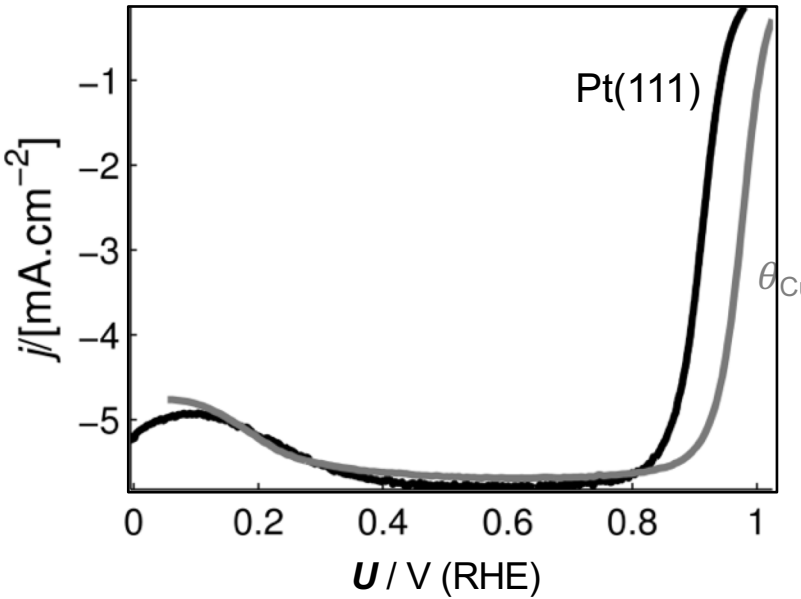
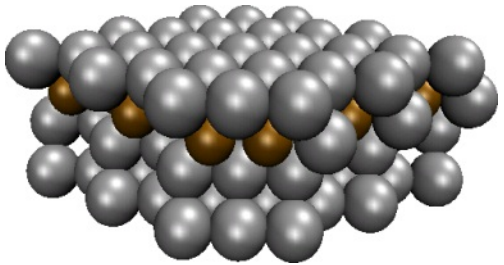


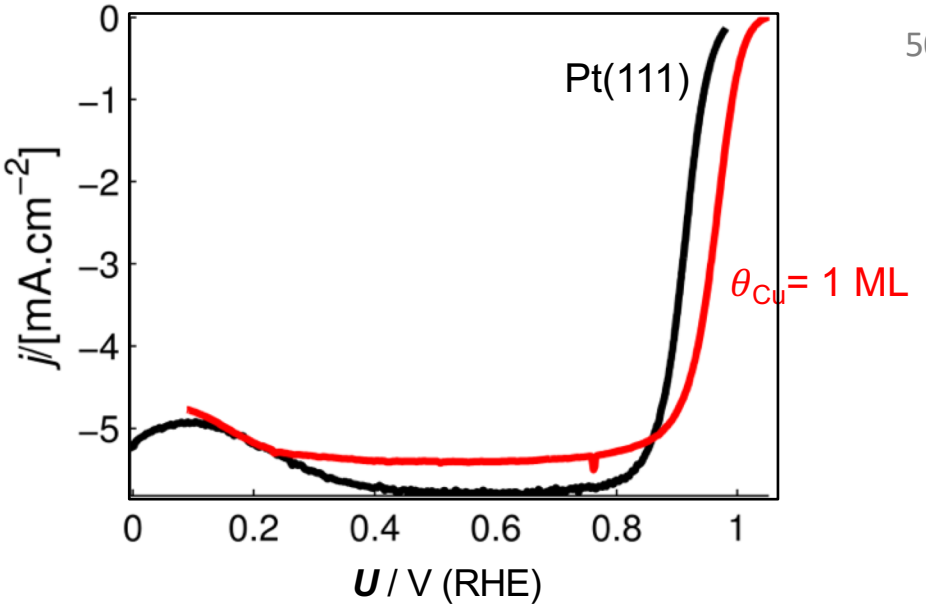
50 mV/s in O_2-saturated 0.1 M KOH, 1600 RPM

θ_{Cu}= 0.77 ML

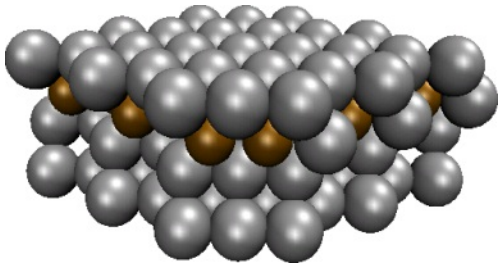


Pt(111) vs Cu/Pt(111) Near Surface Alloys in alkaline media

Jensen, Tymoczko, Bandarenka, Chorkendorff, Rossmeisl Escudero- Escribano, Stephens ***Angew. Chem. Int. Ed.*** 2018



50 mV/s in O_2-saturated 0.1 M KOH, 1600 RPM



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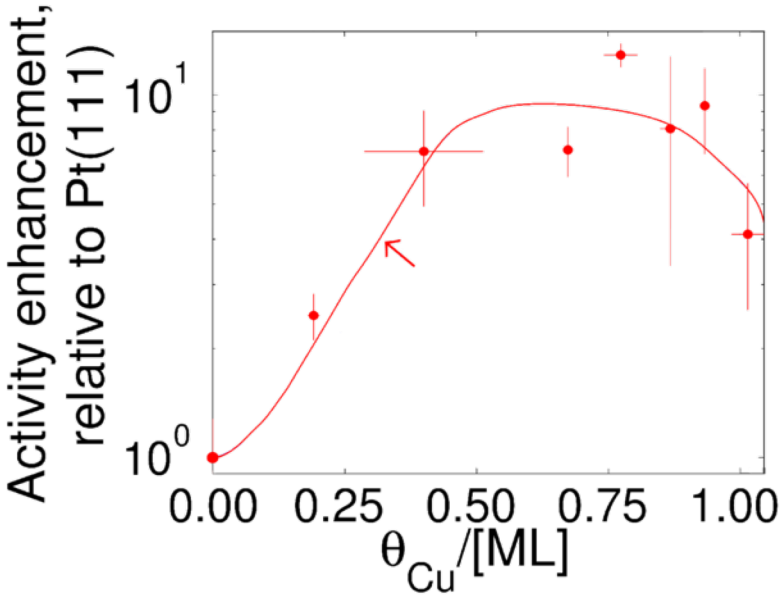
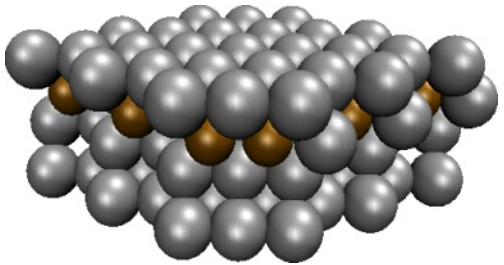
Jensen, Tymoczko, Bandarenka, Rossmeisl, Chorkendorff, Escudero- Escribano, Stephens ***Angew. Chem. Int. Ed.*** 2018

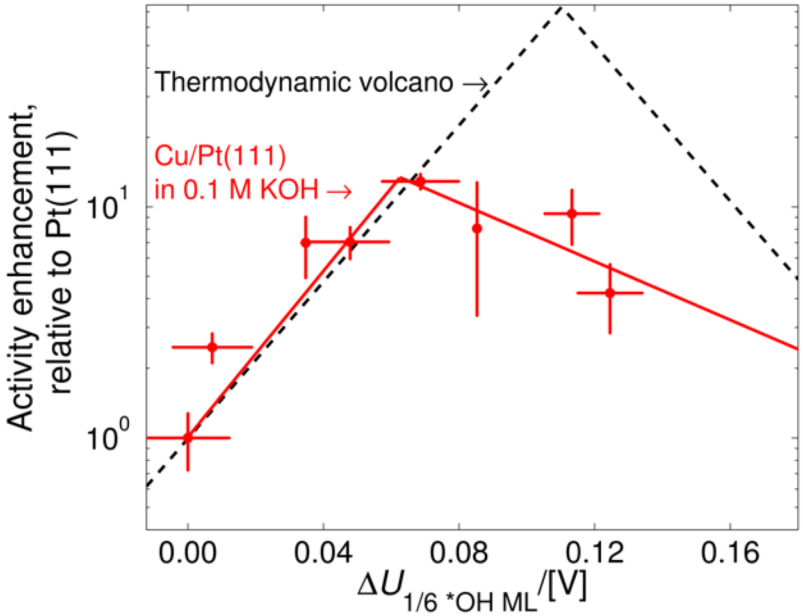


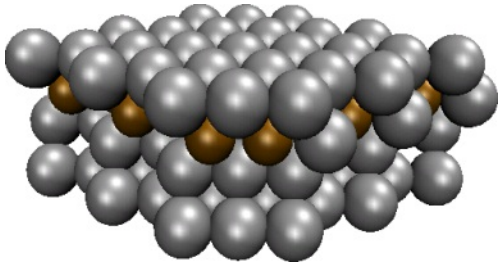
50 mV/s in O_2-saturated 0.1 M KOH, 1600 RPM



Experimental versus theoretical volcano

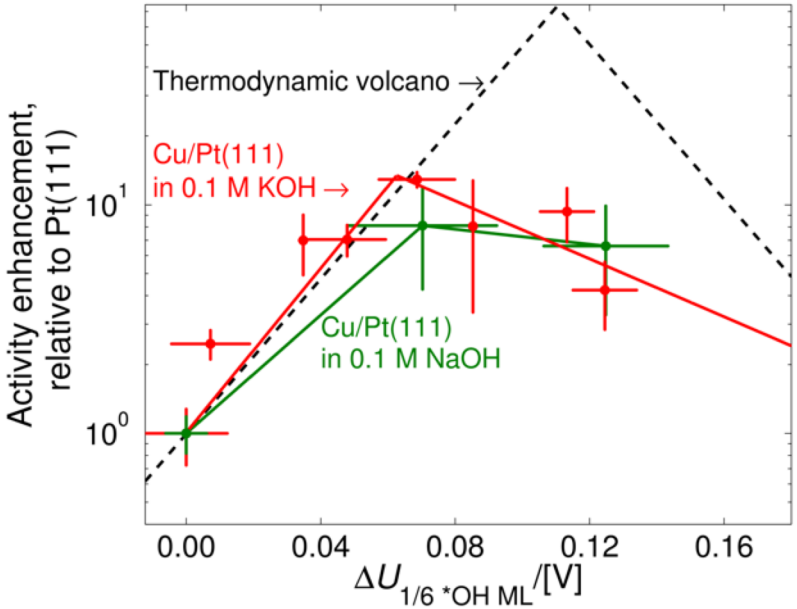
Jensen, Tymoczko, Bandarenka, Chorkendorff, Rossmeisl Escudero- Escribano, Stephens ***Angew. Chem. Int. Ed.*** 2018

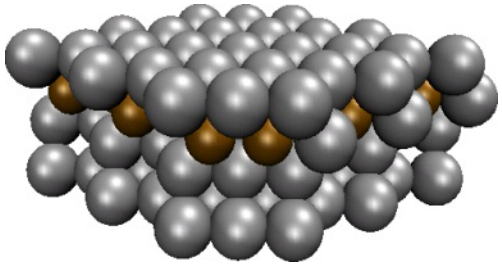




Experimental versus theoretical volcano in base

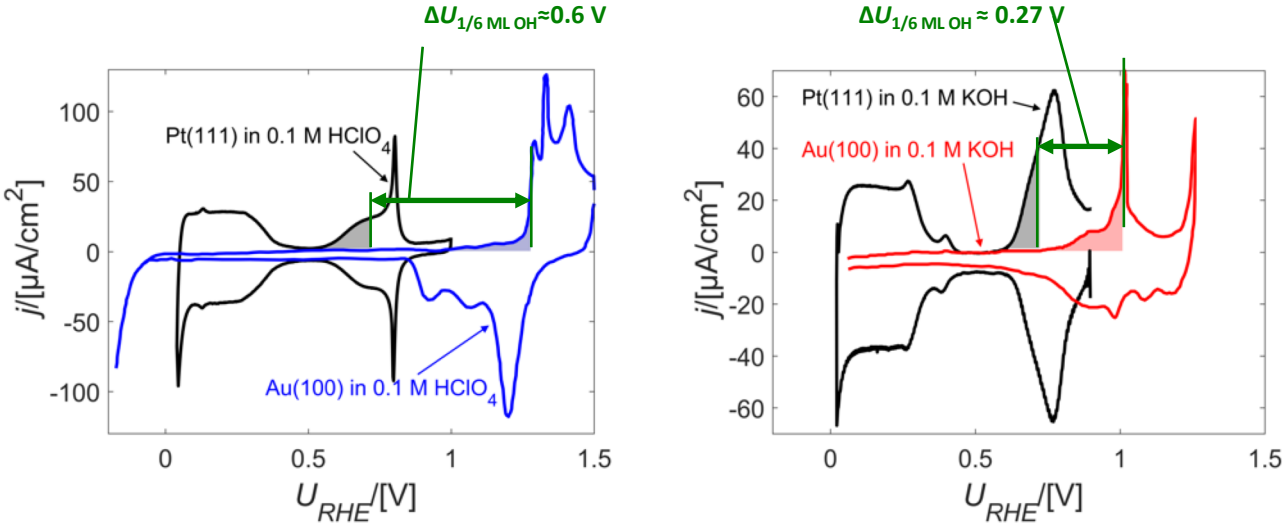
Jensen, Tymoczko, Bandarenka, Chorkendorff, Rossmeisl Escudero- Escribano, Stephens ***Angew. Chem. Int. Ed.*** 2018





What about Au(100)?

Jensen, Tymoczko, Bandarenka, Chorkendorff, Rossmeisl Escudero- Escribano, Stephens ***Angew. Chem. Int. Ed.*** 2018



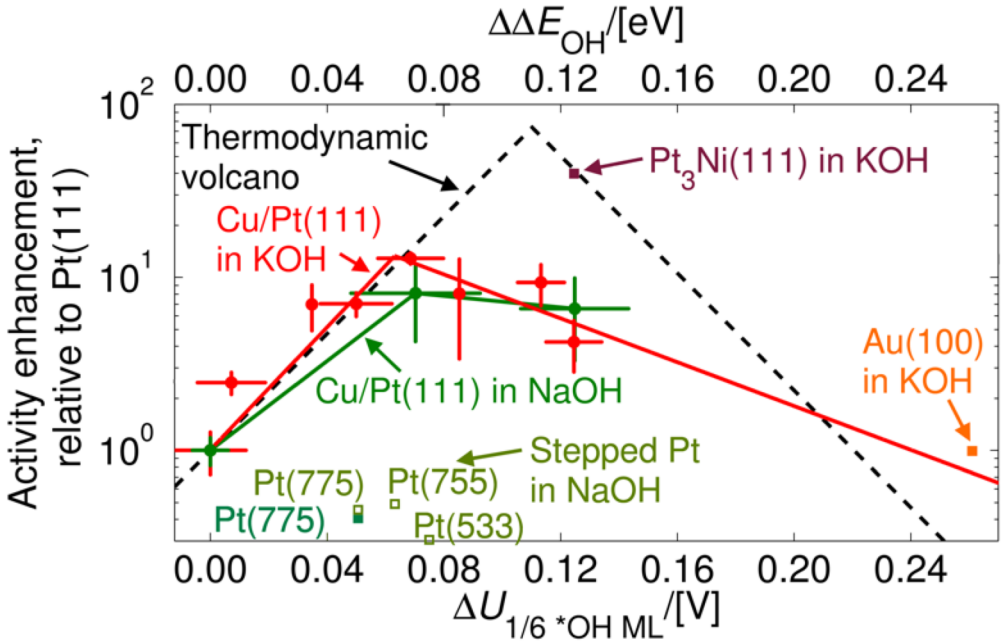
Au(100) from Blizanac, Lucas, Gallagher, Arenz, Ross, Marković, ***JPCB*** *2004* and Staszak-Jirkovský, Subbaraman, Strmcnik, Harrison, Diesendruck, Assary, Frank, Kobr, Wiberg, Genorio, Connell, Lopes, Stamenkovic, Curtiss, Moore, Zavadil & Markovic. ***ACS Catalysis*** 2015

- In 0.1 M $HClO_4$ $\Delta U_{1/6\ ML\ OH} \approx 0.6$ V
- In 0.1 M KOH $\Delta U_{1/6\ ML\ OH} \approx 0.26$ V
- From DFT $\Delta\Delta E_{OH} = 0.35$ V

What causes the destablisation of OH in 0.1 M $HClO_4$ on Au(100)?

Experimental versus theoretical volcano in base

Jensen, Tymoczko, Bandarenka, Chorkendorff, Rossmeisl, Escudero- Escribano, Stephens ***Angew. Chem. Int. Ed.*** 2018



- Low index facets follow theoretical trend
- Stepped surfaces exhibit lower activity, despite exhibiting optimal binding to OH.

Orientation influences proton transfer through double layer?

Conclusions

- Ligand effect can destablise OH using Cu/Pt(111) near surface alloy
- Experimental proof of Sabatier principle for oxygen reduction in 0.1 M $HClO_4$, 0.1 M KOH and 0.1 M NaOH
- Oxygen reduction activity on Pt(111) and Cu/Pt(111) near-surface alloys
  - 0.1 M $HClO_4$ < 0.1 M NaOH < 0.1 M KOH
- In alkaline media, marked difference between near-surface alloys, which have (111) orientation, and stepped surfaces
  - Surface orientation influences catalytic activity by means unrelated to binding of intermediates-*proton transfer through double layer?*

Imperial College London

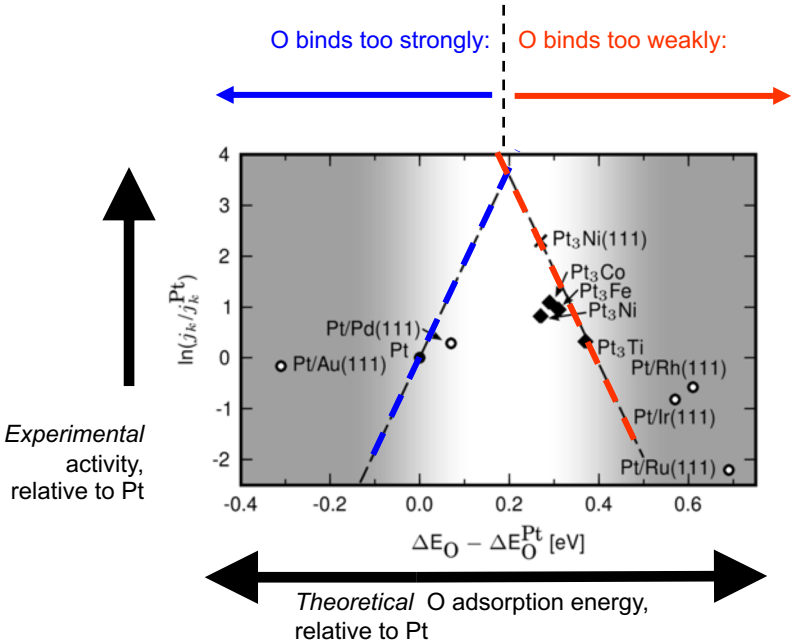
ECLOREL Workshop

24 September 2018

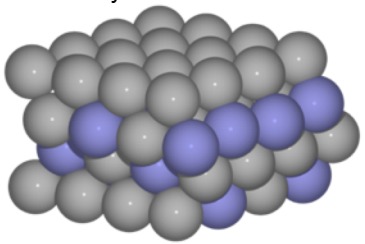
Alloys of Pt and rare earths

Ifan E. L. Stephens

Theoretical trends for oxygen reduction: Using ΔE_O as a 'descriptor' for Pt alloys



All catalysts with Pt-overlayers

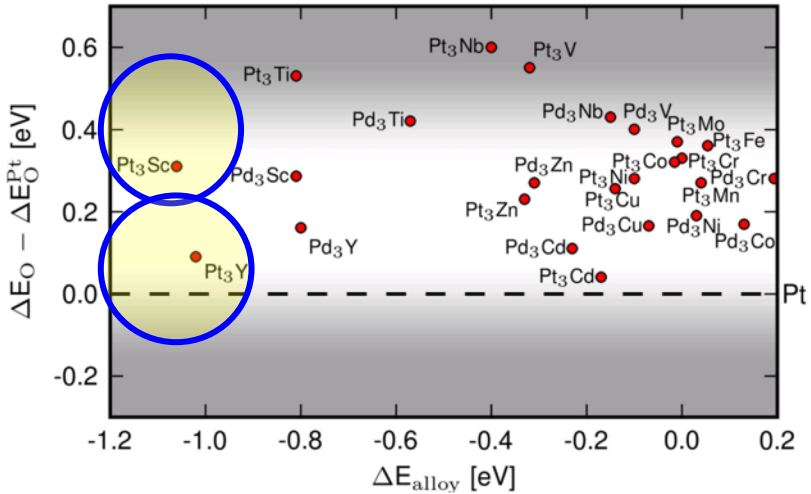


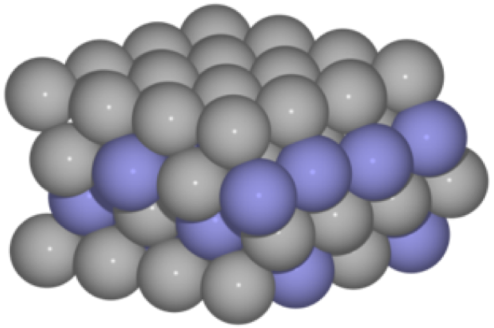
- *Theory from*: Greeley, Stephens, Bondarenko, Johansson, Hansen, Jaramillo, Rossmeisl, Chorkendorff, Nørskov ***Nature Chemistry*** 2009.
- *Experiments from:* Stamenkovic, Fowler, Mun, Wang, Ross, Lucas, Markovic, ***Science*** 2007; Stamenkovic, Mun, Mayrhofer, Ross, Markovic, Rossmeisl, Greeley, Nørskov ***Angew. Chem. Int. Ed.*** 2006; Zhang, Vukmirovic, Xu, Mavrikakis, Adzic, ***Angew. Chem. Int. Ed***. 2005

Theoretical screening study

Greeley, Stephens, Bondarenko, Johansson, Hansen, Jaramillo, Rossmeisl, Chorkendorff, Nørskov ***Nature Chemistry*** *2009*

Activity





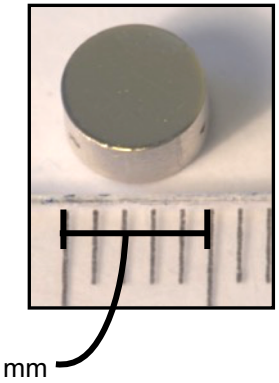
Alloy stability

Theoretical trends for oxygen reduction: Using ΔE_O as a 'descriptor' for Pt alloys

Greeley, Stephens, Bondarenko, Johansson, Hansen,, Jaramillo, Rossmeisl Chorkendorff, Nørskov, ***Nature Chemistry*** 2009.

Predictions from DFT calculations on supercomputer

Smooth, polycrystalline Pt_3X electrode

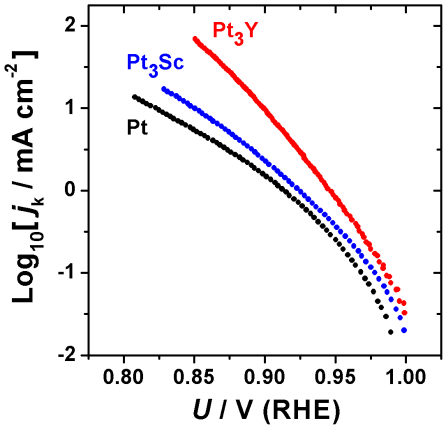


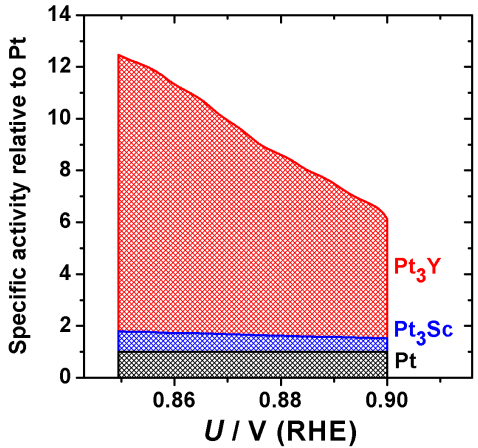
Cleaned and characterised under ultra high vacuum (UHV)

Electrochemical characterisation in 0.1 M $HClO_4$ electrolyte

Pt_3Y and Pt_3Sc as catalysts for oxygen reduction

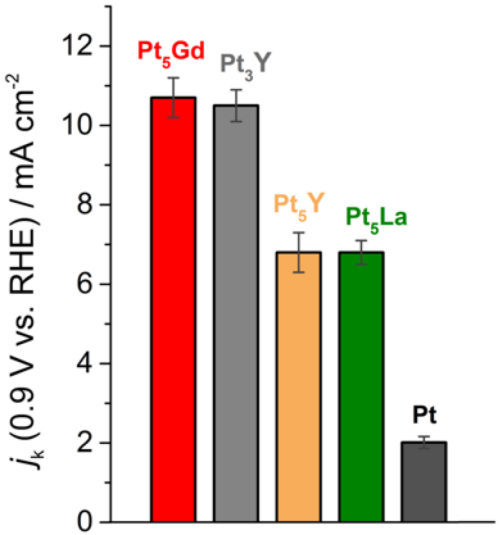
Greeley, Stephens, Bondarenko, Johansson, Hansen,, Jaramillo, Rossmeisl Chorkendorff, Nørskov, ***Nature Chemistry*** 2009.

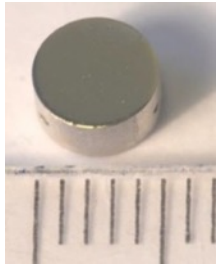




Kinetic current density in O_2-saturated 0.1 M HClO4, 23 °C 20 mV/s, 1600 RPM

Pt_5X alloys also highly active (X = lanthanide)



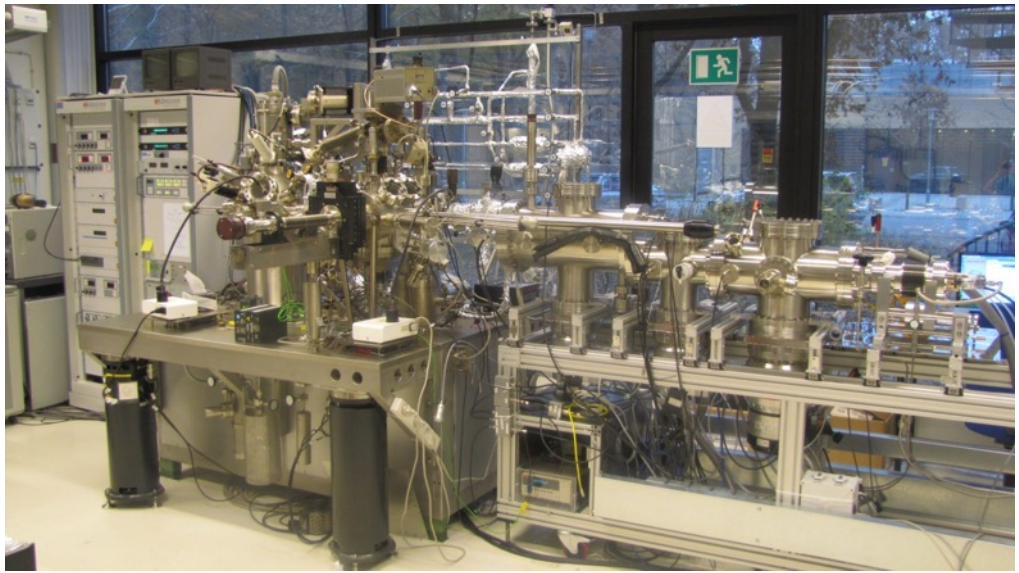


Kinetic current density in O_2-saturated 0.1 M HClO4, 23 °C
50 mV/s, 1600 RPM

- Stephens, Bondarenko, Grønbjerg, Rossmeisl, Chorkendorff, ***Energy Environ. Sci.*** 2012
- Stephens, Bondarenko, Bech, Chorkendorff, **ChemCatChem**, 2012
- Escudero-Escribano, Escudero-Escribano, Verdaguer-Casadevall, Malacrida, Gronbjerg, Knudsen, Jepsen, Rossmeisl, Stephens & Chorkendorff ***J. Am. Chem. Soc***. 2012.

Do Pt_xY and Pt_xGd work in nanoparticulate form????????

Magnetron mass-selected nanoparticle source

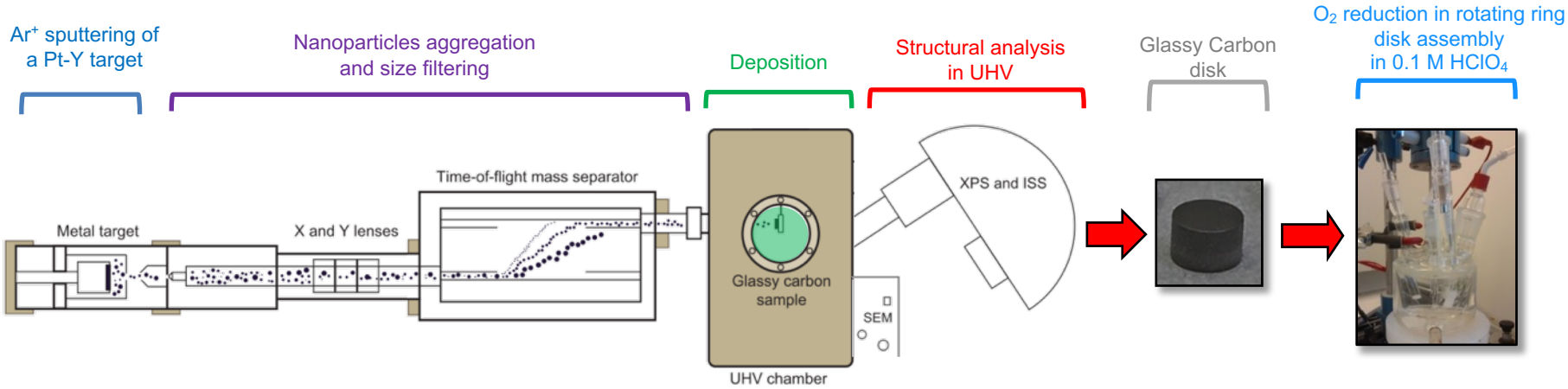


Velázquez-Palenzuela, Masini, Pedersen, Escudero-Escribano, Davide Deiana, Malacrida, Hansen, Friebel, Nilsson, Stephens, Chorkendorff, ***J. Cat.*** *2015.*

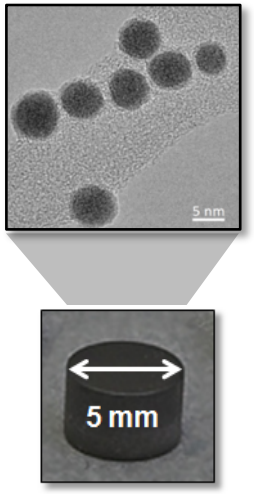
Hernandez-Fernandez, Masini, McCarthy, Strebel, Friebel, Deiana, Malacrida, Nierhoff, Bodin, Wise, Nielsen, Hansen, Nilsson, Stephens, Chorkendorff, ***Nat. Chem,*** 2014.

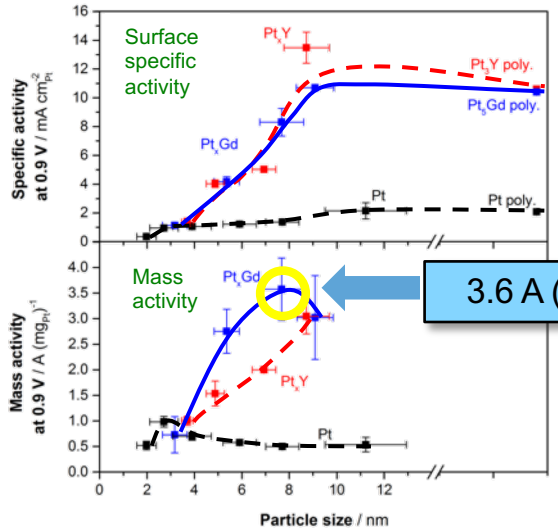
Perez-Alonso, McCarthy, Nierhoff, Hernandez-Fernandez, Strebel, Stephens, Nielsen, Chorkendorff, ***Angew. Chem. Int. Ed*** 2012

Size-selected Pt_xY, Pt_xGd and Pt nanoparticles, from magnetron nanoparticle source



Size-selected Pt_xY, Pt_xGd and Pt nanoparticles, from magnetron nanoparticle source





3.6 A (mg Pt)$^{-1}$

O_2-saturated 0.1 M $HClO_4$, 1600 RPM 23 °C 50 mVs^{-1}

- Pt_xGd from: Velázquez-Palenzuela, Masini, Pedersen, Escudero-Escribano, Davide Deiana, Malacrida, Hansen, Friebel, Nilsson, Stephens, Chorkendorff, ***J. Cat.*** *2015.*
- Pt_xY from: Hernandez-Fernandez, Masini, McCarthy, Strebel, Friebel, Deiana, Malacrida, Nierhoff, Bodin, Wise, Nielsen, [illegible]n, Nilsson, Stephens, Chorkendorff, **Nature Chemistry**,
- Pt from: Perez-Alonso, McCarthy, Nierhoff, Hernandez-Fernandez, Strebel, Stephens, Nielsen, Chorkendorff, ***Angew. Chem. Int. Ed,*** 2012

Comparison with the state-of the art at 0.9 V RHE

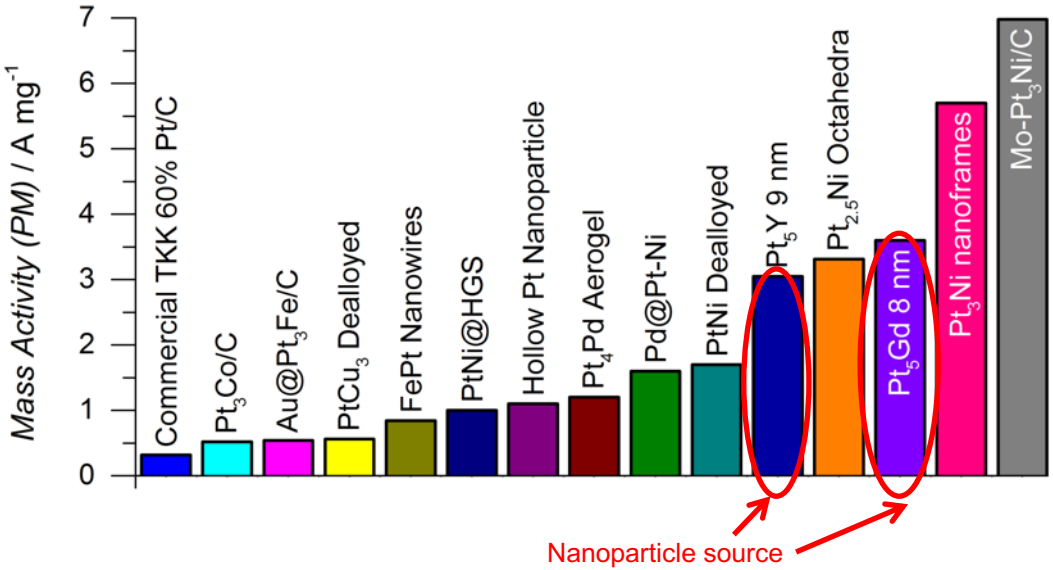


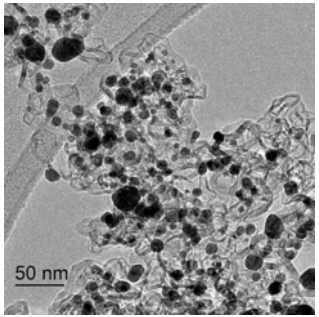
Figure from Pedersen, Escudero-Escribano, Velázquez-Palenzuela, Christensen, Chorkendorff, Stephens, **Electrochimica Acta**,2015.

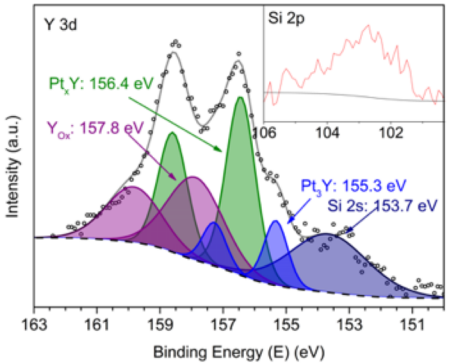
Data from: Wang et al ***Nat. Materials*** 2013; Wang, et al *Nano Lett.* 2011; Guo, et al ***Angew. Chem. Int. Ed.*** 2013; Baldizzone, et al, ***Angew. Chem. Int. Ed.*** 2011; Wang, et al ***JACS*** 2011; Liu, et al. ***Angew. Chem. Int. Ed.*** 2013; Choi, et al ***ACS Nano*** 2014; Cui, et al. ***Nat. Mater*** 2013; Hernandez-Fernandez et al, ***Nat. Chem.*** 2014 Choi, et al. ***Nano Lett.*** 2013; Palenzuela et al ***J. Catal.*** 2015; Chen, et al. ***Science*** 2014; Huang, et al, ***Science*** 2015.

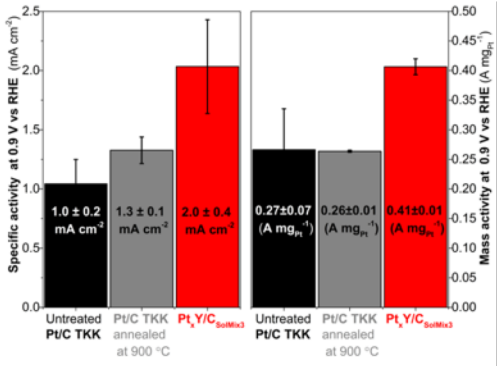
Can Pt_xY and Pt_xGd be synthesised chemically????????

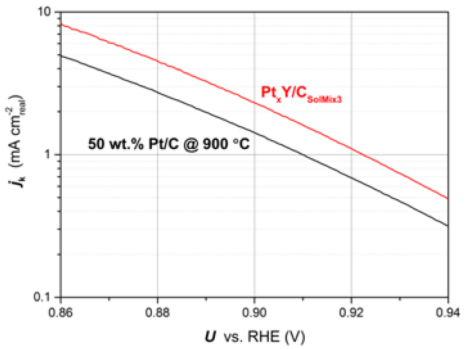
Chemically synthesised Pt_xY nanoparticles

Knudsen, Pedersen, Velazquez-Palenzuela, Stephens, Chorkendorff ***ACS Catalysis*** 2018







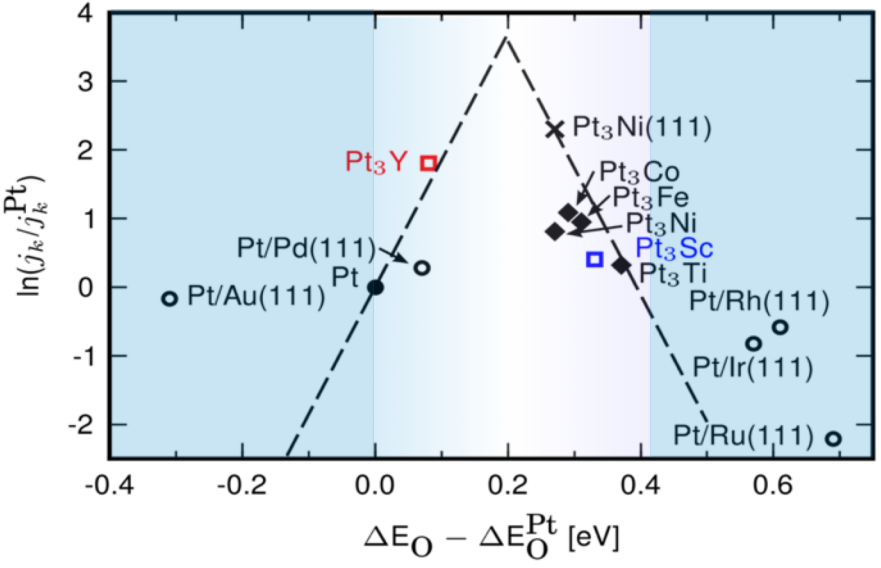


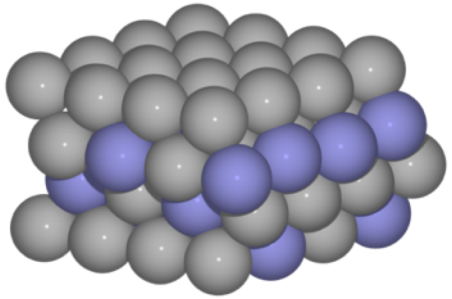
O_2-saturated 0.1 M $HClO_4$,1600 RPM 23 °C 50 mVs^{-1}

Why do these alloys catalyse oxygen reduction so well????????

Recap: Oxygen reduction volcano

Greeley, Stephens, Bondarenko, Johansson, Hansen, Jaramillo, Rossmeisl Chorkendorff, Nørskov, ***Nature Chemistry*** 2009.



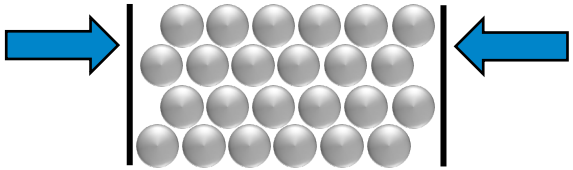


- Surface layer = 100 % Pt
- Alloying weakens binding to O or OH by modification of electronic structure of Pt surface atoms

How to weaken binding of OH and O on Pt towards optimal ORR activity?

1. Compressive lateral strain

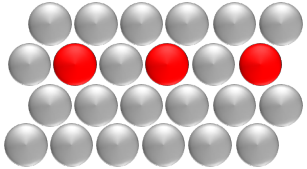
Mavrikakis , Hammer, Norskov ***PRL*** 1998.
Schlapka, Lischka, Gross, Kasberger, Jakob. ***PRL*** 2003



- Lattice parameter of core < Lattice parameter of Pt
- Downshift of d-band centre
- Experimental evidence:
  Strasser, Koh, Anniyev, Greeley, More, Yu, Liu, Kaya, Nordlund, Ogasawara, Toney, Nilsson, ***Nature Chem***., 2010

2. Subsurface alloying/ligand effect

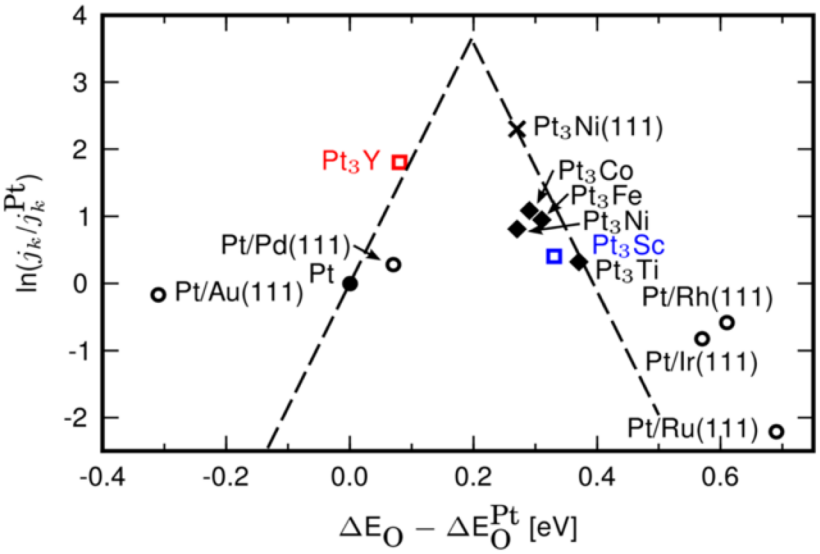
Kitchin, Nørskov, Barteau, Chen, ***J. Chem. Phys.,*** 2004;
Calle-Vallejo, Martinez, Garcia-Lastra, Rossmeisl, Koper, **PRL,** 2012



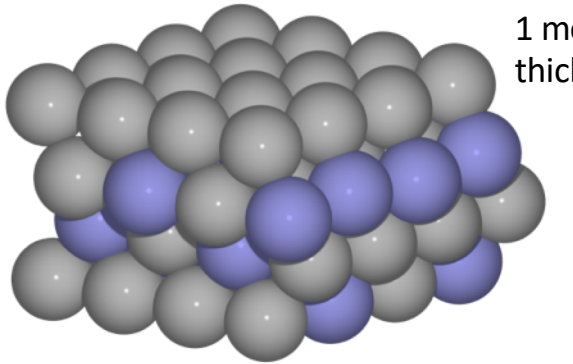
- Solute atom, e.g. Ni, Ti, Co, Cu, Y in 2nd layer
- Experimental evidence:
  Stephens, Bondarenko, Perez-Alonso, Calle-Vallejo, Bech, Johansson, Jepsen, Frydendal, Knudsen, Rossmeisl, Chorkendorff ***JACS.,*** 2011

Our original hypothesis

Greeley, Stephens, Bondarenko, Johansson, Hansen,, Jaramillo, Rossmeisl Chorkendorff, Nørskov, ***Nature Chemistry*** 2009.



- Pt_3Y is under tensile strain (Y larger than Pt)
- Activity reliant on subsurface Y concentration > 25%

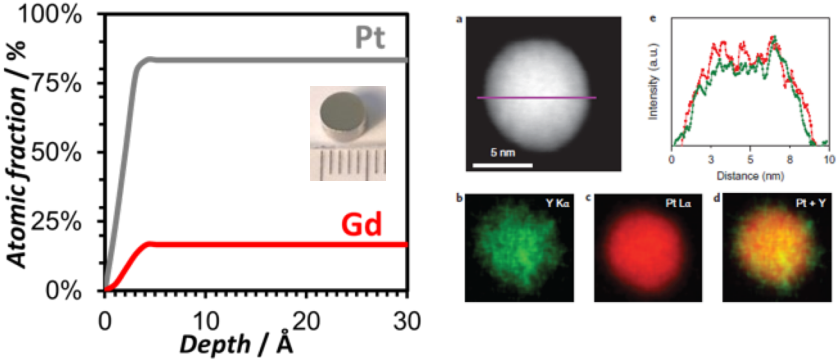


1 monolayer thick Pt overlayer

Before and after electrochemistry

Hernandez-Fernandez, Masini, McCarthy, Strebel, Friebel, Deiana, Malacrida, Nierhoff, Bodin, Wise, Nielsen, Hansen, Nilsson, Stephens, Chorkendorff, **Nat. Chem,** 2014.

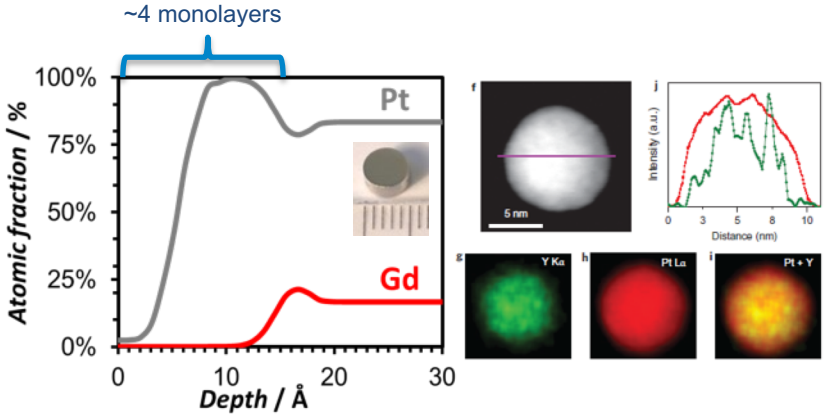
Before electrochemistry



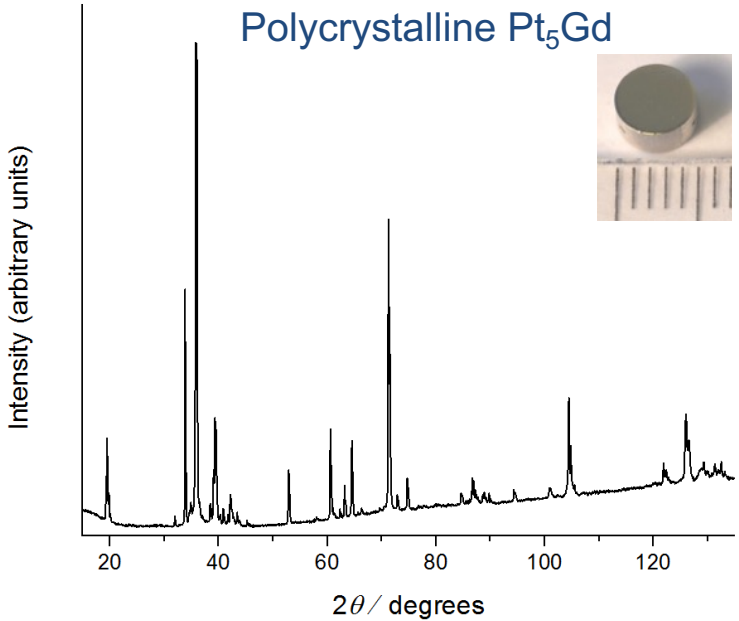
Angle resolved XPS of Pt_5Gd (pc)

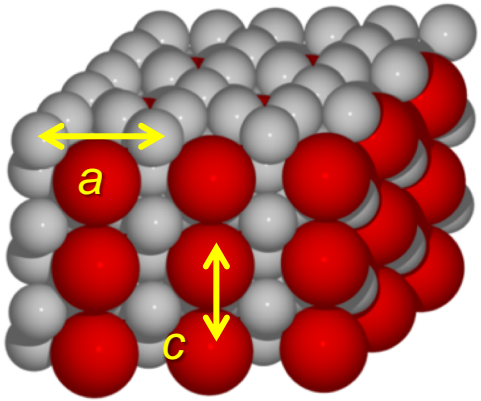
TEM of Pt_xY nanoparticle

After electrochemistry



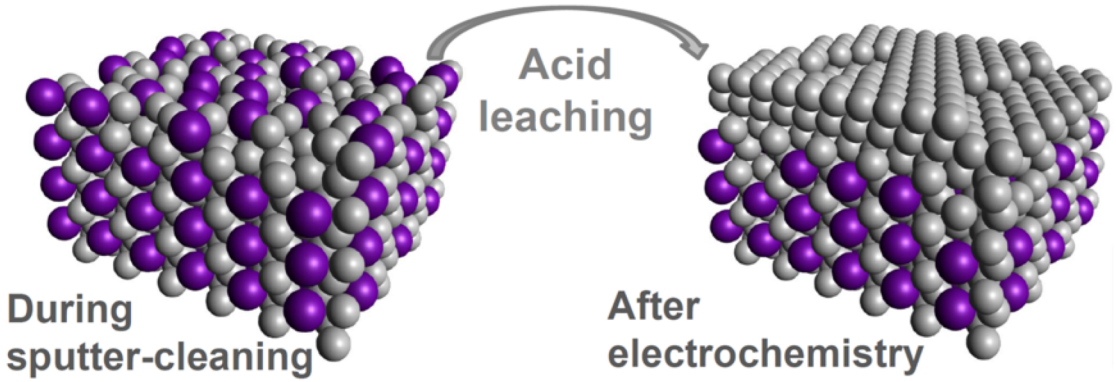
Bulk structure of Pt_5M alloys: X-ray diffraction





- Cu_5Ca structure: Not closely packed
- Pt-Pt distance in bulk of alloy < pure Pt

Before and after electrochemistry



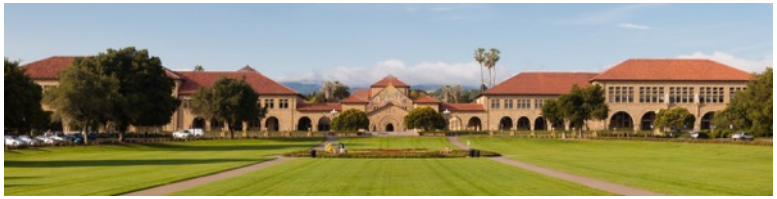
Stephens, Bondarenko, Bech, Chorkendorff, ***ChemCatChem*** 2012

Escudero-Escribano, Verdaguer-Casadevall, Malacrida, Grønbjerg, Knudsen, Jepsen, Rossmeisl, Stephens, Chorkendorff, ***J. Am. Chem. Soc.*** 2012.

Malacrida, Escudero-Escribano, Verdaguer-Casadevall, Stephens, Chorkendorff, ***J. Mater. Chem.*** *A* 2014.

(Similar to Pt_xFe and Pt_xCo : Toda, Igarashi, Uchida, Watanabe, *J. Electrochem. Soc.* 1999)

Synochotron X-ray source

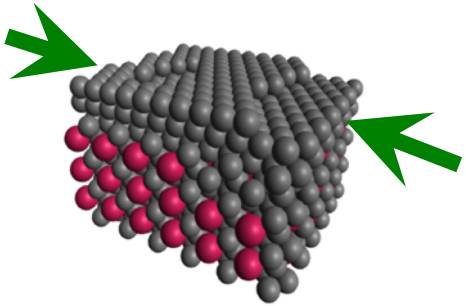


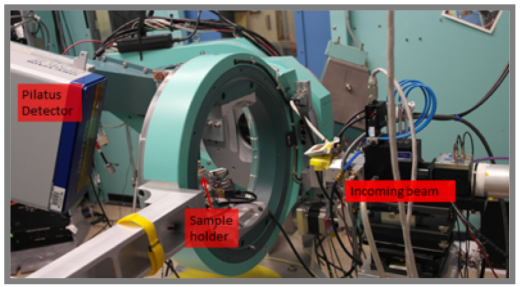
Stanford University

SLAC

Structure of Y/Pt(111) and Gd/Pt(111): Surface XRD

Pedersen, Ulrikkeholm, Escudero-Escribano, Johansson, Malacrida, Pedersen, Hansen, Jensen, Rossmeisl, Friebel, Nilsson, Chorkendorff , Stephens
***Nano Energy**, 2016.*

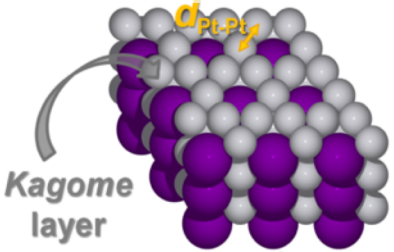


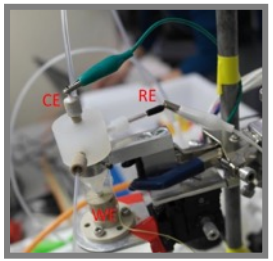


After electrochemistry measurements:

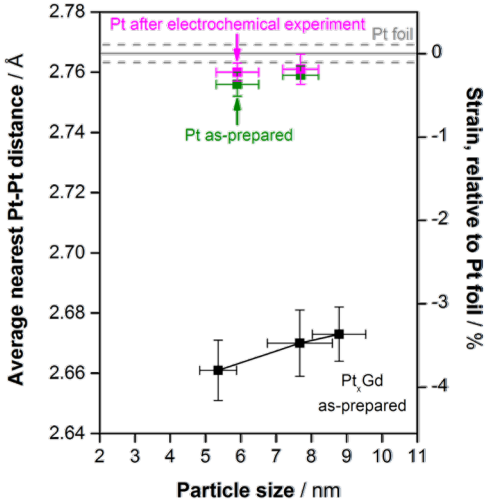
- Crystalline Pt overlayer formed
- Compressive lateral strain up to 1.4%
- 1st surface layer structure unknown (need STM)

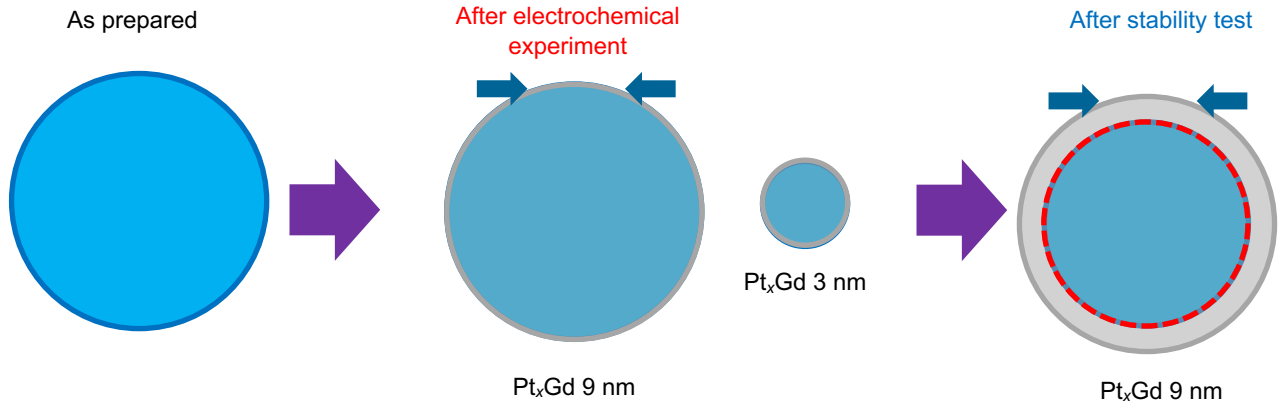
Bulk structure of Pt_xGd





Ex-situ extended X-ray absorption fine structure (EXAFS) of Pt and Pt_xGd nanoparticles

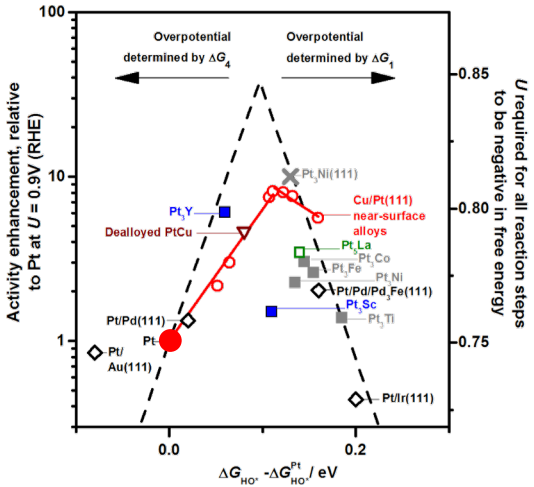


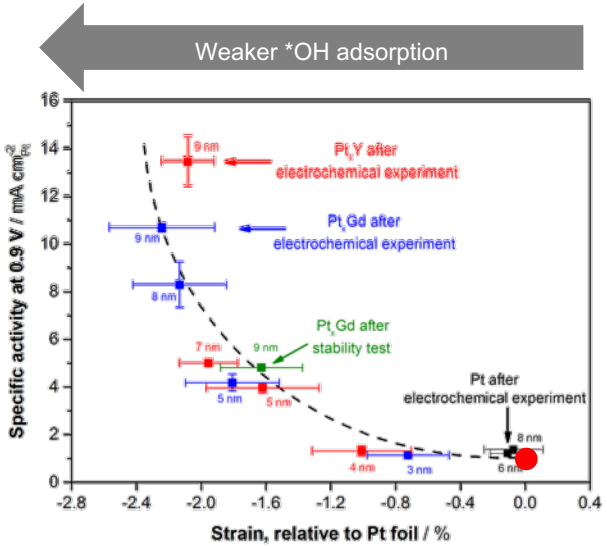


Velázquez-Palenzuela, Masini, Pedersen, Escudero-Escribano, Davide Deiana, Malacrida, Hansen, Friebel, Nilsson, Stephens, Chorkendorff, **J. Cat**, 2015;

Perez-Alonso, McCarthy, Nierhoff, Hernandez-Fernandez, Strebel, Stephens, Nielsen, Chorkendorff, **Angew. Chem. Int. Ed**, 2012

Correlating activity to Pt-Pt distance





Stephens, Bondarenko, Grønbjerg, Rossmeisl, Chorkendorff, ***Energy Environ. Sci*** 2012

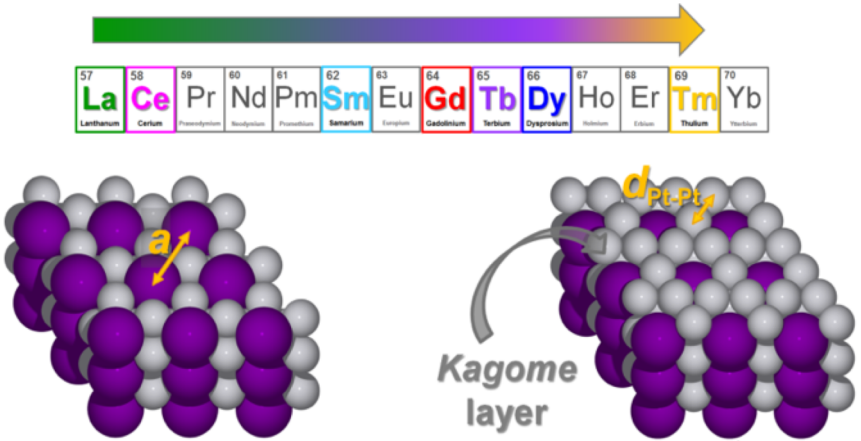
Hernandez-Fernandez, Masini, McCarthy, Strebel, Friebel, Deiana, Malacrida, Nierhoff, Bodin, Wise, Nielsen, Hansen, Nilsson, Stephens, Chorkendorff, ***Nat. Chem***, 2014.

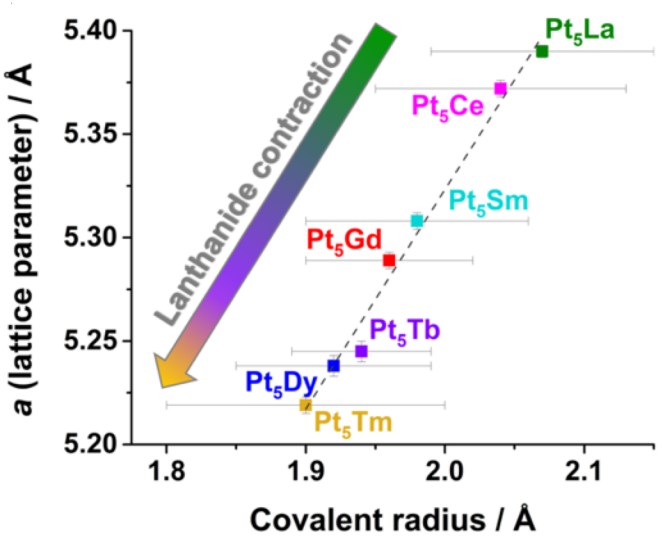
Velázquez-Palenzuela, Masini, Pedersen, Escudero-Escribano, Davide Deiana, Malacrida, Hansen, Friebel, Nilsson, Stephens, Chorkendorff, ***J. Cat***, 2015;

Perez-Alonso, McCarthy, Nierhoff, Hernandez-Fernandez, Strebel, Stephens, Nielsen, Chorkendorff, ***Angew. Chem. Int. Ed***, 2012

Tuning bulk strain via the lanthanide contraction

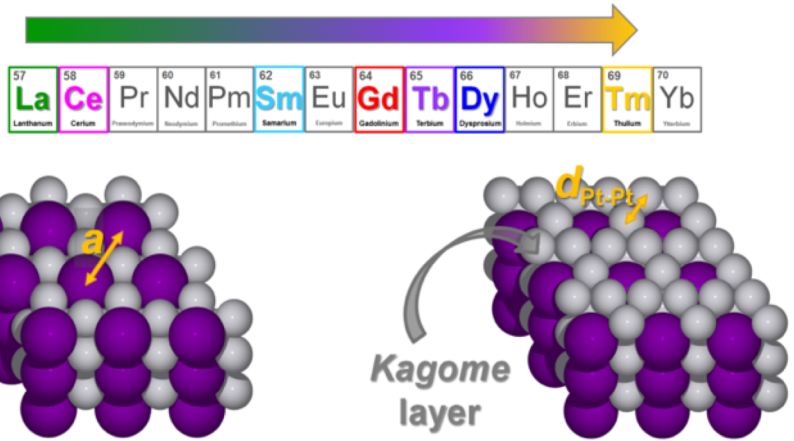
Escudero-Escribano, Malacrida, Velazquez-Palenzuela, Grønbjerg, Hansen, Tripkovic, Schiøtz, Rossmeisl, Stephens, Chorkendorff, **Science,** 2016.

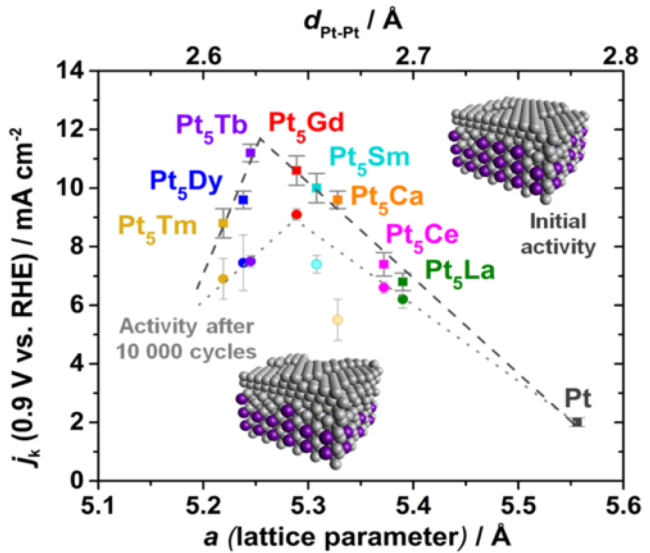




Bulk Pt-Pt distance as a descriptor for Pt_5M activity

Escudero-Escribano, Malacrida, Velazquez-Palenzuela, Grønbjerg, Hansen, Tripkovic, Schiøtz, Rossmeisl, Stephens, Chorkendorff, **Science,** 2016.

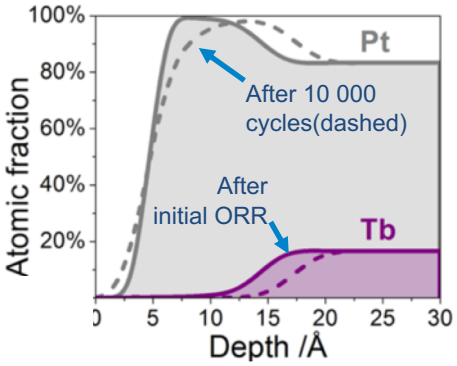


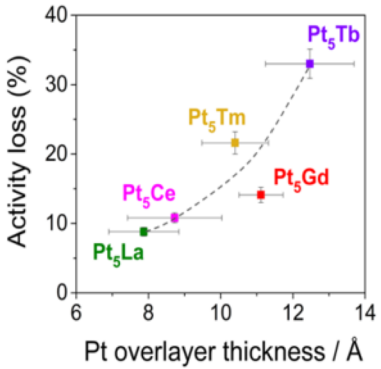


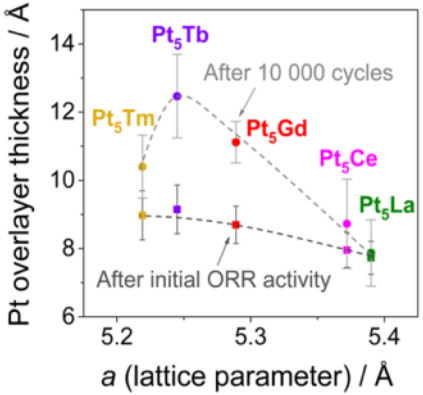
50 mV/s in O_2-saturated 0.1 M $HClO_4$, 1600 PRM

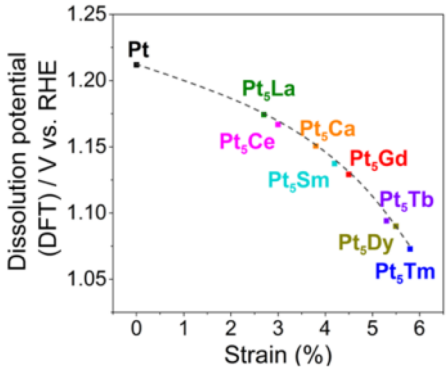
Trends in Pt_5M stability and overlayer thickness

Escudero-Escribano, Malacrida, Velazquez-Palenzuela, Grønbjerg, Hansen, Tripkovic, Schiøtz, Rossmeisl, Stephens, Chorkendorff, **Science,** 2016.





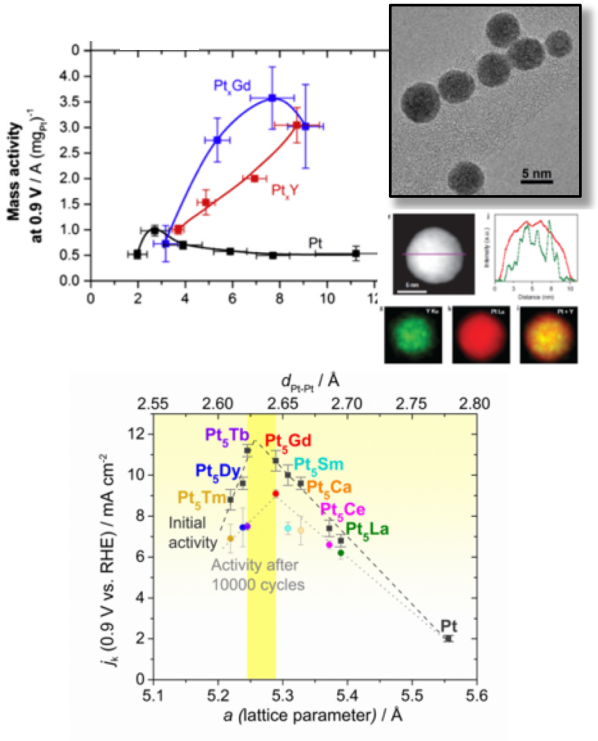




How well do these studies translate to real fuel cells?

Conclusions on Pt-rare earth alloys

- Pt and rare earths are active and stable catalysts for oxygen reduction
  - Extended surfaces and nanoparticles
- Origin of activity:
  - Structure in original DFT calculations was unstable
  - Compressed Pt overlayer
- Can negative alloy formation energy provide long term stability?
- Can they be synthesised on a large scale?
- How well do these results translate to real devices?



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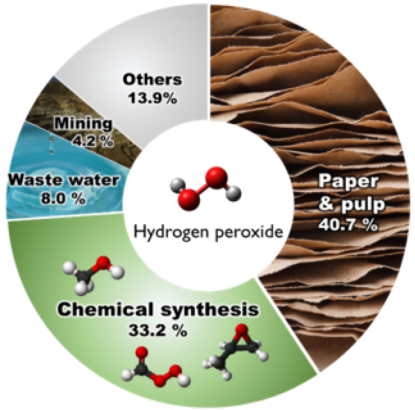
Electrolytic H_2O_2 production

Ifan E. L. Stephens

H_2O_2 consumption and production

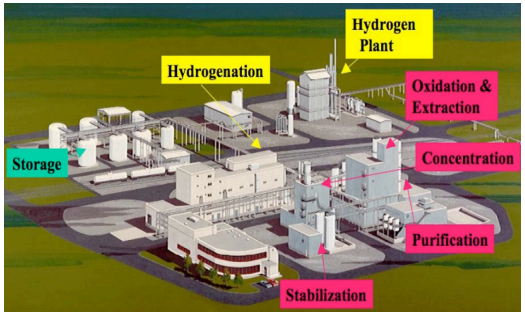
Yang, Verdaguer-Casadevall, Arnarson, Silvioli, Čolić, Frydendal, Rossmeisl, Chorkendorff, Stephens ***ACS Catalysis*** 2018

Consumption



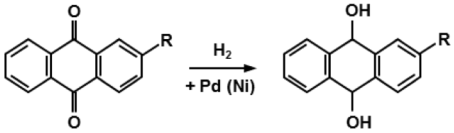
- 5.5 million tons globally (2015)
  Data from https://www.gminsights.com/

Production via anthraquione process

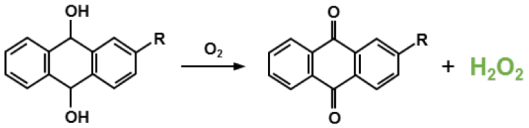


- ~55 plants in the world
  Anderson, Southeastern TAPPI and TAPPI Bleaching Committee Joint Meeting, St. Augustine (FL USA), 2002.

Hydrogenation



Oxidation



Safety risks of transporting H_2O_2 at high concentrations

http://helenair.com/news/local/article_8984de1d-0792-5aad-8021-fba2af1f35f1.html
http://news.bbc.co.uk/2/hi/uk_news/england/london/4197500.stm

Trainwreck in Montana, USA (1989)

M25 Motorway, London (2005)

- Many applications require lower concentrations of H_2O_2
  - Wastewater treatment: < 0.1%

Electrolytic H_2O_2 production

Yamanaka, Murayama, ***Angew. Chem., Int. Ed.*** 2008
Yang, Verdaguer-Casadevall, Arnarson, Silvioli, Čolić, Frydendal, Rossmeisl, Chorkendorff, Stephens ***ACS Catalysis*** 2018

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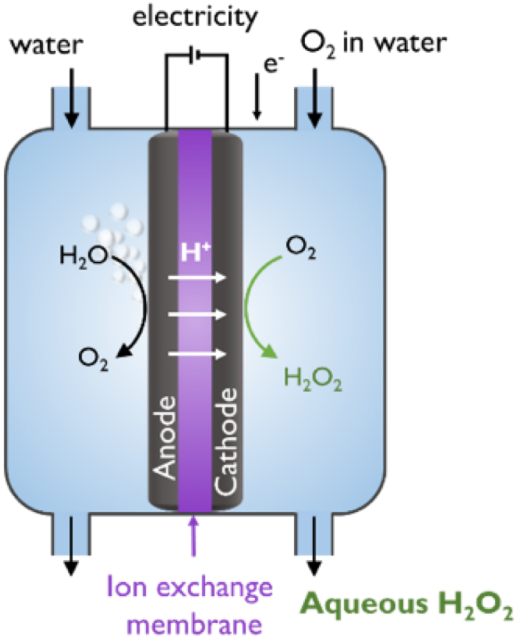


- On-site production
- Only requires **water, air, and electricity**
- H_2 and O_2 mixture is avoided
- Continuous, flow process
- **Effluent of dilute H_2O_2 in pure H_2O**

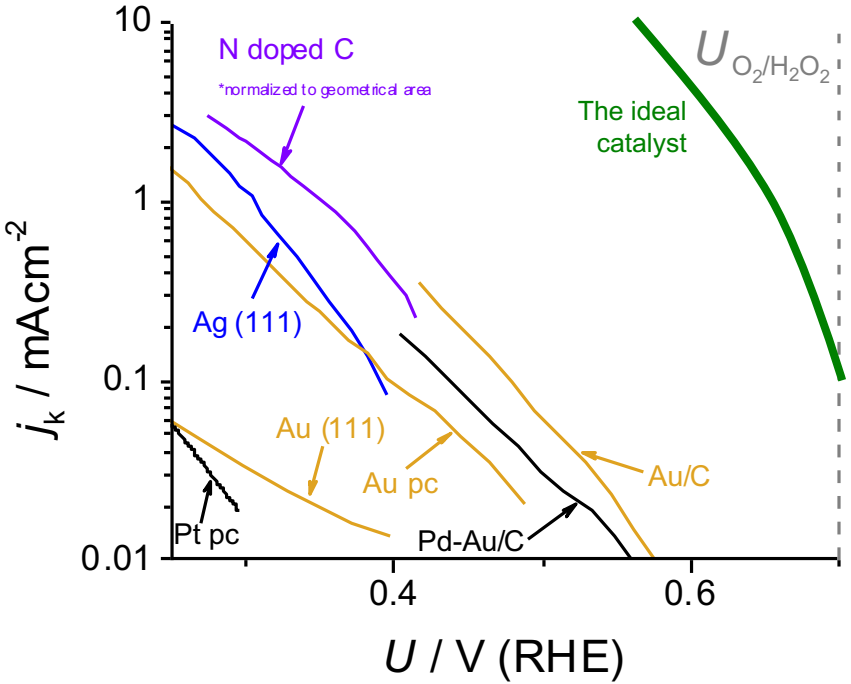
- *Selective*, *active* and stable catalyst needed for:

$O_2 + 2H^+ 2e^- \rightarrow H_2O_2$ ☺

$O_2 + 4H^+ + 4e^- \rightarrow 2H_2O$ ☹

- **Proton conducting membrane = pH 0**

State-of-the art H_2O_2 electrocatalysts (back in 2013)



- Au/C

  Jirkovsky, Halasa, Schiffrin, ***PCCP*** 2010
  - most active
  - 80% selective to H_2O_2
- Pd-Au/C

  Jirkovsky, Panas, Ahlberg, Halasa, Romani, Schiffrin ***JACS*** 2011
  - High selectivity (90%) and activity
- Total H_2O_2 current plotted from:

  Alvarez-Rizatti, Jüttner, ***J. Electronal. Chem.*** 1983; Jirkovsky, Panas, Ahlberg, Halasa, Romani, Schiffrin **JACS** 2011; Jirkovsky, Halasa, Schiffrin, ***PCCP*** 2010; Blizanac, Ross, Markovic, ***Electrochim. Acta*** 2007; Fellinger, Hasche, Strasser, Antonietti ***JACS*** 2012.

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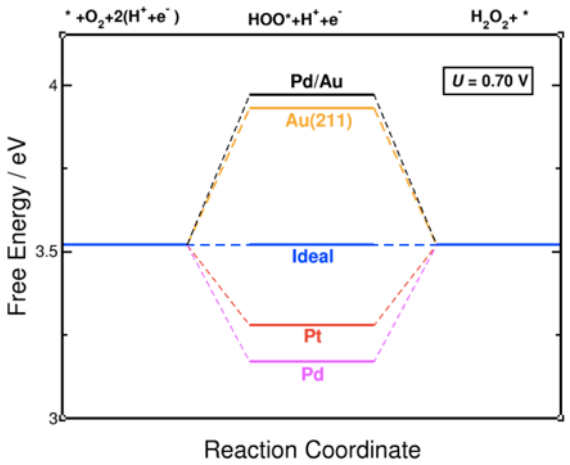
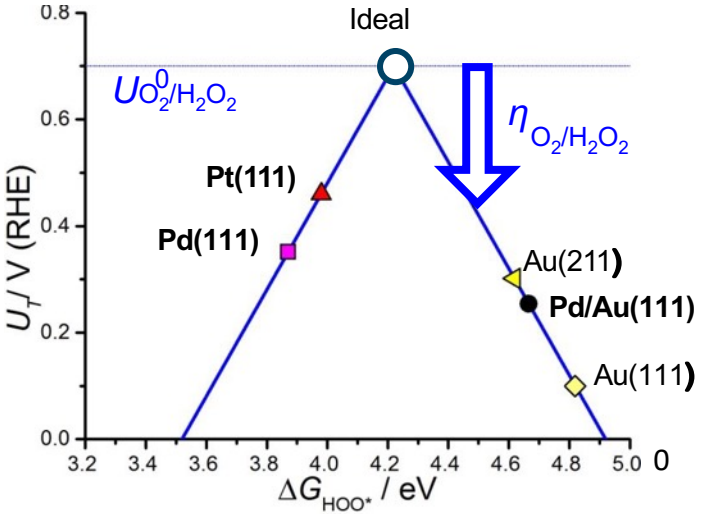
Design principles for H_2O_2 production

Ifan E. L. Stephens

The 2 electron volcano, from DFT

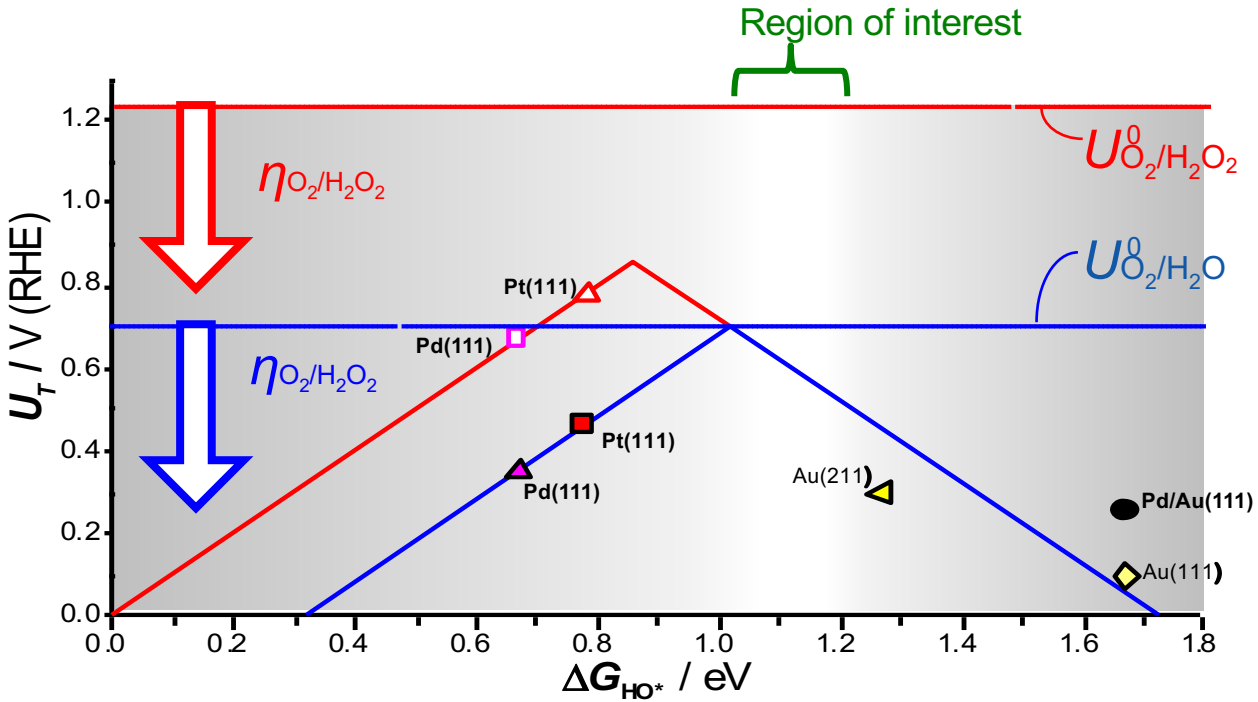




High currents should be possible within close vicinity of U^0

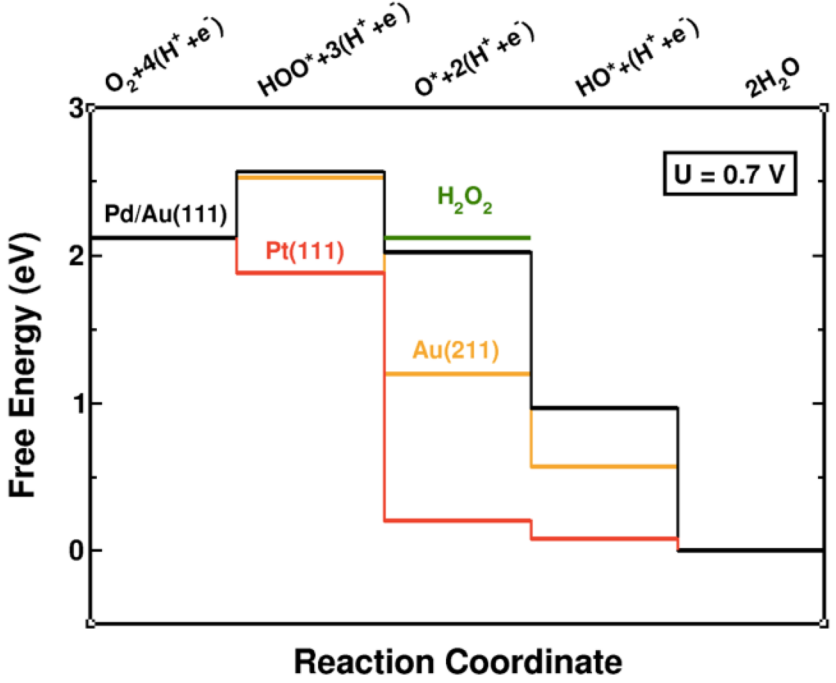
- Single intermediate (*OOH) = simple to catalyse e.g. H_2 evolution/oxidation, Cl_2 evolution
  Nørskov, Bligaard, Logadottir, Kitchin, Chen, Pandelov, Stimming, *J. Electrochem. Soc.* 2005 Zalitis, Kramer, Kucernak, *PCCP* 2013. Hansen, Man, Studt, Abild-Pedersen, Bligaard, Rossmeisl, *PCCP*, 2009 Koper, M.T.M. *J. Electroanal. Chem*, 2011

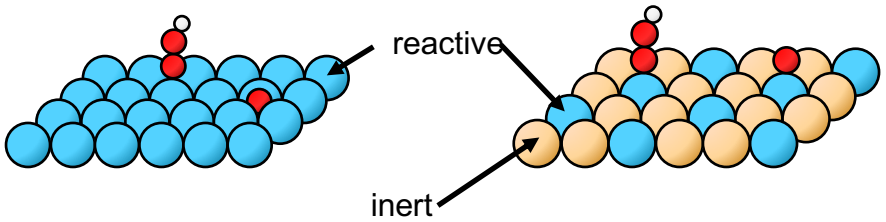
Selectivity: 4 electron vs. 2 electron volcano



Isolated reactive sites for high H_2O_2 selectivity (geometric effects)

Siahrostami, Verdaguer-Casdevall, Karamad, Chorkendorff, Stephens & Rossmeisl. ***Electrochemical Society Transactions*** 2013



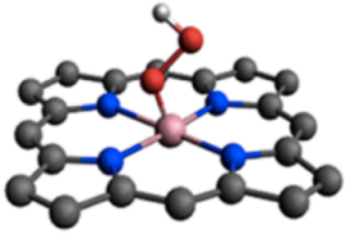


- ΔG(HOO*) controls activity
- $\Delta G(H_2O_{2(l)})$-ΔG(O*) controls selectivity
- High selectivity of cobalt porphyrins has similar origin

Siahrostami, Bjorketun, Strasser, Greeley, Rossmeisl, ***PCCP*** 2013.

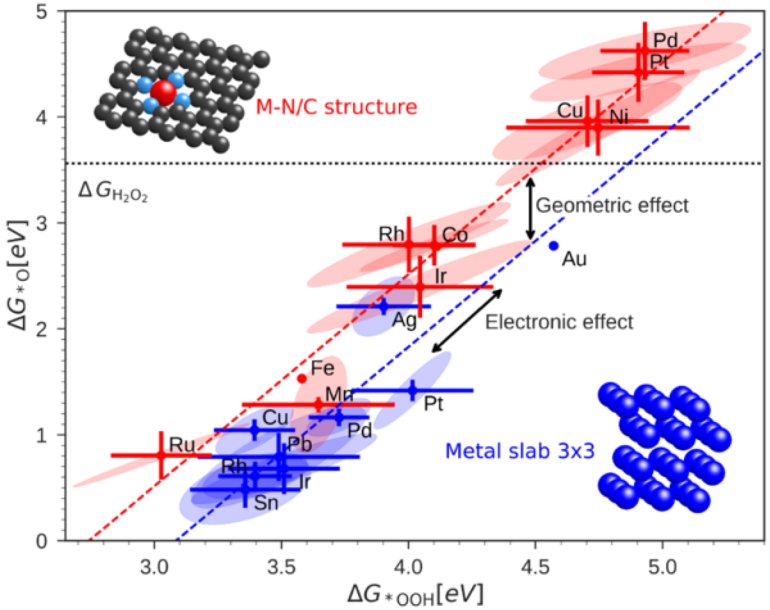
Isolated reactive sites for high H_2O_2 selectivity (geometric effects)

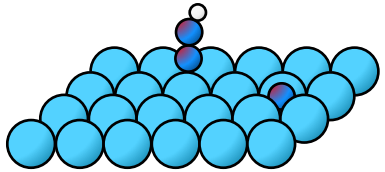
Yang, Verdaguer-Casadevall, Arnarson, Silvioli, Čolić, Frydendal, Rossmeisl, Chorkendorff, Stephens ***ACS Catalysis*** 2018



M-N/C structure
(Porphyrin like)

Isolated reactive sites
(Only atop sites available)





Metal slab

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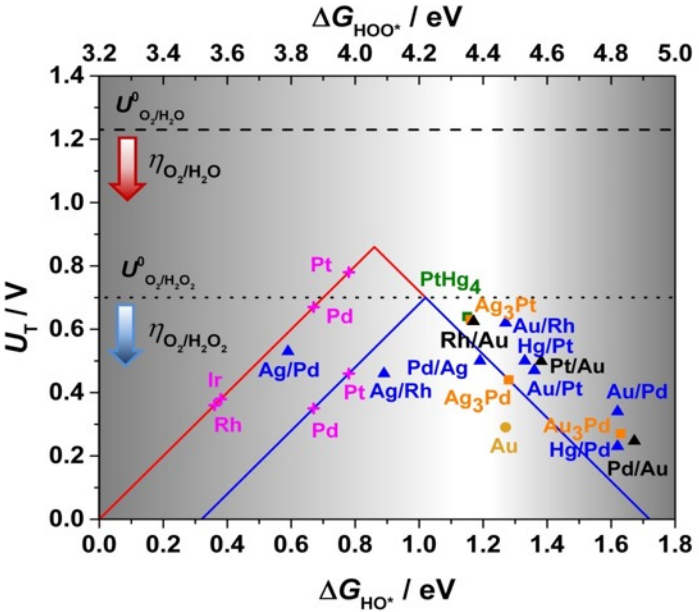
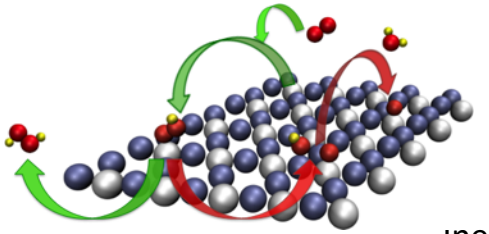
Theoretical screening

Ifan E. L. Stephens

Theoretical screening

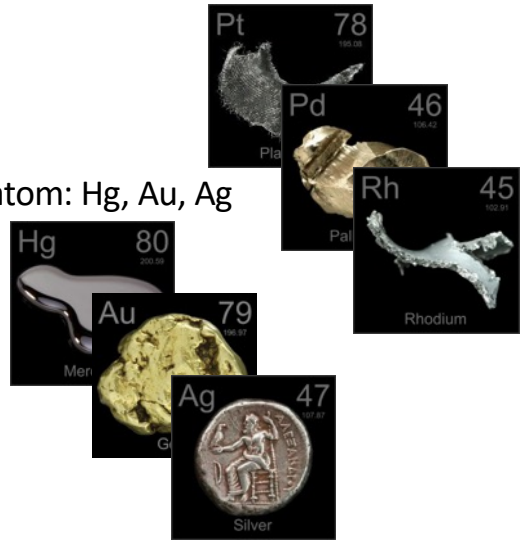
Siahrostami, Verdaguer-Casadevall, Karamad, Deiana, Malacrida, Wickman, Escudero-Escribano, Paoli, Frydendal, Hansen, Chorkendorff, Stephens, Rossmeisl, ***Nature Materials***, 2013.





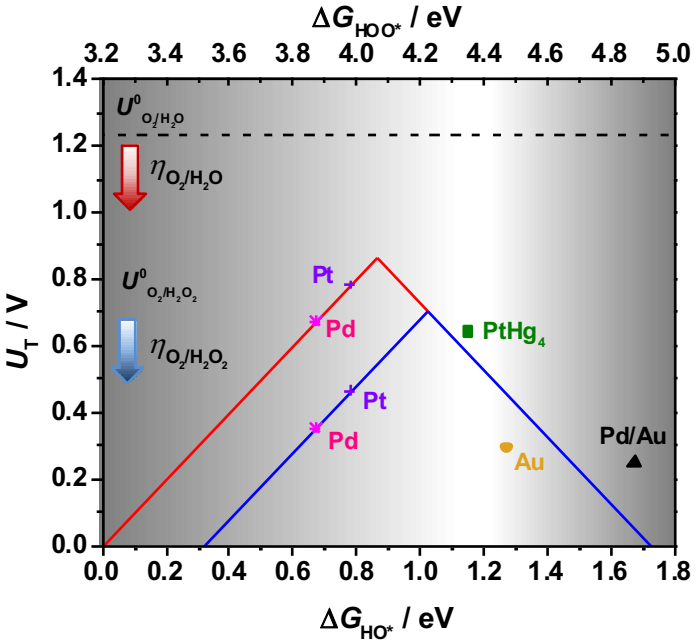
Reactive atom: Pt, Pd, Rh

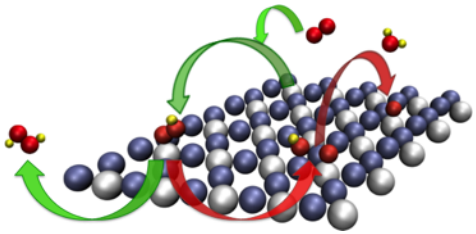
Inert atom: Hg, Au, Ag

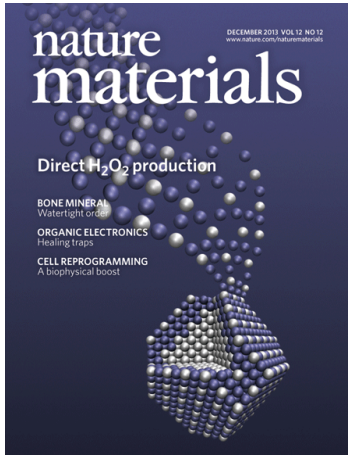


Theoretical screening

Siahrostami, Verdaguer-Casadevall, Karamad, Deiana, Malacrida, Wickman, Escudero-Escribano, Paoli, Frydendal, Hansen, Chorkendorff, Stephens, Rossmeisl, ***Nature Materials***, 2013.

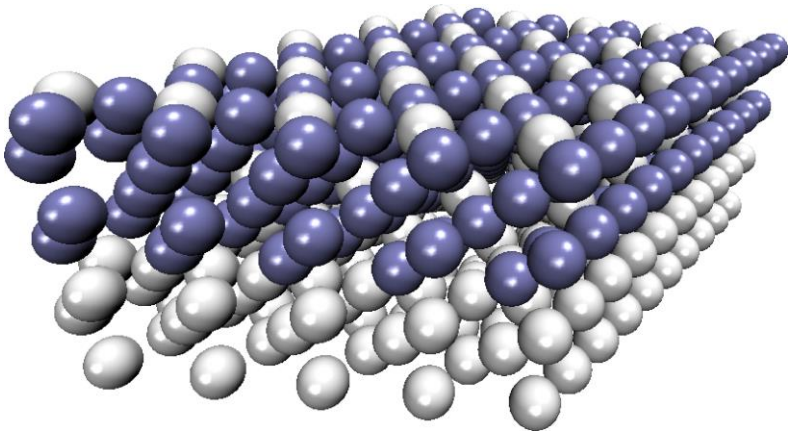






Verification of theory

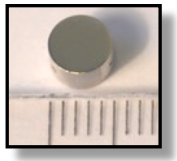
$PtHg_4$ as a catalyst for H_2O_2 production???



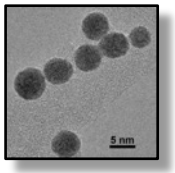
- Surface structure of PtHg4(110) established experimentally
  Wu, Yau, Zei, *Electrochim. Acta* 2008
  - In-situ using electrochemical scanning tunnelling microscopy (STM)
  - Reflection high energy electron diffraction (RHEED)
- Forms self-organised, stable crystalline structure at room temperature
  - Electrodeposition of Hg^{2+} onto Pt from HClO4.

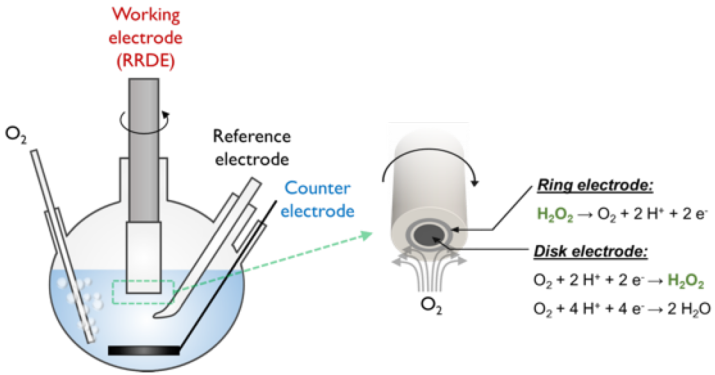
Experimental verification of theory using Rotating Ring Disk Electrode (RRDE) measurements

Single crystals

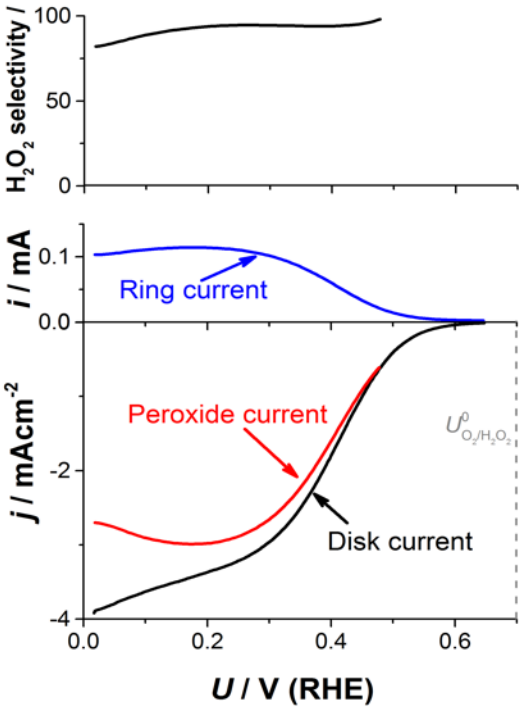


Nanoparticles



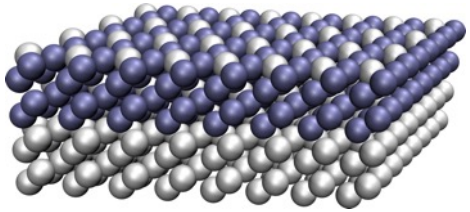


Experimental results: Hg electrodeposited on Pt(pc)

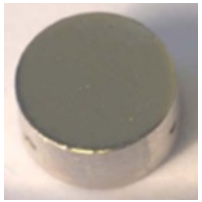


Siahrostami, Verdaguer-Casadevall, Karamad, Deiana, Malacrida, Wickman, Escudero-Escribano, Paoli, Frydendal, Hansen, Chorkendorff, Stephens, Rossmeisl, ***Nature Materials***, 2013

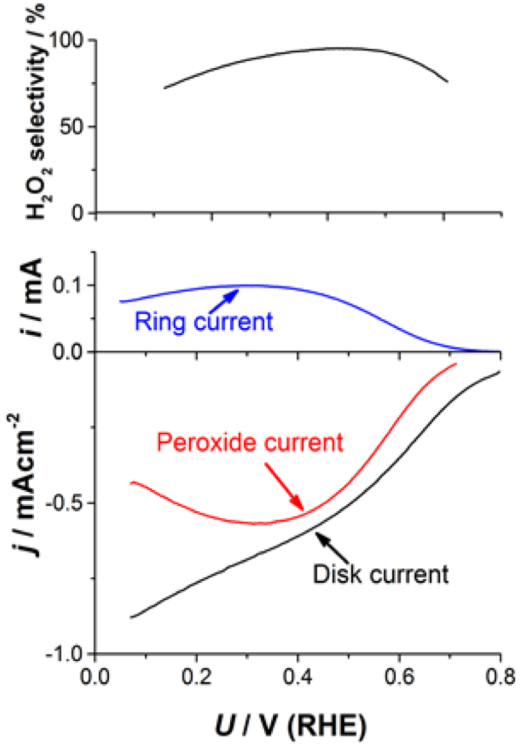
- Onset ~ 0.6 V
- %H_2O_2(0.2 V<*U*<0.4 V) ~ 96 %



50 mVs^{-1} in O_2-purged 0.1 M $HClO_4$; room temperature in rotating ring disk electrode assembly

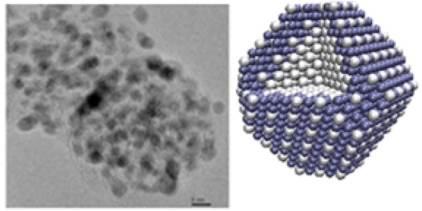


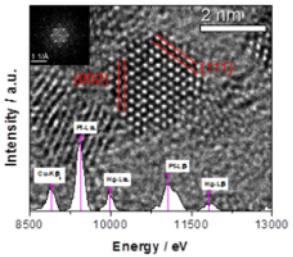
Hg electrodeposited on Pt/C nanoparticles



Siahrostami, Verdaguer-Casadevall, Karamad, Deiana, Malacrida, Wickman, Escudero-Escribano, Paoli, Frydendal, Hansen, Chorkendorff, Stephens, Rossmeisl, ***Nature Materials***, 2013

- Onset ~ 0.7 V
- %H_2O_2(0.3 V<*U*<0.5V) ~ 90 %
- 4-5 times as active as extended surface of Hg-Pt
- No measurable losses after 8,000 cycles between 0.05 and 0.8 V

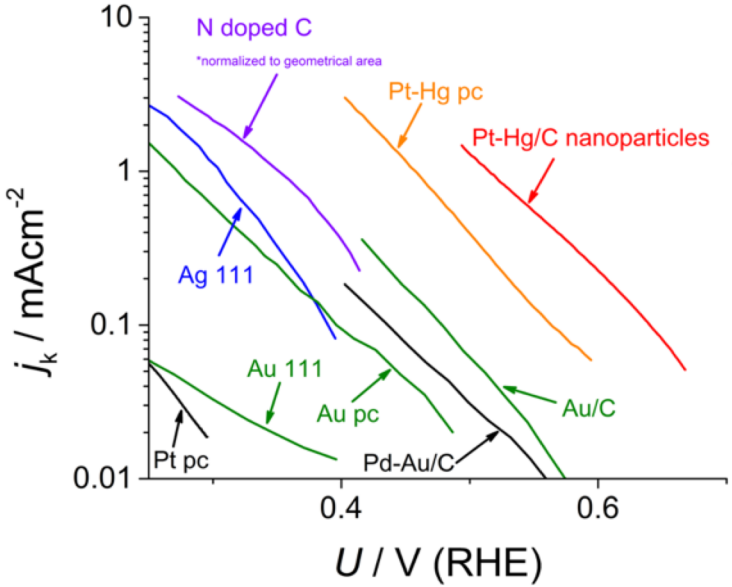


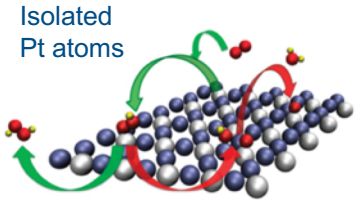


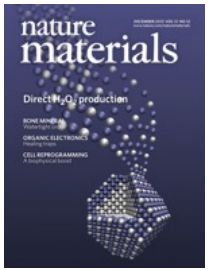
50 mVs^{-1} in O_2-purged 0.1 M $HClO_4$; room temperature in rotating ring disk electrode assembly

Comparison with state-of-the art

Siahrostami, Verdaguer-Casadevall, Karamad, Deiana, Malacrida, Wickman, Escudero-Escribano, Paoli, Frydendal, Hansen, Chorkendorff, Stephens & Rossmeisl. ***Nature Materials*** **2013**





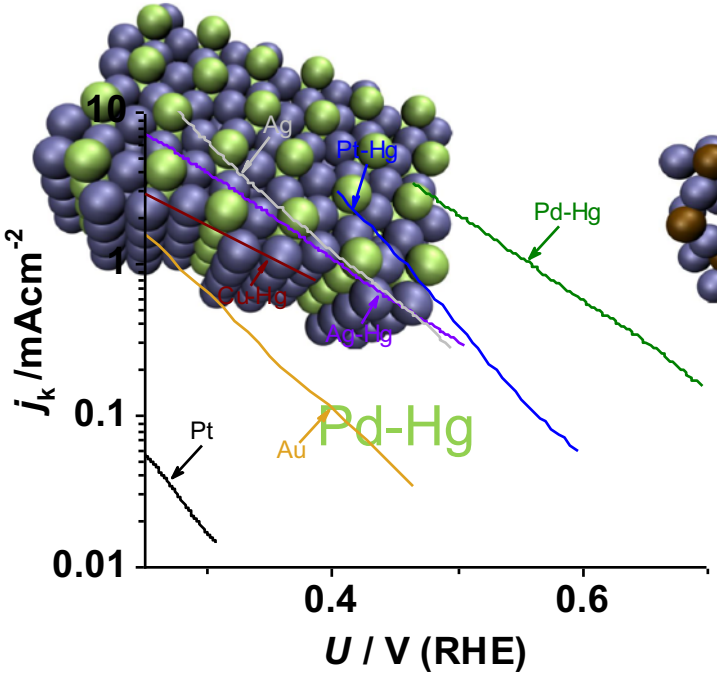


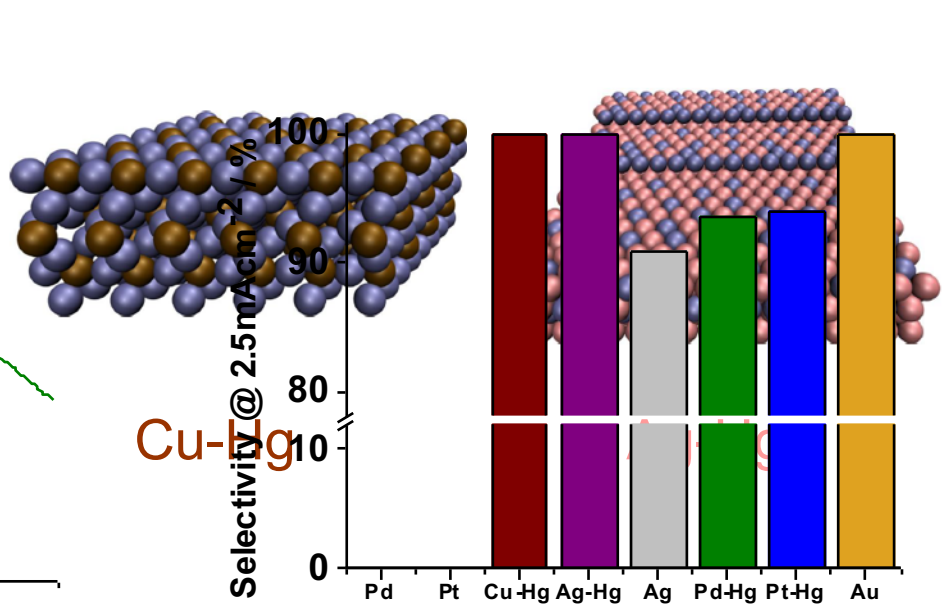
- Pt-Hg nanoparticles show >10-fold higher activity for H_2O_2 over prior state-of-the-art

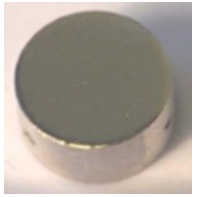
Comparison with state-of-the-art: Alvarez-Rizatti, M. and Jüttner, K. *J. Electronal. Chem*. 1983; Jirkovsky, J.S. *J. Amer. Chem Soc*. 2011; Jirkovsky, J.S *PCCP*. 2010; Blizanac, B. et al *Electrochim. Acta* 2007; Fellinger et al*, J. Amer. Chem. Soc* 2012

Hg alloys with Pd, Cu and Ag

Verdaguer-Casadevall, Deiana, Karamad, Siahrostami, Malacrida, Hansen, Rossmeisl, Chorkendorff, Stephens, ***Nano Letters*** (2014).

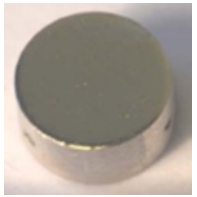


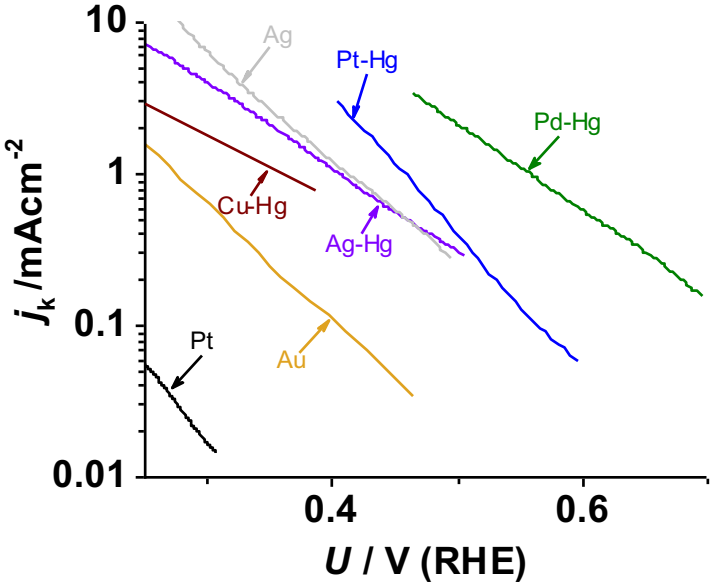


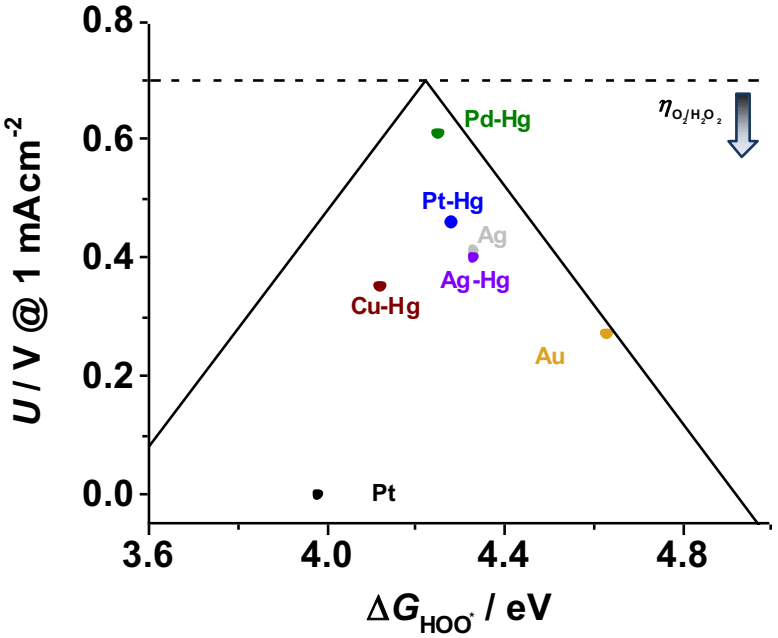


Hg alloys with Pd, Cu and Ag

Verdaguer-Casadevall, Deiana, Karamad, Siahrostami, Malacrida, Hansen, Rossmeisl, Chorkendorff, Stephens, ***Nano Letters*** (2014).







Conclusions for H_2O_2

- Design principles:
  - ΔG(HOO*) controls activity
  - $\Delta G(H_2O_{2(l)})$-ΔG(O*) controls selectivity
- Theoretical prediction that high H_2O_2 production activity should be possible at low overpotentials, similar to other 2-electron reactions
  - Realised using Pt-Hg and Pd-Hg
- Hg unsuitable for industrial applications
- Spin off company established in 2015
- *Electrochemistry can provide the ideal solution for the localised production of our most coveted chemicals*.

HPNow

Imperial College London

ECLOREL Workshop

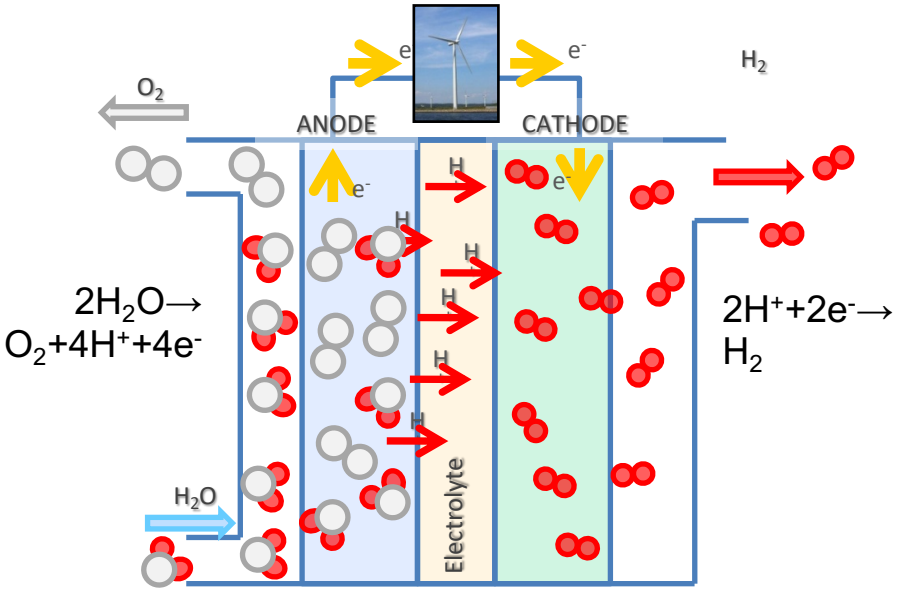
24 September 2018

Oxygen evolution in acid on non-precious metal oxides

Frydendal, Paoli, Chorkendorff,Rossmeisl, Stephens ***Advanced Energy Materials*** 2015

Ifan E. L. Stephens

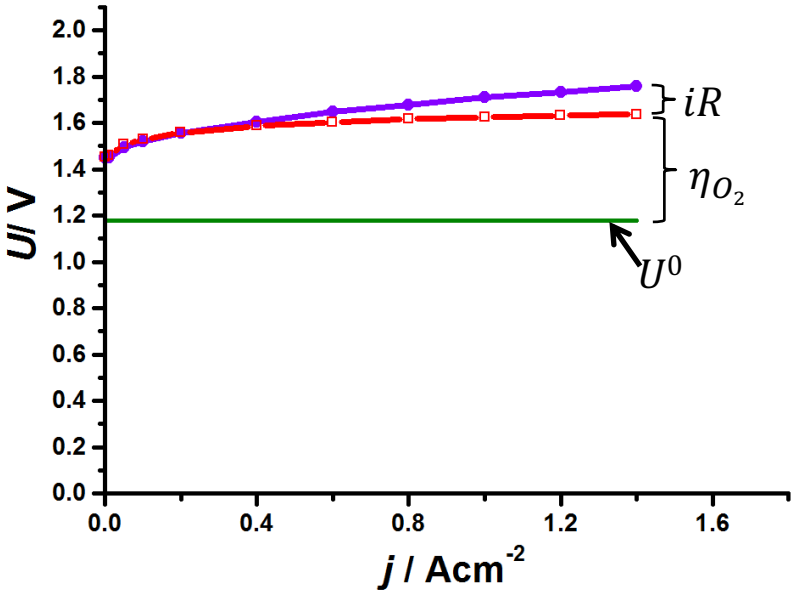
Electricity storage through Polymer Electrolyte Membrane (PEM) Electrolysis



Ayers, Dalton & Anderson. ***ECS Transactions*** 2012

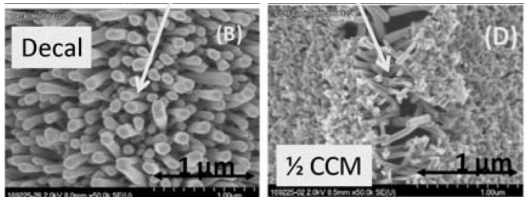
- Little infrastructure:
  - close to point of consumption
- Ambient conditions
- Fast start-up and shut-down
  - *ideal for intermittent renewables*

What limits the efficiency of a PEM Electrolyser?



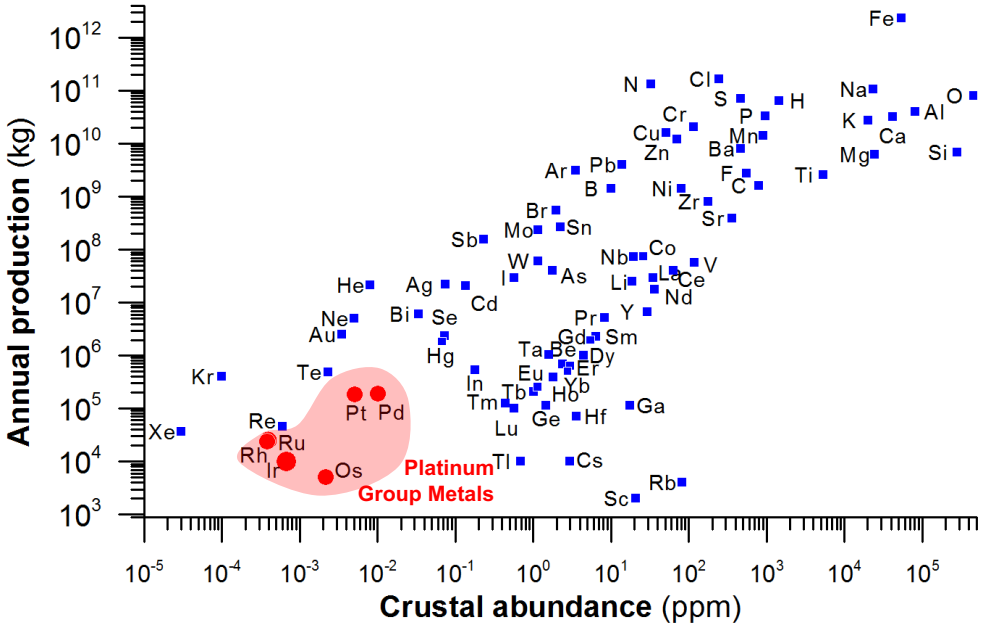
$$U = U^0 + iR + \eta_{O_2} + \eta_{H_2}$$

- *iR*< 120 mV
- Cathode: η_{H_2} < 2mV possible with 0.05 mg/cm^2 Pt
  Neyerlin, Gu, Jorne, Gasteiger ***JECS*** 2007.
  Kucernak & Zalitis. ***J. Phys. Chem. C*** 2016
- Anode: 270mV< η_{O_2}<440 mV with $PtIrO_x$;
  0.3 mg/cm^2 precious metal
  Debe, Hendricks, Vernstrom, Meyers, Brostrom, Stephens, Chan, Willey, Hamden, Mittelsteadt, K.; Capuano, Ayers, Anderson, ***JECS*** 2012



Nanostructured thin film of Pt-Ir-O_x whiskers (3M)

Is PEM Electrolysis scalable to the TW level?

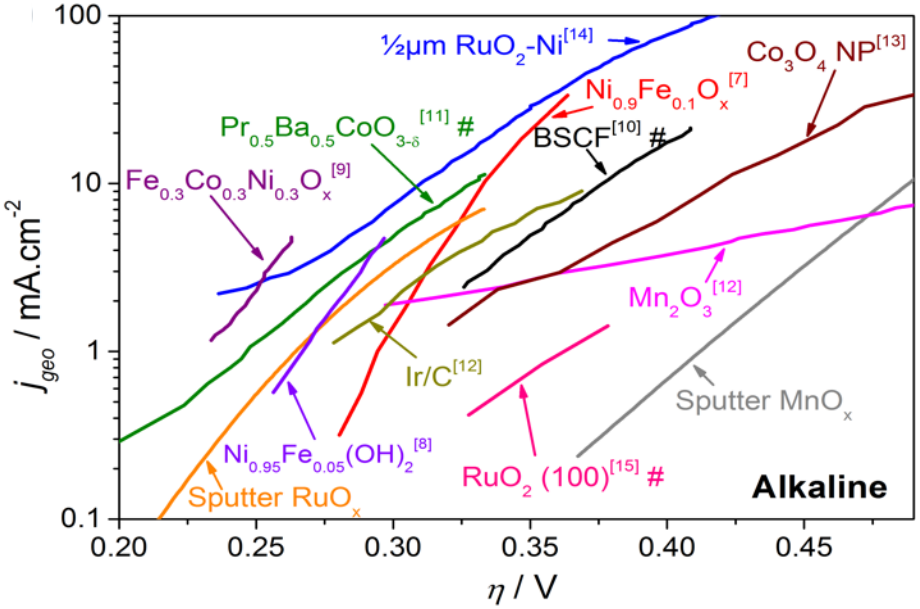


Adapted from Vesborg, Jaramillo, ***RSC Advances*** 2012

Also see: Paoli, Masini, Frydendal, Deiana, Schlaup, Malizia, Hansen, Horch, Stephens, Chorkendorff. ***Chem. Sci.*** 2015,

State-of-the-art oxygen evolution catalysis in alkaline media

Frydendal, Paoli, Knudsen, Wickman, Malacrida, Stephens, Chorkendorff **ChemElectroChem** 2014



[7] L. Trotochaud, J. K. Ranney, K. N. Williams, S. W. Boettcher, *J. Am. Chem. Soc.* **2012**,

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[10] J. Suntivich, K. J. May, H.A. Gasteiger, J. B. Goodenough, Y. Shao-Horn, *Science* **2011**

[11] A. Grimaud, K. J. May, C. E. Carlton, Y.-L. Lee, M. Risch, W. T. Hong, J. Zhou, Y. Shao-Horn, *Nat. Commun.* **2013**,

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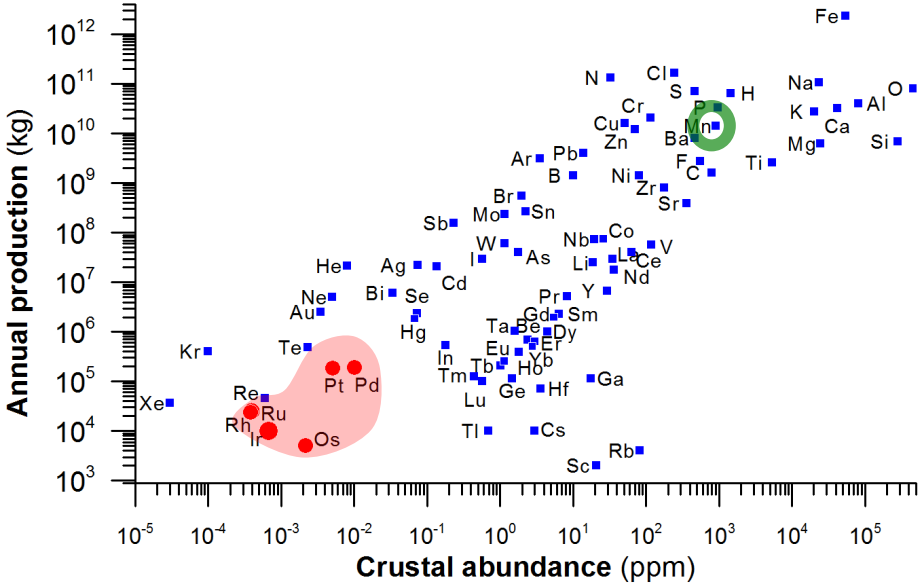
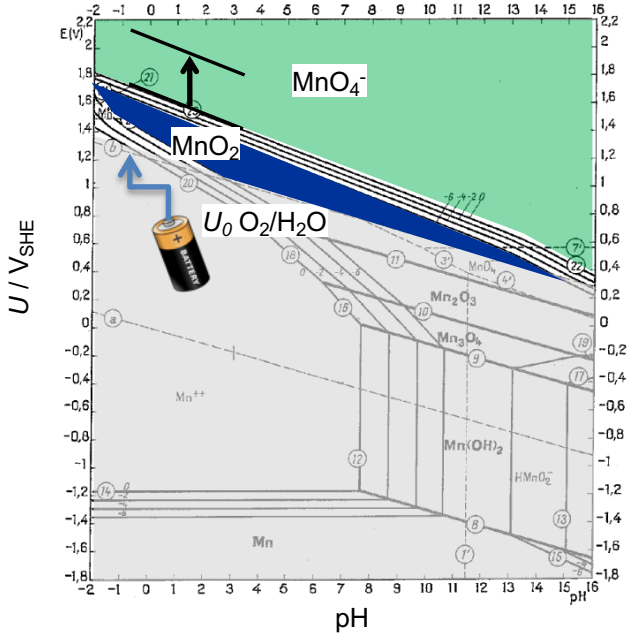
MnO_2: active and stable?

Frydendal, Paoli, Chorkendorff,Rossmeisl, Stephens ***Advanced Energy Materials*** 2015

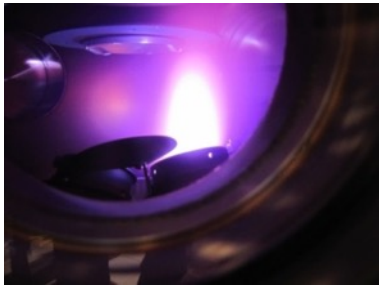


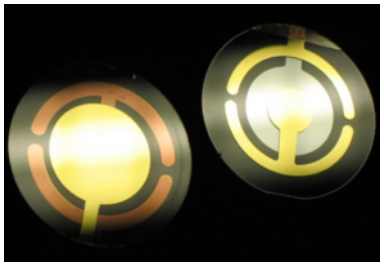
Adapted from Vesborg, Jaramillo, **RSC Advances** (2012); Pourbaix, **Atlas of Aqu. Equil.** 1966

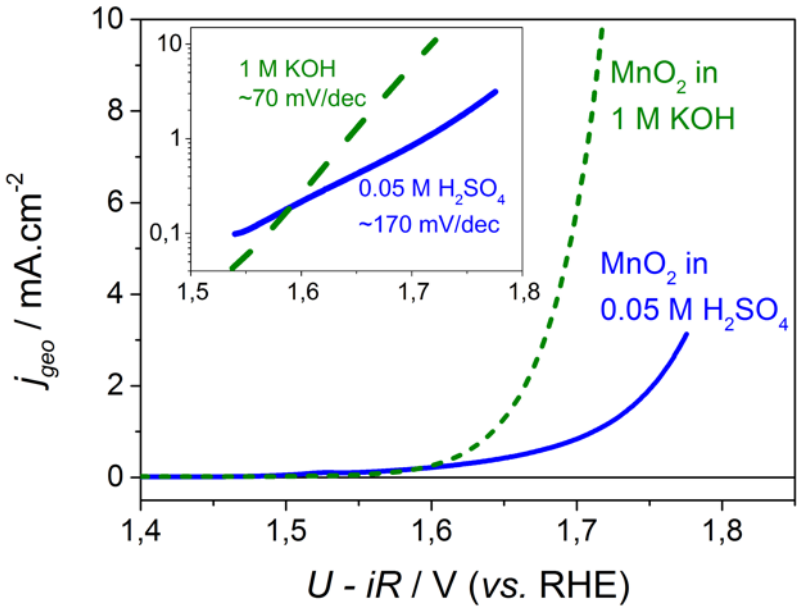


MnO_2: active and stable?

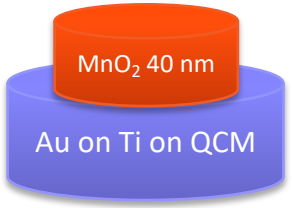
Frydendal, Paoli, Chorkendorff,Rossmeisl, Stephens ***Advanced Energy Materials*** 2015

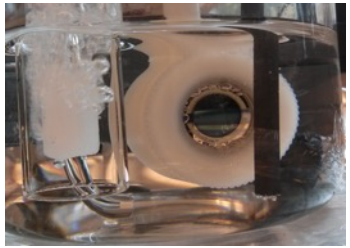






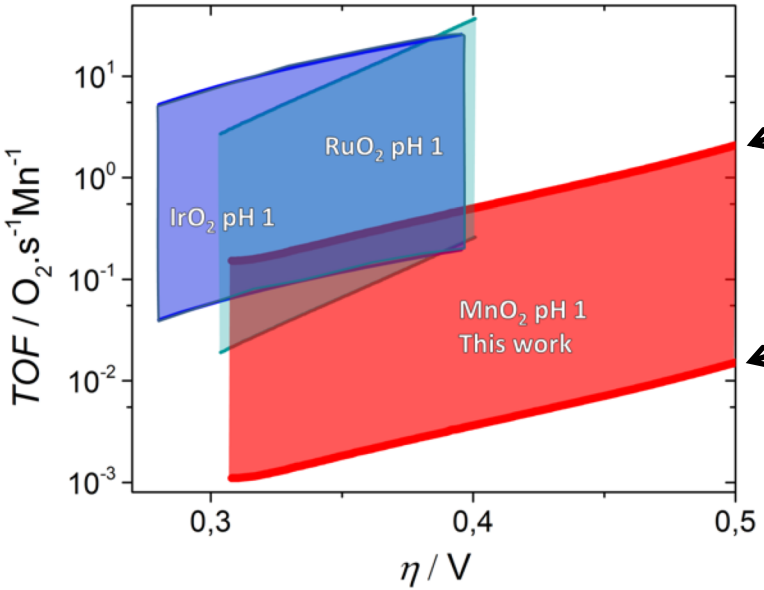
5 mV/s, N_2 saturated





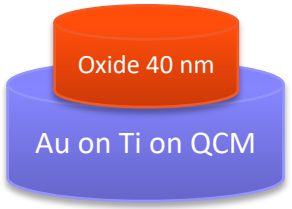
Turnover frequency (TOF) versus RuO_2 and IrO_2 in acid

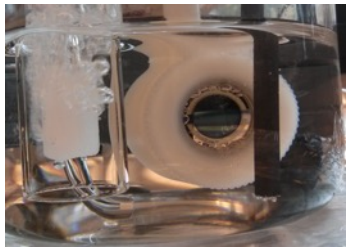
Frydendal, Paoli, Chorkendorff,Rossmeisl, Stephens ***Advanced Energy Materials*** 2015



TOF $_{max}$ = only surface sites are active

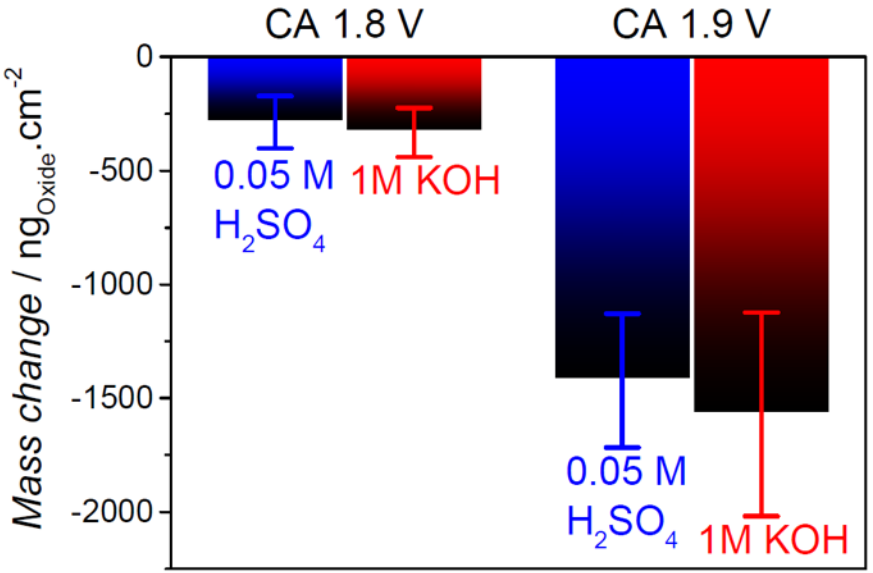
TOF $_{min}$ = all sites in bulk are active

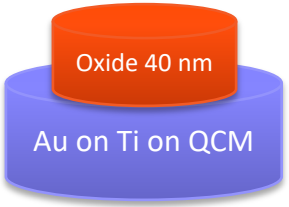


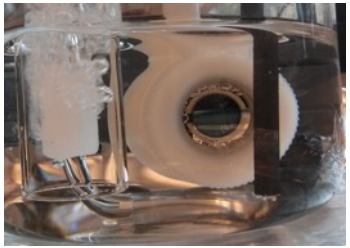


Stability of MnO_2 thin films (from quartz crystal microbalance)

Frydendal, Paoli, Chorkendorff,Rossmeisl, Stephens ***Advanced Energy Materials*** 2015







- Consistent with dissolution probed by ICP-MS

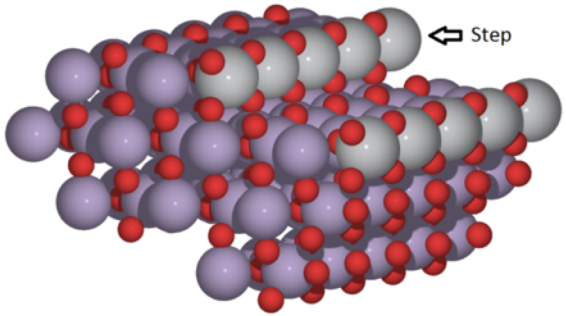
Frydendal, Paoli, Knudsen, Wickman, Malacrida, Stephens, Chorkendorff ***ChemElectroChem*** *2014*

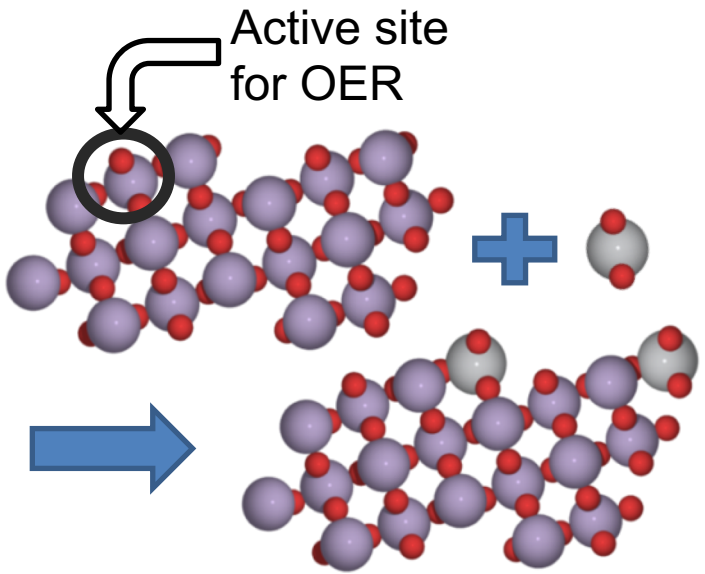
Frydendal, Paoli, Chorkendorff,Rossmeisl, Stephens ***Advanced Energy Materials*** 2015

How to Improve Stability of MnO_2, from DFT

Frydendal, Paoli, Chorkendorff,Rossmeisl, Stephens *Advanced Energy Materials* 2015

- Dissolution occurs at undercoordinated sites
  Jinnouchi, Toyoda, Hatanaka, Morimoto. **JPCC**, 2010
- Activity due to terraces
  Su, Gorlin, Man, Calle-Vallejo,. Nørskov, Jaramillo, Rossmeisl. **PCCP**. 2012
- **Step termination** → higher dissolution potential – without decreasing activity



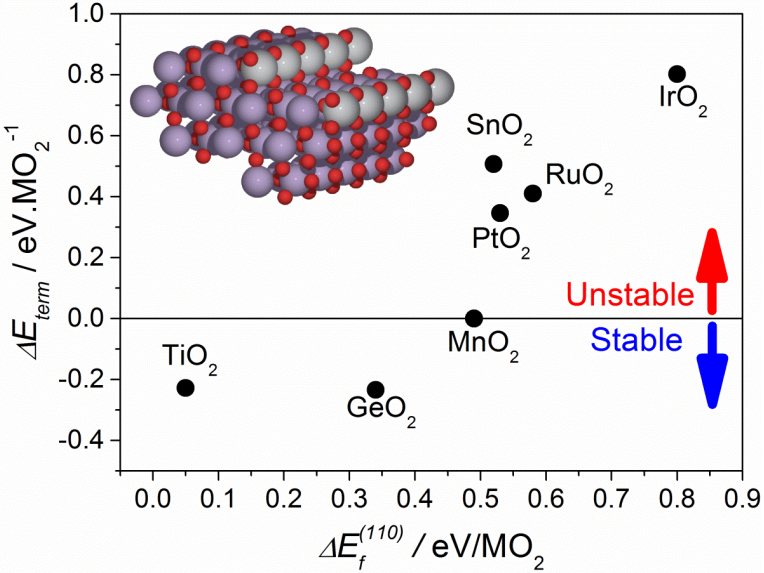


How to Improve Stability of MnO_2, from DFT

Frydendal, Paoli, Chorkendorff,Rossmeisl, Stephens *Advanced Energy Materials* 2015

- DFT calculations on a stepped MnO_2 surface
- TiO_2 sits preferably at steps
  - Not on flat surface or in bulk
- Termination with TiO_2 is feasible
- TiO_2 is stable in acid > 2 V

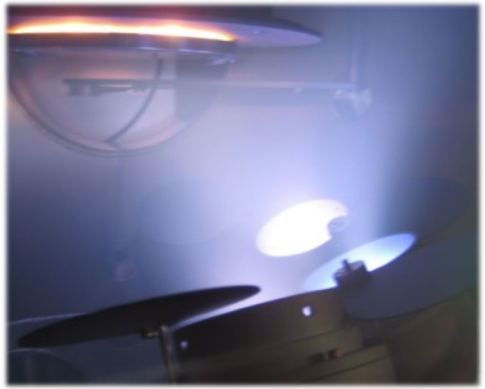
$$\Delta E_{term} = E_{term} - E_{MnO_2} - (E_{bulk,Guest} - E_{bulk,MnO_2})$$

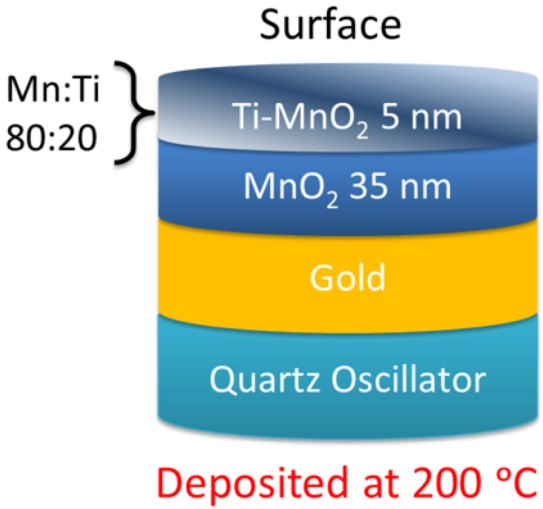


Experimental verification

Frydendal, Paoli, Chorkendorff, Rossmeisl, Stephens *Advanced Energy Materials* 2015

- Co-deposition of Mn and Ti

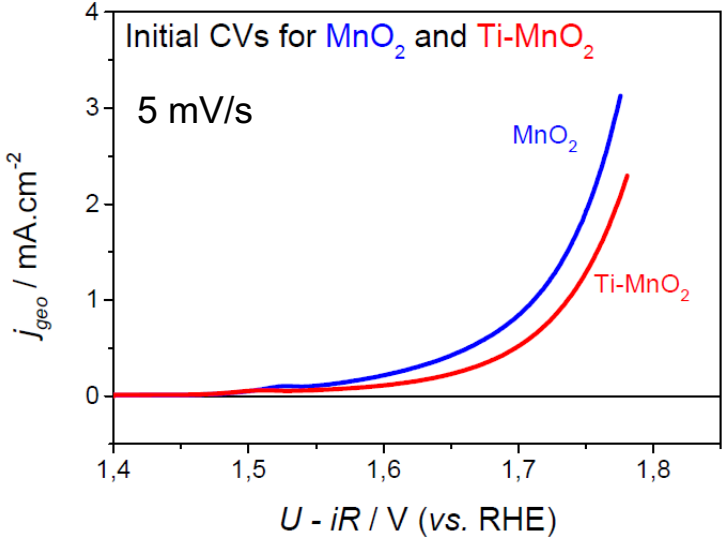


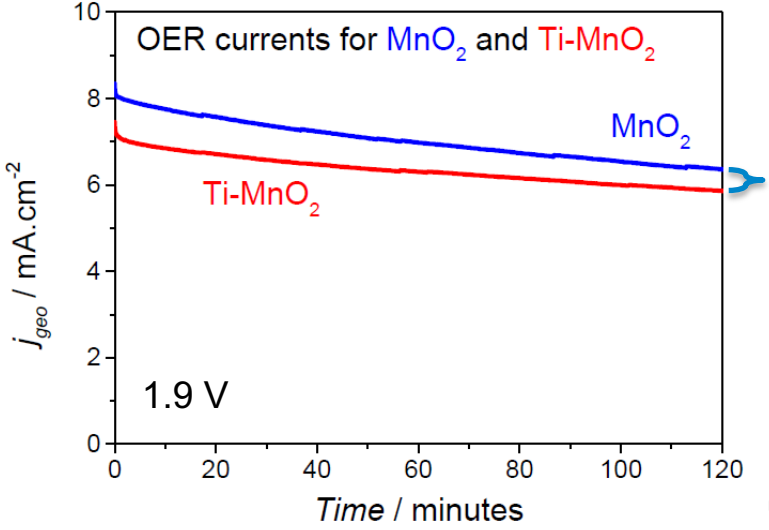


- Characterisation
  - XPS → 20 % Ti (metals basis)
  - XRD → Disordered oxide

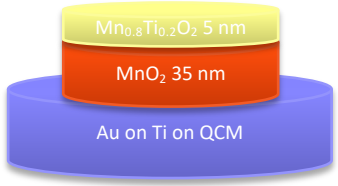
Experimental verification

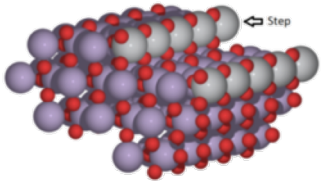
Frydendal, Paoli, Chorkendorff,Rossmeisl, Stephens *Advanced Energy Materials* 2015





Difference ~ 10 %

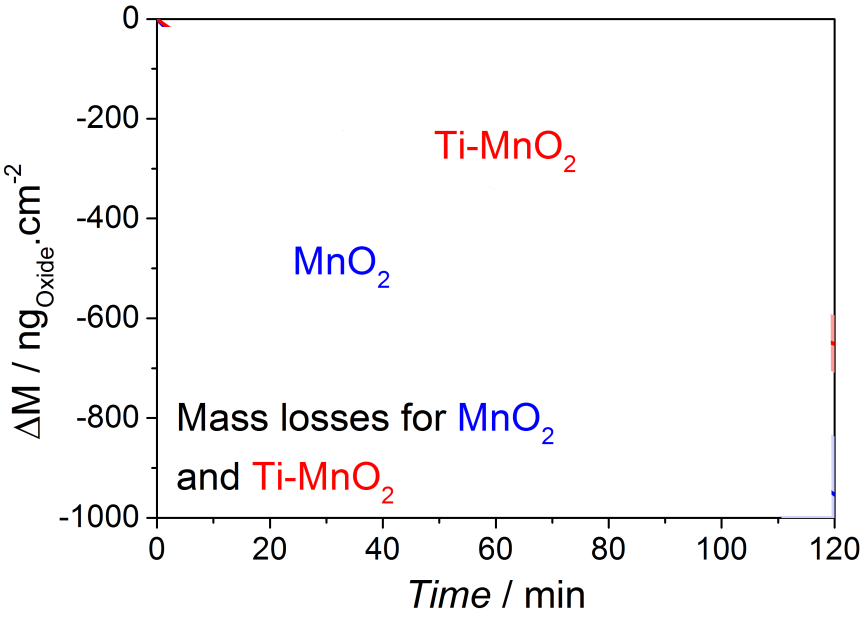




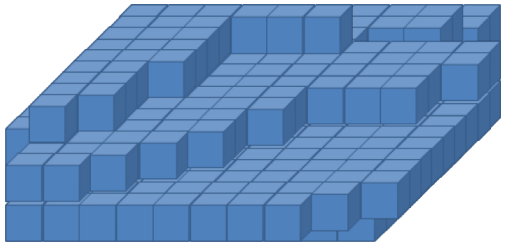
0.05 M H_2SO4

Monitoring mass losses at 1.9 V

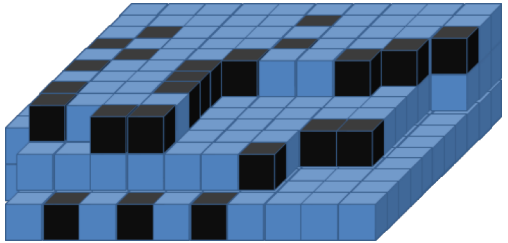
Frydendal, Paoli, Chorkendorff,Rossmeisl, Stephens *Advanced Energy Materials* 2015



MnO$_2$

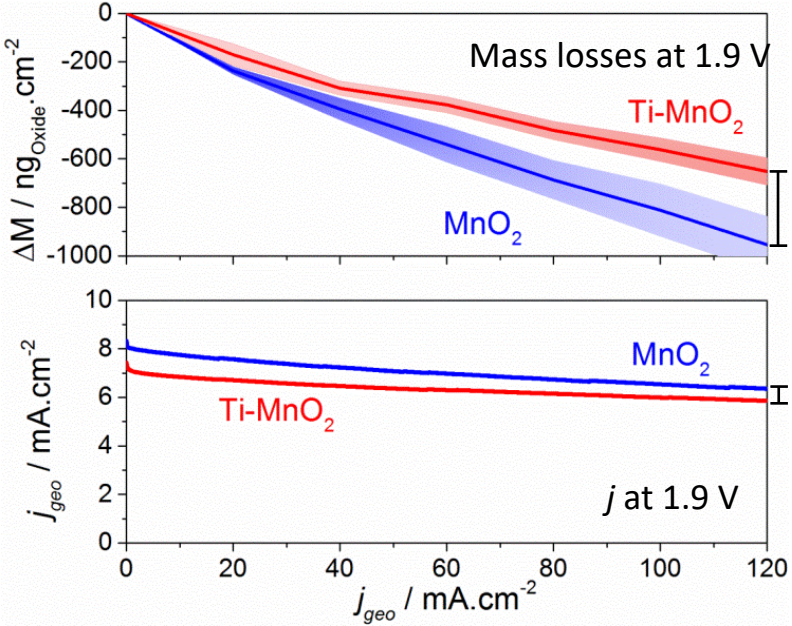


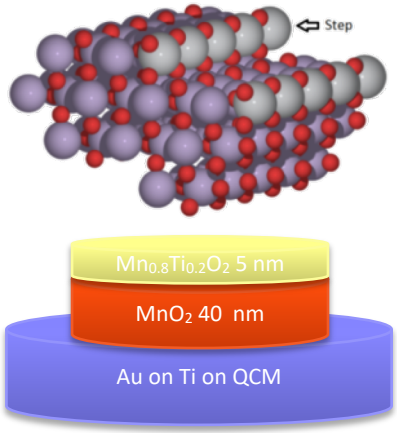
Ti-MnO$_2$

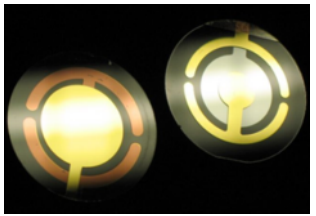


Activity and stability

Frydendal, Paoli, Chorkendorff,Rossmeisl, Stephens *Advanced Energy Materials* 2015

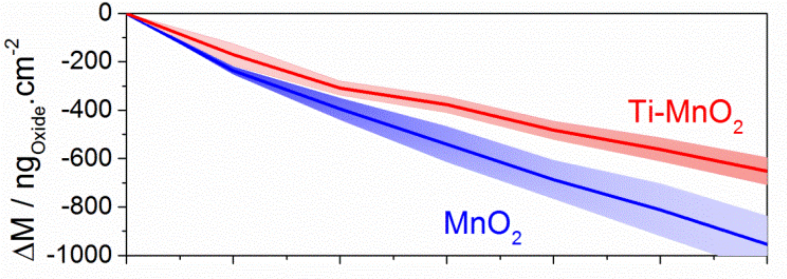


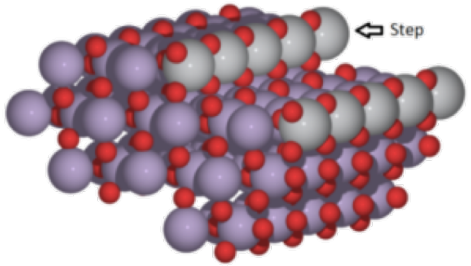




Conclusions on oxygen evolution

- MnO_x-Ti:
  - Prediction from theory that Ti at steps should stabilise MnO_2 against corrosion
  - Modest stability confirmed on Ti-MnO_2 thin film





Imperial College London

Conclusions

Ifan E. L. Stephens

Collaborating with theorists

1. Be open: experiment might be wrong
2. Build trust
3. Meet often and for extended time periods
4. **Strength of collaboration α log 1/(distance)**
   same office>same corridor>same building>same country>same continent
5. Try to distinguish certainty from uncertainty in calculations, e.g.
   a) Individual data points are less important than trend
   b) At constant surface orientation, trends should be more easy to calculate than between different orientations (e.g. stepped Pt in alkaline media)
   c) Effects of solvation on binding of intermediates seems to particularly challenging to account for
   d) Charge transfer barriers are particularly challenging to model (Hannes Jonsson's talk)

Collaborating with theorists ...continued

6. Close comparison between experiment and theory can answer or open questions:
   a) *Provide answers to old questions:* Steps improve oxygen reduction in activity in acid by decreasing OH binding on adjacent terraces
   b) *Open new questions:* Why is stepped Pt so inactive in base? Why is Au so inactive for oxygen reduction in acid?
7. Structure formed under reaction conditions is highly challenging to predict *a priori*
   a) Theoretical screening might lead to high activity for the wrong reasons (e.g. Pt_3Y)
8. Use well-defined surfaces
   a) *Capitalise on systems which have already been the subject of detailed surface science investigations:* Cu/Pt(111), Hg/Pt
   b) Perform your own detailed surface science investigations: Y/Pt(111) or Gd/Pt(111)

Current and former collaborators at the Technical University of Denmark (DTU)

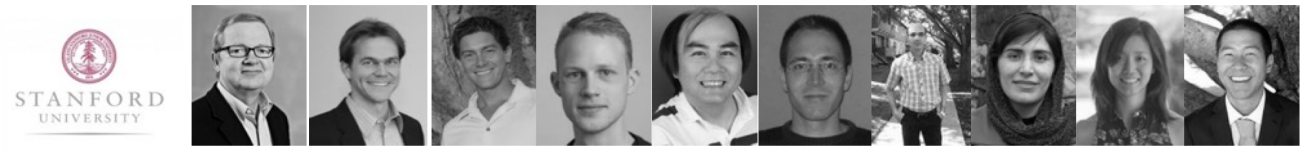
Electrocatalysis Group

Other researchers

Faculty members

DTU

Selected external collaborators



Acknowledgements