



# Structures of interfaces

## relevant in chemical energy conversion

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Thanks to the group leaders:

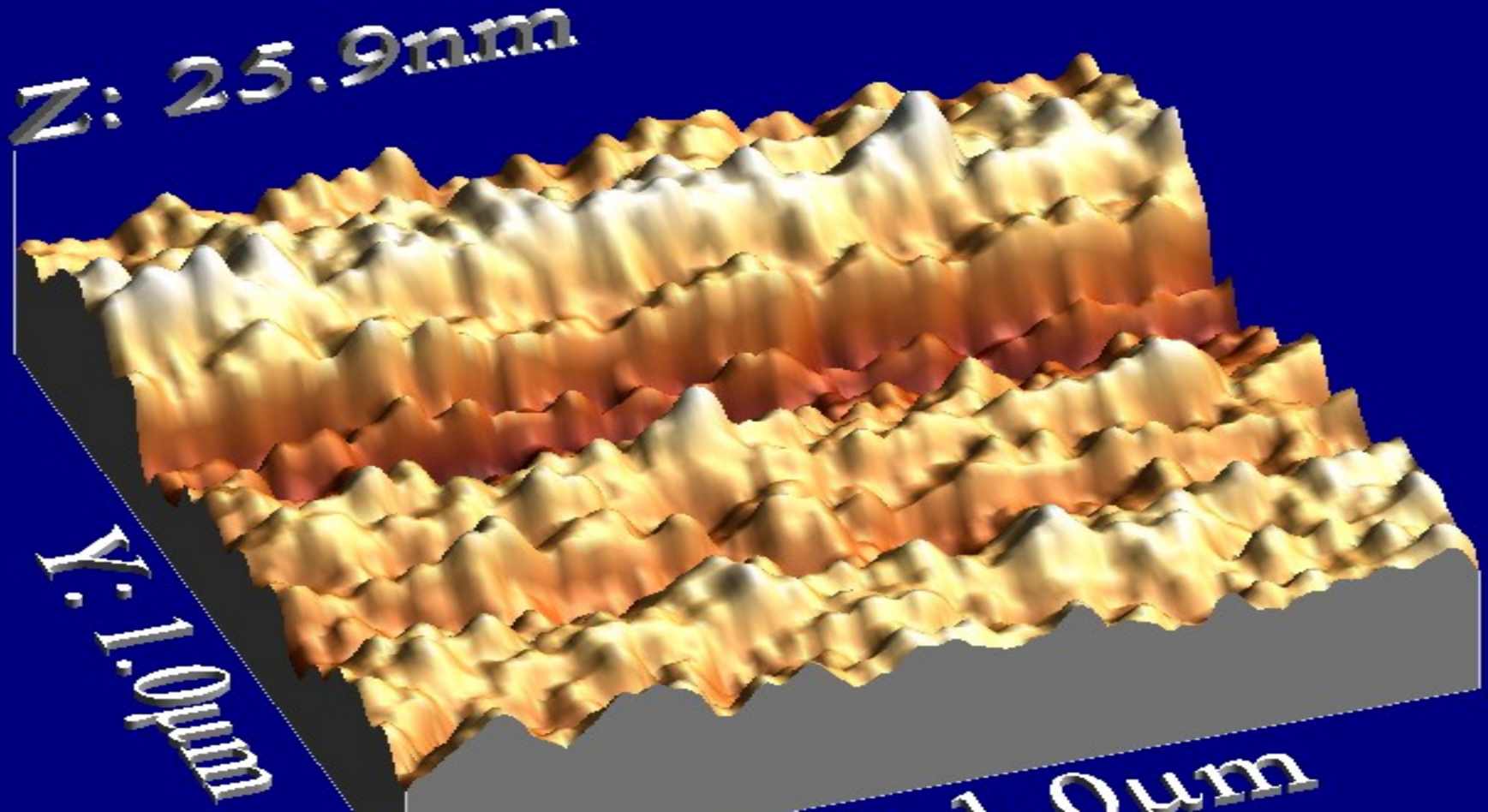
M. Behrens, (R. Horn), A. Knop-Gericke, J. Tornow, A. Trunschke, M. Willinger



# The standard model (Langmuir, Ertl)

- A heterogeneous catalysts can be approximated by a single crystal surface.
- The terminating atoms are all equal and active.
- Adsorption strength may change this: perimeter of islands in CO oxidation; (dynamics).
- Surface atoms can be defined precisely with atom co-ordinates.
- They can be studied by surface science structural tools.
- Single crystal approach.

# More complexity: Active sites





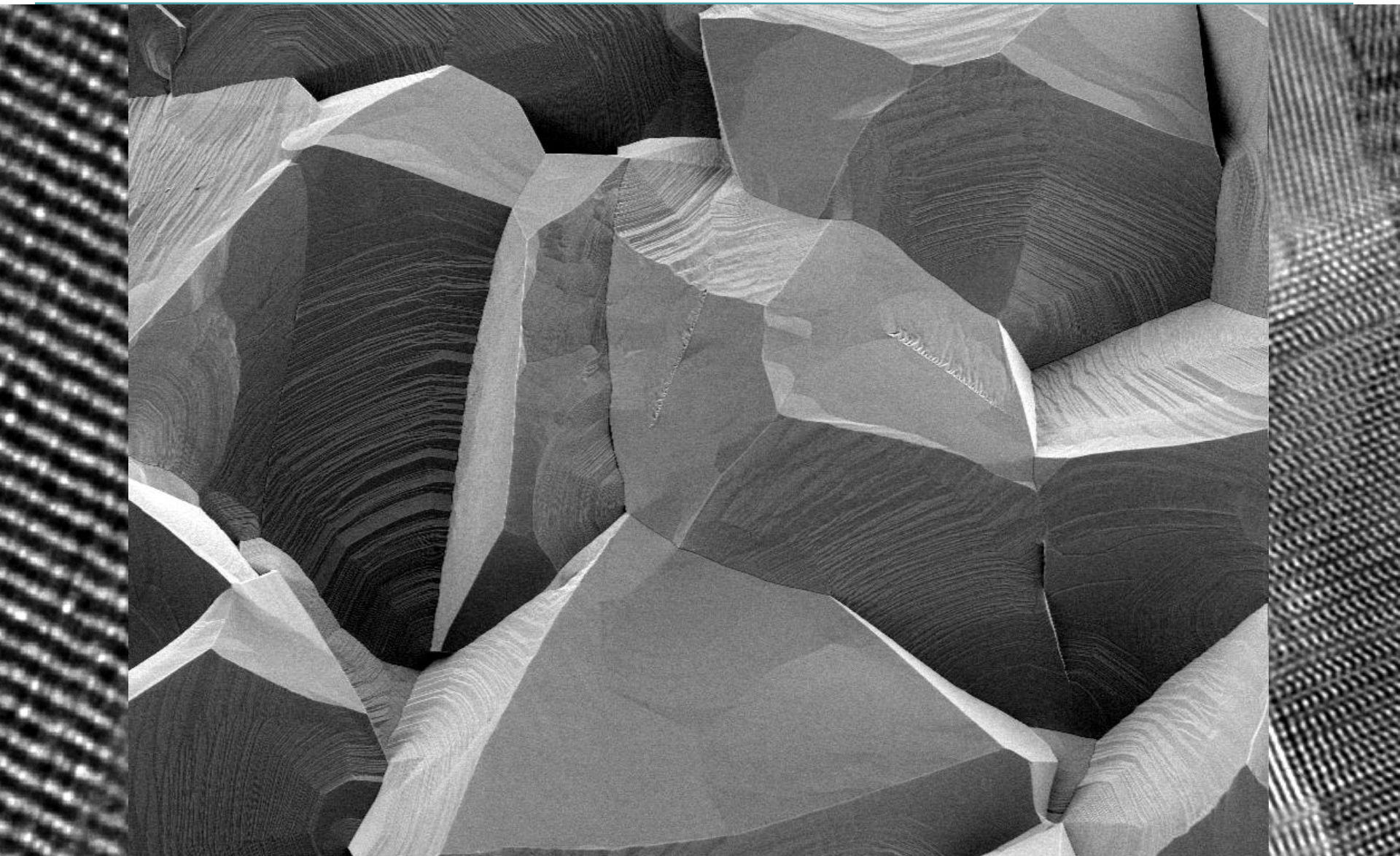


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# Catalyst dynamics: lattice oxygen an early manifestation

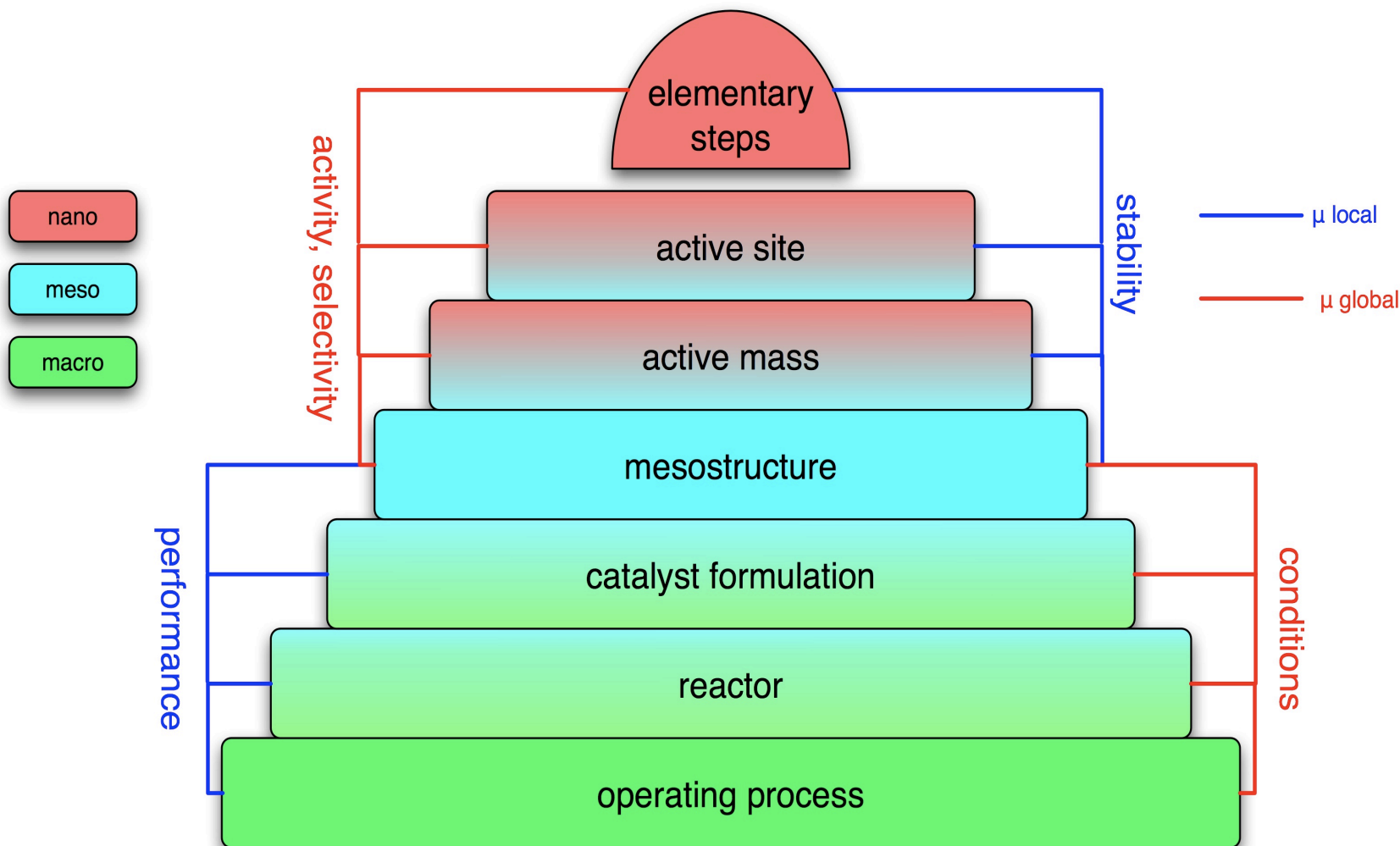
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# Catalysis is a multi-scale phenomenon

## We exclude much of it here!





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# Energy systems:

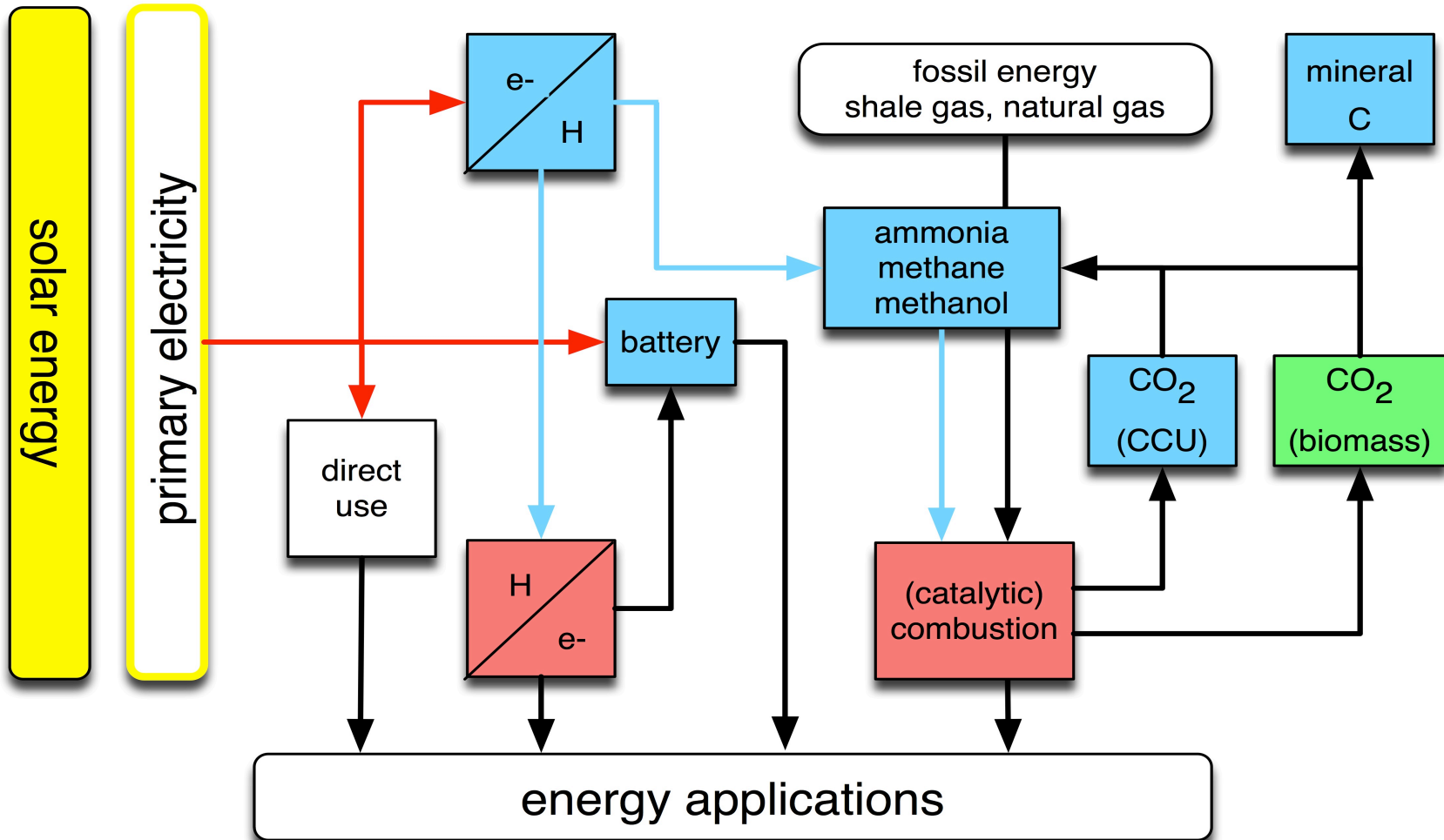
from requirements rather than from the past

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- **Sustainable** : closed material flows for all harmful species.
- **Scalable**: use processes and materials working on abundant resources without open risks.
- **Subsidiary**: address challenges locally where they arise.
- **Stable**: interconnect solutions to ensure system stability where necessary.
- The consequence is an increase in complexity and a change in our target function (complete economics).
- Time scales are long (lifetime of infrastructure systems) also long transition periods: chance for novel approaches.

# Energy storage: Two ways one target: pack sunlight into a tank



The „renewables“ power station



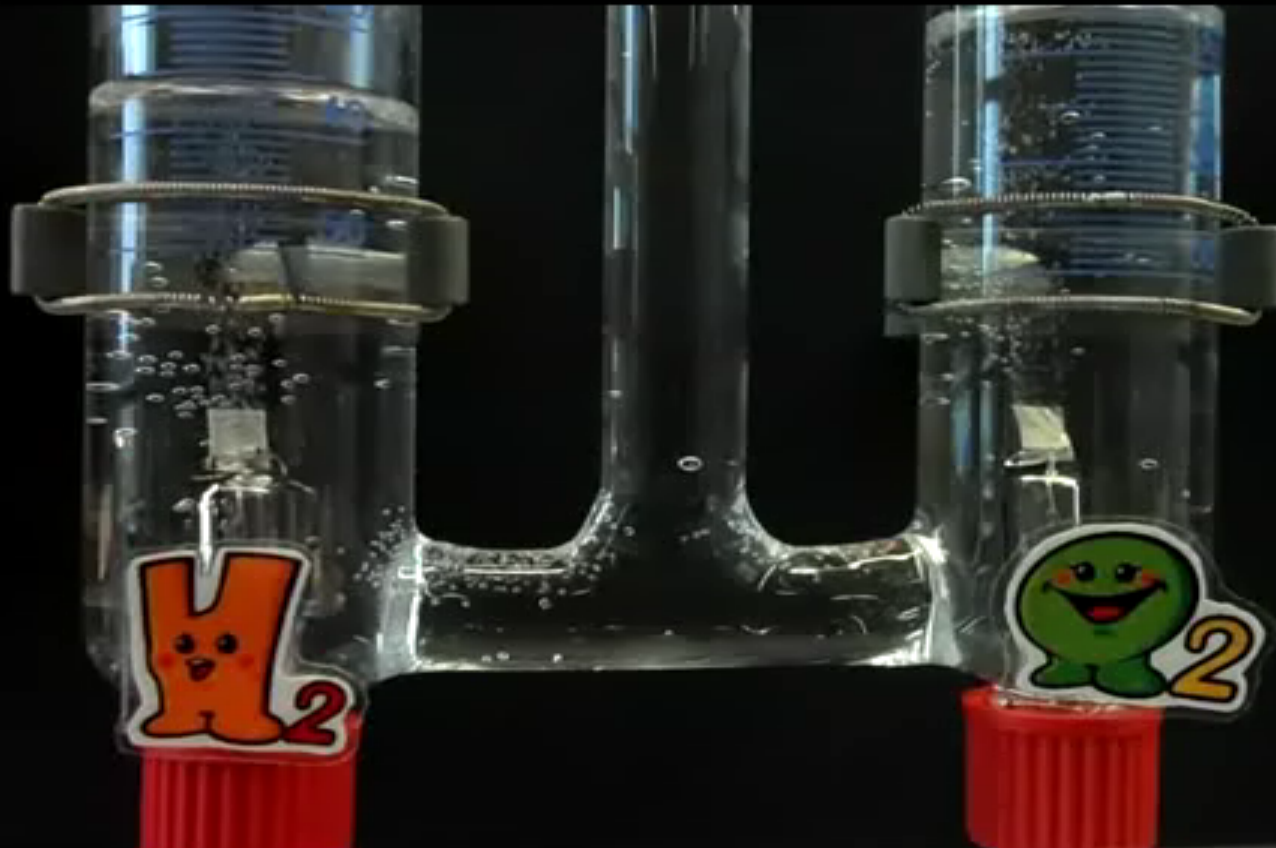


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# Inter-industry systems approach: Power-to-gas

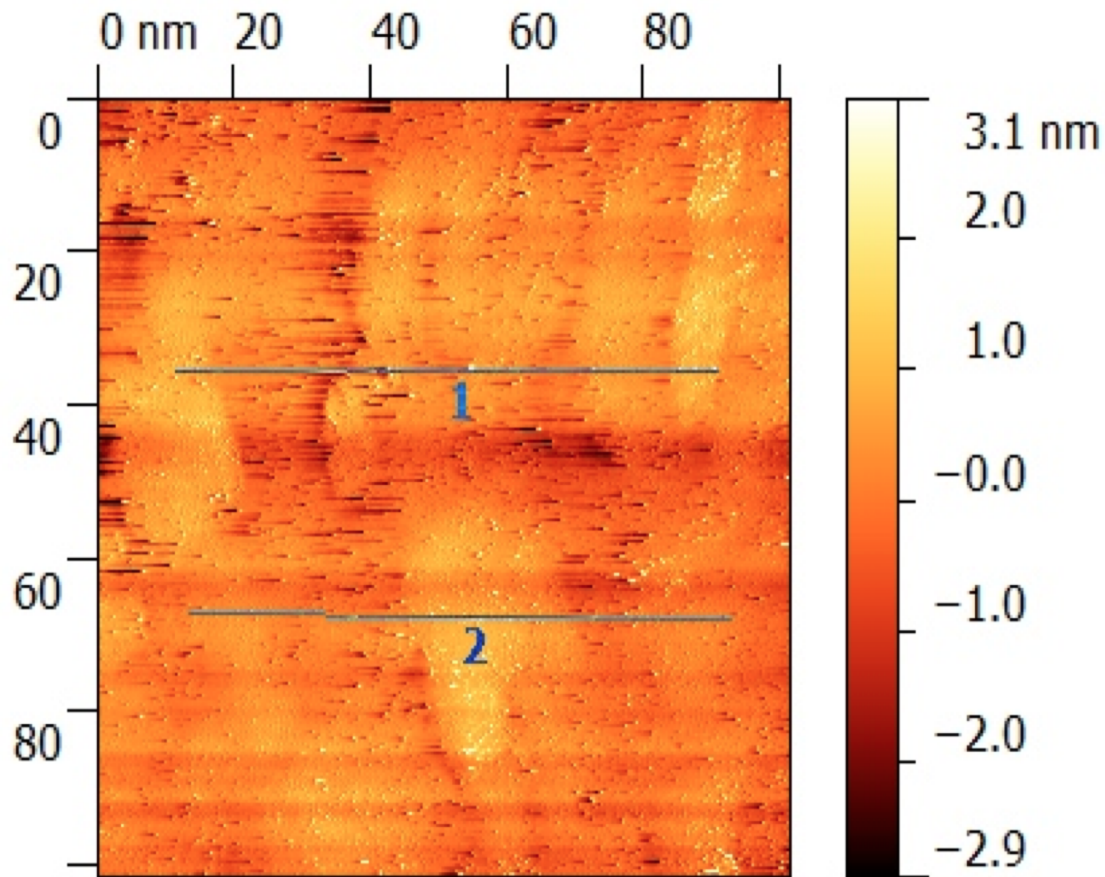
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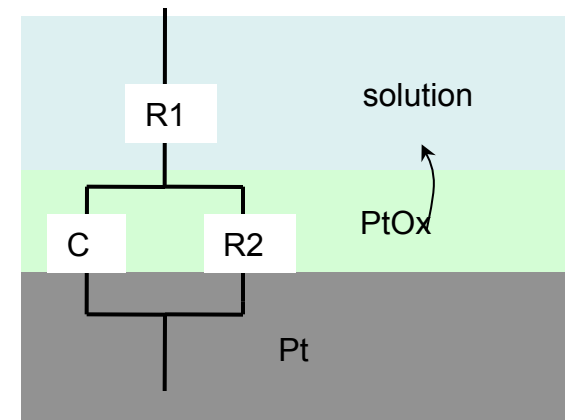




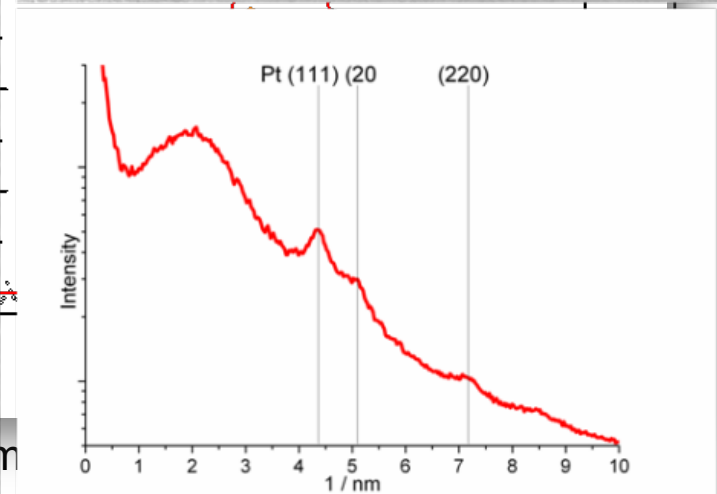
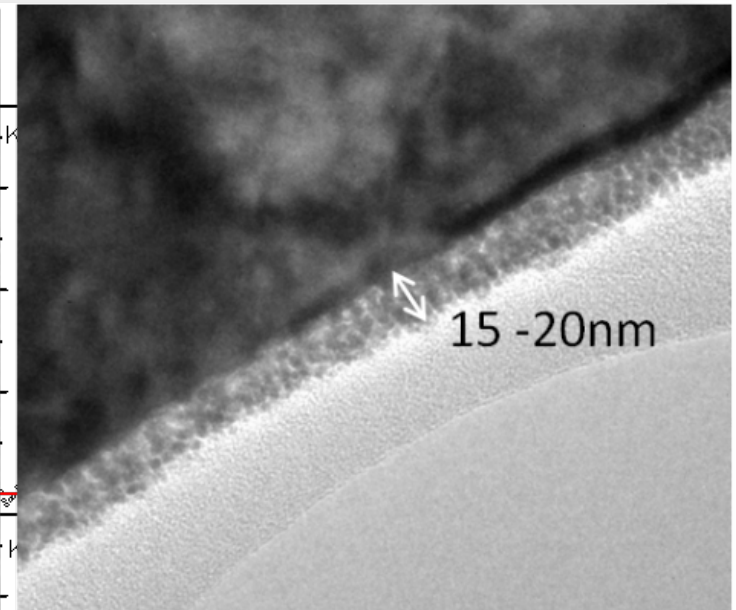
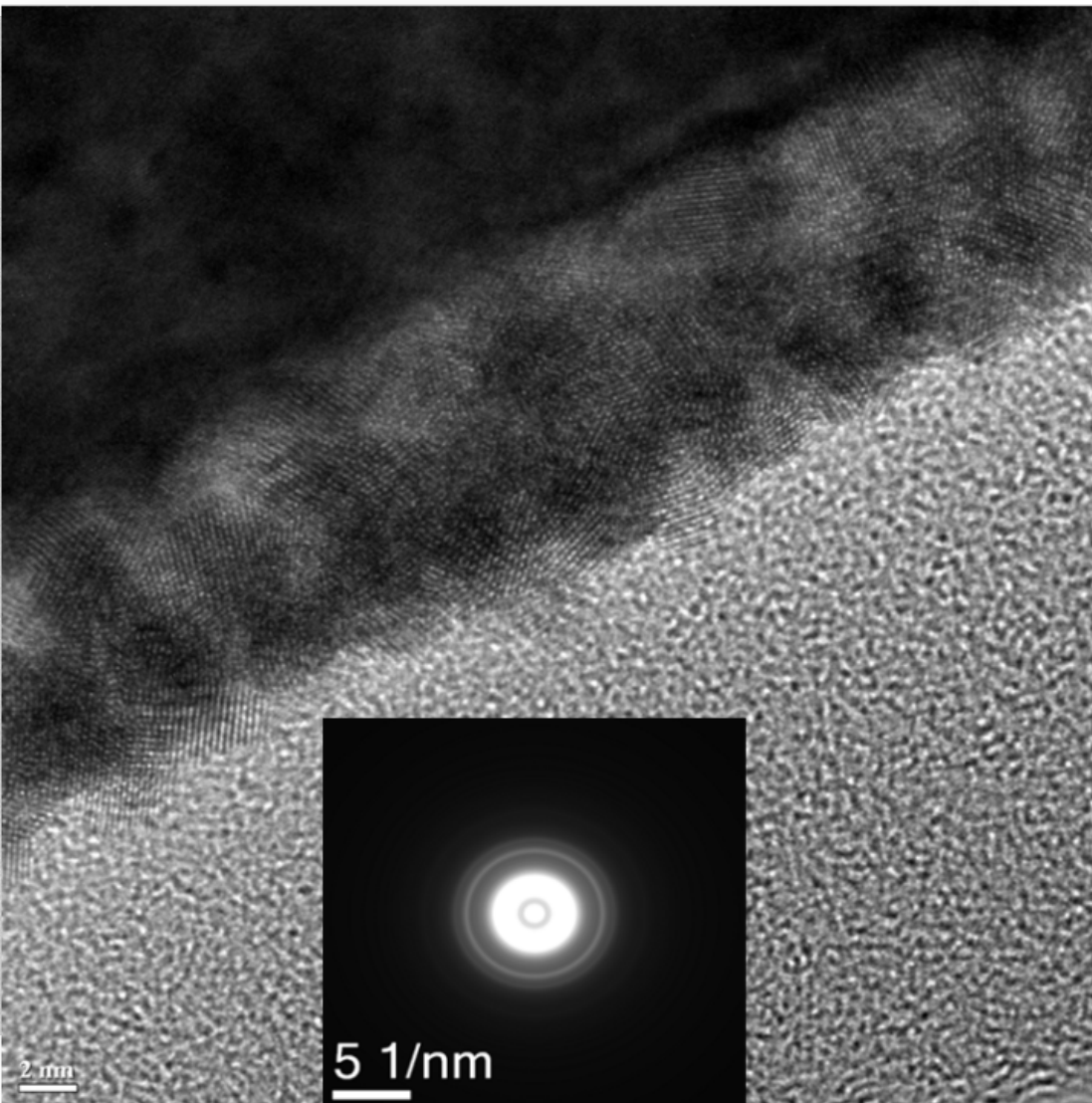
# Dynamics of Pt in OER



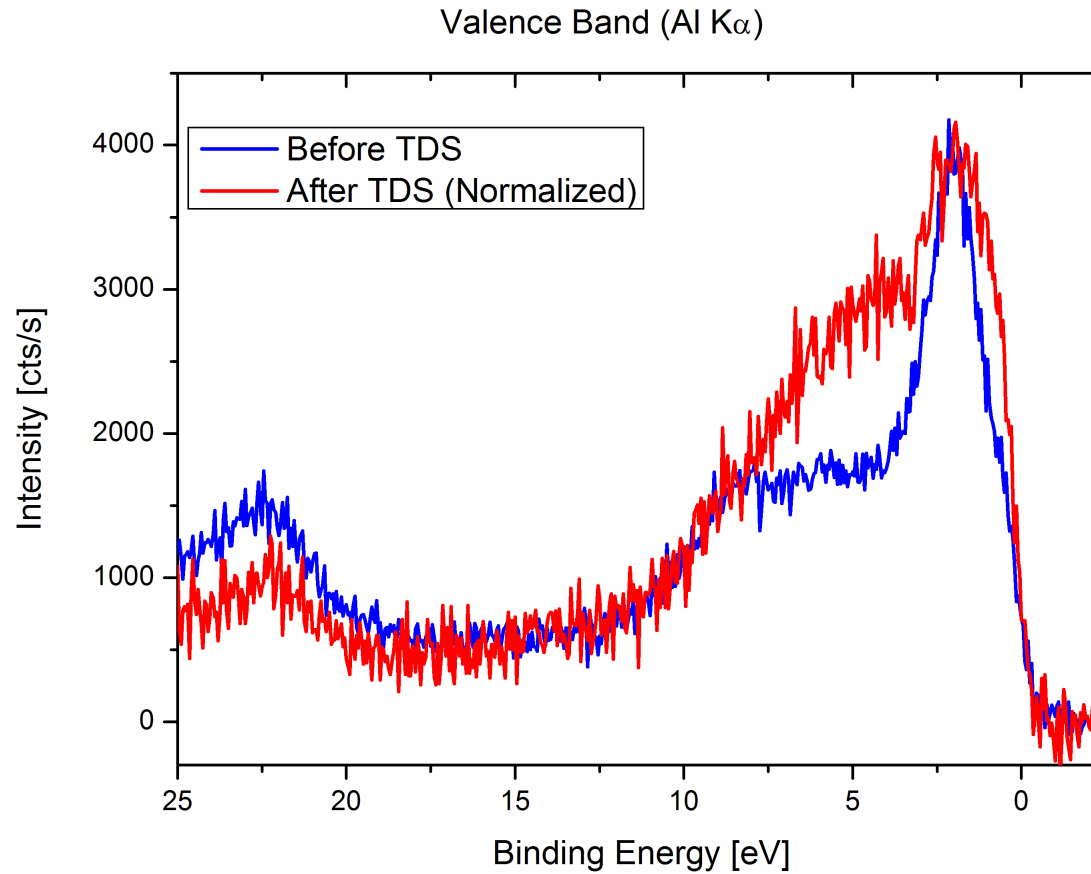
2	1-Set	21-set
	1.68	1.69
	51	48.9
	<b>2901</b>	<b>5 151</b>



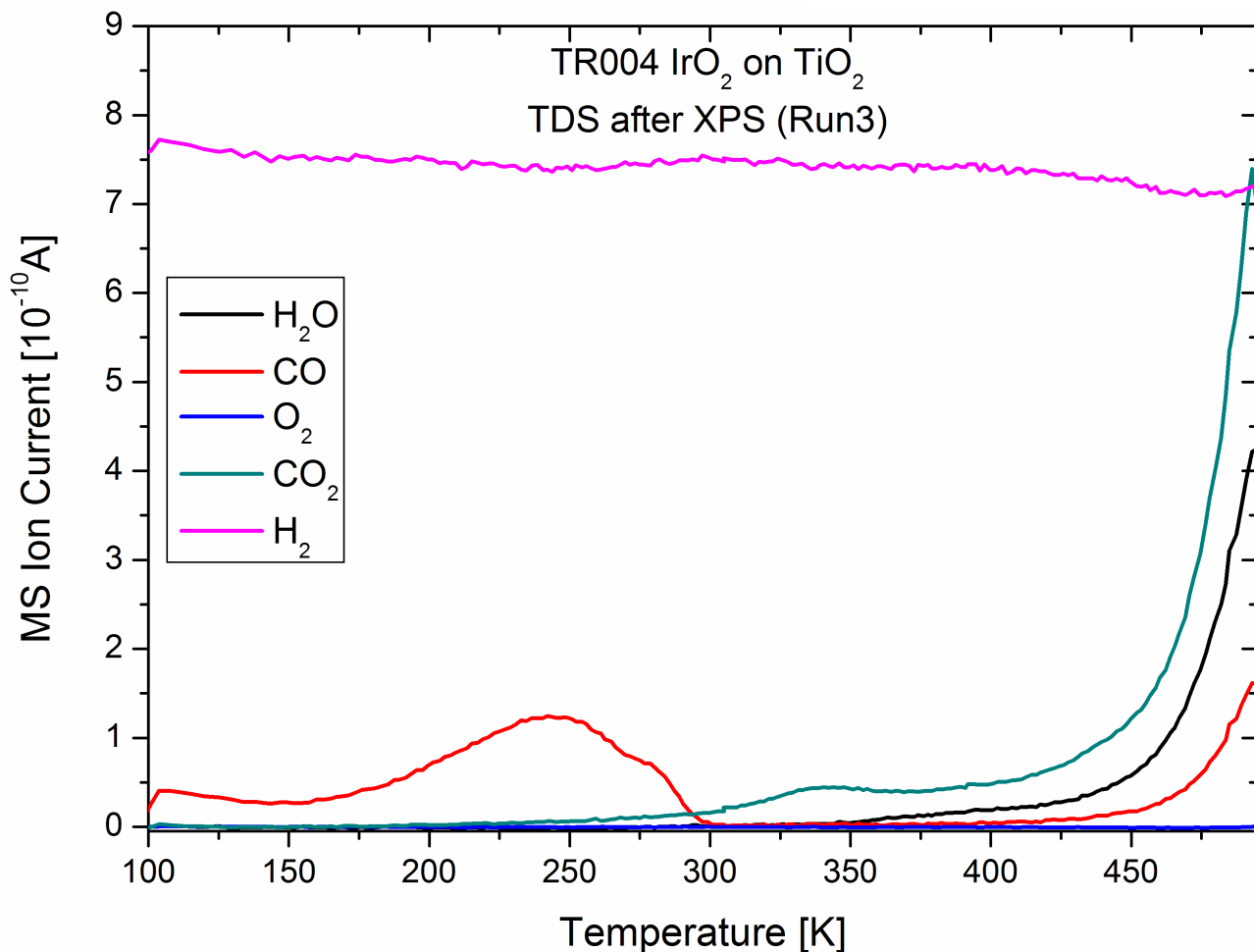
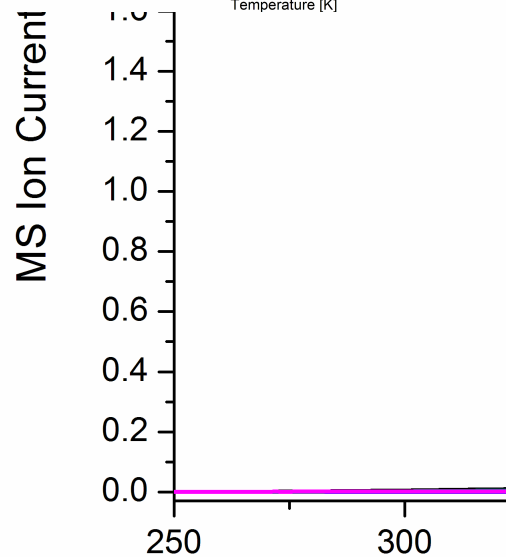
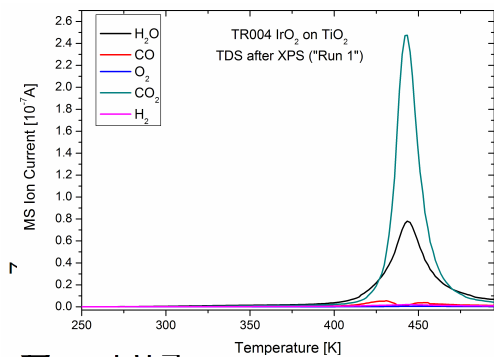
# Nature of the Pt rust



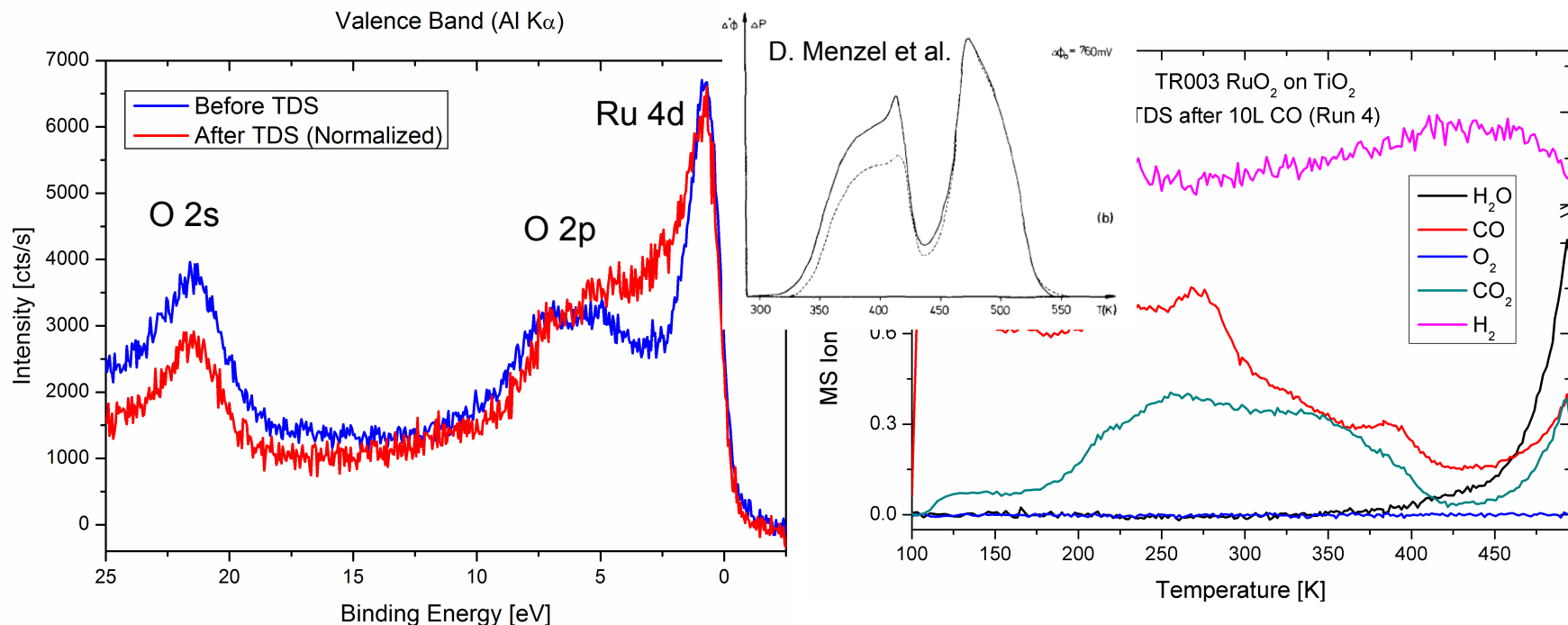
# IrOx: electronic structure



# IrOx: TDS



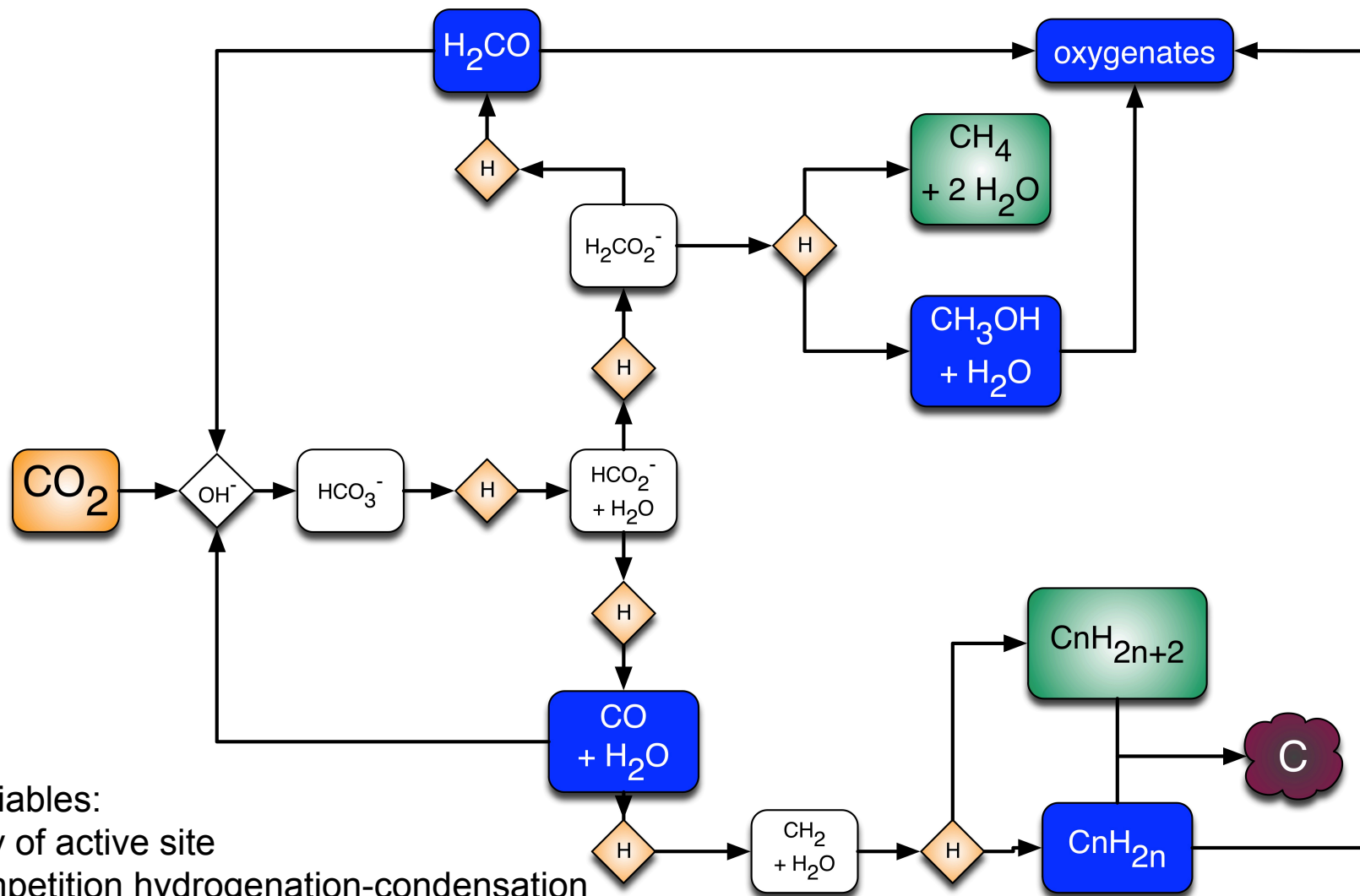
# Properties of RuO<sub>x</sub> electrodes: a challenge for characterization



The electrode is a conducting oxide.  
CO TDS up to 550 K causes reduction: no RuO<sub>2</sub>, suboxide

Equilibrated CO TDS senses oxidic sites with traces of metallic sites: suboxide

- 
- Pt is not the best of all materials but conclusions hold also for Ru and Ir systems.
  - In OER dimensional instability for large surfaces unavoidable.
  - Complex reaction sequence from sub-surface oxide, to divalent and at high load tetravalent species with a large number of coordinated water:
  - Product is a hydrated oxide mix “metal black”.
  - Metastable with respect to re-formation of metal NP at open circuit conditions.
  - Storage of peroxo-compounds in hydrated oxide.



Control variables:

Oxophilicity of active site

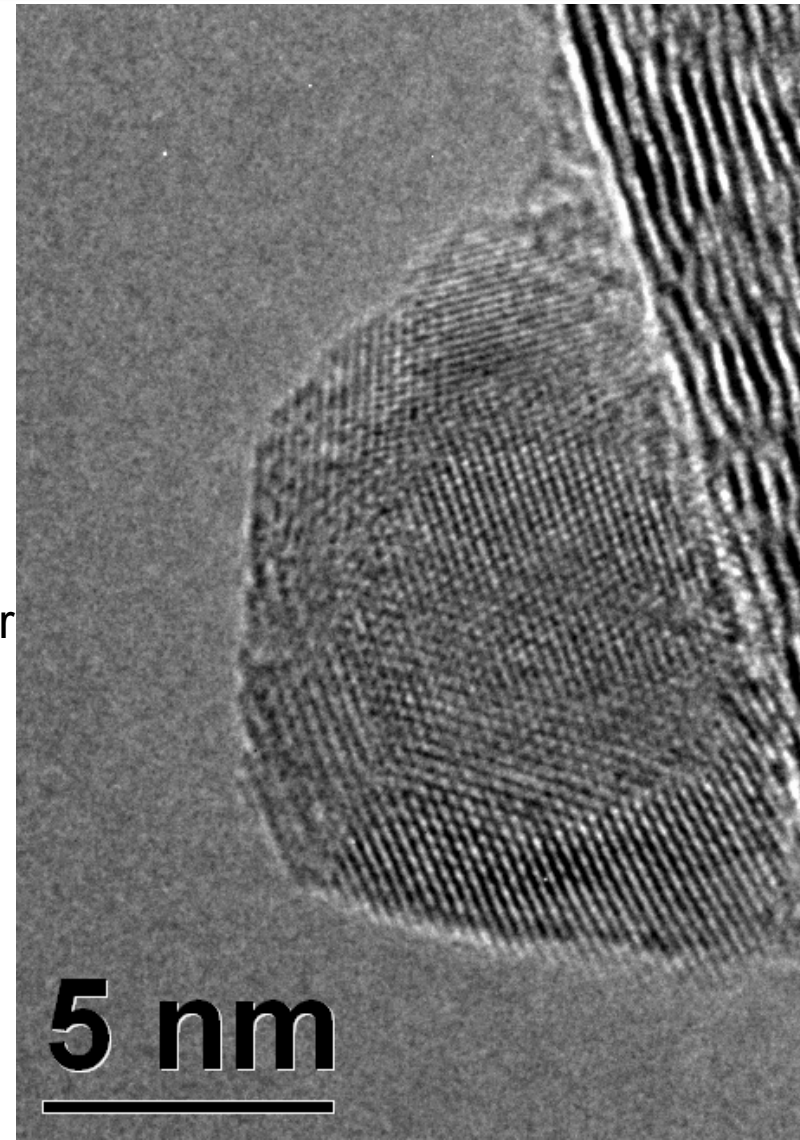
Kinetic competition hydrogenation-condensation



Deposition of carbon limits catalyst performance: loss of active phase through CNT formation.

Technical solution: operate under highly dilute conditions: stable but low productivity.

Protection through carbide formation: labile under reaction conditions: catalyst design allowing for facile carbon dissolution.

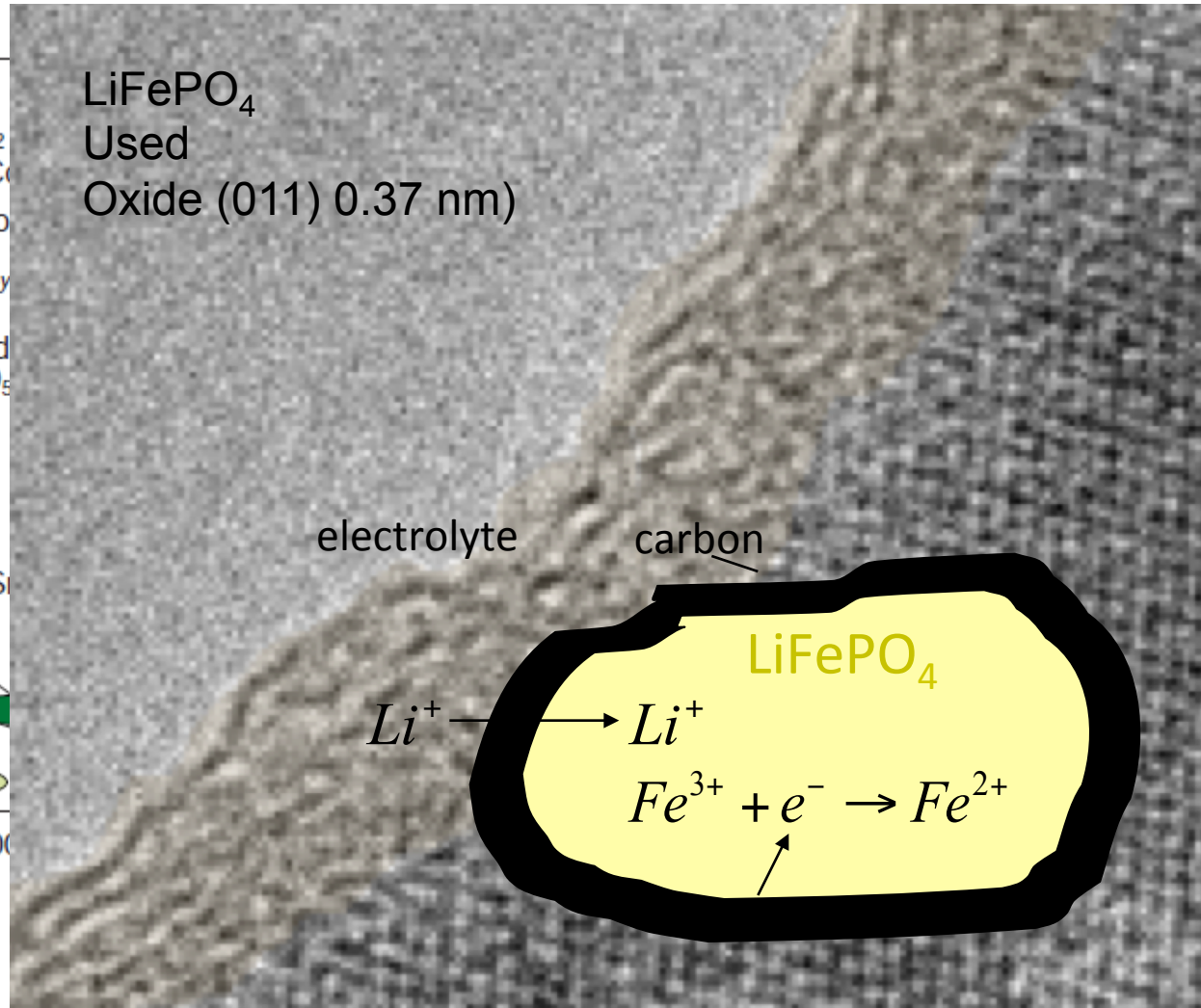
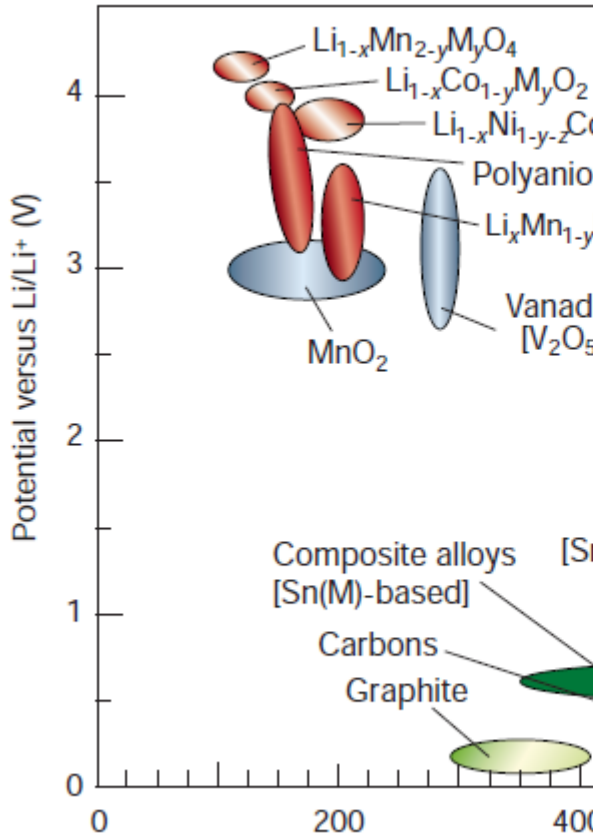




# Operational reality: Dynamics of catalysts Ni under hydrogenation conditions

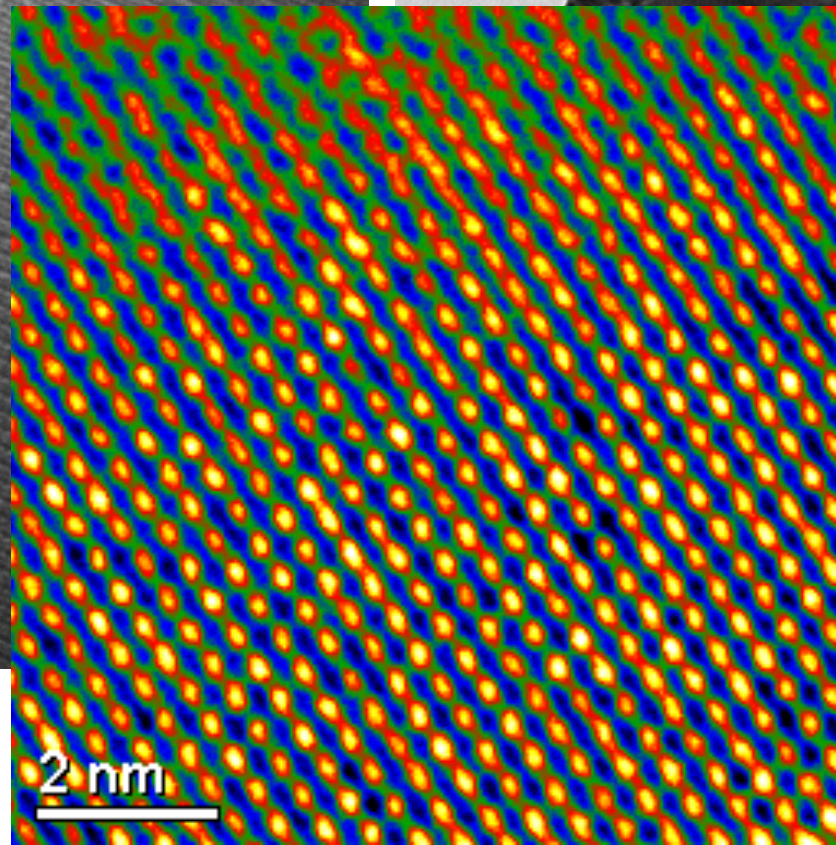
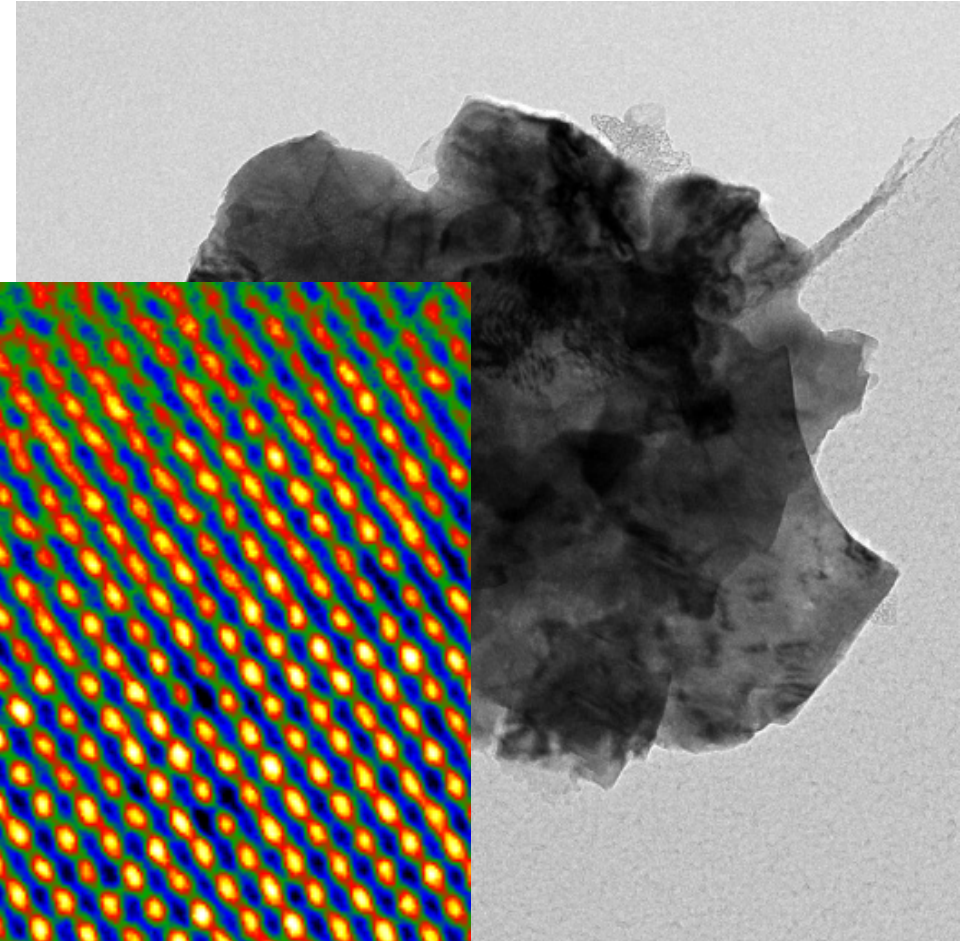
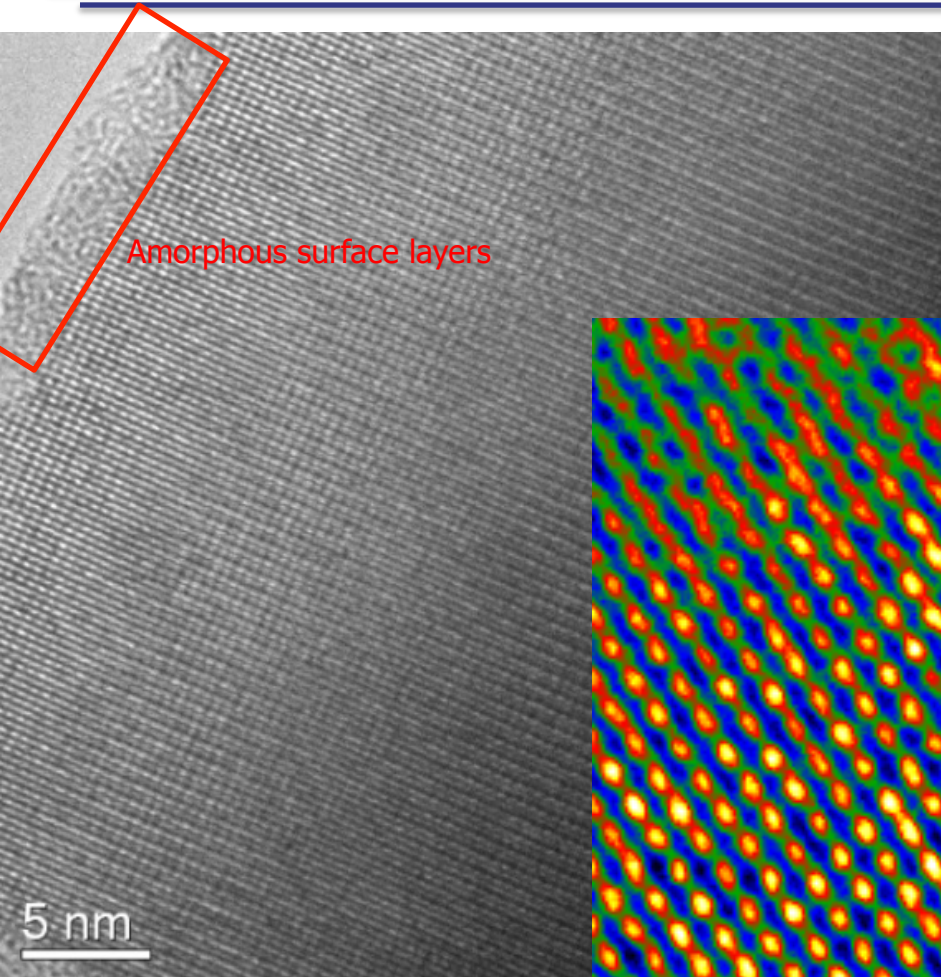


# Batteries: an important component of new energy systems

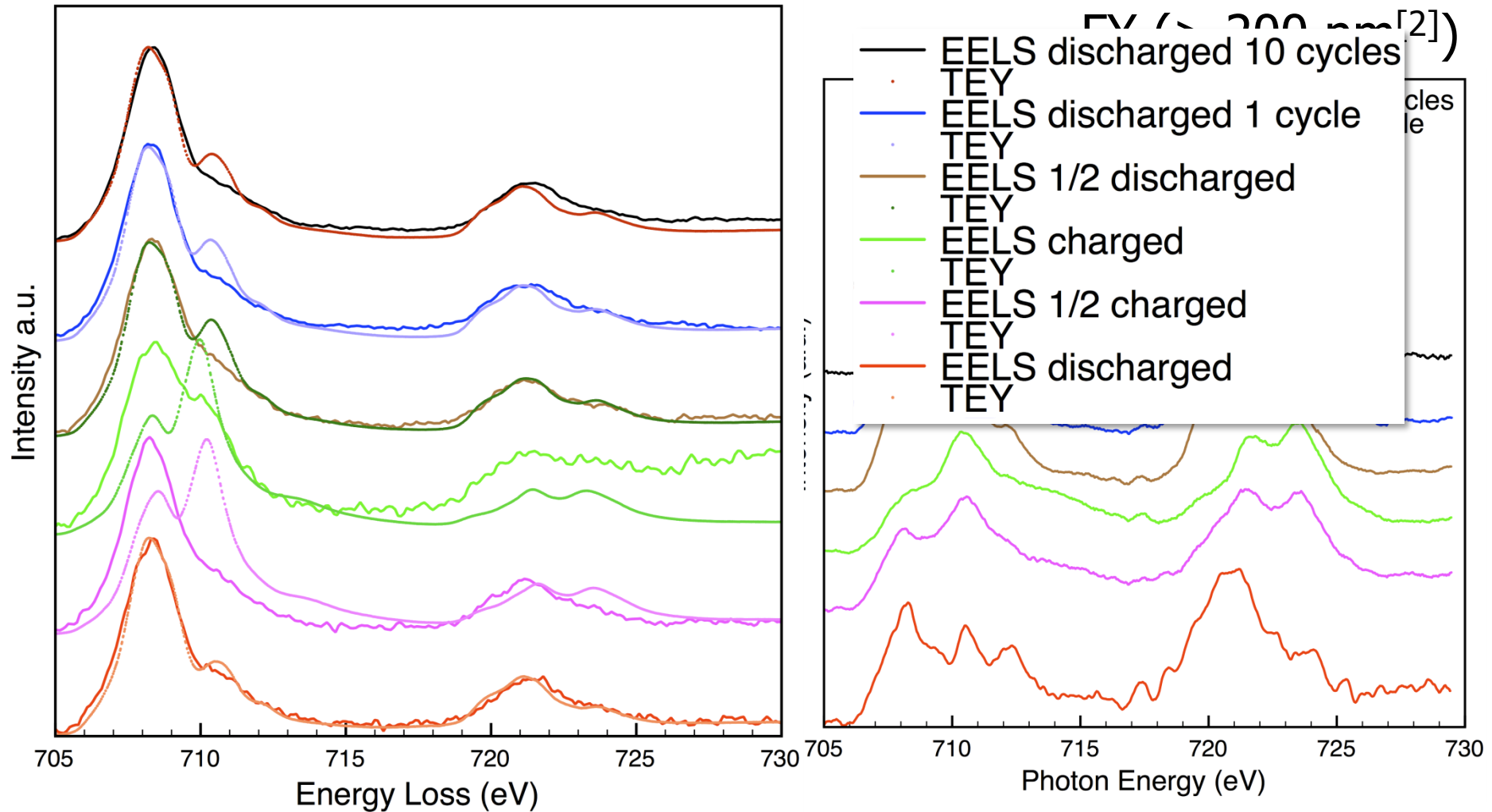




# Where is what type of Li ? Structure



# Where is what type of Li ? Spectroscopy



[1] A. Krol, et al. *Phys. Rev. B: Condens. Matter*, 1990, 42, 2635.

[2] B. L. Henke et al., *At. Data Nucl. Data Tables*, 1993, 54, 181–342.

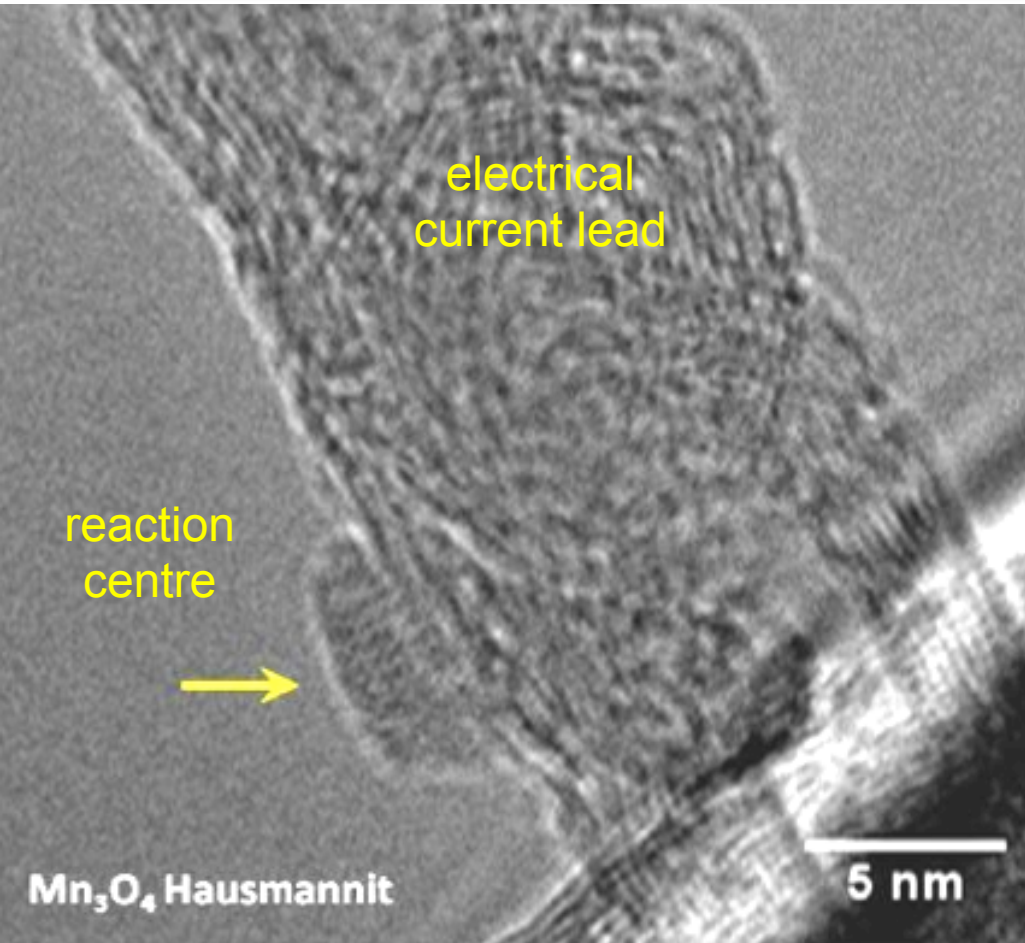
- A severe material problem limits the performance of Li batteries (accumulators).
- Charge storage highly inhomogeneous in oxides such as iron- or cobaltates: is the bulk needed?
- Charge storage mechanism unclear: no evidence for Li ions by spectroscopy.
- No clean host-guest separation such as in Li graphite.
- Synthesis of homogeneous interfaces critical (also for Li air battery).

## To take home

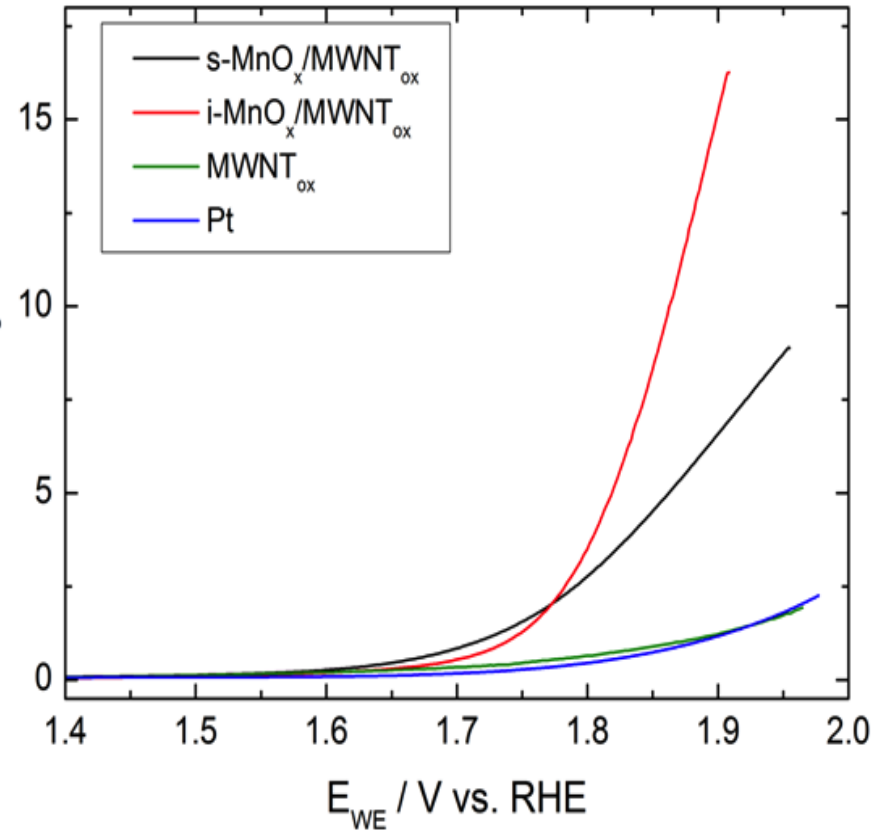
- Catalytic reactions are networks being activated by a catalyst in several routes simultaneously.
- Performing catalytic surfaces are dynamical in structure and composition.
- They react with reagents and form active phases not initially present.
- Nanostructuring allows rapid equilibration to the local chemical potential.
- Beware of directly correlating high performance data with those from extended model surfaces.



# Non-noble metal electrolysis: practice the conclusions



0 100 200 300 400 500 600  
Temperature / °C



Nano-  $Mn_2O_3$  made electrically contacted  
by functionalized CNT

Dem Anwenden muss das Erkennen vorausgehen

Max Planck



Thank You



