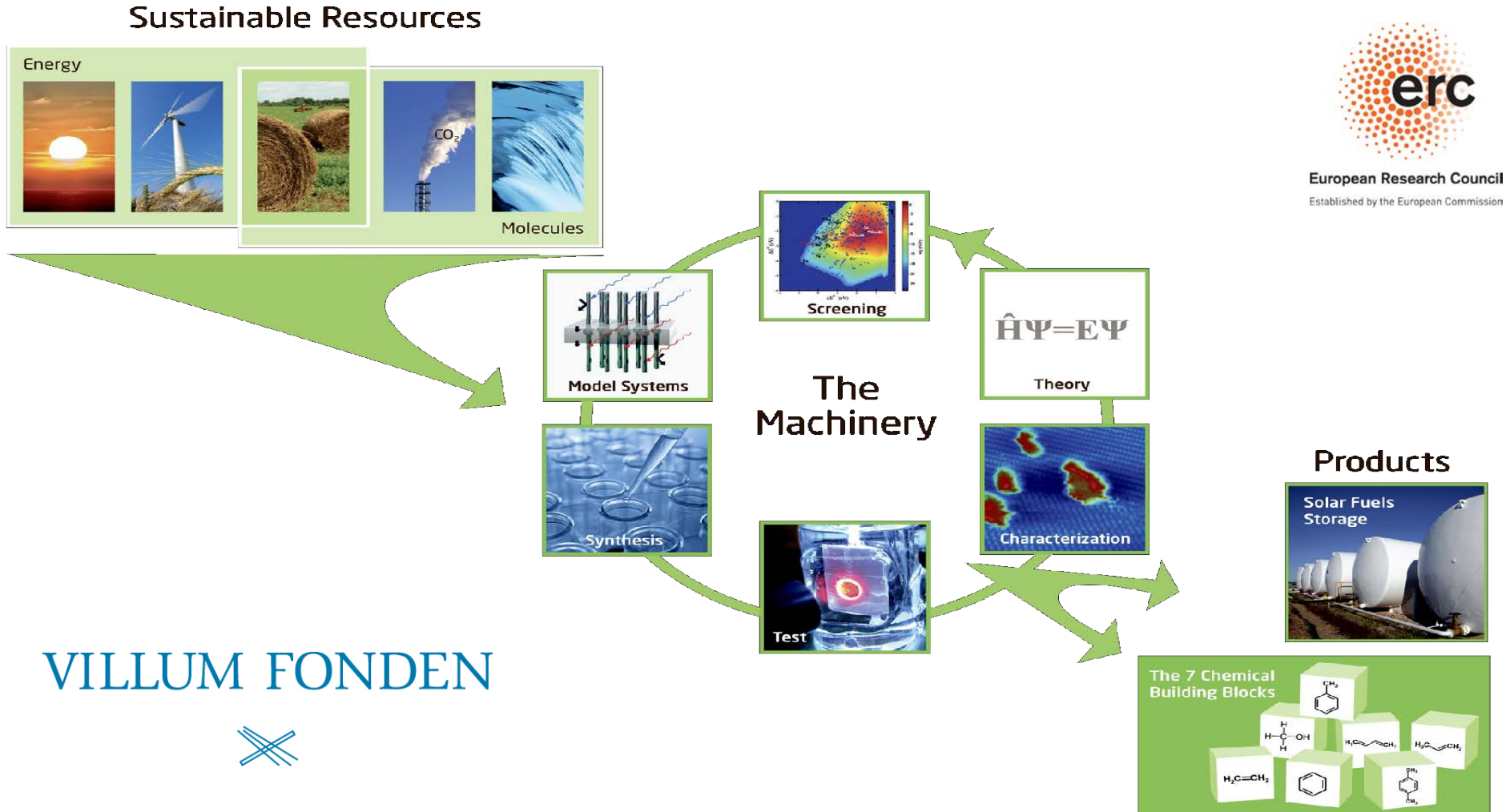
Netherlands conference on Electrochemical Conversion & Materials (ECCM)

Ib Chorkendorff

Surface Physics and Catalysis

Department of Physics, DTU



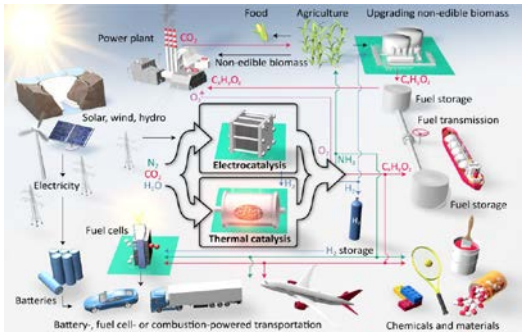
European Research Council

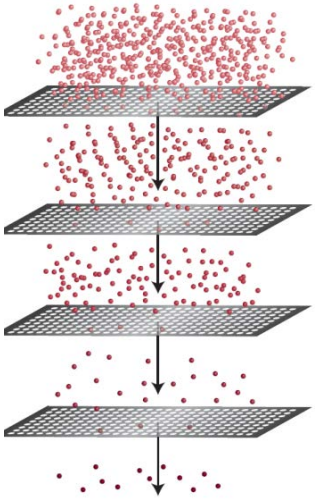
Established by the European Commission

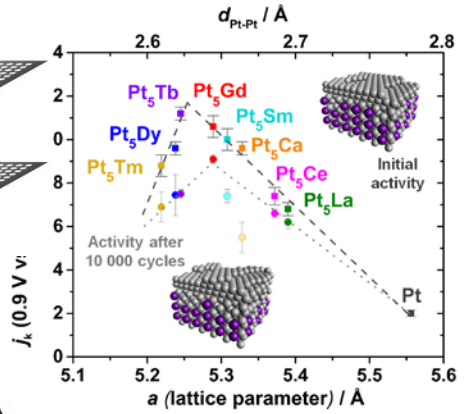
VILLUM FONDEN

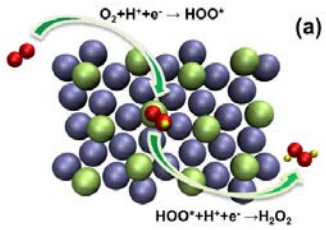
Outline

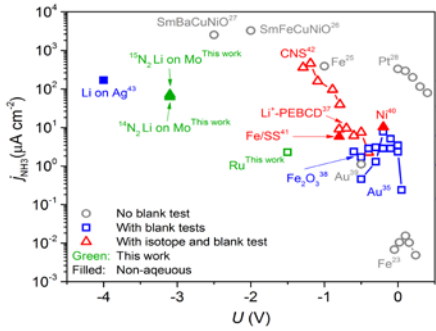
- **Motivation**
- **Approach**
- **Oxygen Reduction (ORR)**
- **Hydrogenperoxide production**
- **Electrochem hydrogenation of N_2 to ammonia**



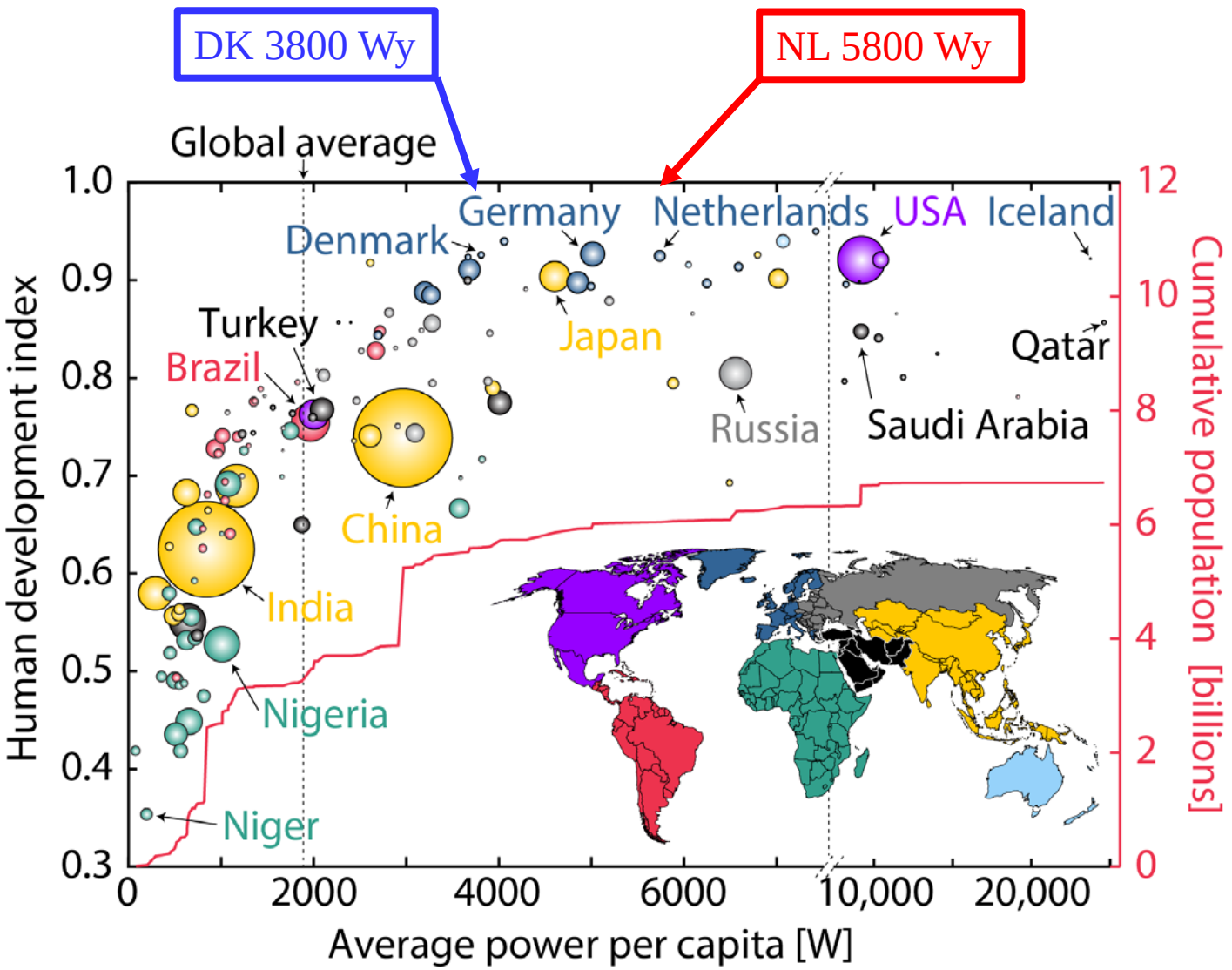








Human Development and Energy Usage

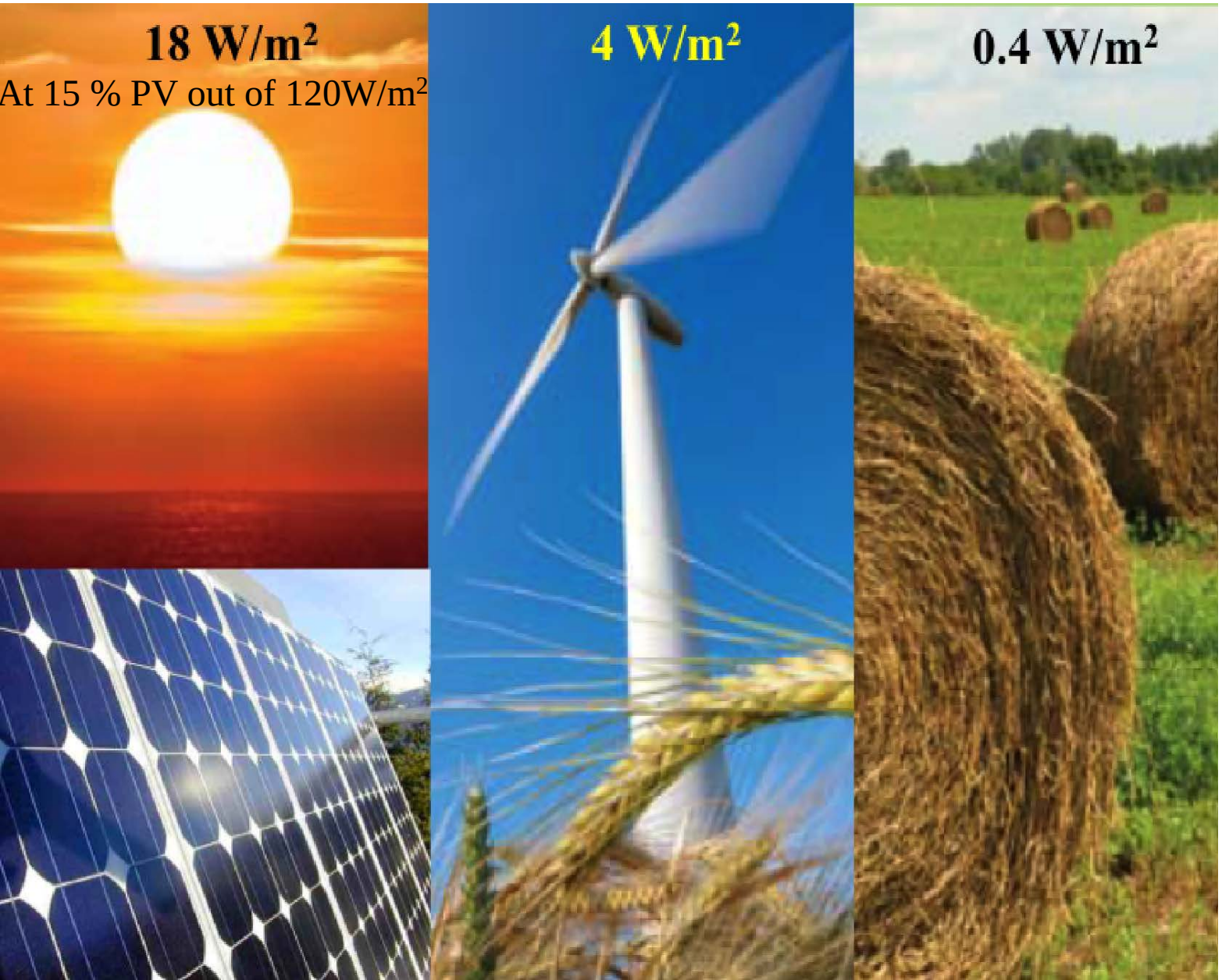


Energy: 80 % comes from fossil fuels
Expected to increase from 18 TWy to 30 TWy by 2050

In Denmark we use 3800 Wy per person or roughly 40 times our basic metabolism.
We need to produce some 0.6Wy/m^2 per capita.
(NL 2,4Wy/m^2)

DK plan to be fossil free in 2050 (2016: DK 31% NL 6%)

The Good News- we have plenty of it!



Sustainable Energy Denmark

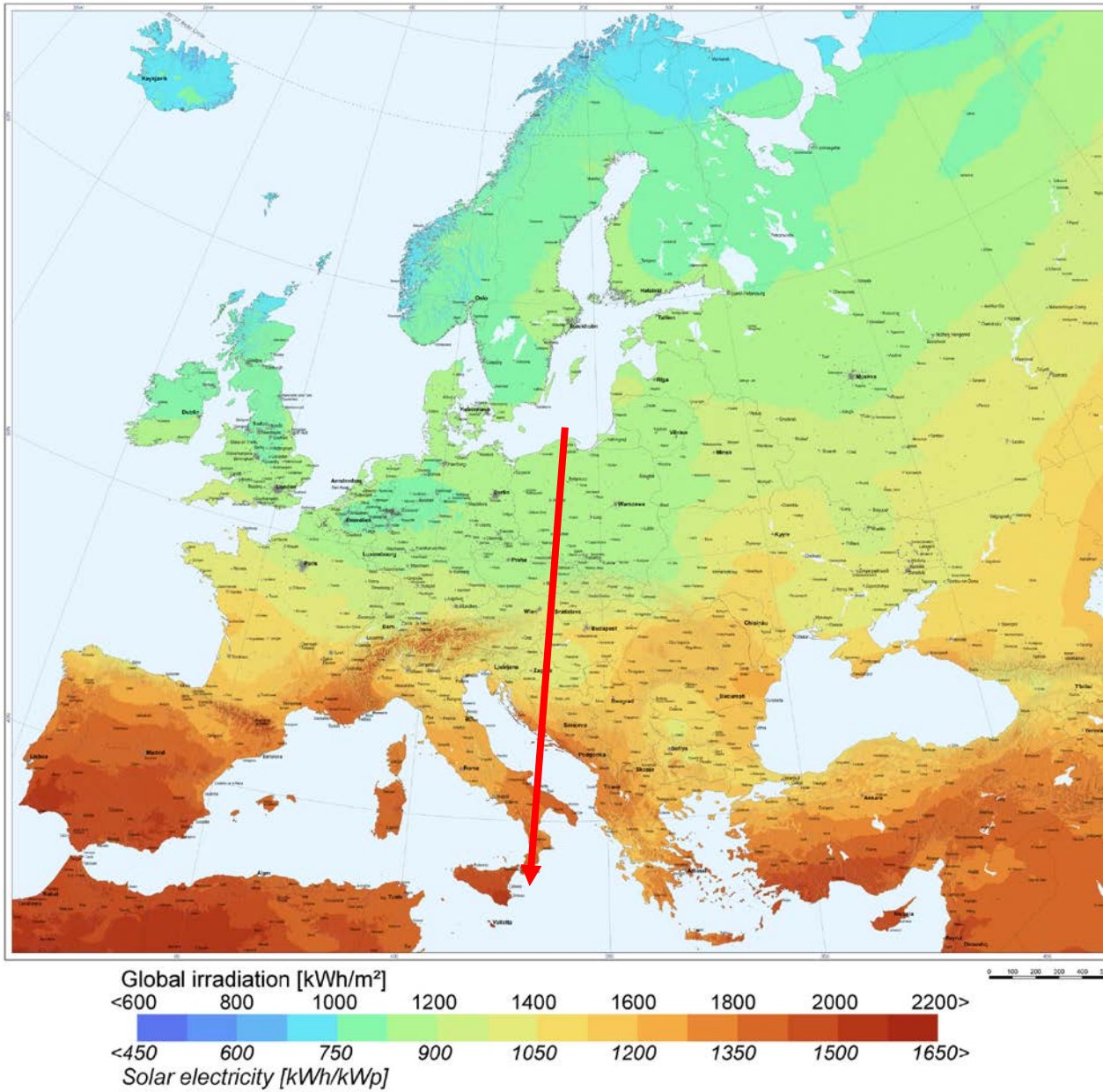
In Denmark we use 0.6Wy/m² per capita

In NL 2,4Wy/m²

The Solar Resources Europe

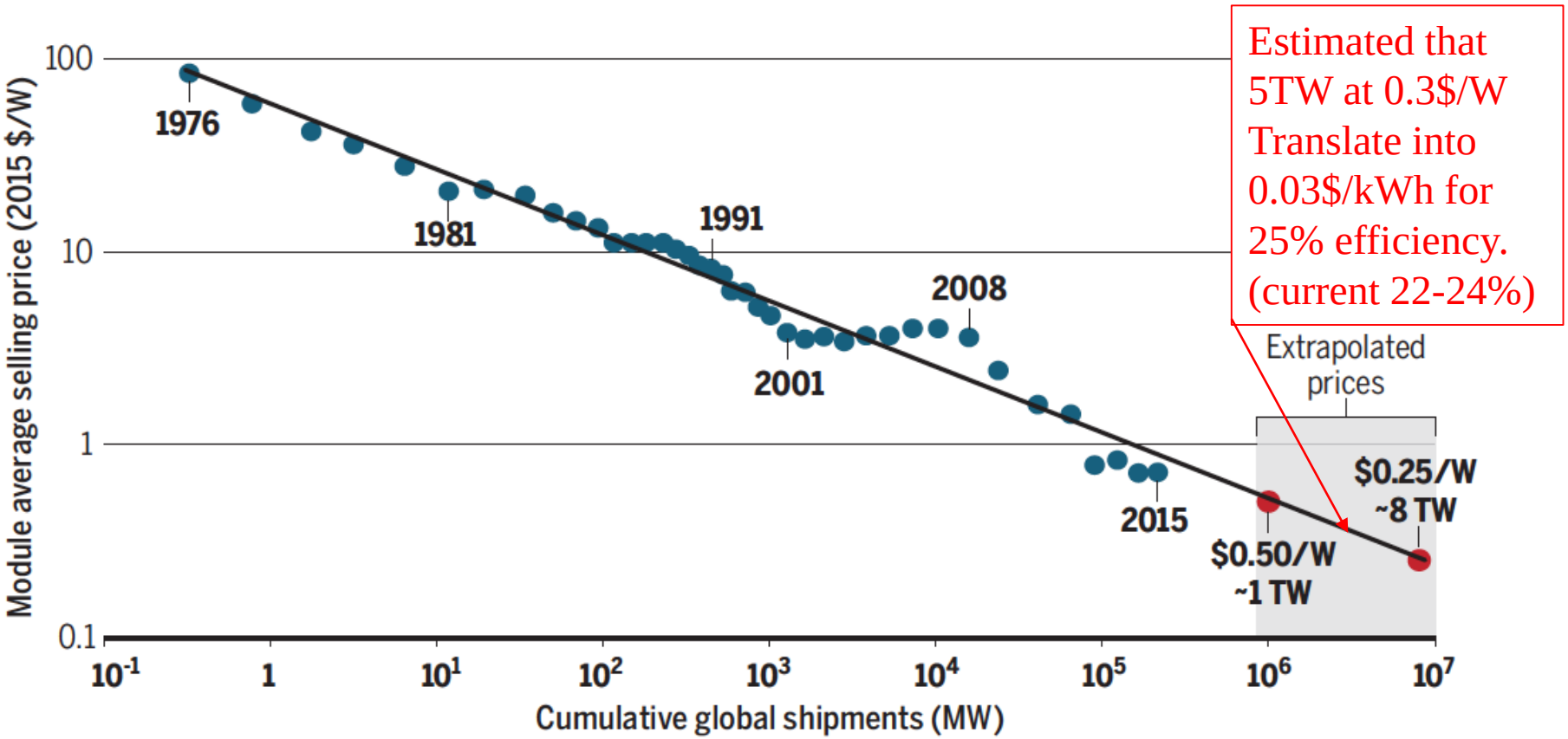
Horizontal DK
Ca. 1050 kWh/m^2 year
Or 120Wy/m^2
averaged over a year

Globally use 18 TWy
Sun in: 120000 TWy:
A factor of 1:6700



http://re.jrc.ec.europa.eu/pvgis/apps4/pvest.php#

PV learning curve



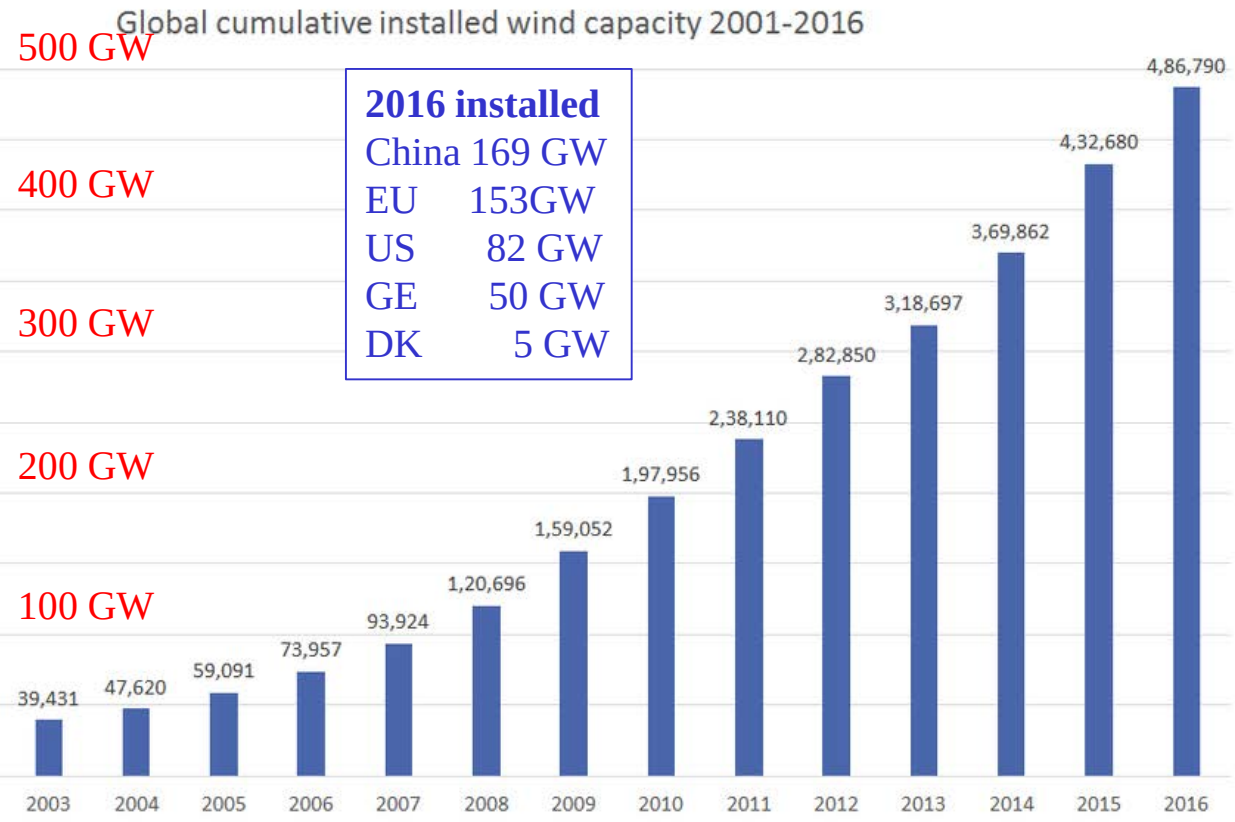
Estimated that 5TW at 0.3$/W Translate into 0.03$/kWh for 25% efficiency. (current 22-24%)

N. M. Haegel et al. Science 356 (2017) 6334

SurfCat

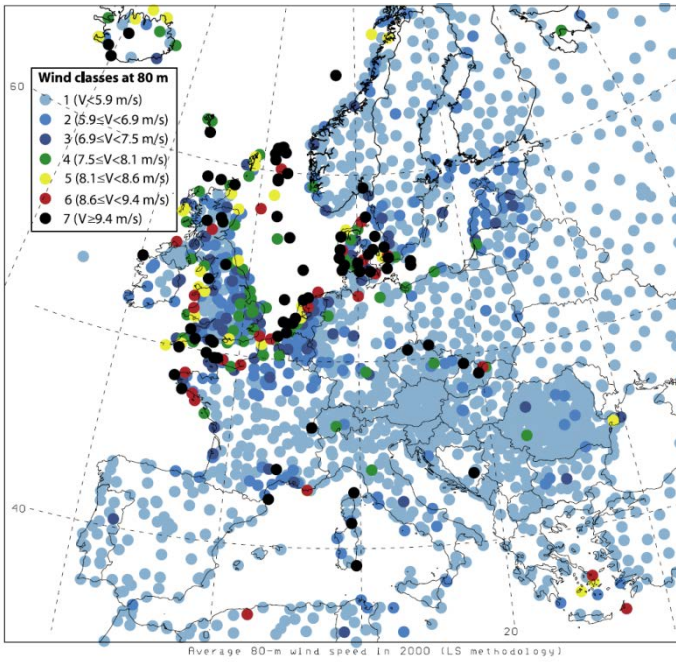
Global Wind Capacity

DTU



Estimated Wind potential
70 TW (land only)!

J. GEOPHYSICAL RESEARCH, 110, D12110, doi:10.1029/2004JD005462, 2005
M. Jacobson

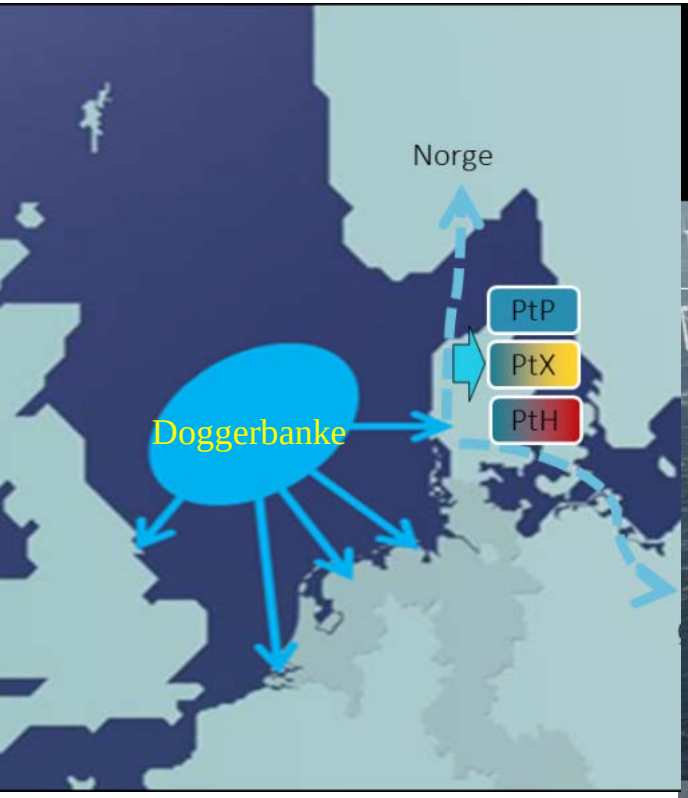


Wind learning curve

Kriegers Flak (600 MW offshore wind farm)
The lowest bid: 6.2 US cents /kWh
http://efkm.dk

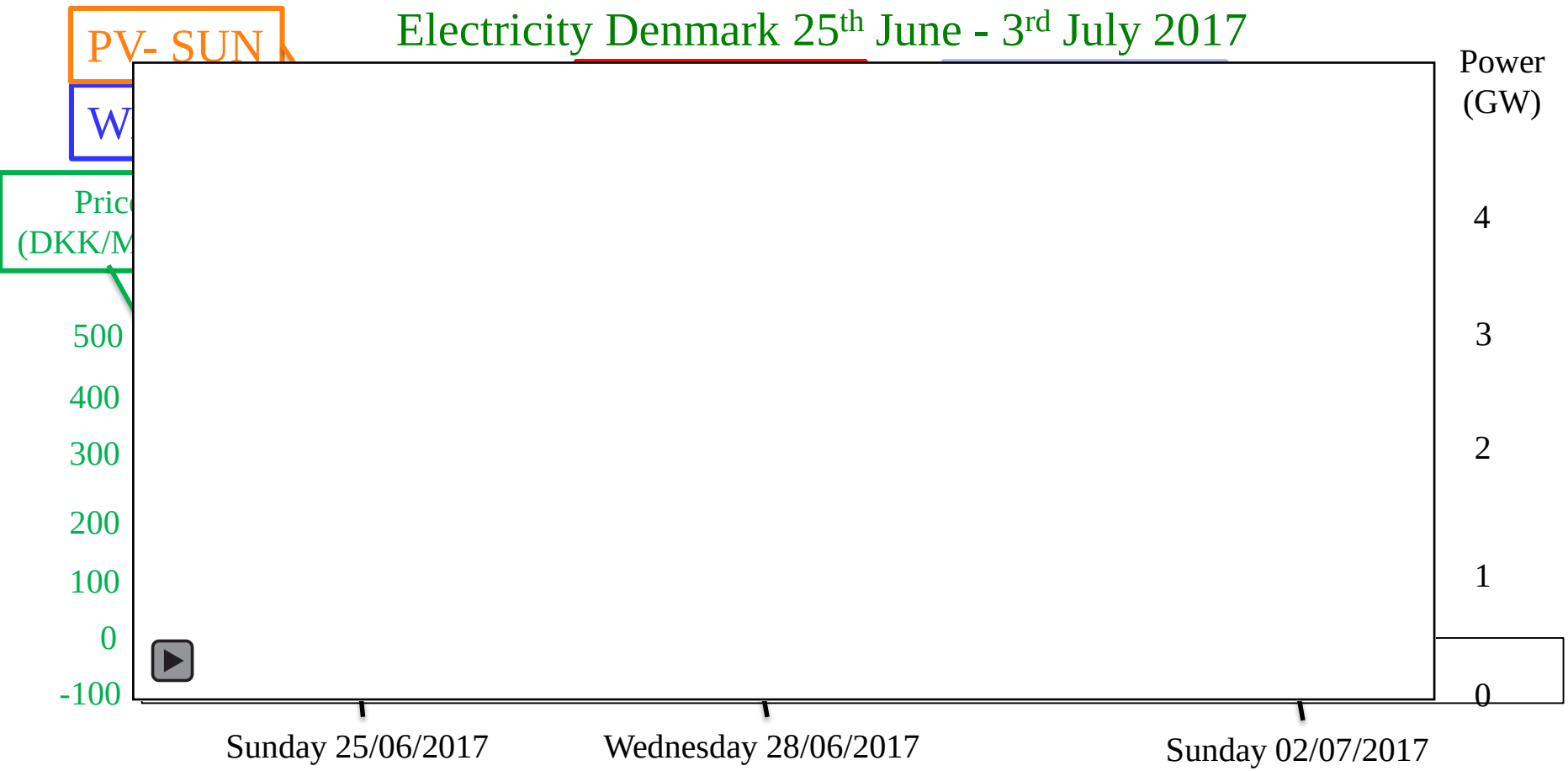
Crude oil price March 2018:
~ 60 USD per barrel = ~ 3.5 US cents per kWh

Nobody want wind turbines at land so…



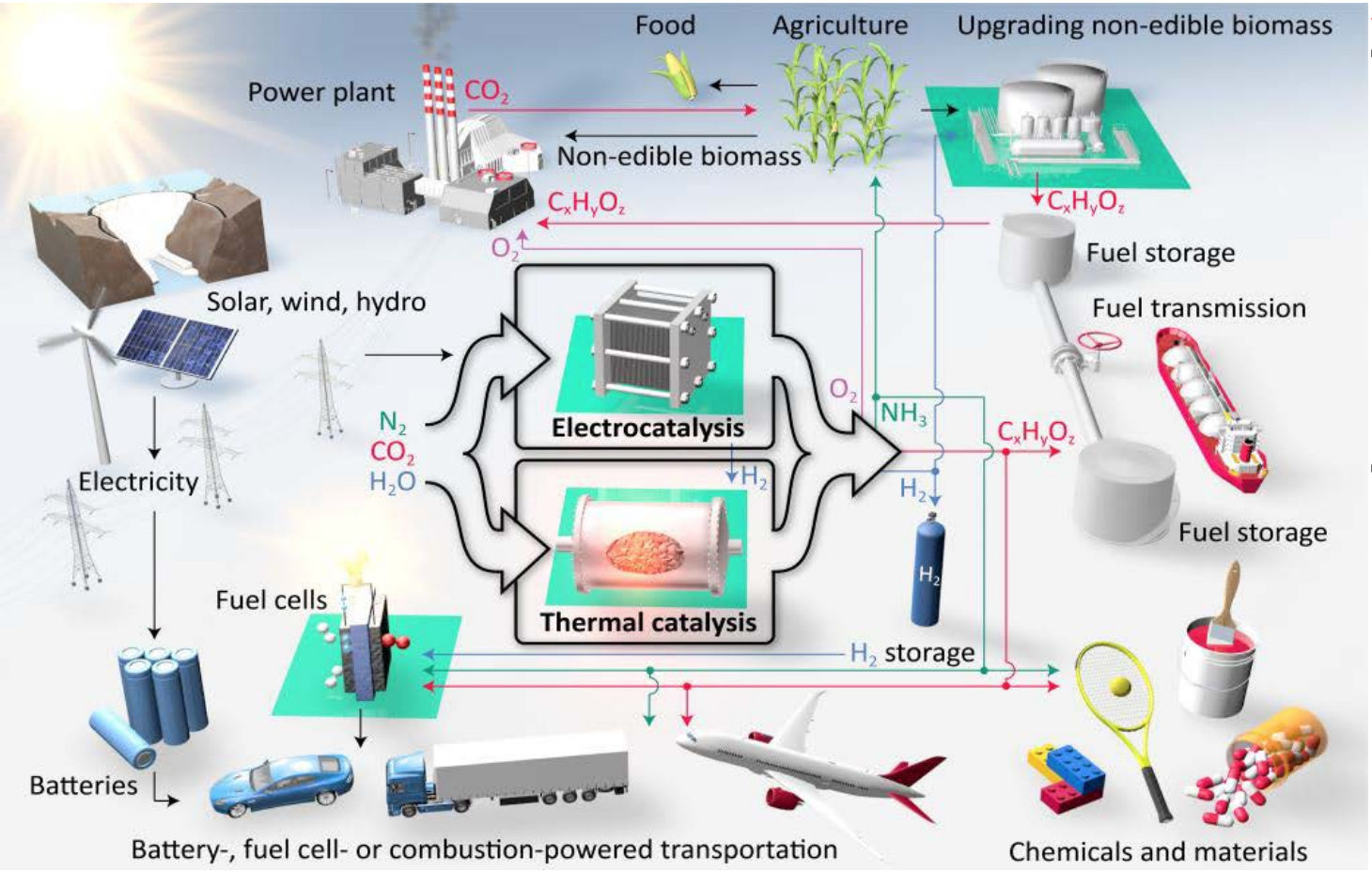
Say 200*200Km^2 means 4*10^{4}km or 4*10^{10}m^2 or 160 GW

Sustainable energy is inherently intermittent!



EU	Total	Power	
EU	2200	320	
DK	23	3,6	
NL	105	12	All GWy

Power to X



Europe uses:

Total 2,2 TWy

~5% for Chemicals

~5% for Steel prod.

~3% for Aviation fuel

~?% for seasonal aveageing

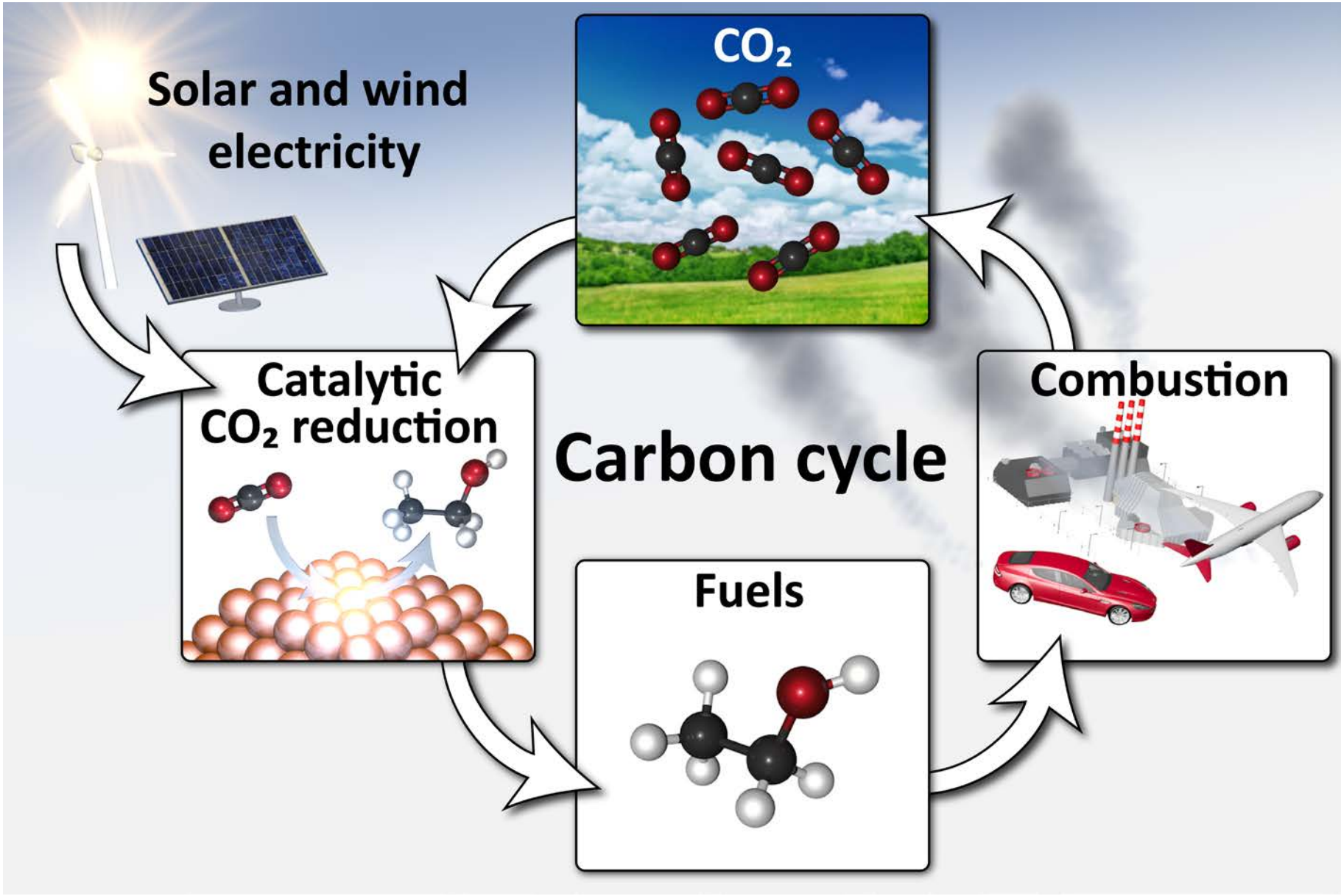
Trucks, Ships?

Where shall the CO_2 come from?

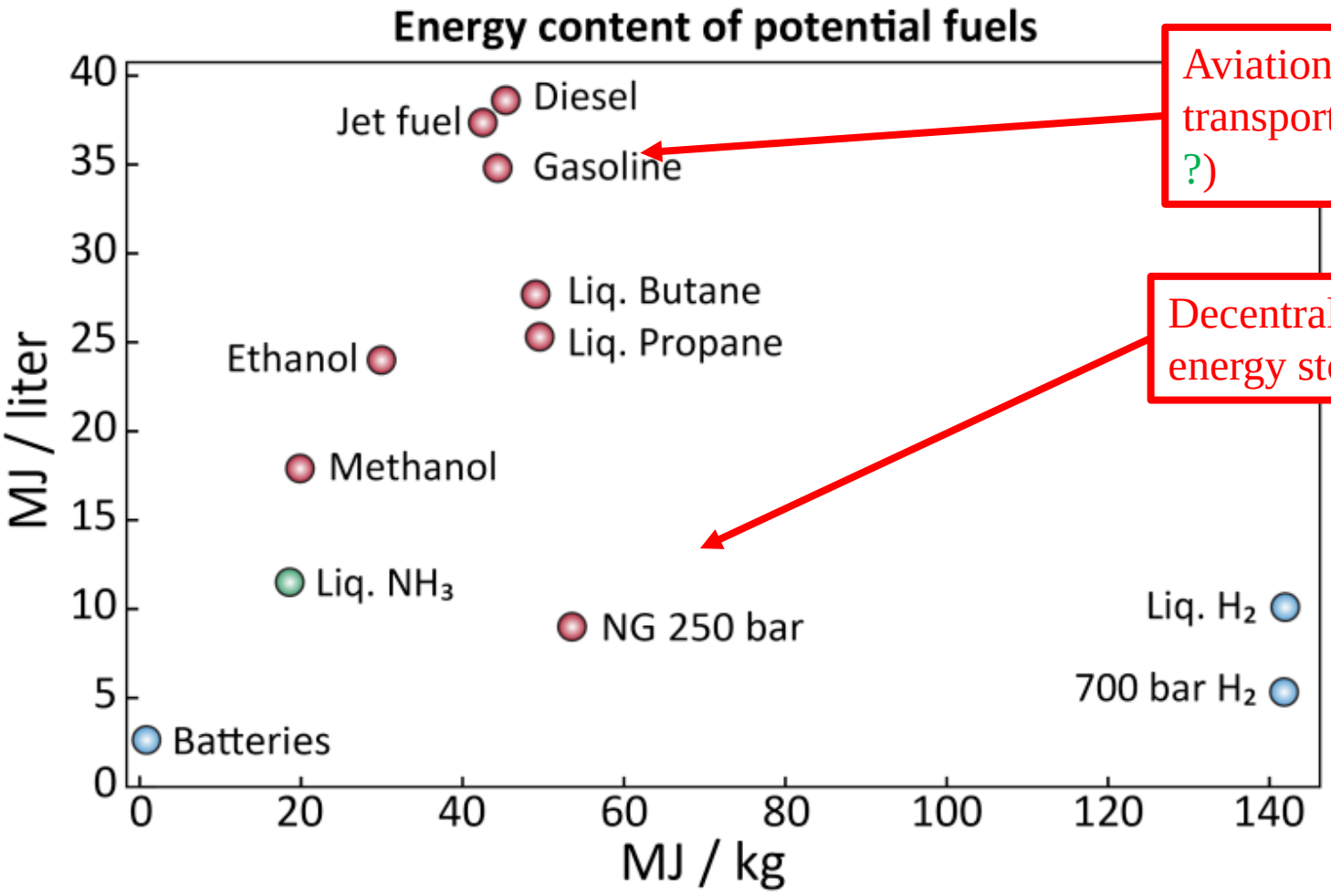
Concrete production

Biomass using O_2 from Electrolysis.

CO_2 (N_2) reduction



Fuel Densities mainly important for Transport

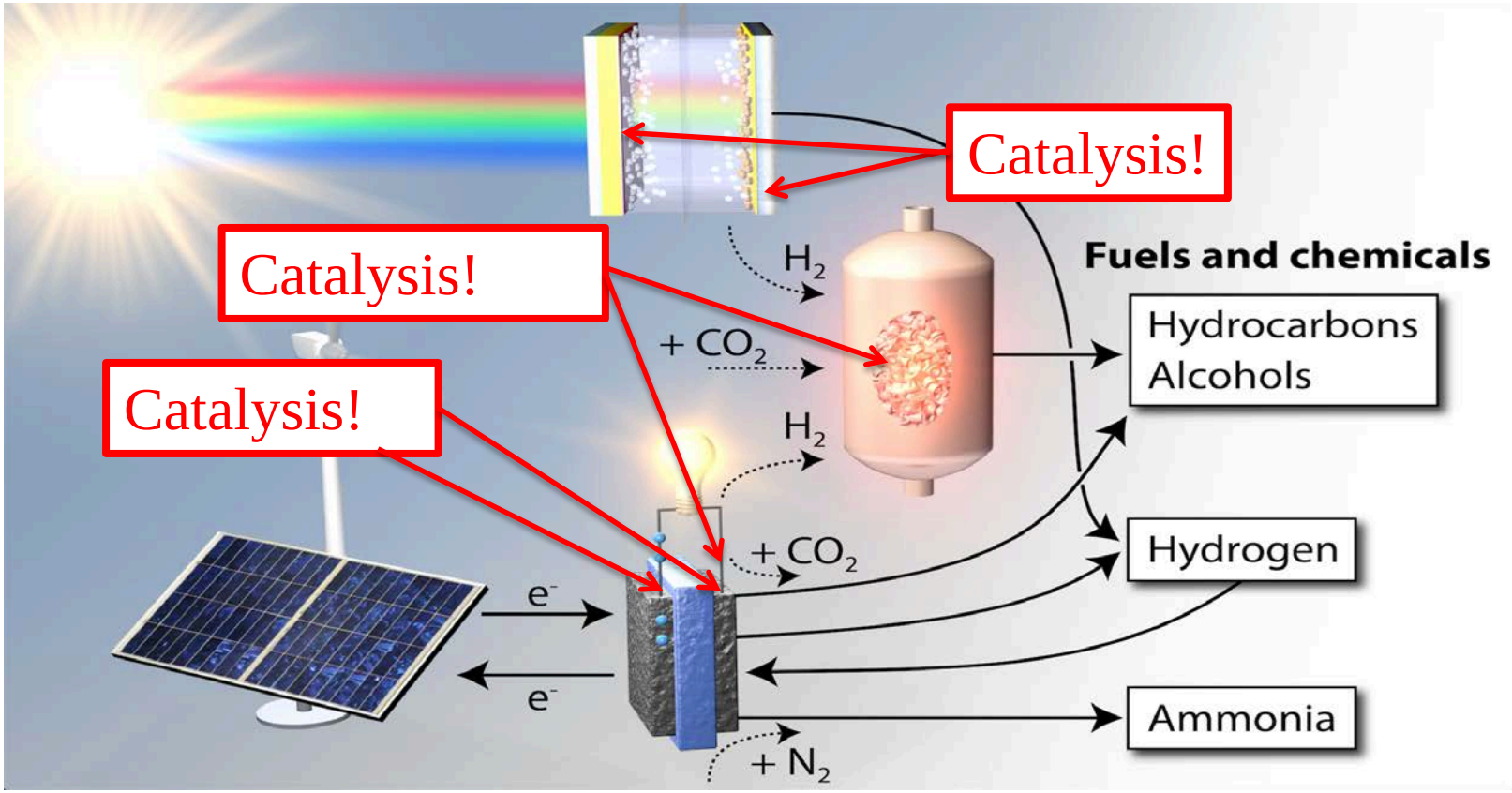


Aviation and long transport (trucks ? & ships ?)

Decentralized long term energy storage ~ months

Notice: If we change all 253 mio. Cars in Europe to the new Tesla S with 100 kWh batteries and they all are fully charged we can only run Europe for some 12 hours.
USA 235 mio. cars gives 10 hours

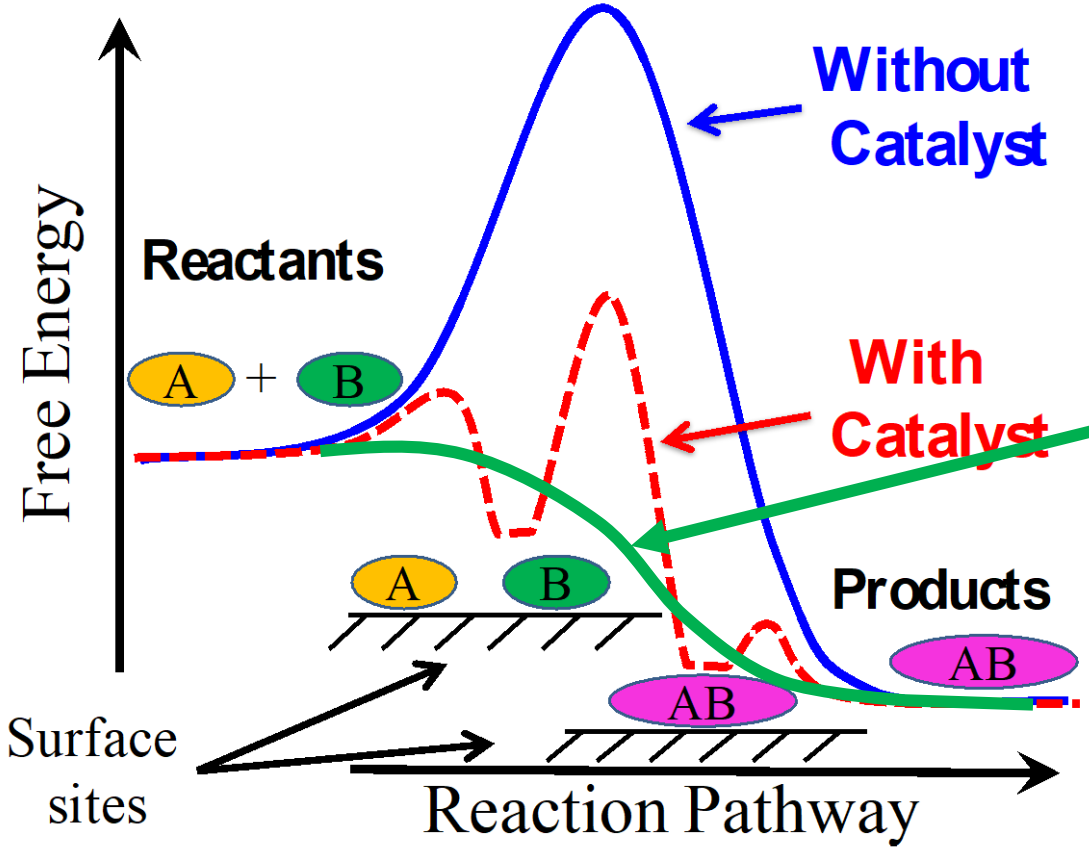
Energy storage and sustainable chemical production



The Challenge: We need new catalysts with:

- High efficiency
- High selectivity
- High stability
- Abundant elements, preferably

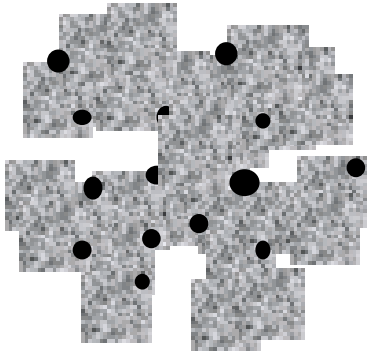
What is a catalyst doing?

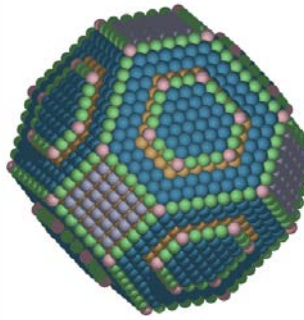


The surface is essential since all happens there. So how do we get lots of surface??

The ideal case

~100m^2/g





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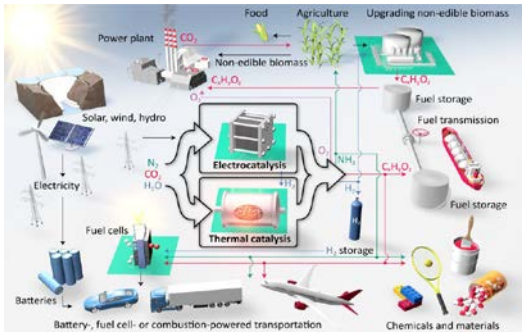
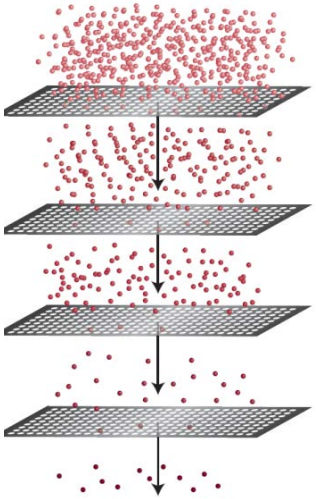
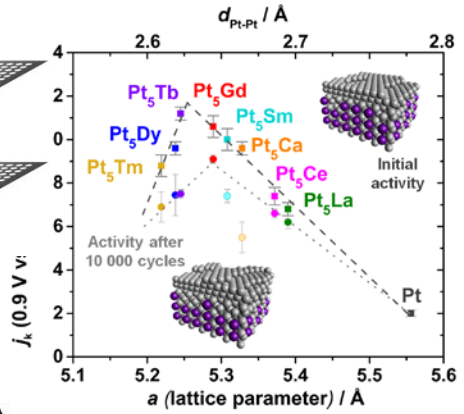
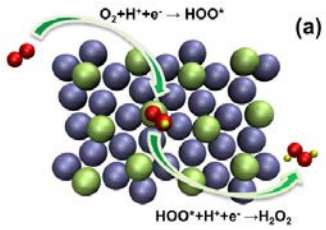
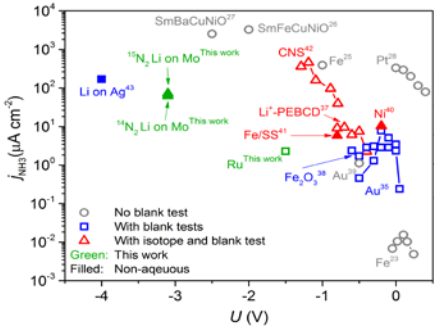






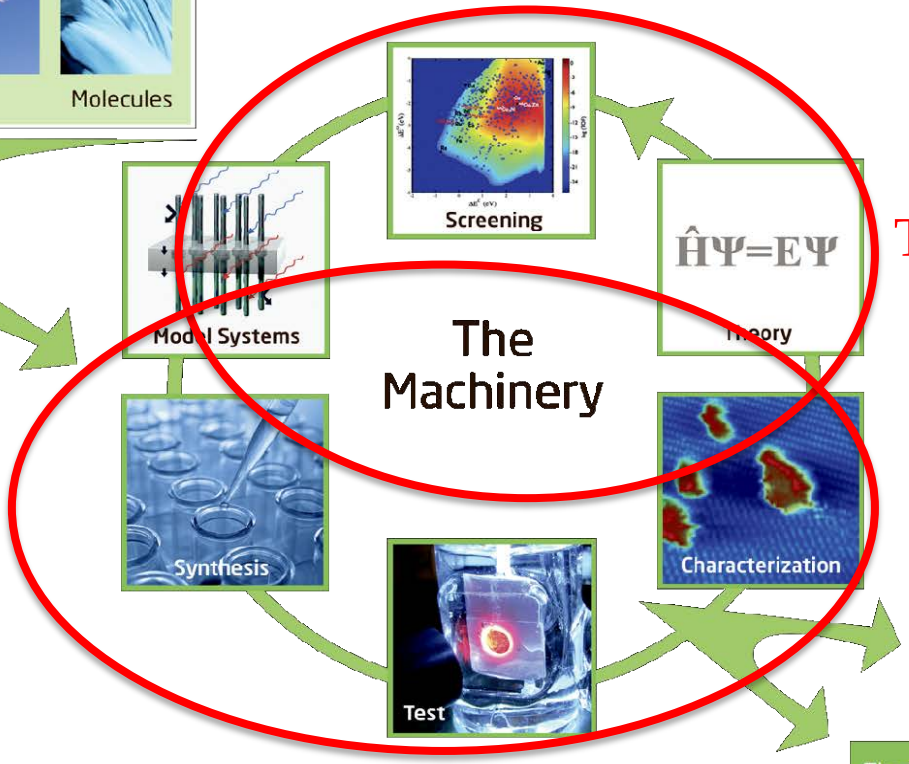




The machinery (the unifying principle)

Sustainable Resources

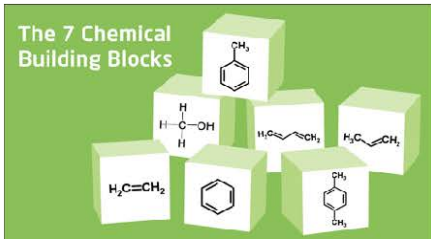
Basic research approach to solving important technological and societal problems



Theory

Experiment

Products



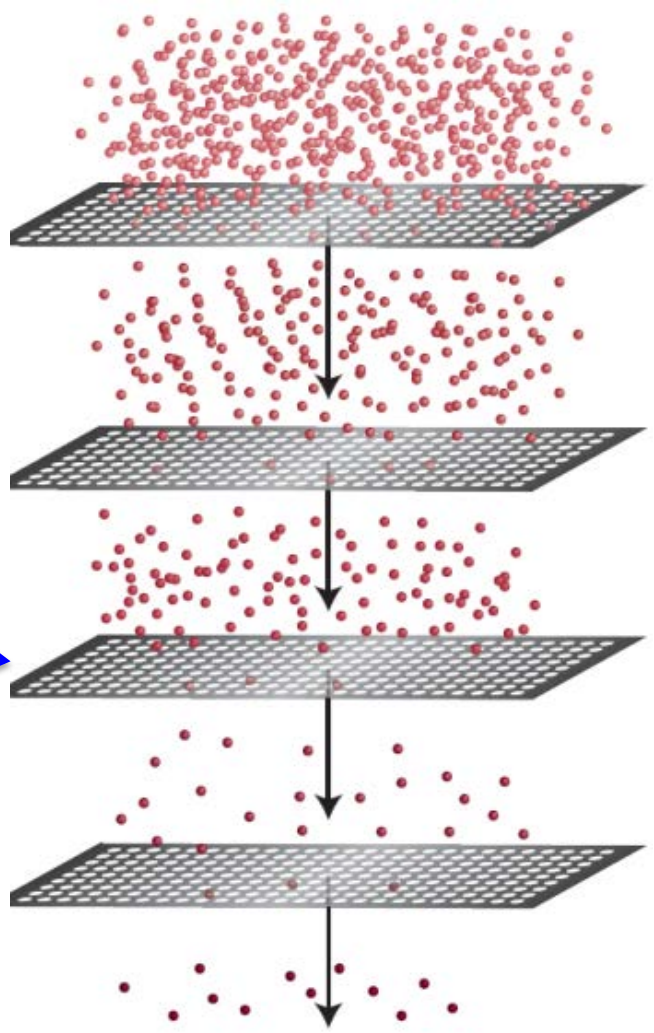
VILLUM FONDEN

Computational screening of catalyst candidates

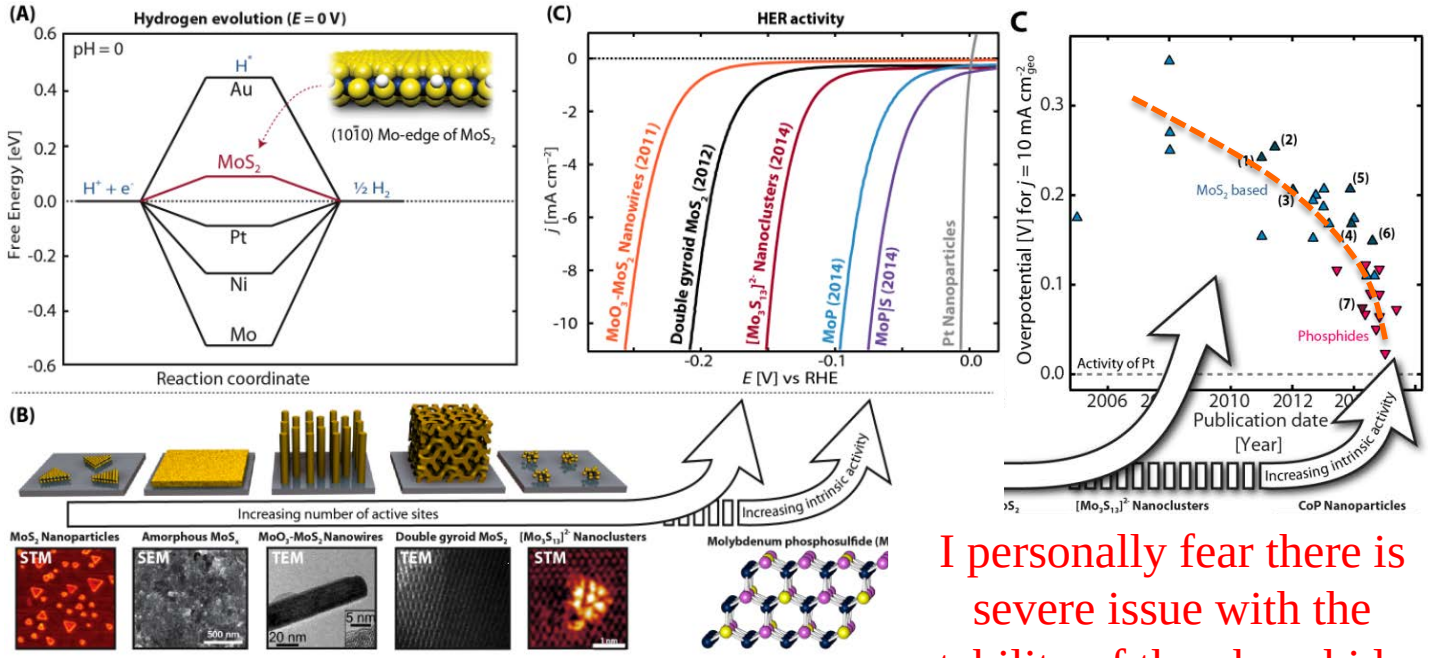
Electronic structure theory now has **predictive power** in many cases

Establish a reaction pathways and
identify **descriptors** of catalytic activity

- Check catalytic activity
- Check for stability under reaction conditions
- Check for selectivity
- Establish lead candidates for experimental investigation (Abundance)



Tremendous Development in HER



I personally fear there is severe issue with the stability of the phosphides

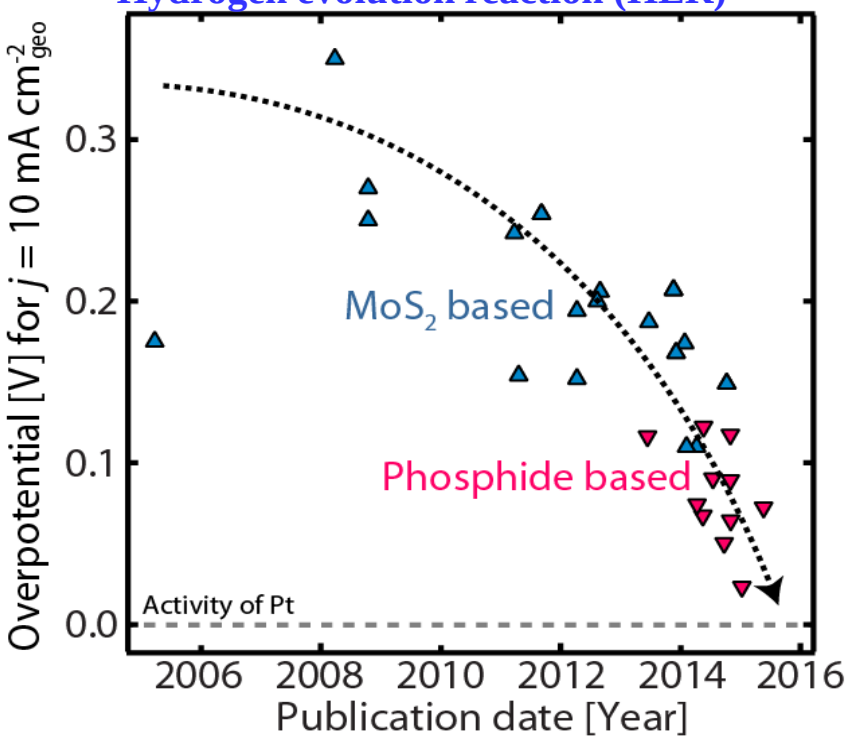
- Identifying and optimizing active sites (incl. selectivity and stability)
- Theoretical screening identifying most potential candidates
- Optimizing number of active sites by nanotechnology

Z. W She, J. Kibsgaard, C. F. Dickens, I. Chorkendorff, J. K. Nørskov, T. F. Jaramillo, Science (2017) 355

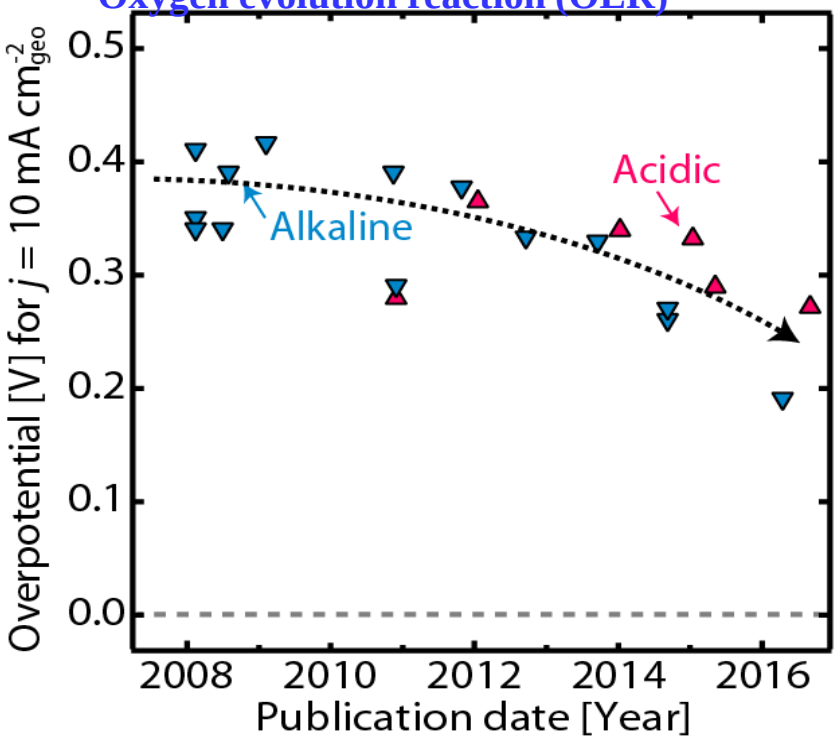
The other side: Oxygen evolution

$$2\,H_2O \rightarrow 2H_2 + O_2$$

Hydrogen evolution reaction (HER)

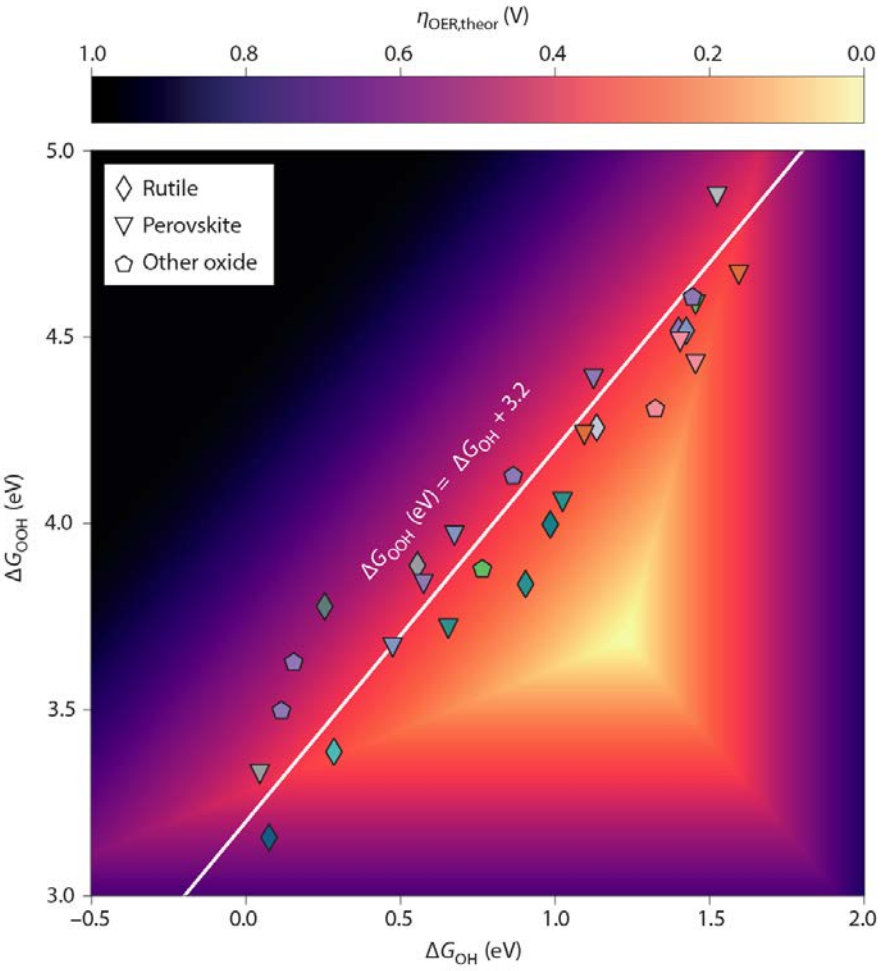


Oxygen evolution reaction (OER)

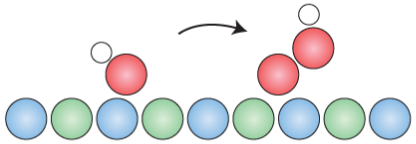


Z. W. Seh, J. Kibsgaard, C. F. Dickens, I. Chorkendorff, J. K. Nørskov, T. F. Jaramillo, *Science.* **2017**, *355* (6321).

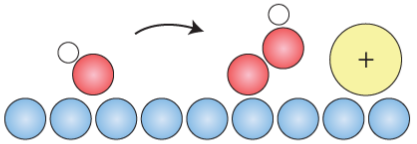
This insight leads the route forward



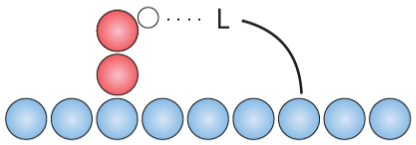
Bifunctionality



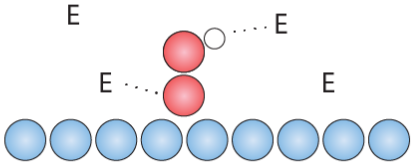
Promoters



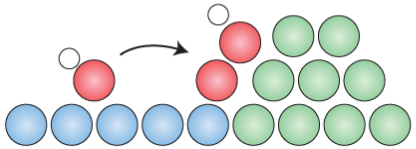
Tethering/functionalization



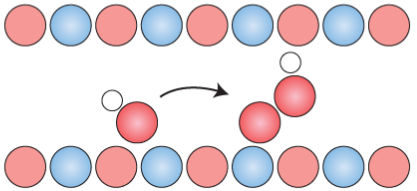
Electrolyte engineering



Interfacial sites



Confinement



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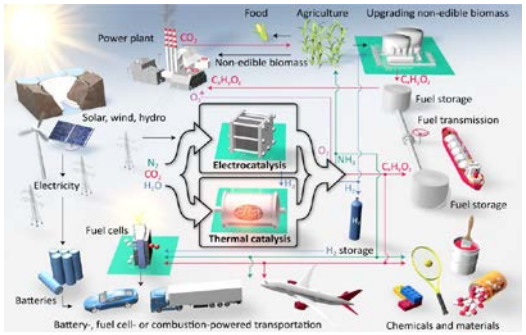
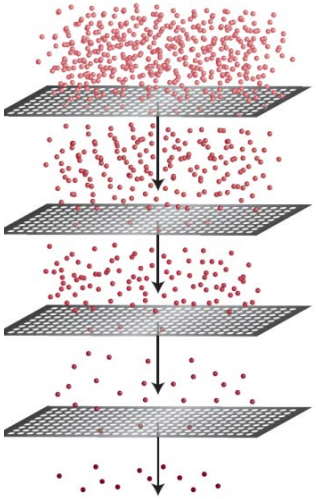
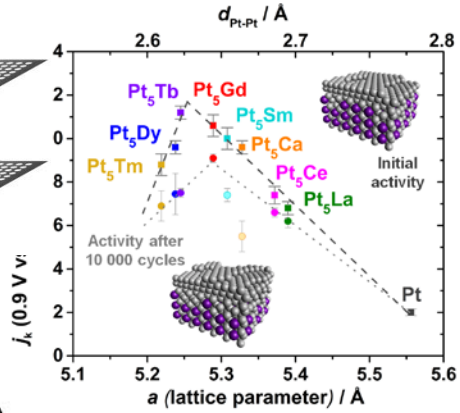
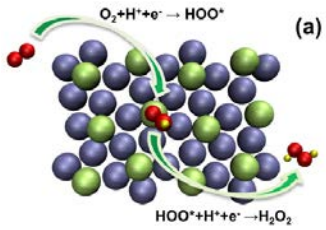
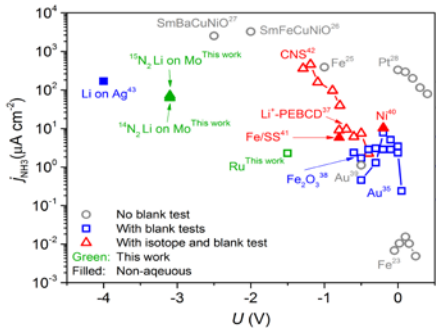




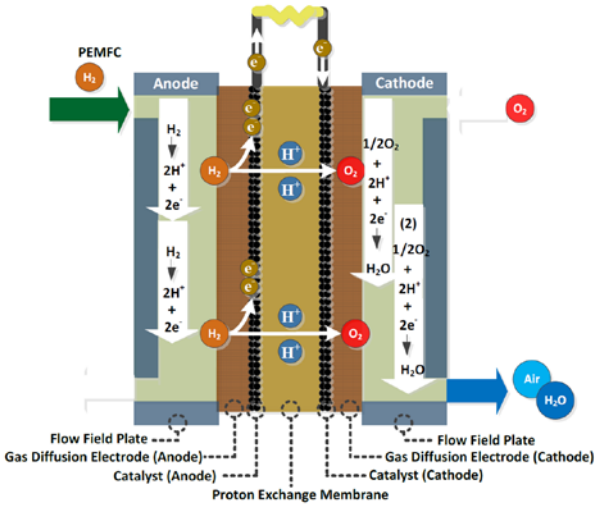


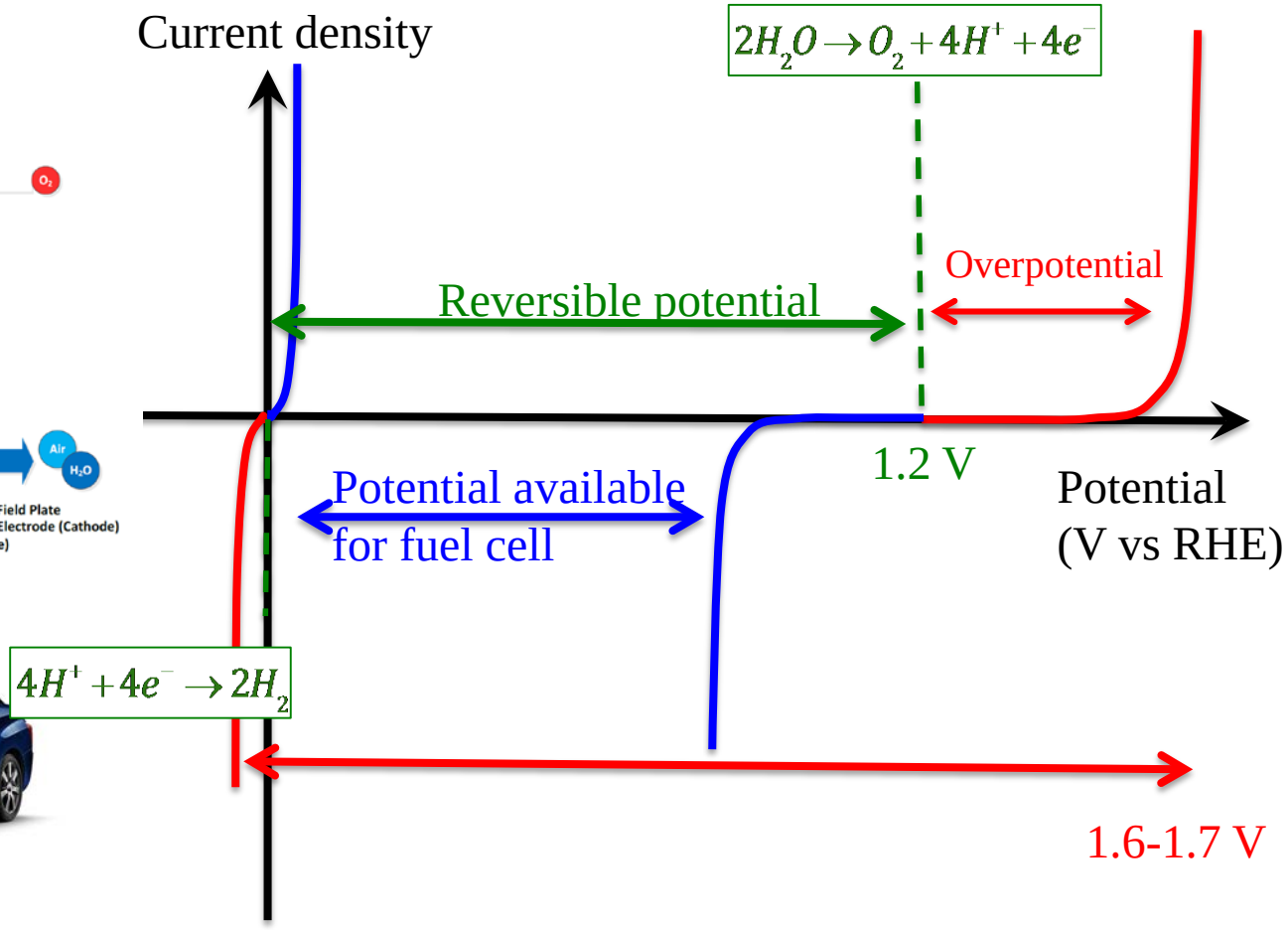




$$2H_2O \xleftarrow[\text{Energy}]{\text{Catalysis}} 2H_2 + O_2$$

DTU

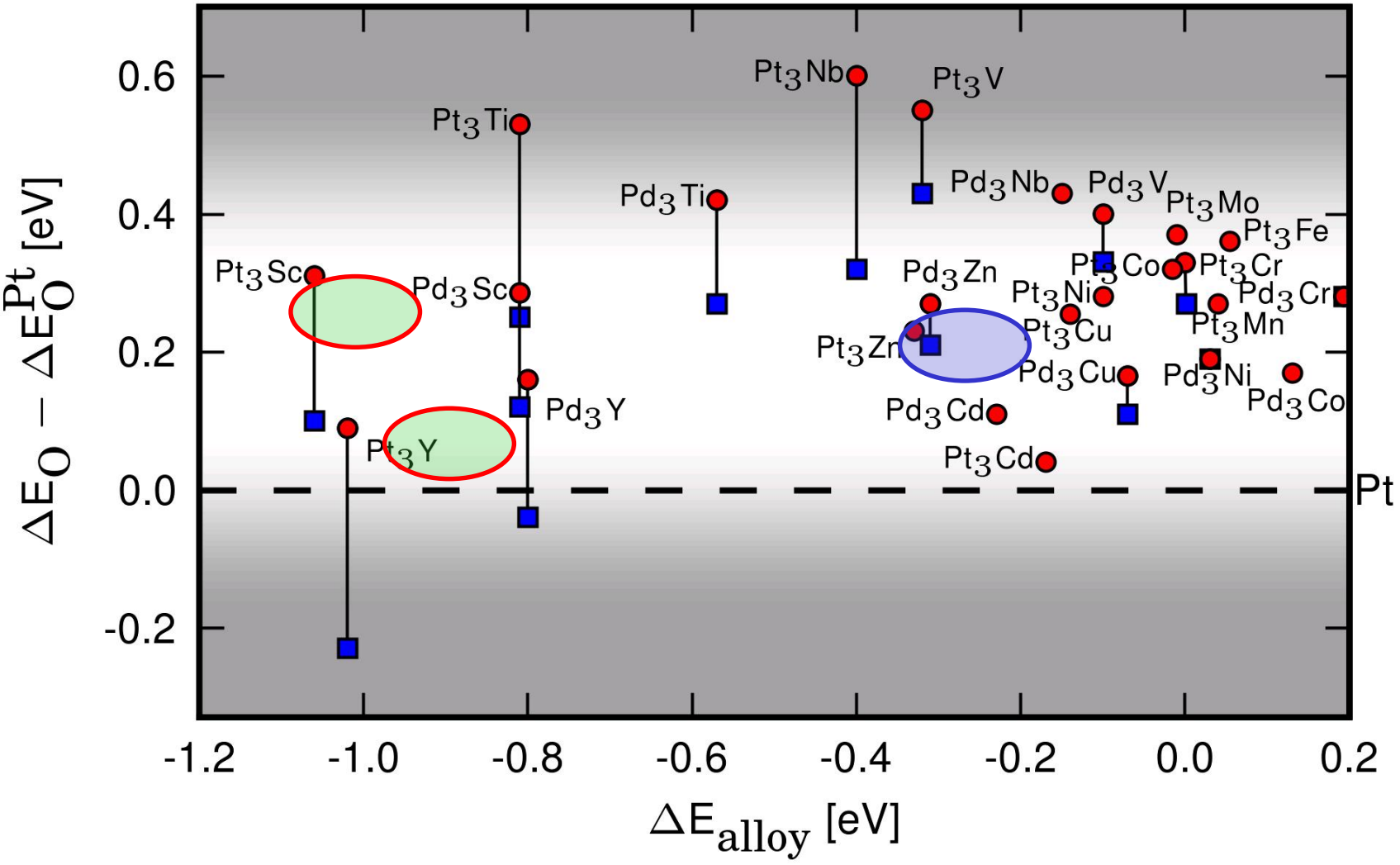




SurfCat

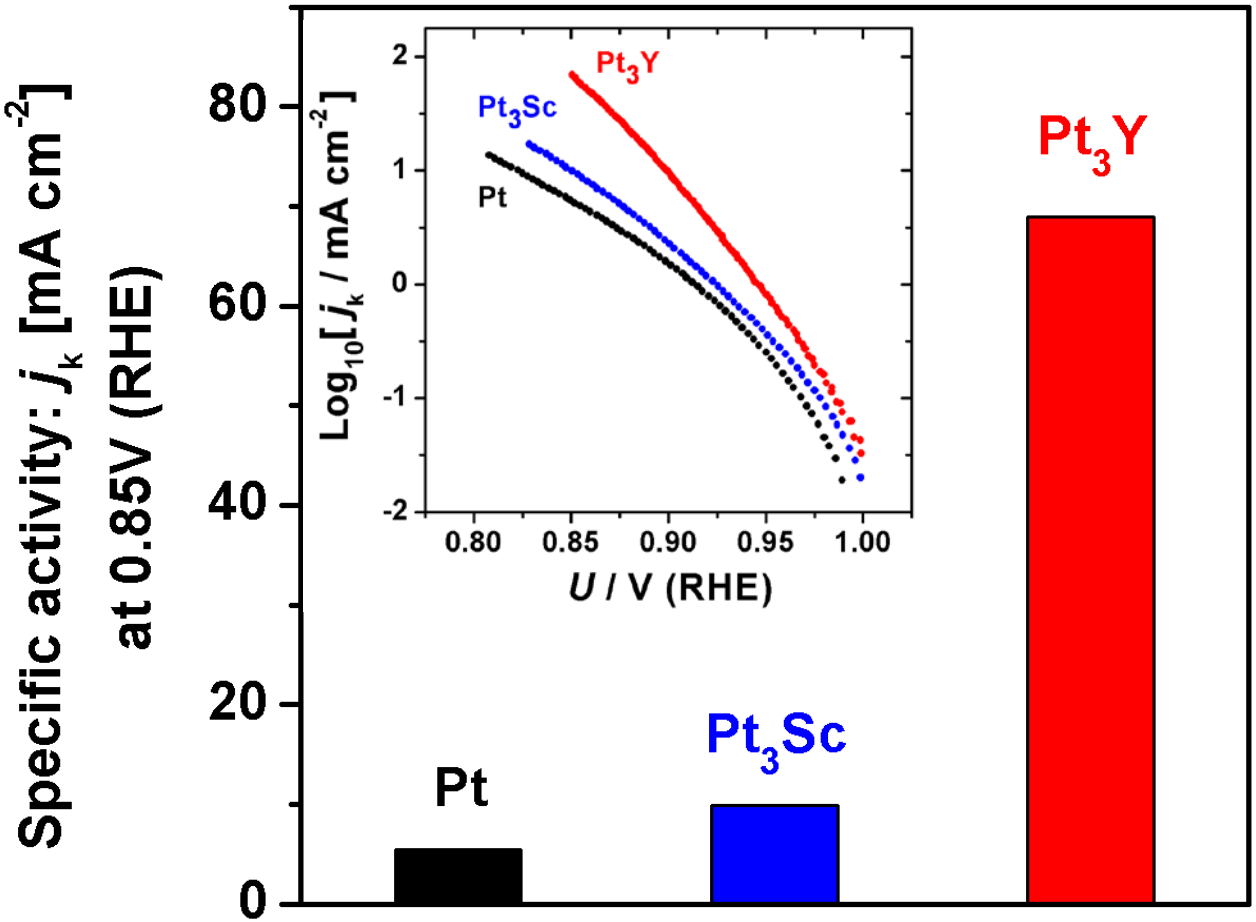
Screening of Pt_3X and Pd_3X alloys

DTU



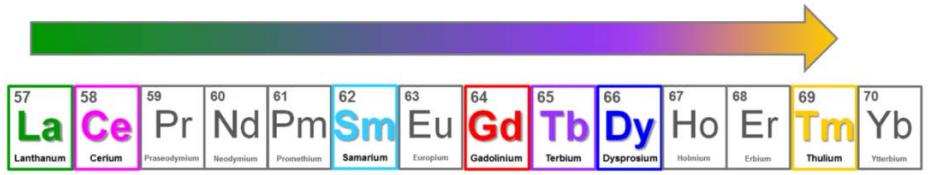
Greeley, Stephens, Bondarenko, Johansson, Hansen, Jaramillo, Rossmeisl, Chorkendorff, Nørskov (2009) Nature Chemistry 1 (2009) 522

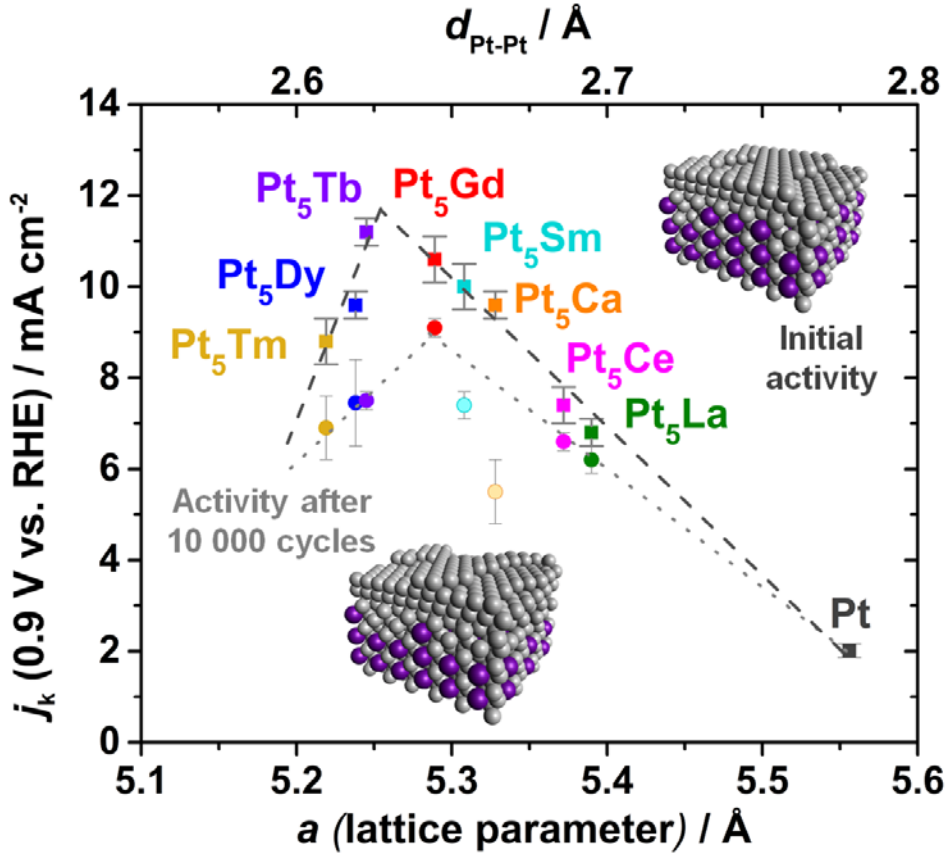
Kinetic rates

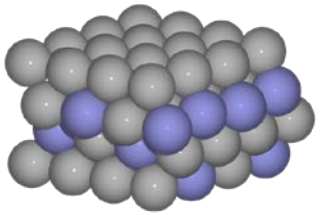


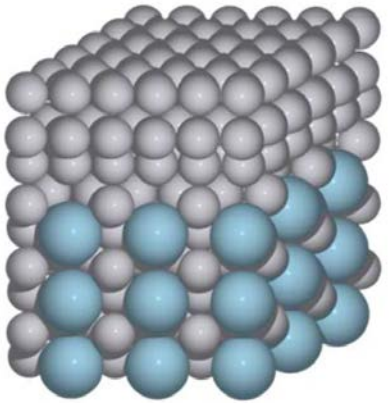
Greeley, Stephens, Bondarenko, Johansson, Hansen, Jaramillo, Rossmeisl, Chorkendorff, Nørskov (2009) Nature Chemistry 1 (2009) 522

Experimental activity-lattice parameter volcano





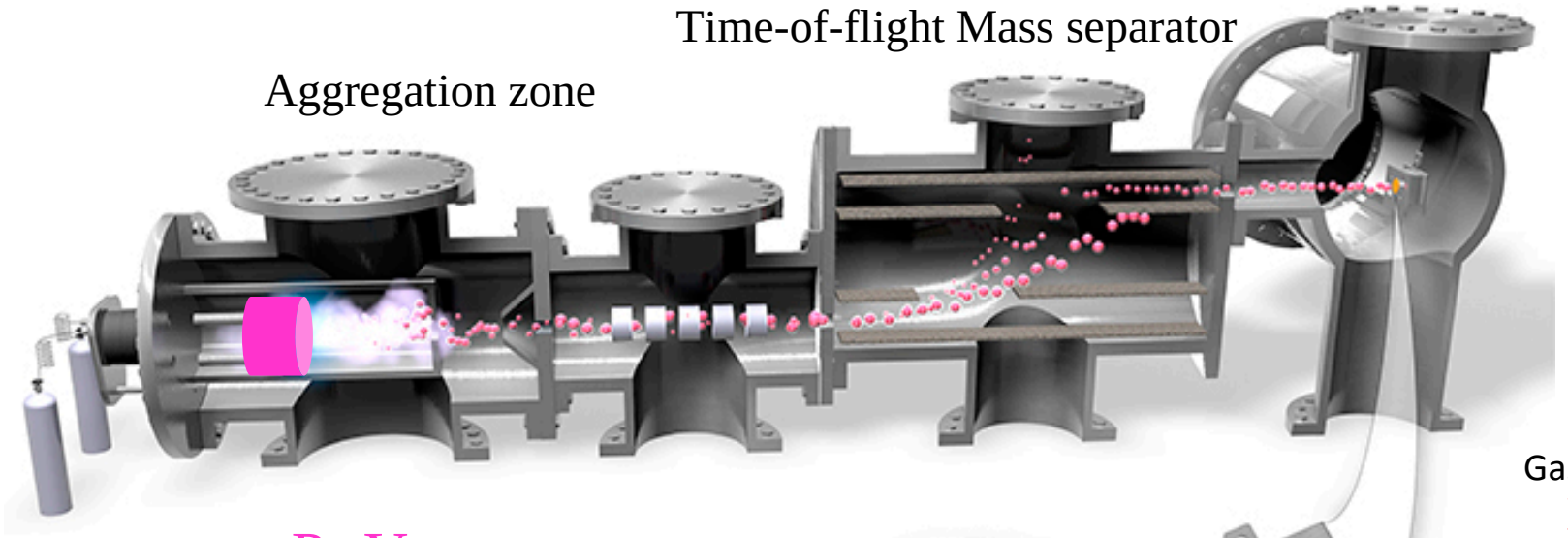




Lattice parameter: activity and stability *descriptor*

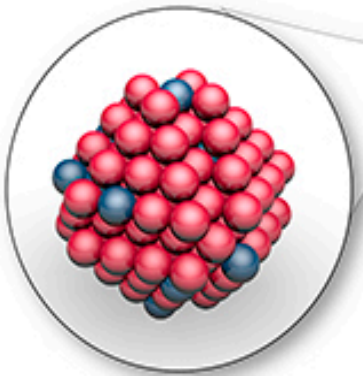
Escudero-Escribano, Malacrida,… , Rossmeisl, Stephens, Chorkendorff, *Science* **2016**, *352*, 73.

Schematic representation of the cluster source



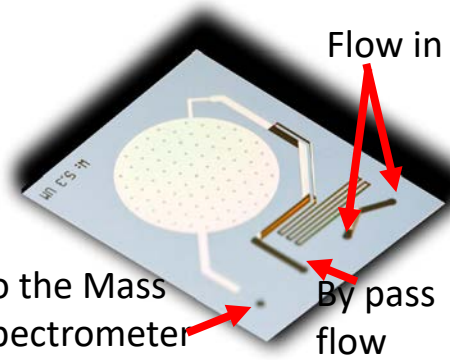
UHV
With
XPS,
AES,
ISS,
SEM,
STM

Pt_9Y



TEM grid or
Microreactor

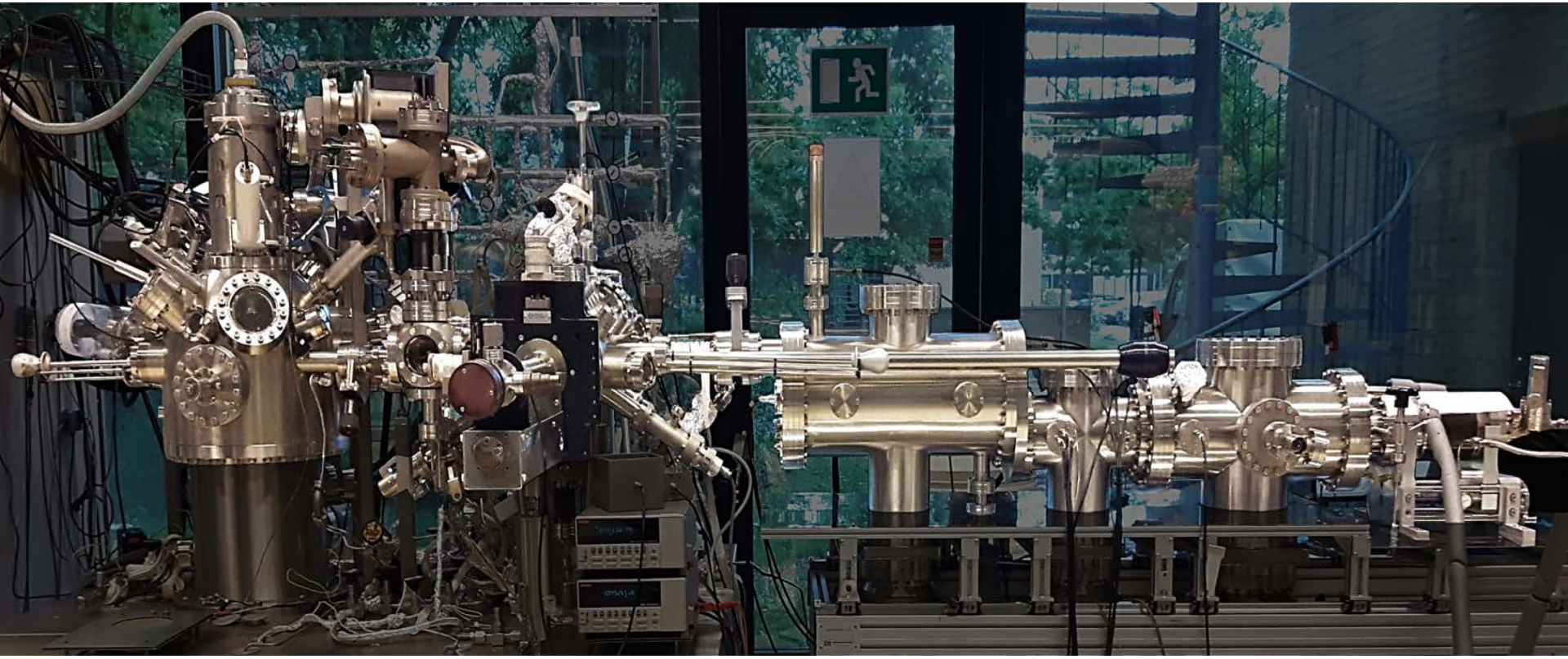
Gas phase reactor
phase reactor



SurfCat

TOF apparatus

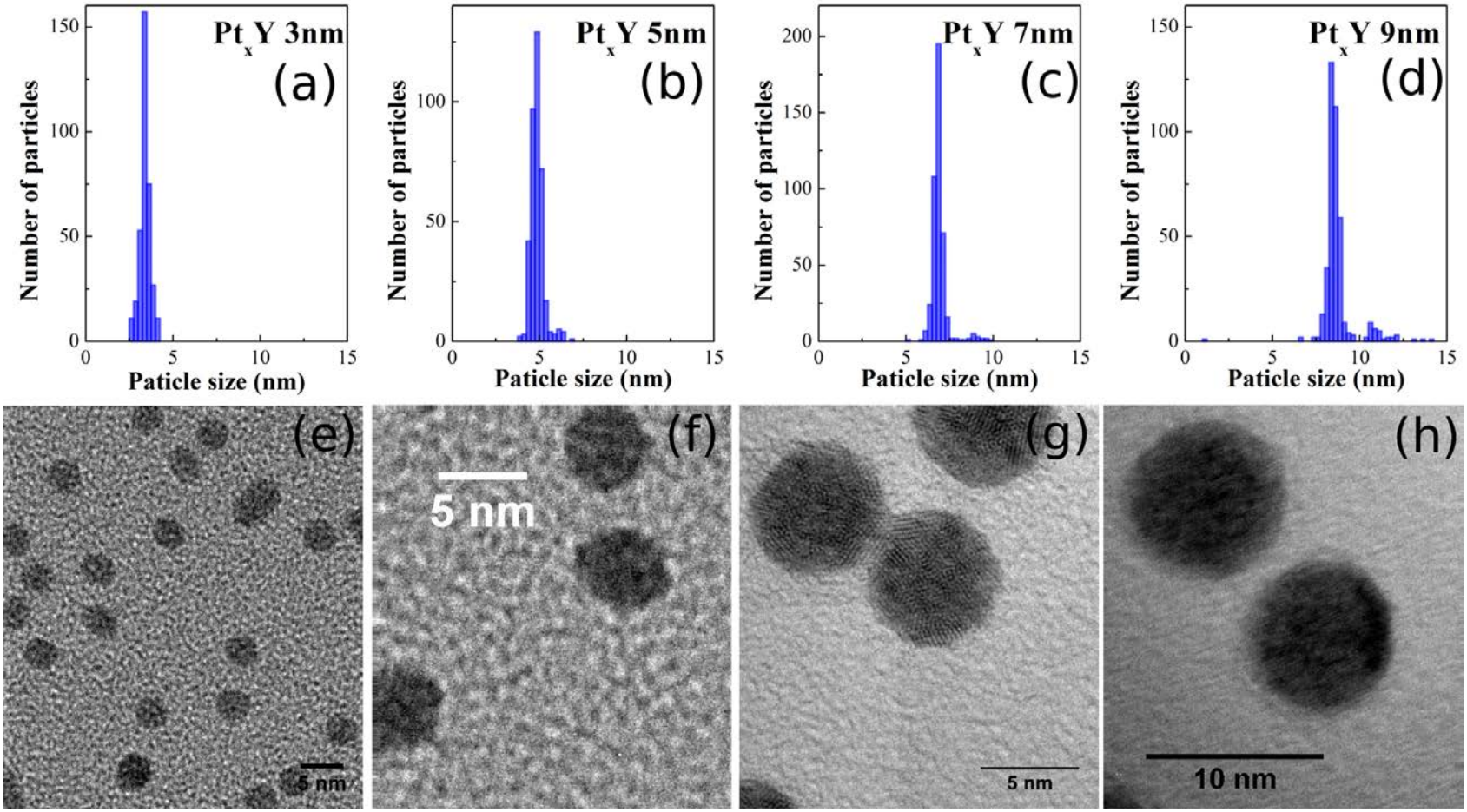
DTU



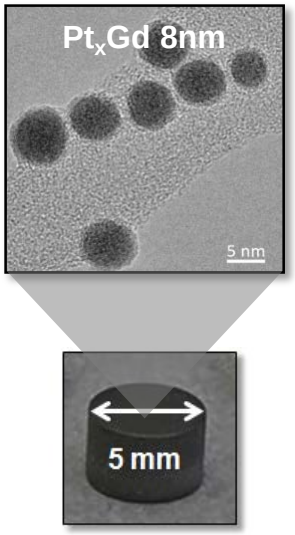
SurfCat

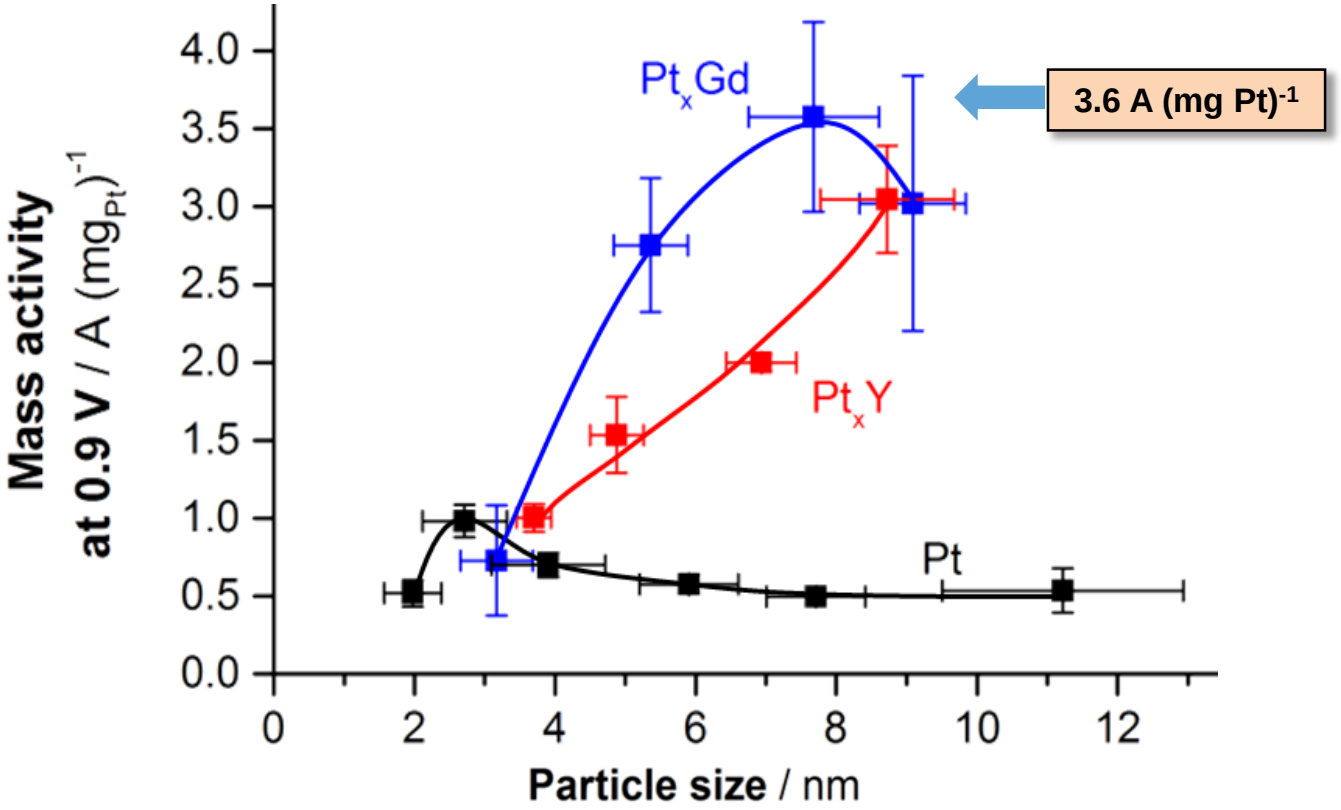
Mass selected Pt_xY Nanoparticles

DTU



Activity of Mass-selected NP of Pt, Pt_xY, Pt_xGd



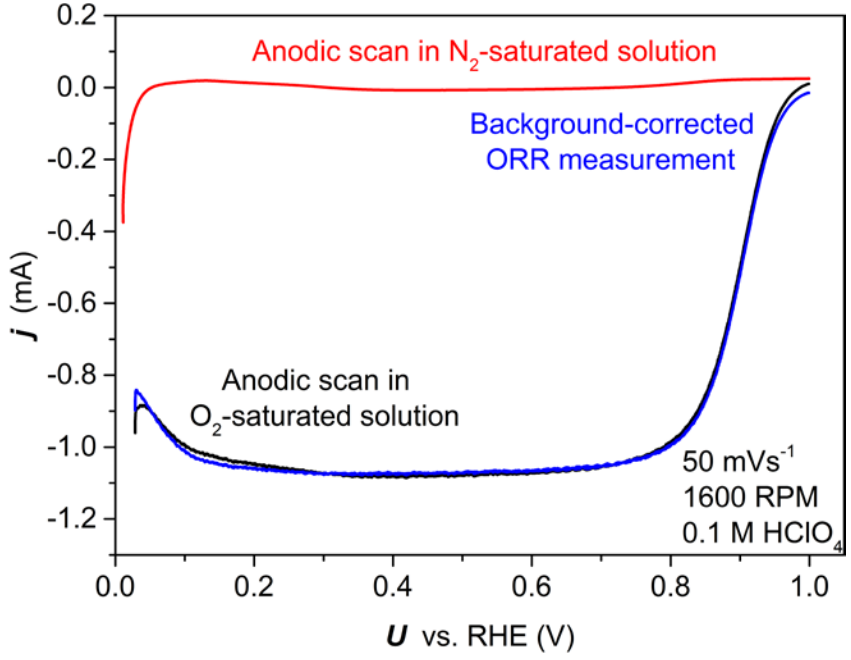


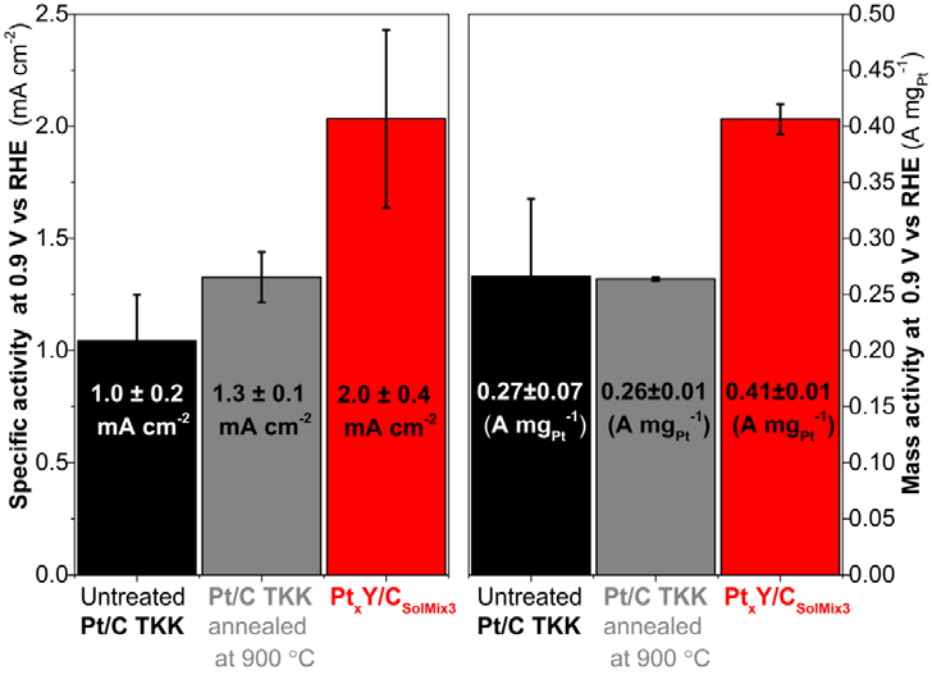
Pt_xGd nanoparticles: Velázquez-Palenzuela, Masini, Pedersen, Escudero-Escribano, Deiana, Malacrida, Hansen, Friebel, Nilsson, Stephens, Chorkendorff, J. Catal. 328 **2015** 297

Pt_xY nanoparticles: Hernandez-Fernandez,…, Stephens, Chorkendorff, *Nature Chem*. **2014**, 6, 732.

Pt nanoparticles: Perez-Alonso, ….. Hernandez-Fernandez, Strebel, Stephens, Nielsen, Chorkendorff, *Angew. Chem. Int. Ed*. **2012**, *51*, 4641.

SurfCat Oxygen Reduction Reaction in RDE Setup

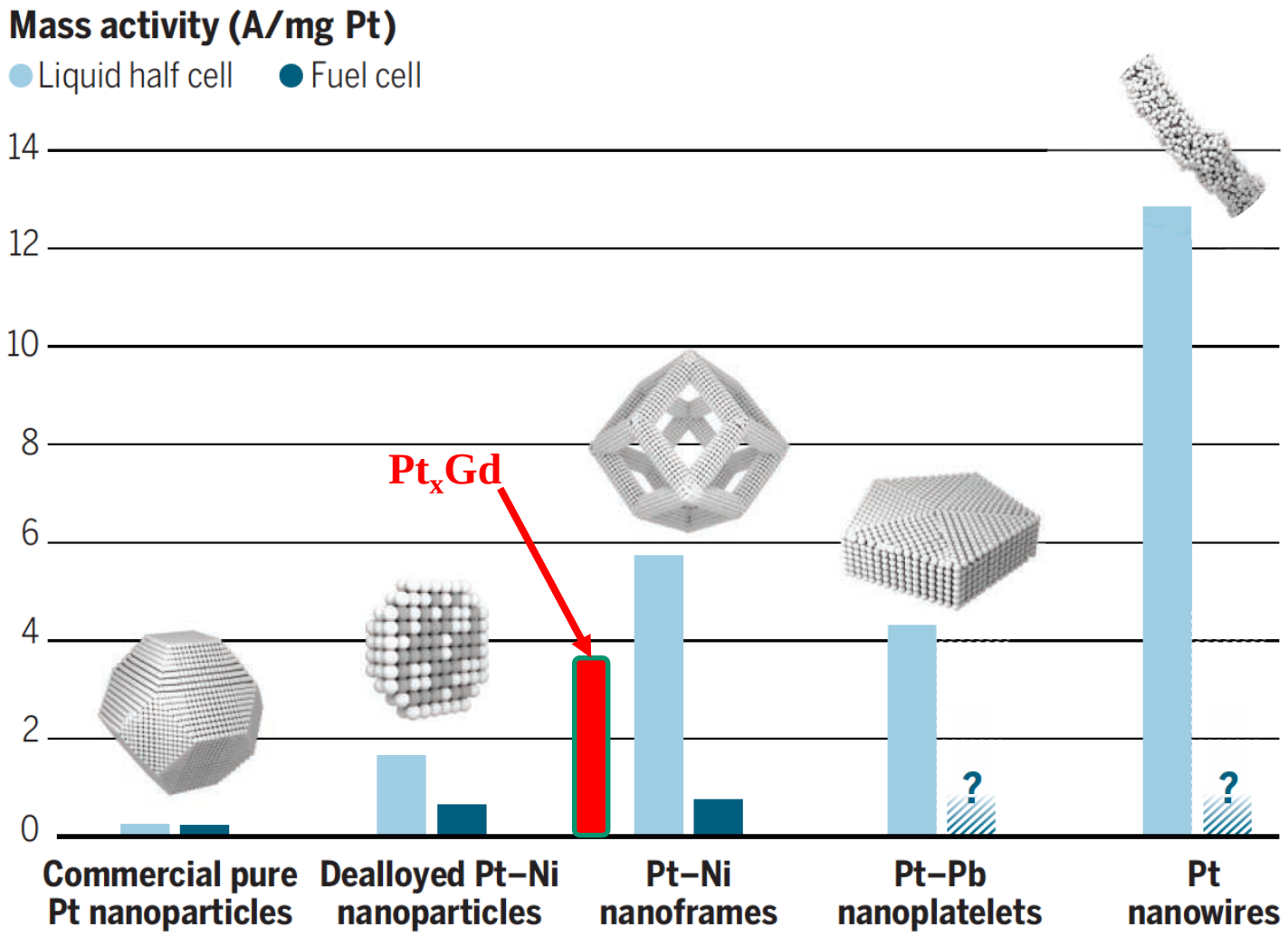




Significant increase in specific and mass activity, but nearly an order of magnitude lower than the specific mass activity observed for the Mass-selected Pt_xGd (3.5 Amg^{-1})

C. Roy, B. P. Knudsen, C. M. Pedersen, A. Velázquez-Palenzuela, L. H. Christensen, C. D. Damsgaard, I. E. L. Stephens, and I. Chorkendorff, ACS Catal. 8 (2018) 2071−2080

Outlook/Perspective

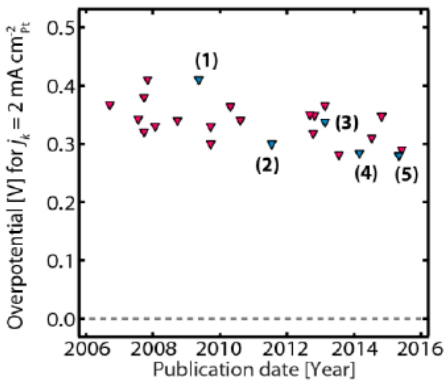


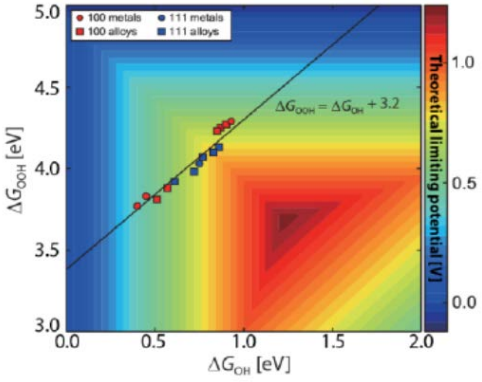
I. F. L. Stephens, J. Rossmeisl, I. Chorkendorff, Science 354 (2016) 1378-79.

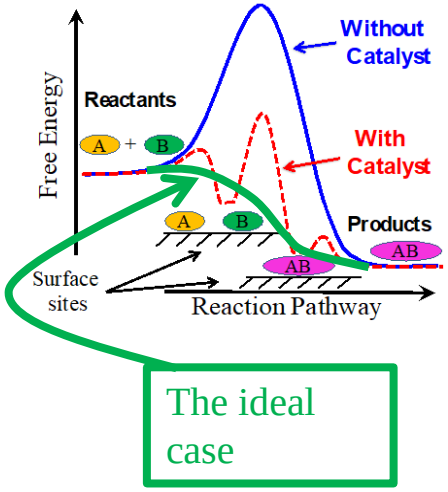
The need for a disruptive approach:

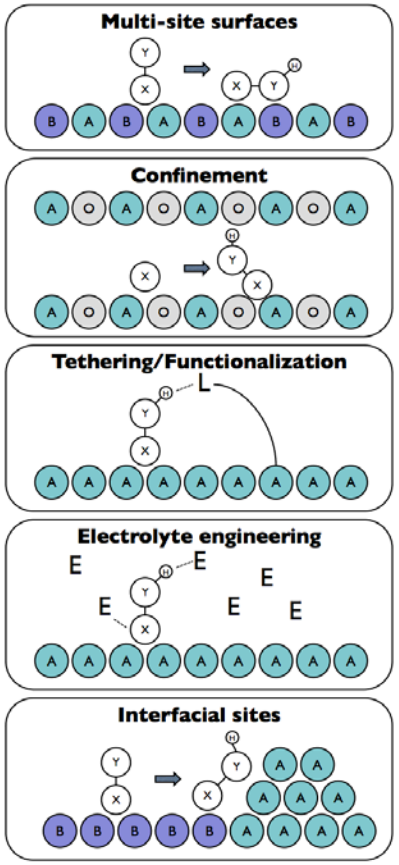
We have identified main obstacles – defines the approach forward

Fuel cell catalysts (ORR)





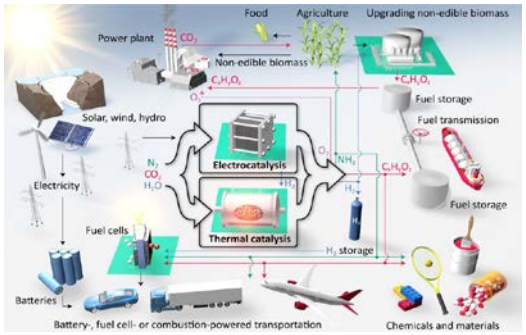


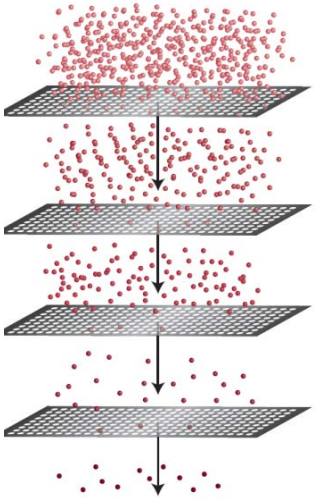


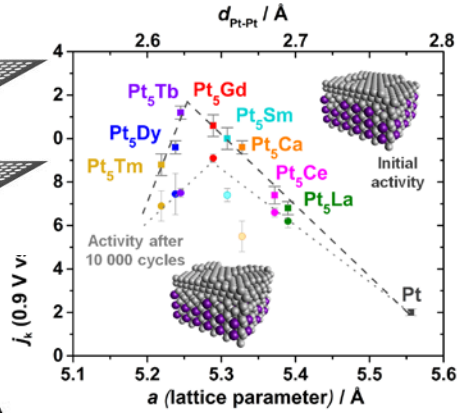
Z. W. Seh, J. Kibsgaard, C. F. Dickens, I. Chorkendorff, J. K. Nørskov, T. F. Jaramillo, *Science*. **2017**, *355* (6321).

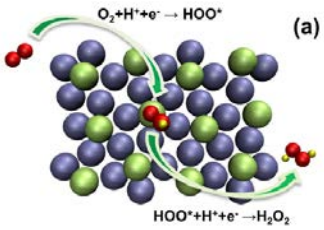
Outline

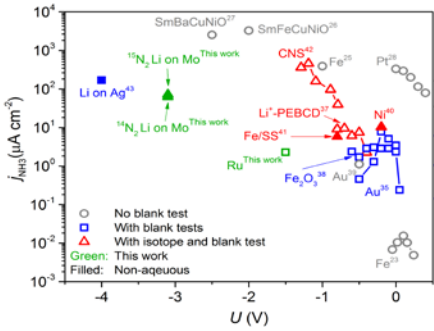
- **Motivation**
- **Approach**
- **Oxygen Reduction (ORR)**
- **Hydrogenperoxide production**
- **Electrochem hydrogenation of N_2 to ammonia**







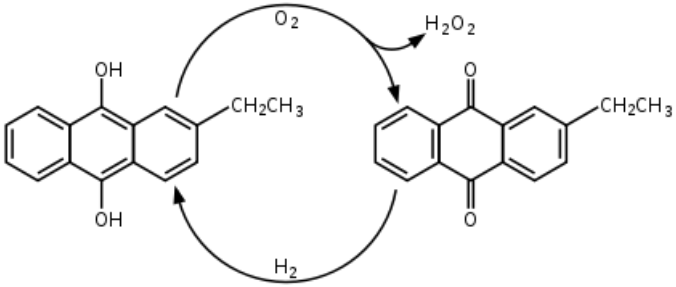




SurfCat

H_2O_2 by the anthraquinone process

DTU

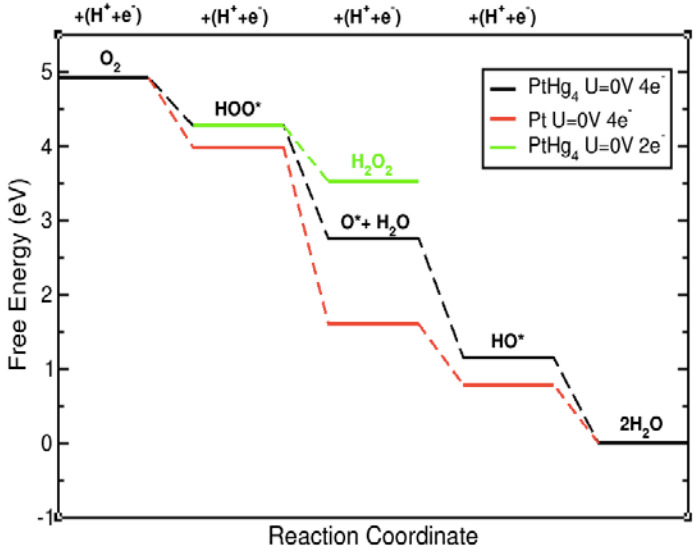


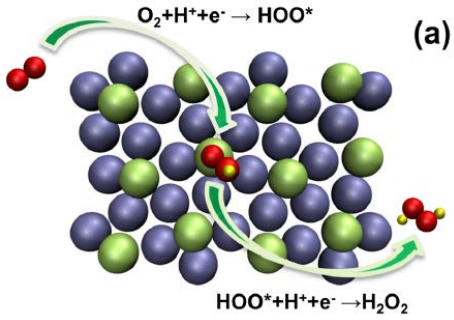
The anthraquinone process

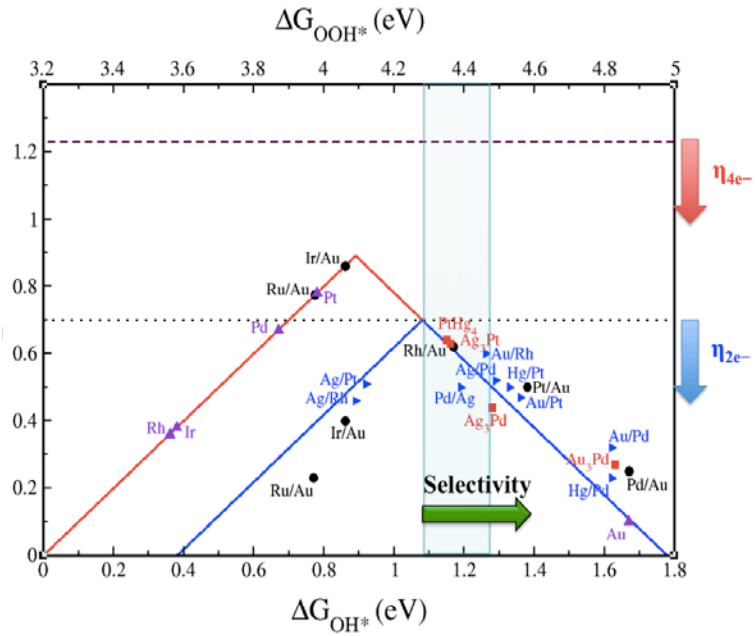
H_2O_2 plant in Rotterdam, the Netherlands

- Batch synthesis method
- Requires huge plants (just about 60 in the whole world)

New heterogeneous catalyst Pd/Au for a "Dream Reaction"

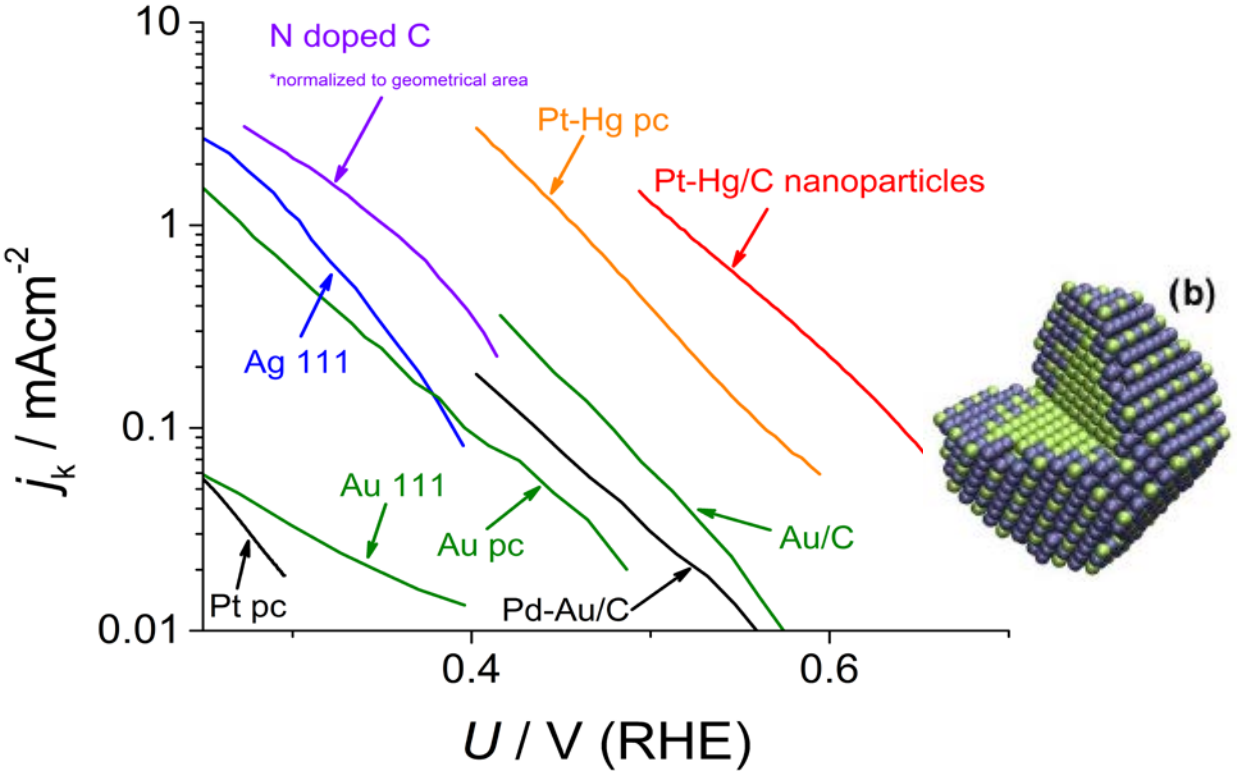


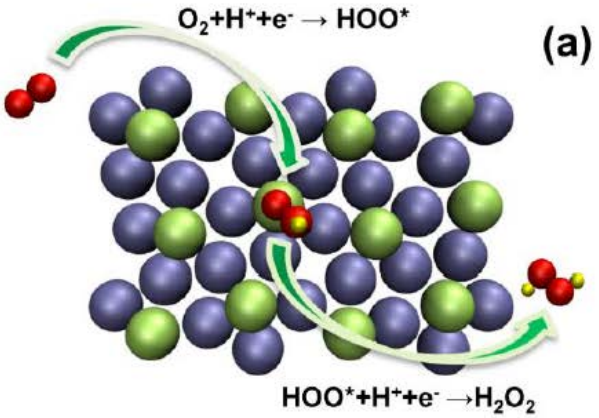




SurfCat Comparison to other electrocatalysts

HPNow

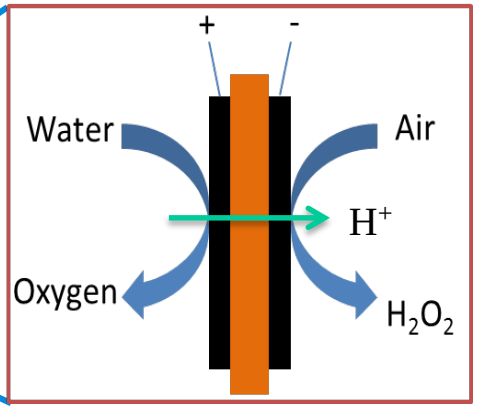




S. Siahrostami, A. Verdaguer-Casadevall, M. Karamad, P. Malacrida, B. Wickman, M. Escudero-Escribano, I. Chorkendorff, I. Stephens, J. Rossmeisl, Nature Mat. 12 (2013) 1137 .

Electrochemical H_2O_2 generation

HPNow



- Electrolytic reaction between **Oxygen** and **protons** from water
- Safe to operate
- Concentration controlled by adjusting power input and water flow

Outline

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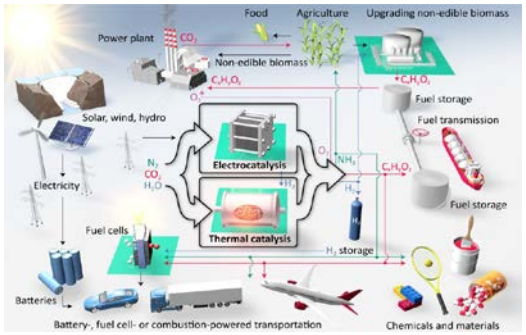
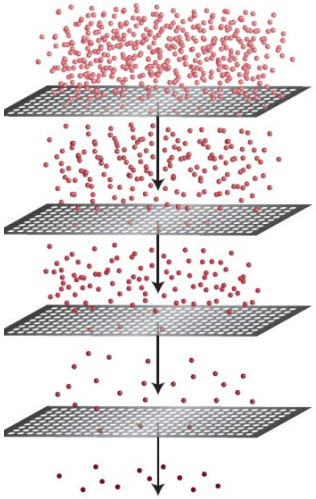
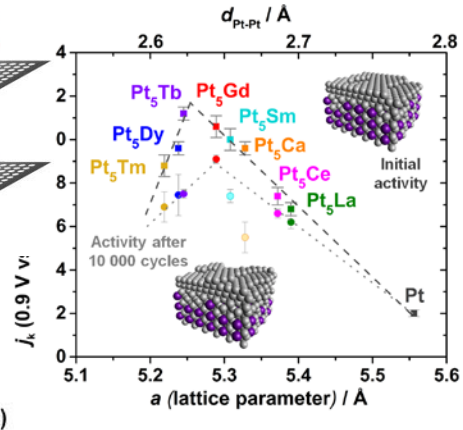
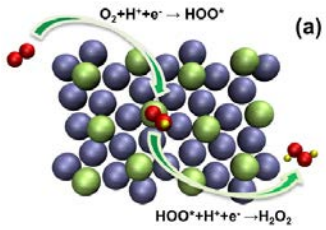
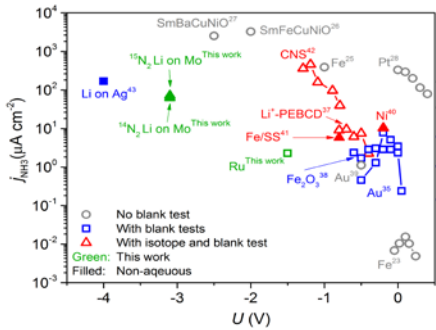




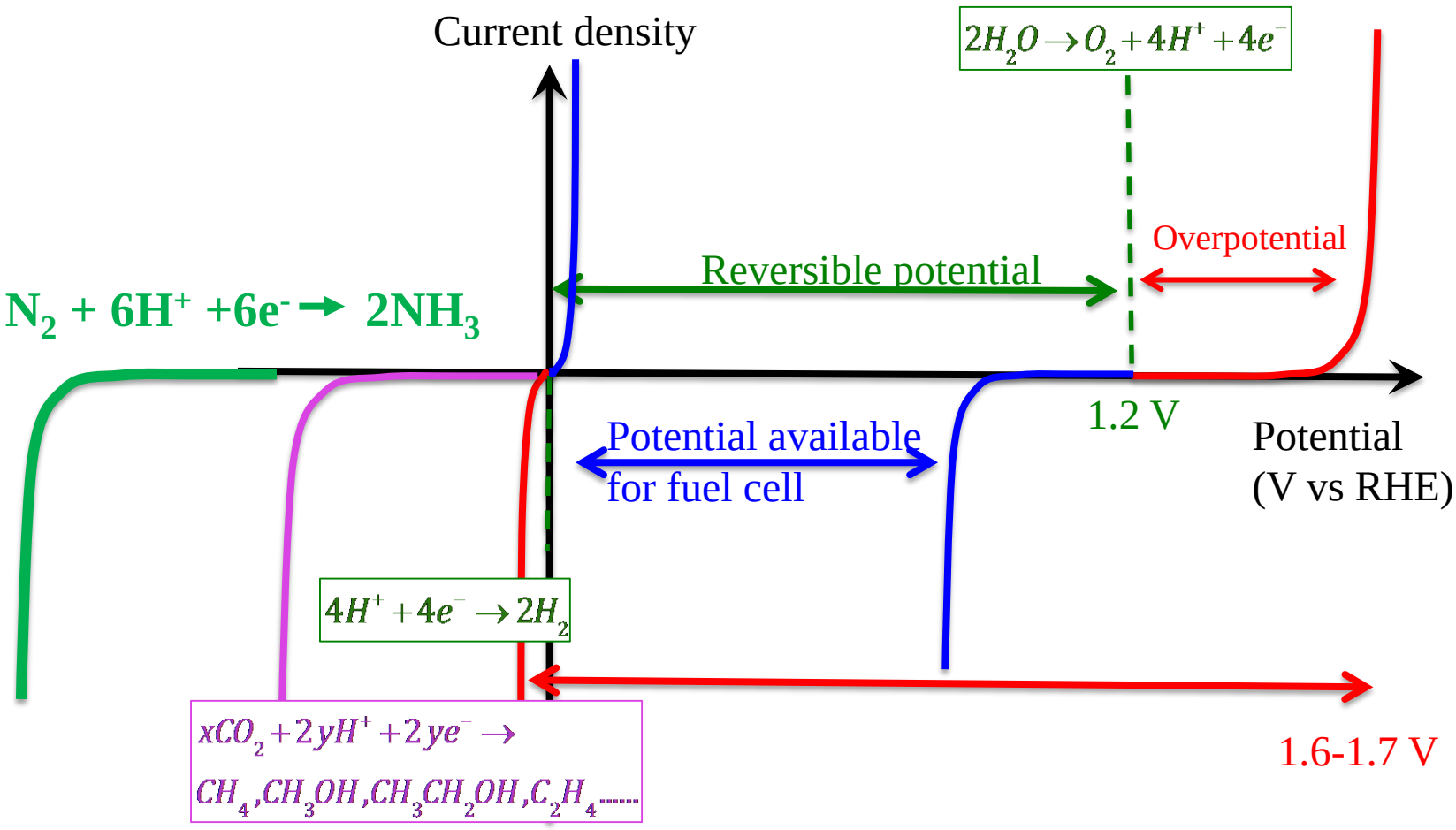






$$2H_2O \xleftarrow[Energy]{Catalysis} 2H_2 + O_2$$

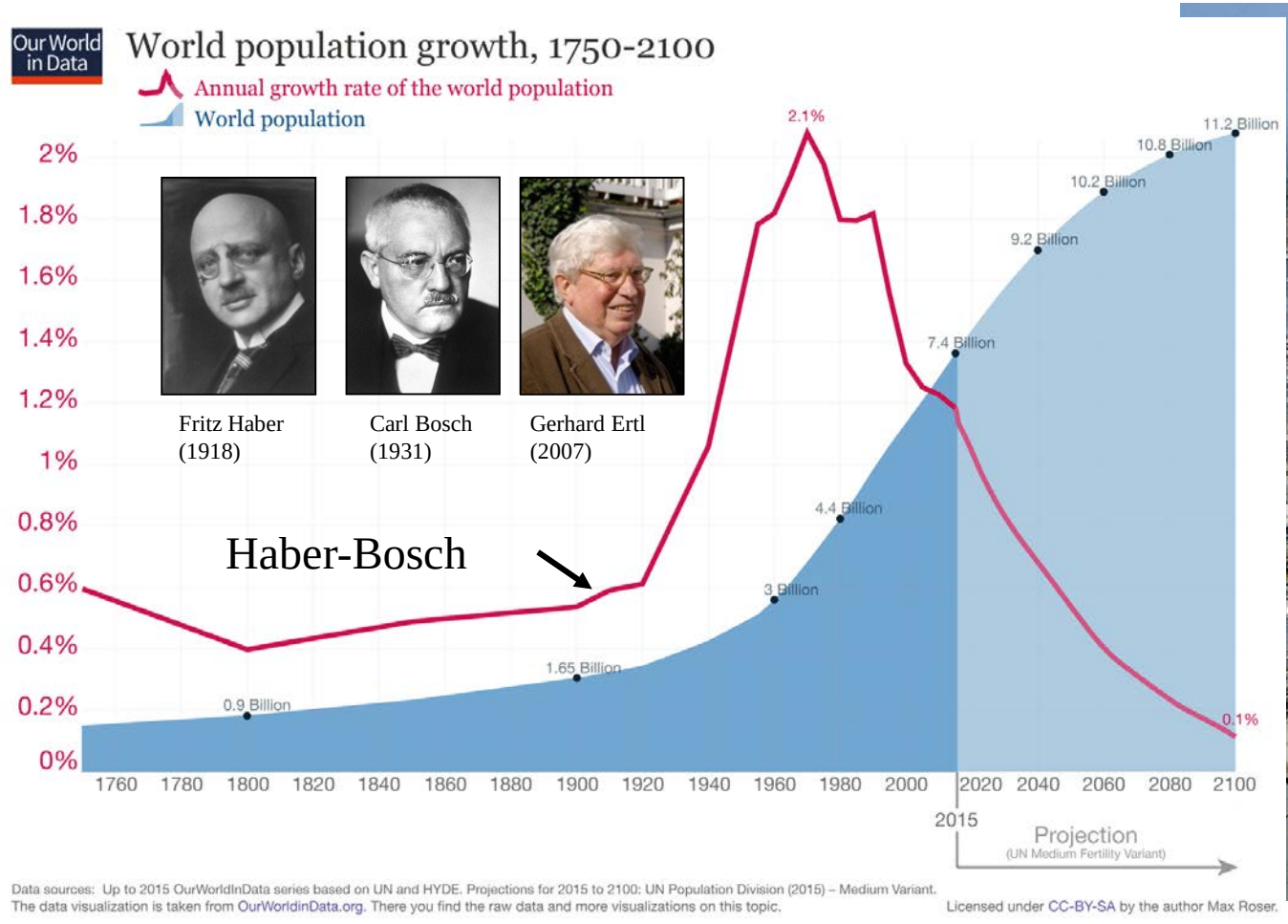
DTU



SurfCat

Why ammonia?

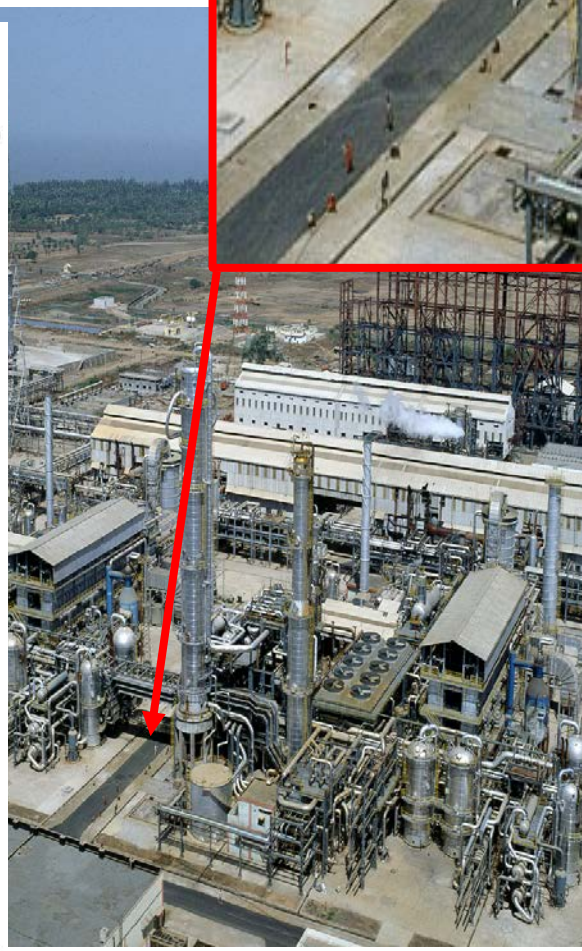
DTU



Fritz Haber
(1918)

Carl Bosch
(1931)

Gerhard Ertl
(2007)

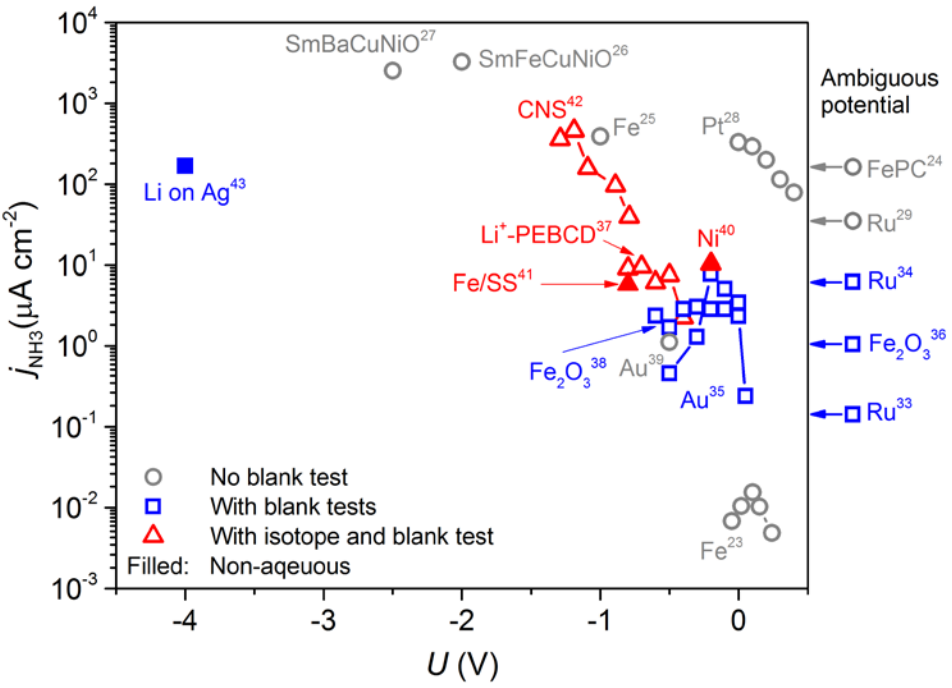


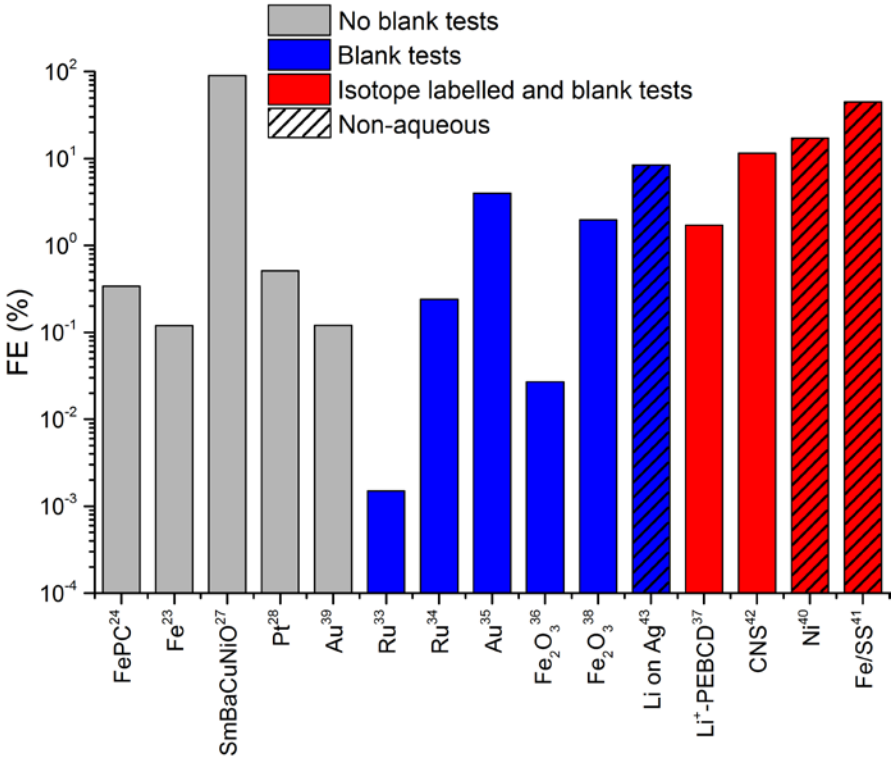
Use 1 % of our total energy Consumption

SurfCat

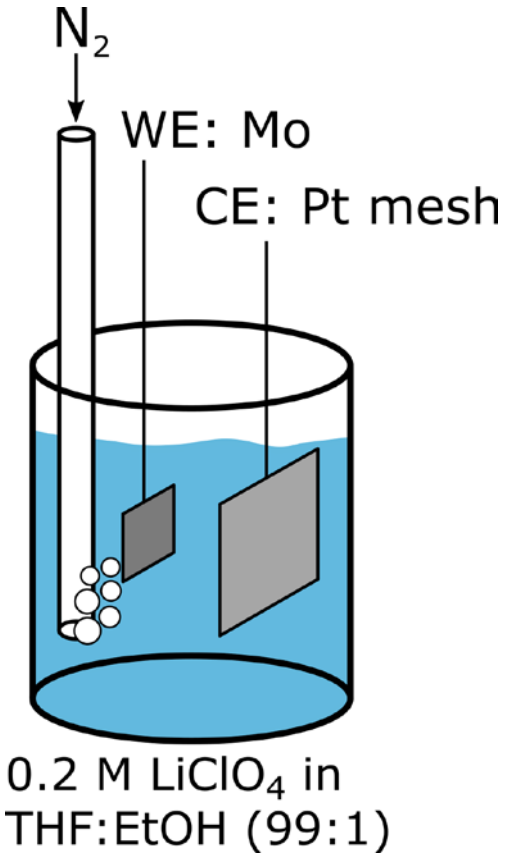
State-of-the-art in the field

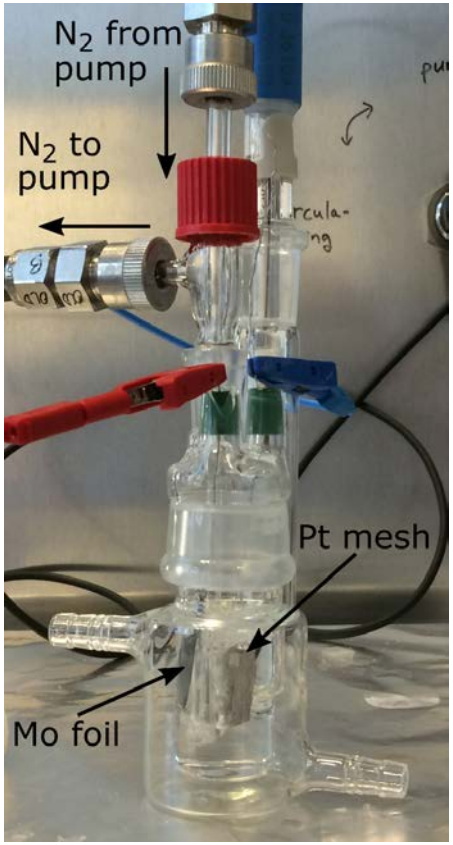
DTU





SurfCat A rigorous repeat of A. Tsuneto's work from 1993





Cleaned N_2 gas prior to measurement with Cu catalyst to reduce NO_x. Use cold trap to trap any ammonia in stream.

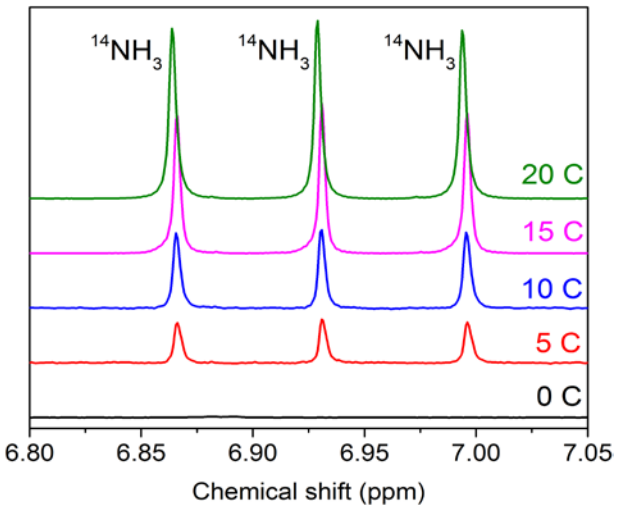
Use glass pump to cycle gas for duration of experiment (use 200 mL isotope labelled nitrogen).

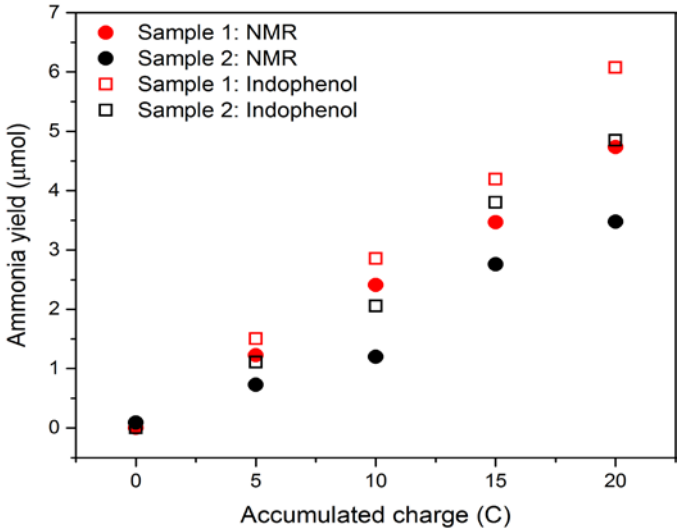
Include background measurements with Ar with potential and N_2 at OCP (no significant contribution)

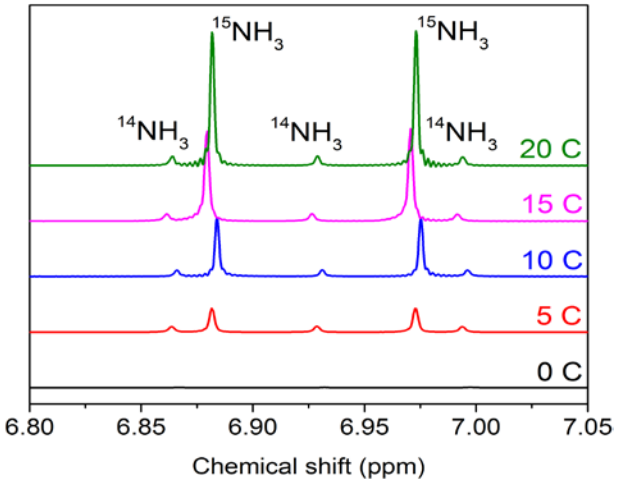
Need <-3.04 V to electrodeposit lithium

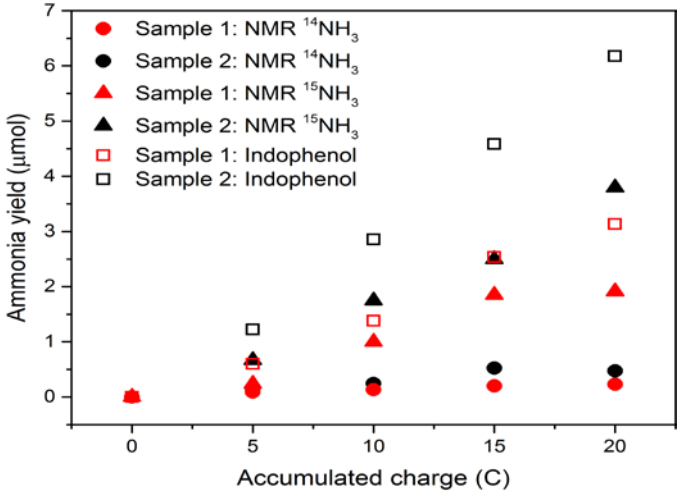
A. Tsuneto, A. Kudo, & T. Sakata Chemistry Letters 851-854 (1993)

NMR spectroscopy of isotope labelled NH_3







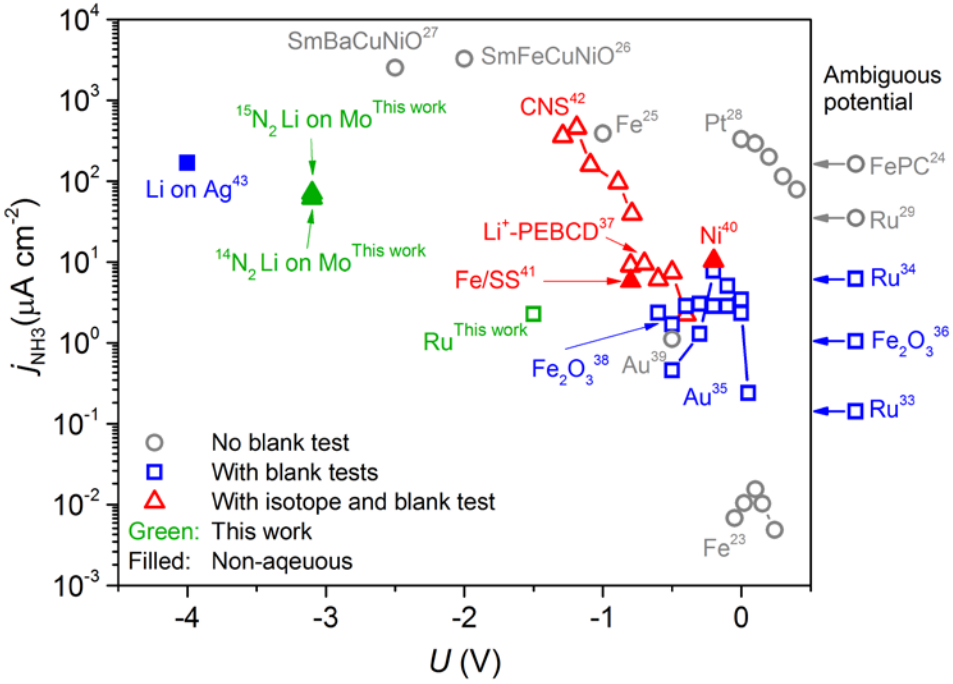


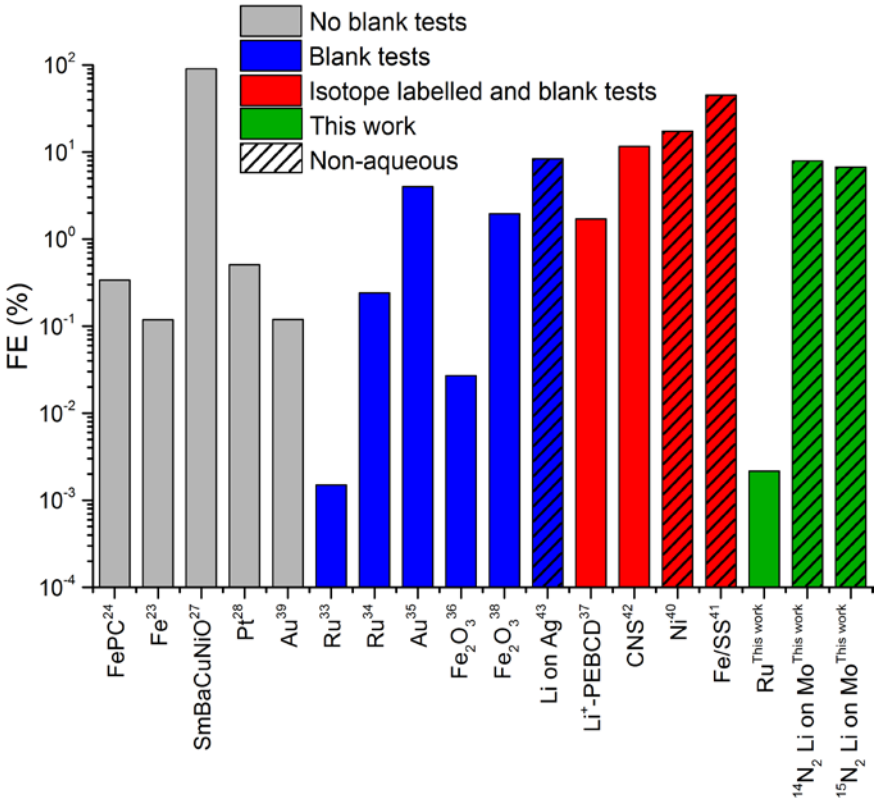
A. Tsuneto, A. Kudo, & T. Sakata Chemistry Letters 851-854 (1993)

Quantitative $^{15}N_2$ conversion to ammonia is **Mandatory!!**

"Assessing the Current State of Catalyst Development for the Electrochemical Reduction of N2 to NH3"
S. Z. Andersen, V. Čolić, S. Yang, J. A. Schwalbe, A. C. Nielander, J. M. McEnaney, J. G. Baker, A. R. Singh, B. A. Rohr, M. J. Statt, S. J. Blair, S. Mezzavilla, K. Enemark-Rasmussen, J. Kibsgaard, P. C. K. Vesborg, M. Cargnello, S. F. Bent, T. F. Jaramillo, I. E. L. Stephens, J. K. Nørskov, I. Chorkendorff. Submitted (2018).

State-of-the-art in the field





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Summary

We need to make Sustainable Energy cheaper than Fossil Fuels

- **What is definitively needed: Better OER catalysts in particular for acid**
- **We should consider new processes for delocalized production, whether it is Thermal or Electrochemical does not matter as long it is efficient and selective**
- **This provides new opportunities: SurfCat have started three spin-off companies since 2014.**

SpectroInlets
Enabling real-time analysis

HPNow

RenCat