The Abdus Salam International Centre for Theoretical Physics

United Nations Educational, Scientific and Cultural Organization

IAEA International Atomic Energy Agency

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Workshop on New Materials for Renewable Energy

17 - 21 October 2011

Material challenges in electro-catalysis

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www.fhi-berlin.mpg.de

Special thanks to:

M. Behrens, R. Horn, A. Knop-Gericke, D. Su, J. Tornow, A. Trunschke, M. Willinger

unicat Unifying Concepts in Catalysis P. Strasser

The understanding of heterogeneous reactions has made fundamental progress over the last decade.

- New techniques in theory and experiment allow unravelling the complexity of real interfaces.
- Reactive systems are dynamical and couple with their environment.
- The static picture of solid surfaces or “nanoparticles” is oversimplified.
- The emerging control of solid state dynamics as key to adaptive active materials.
- Theory is capable of meeting the complexity of reacting systems.

A realistic model of a working catalyst

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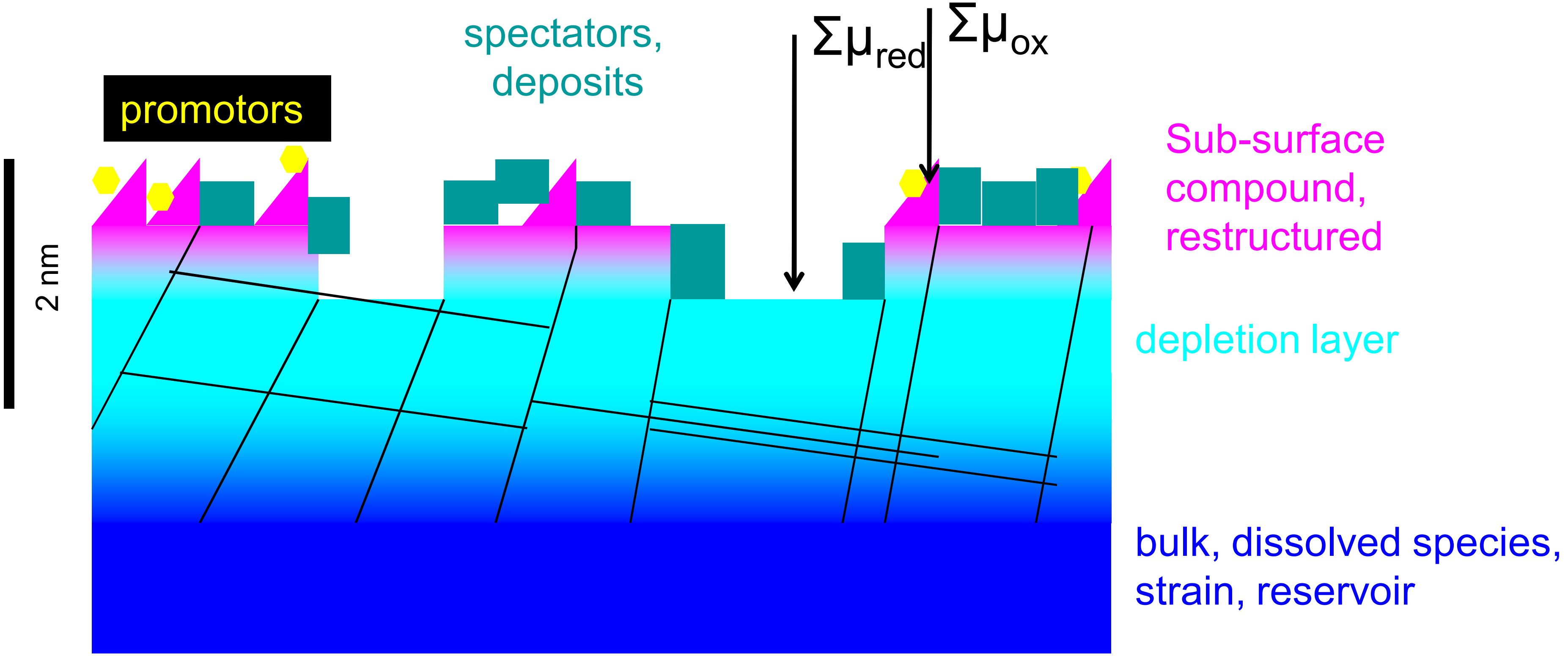


A functional material with metastable features induced by contact with its environment

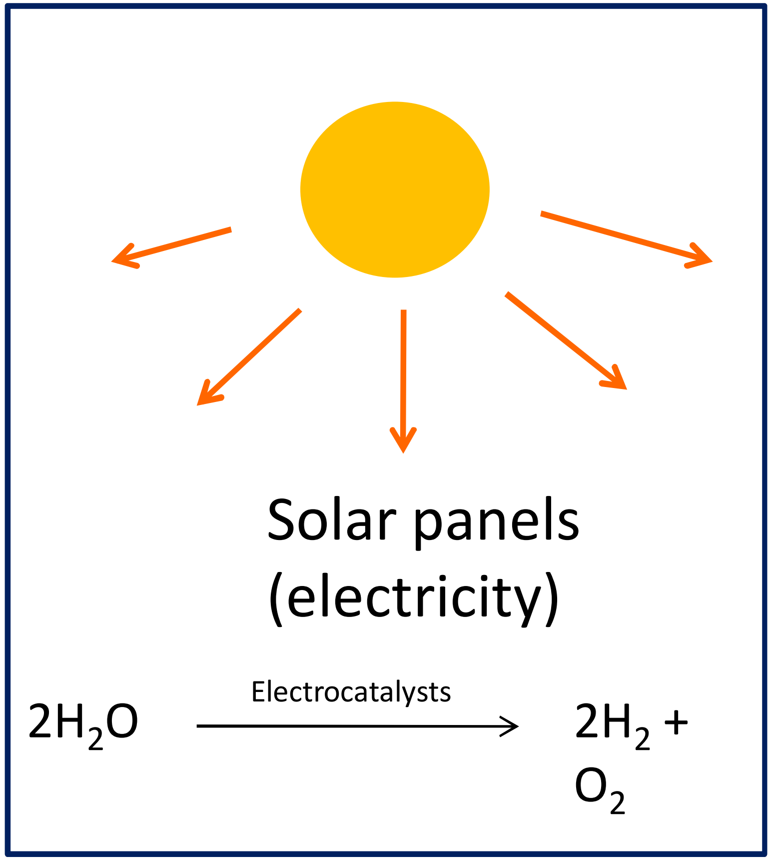
One bottleneck in energy storage: hydrogen

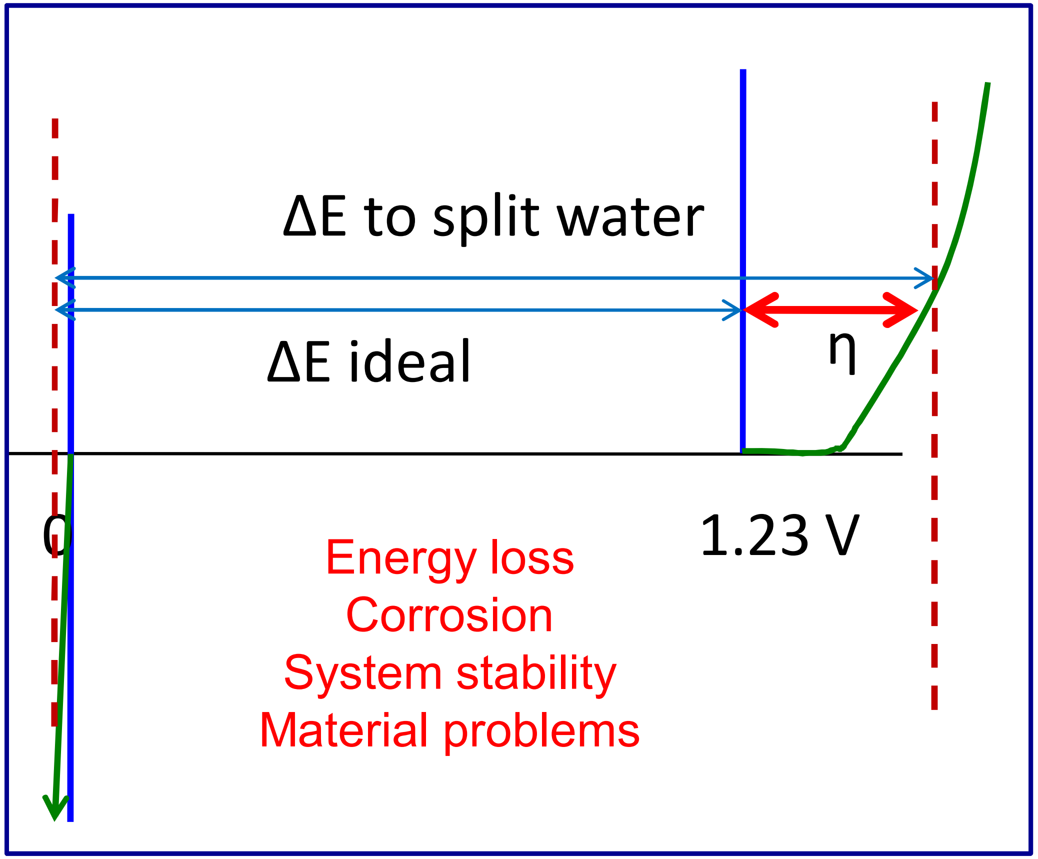
- Converting water to hydrogen and oxygen is today not possible in a technological dimension.

$$2\ H_2O \leftrightarrow 2\ H_2 + O_2$$

- Solar hydrogen as platform storage system.
- No interferences with the biosphere.
- Critical process for “solar refinery”.
- Missing basic knowledge about controlling energy barriers of the reactions of the most simple molecules.

A (not new) idea and its challenge

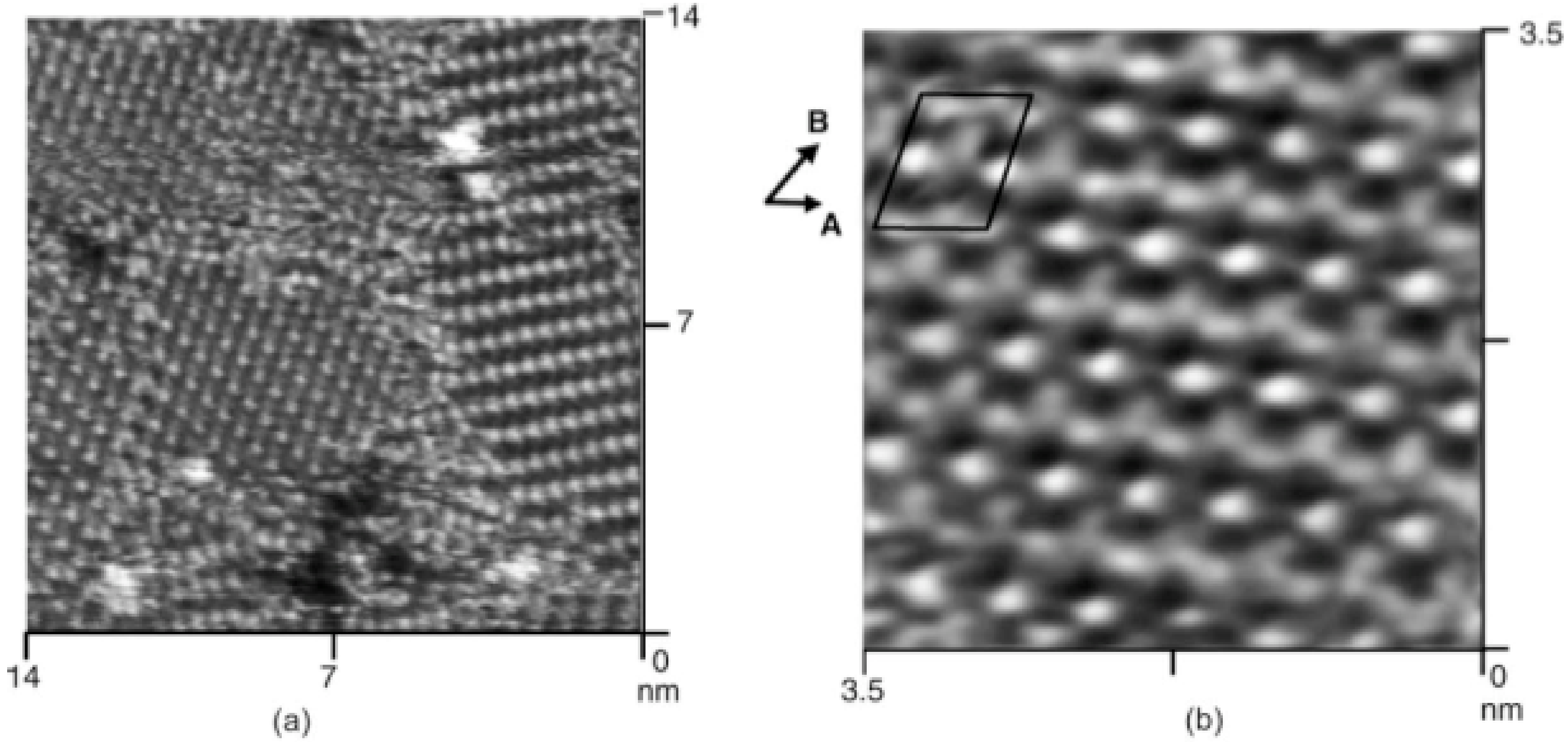




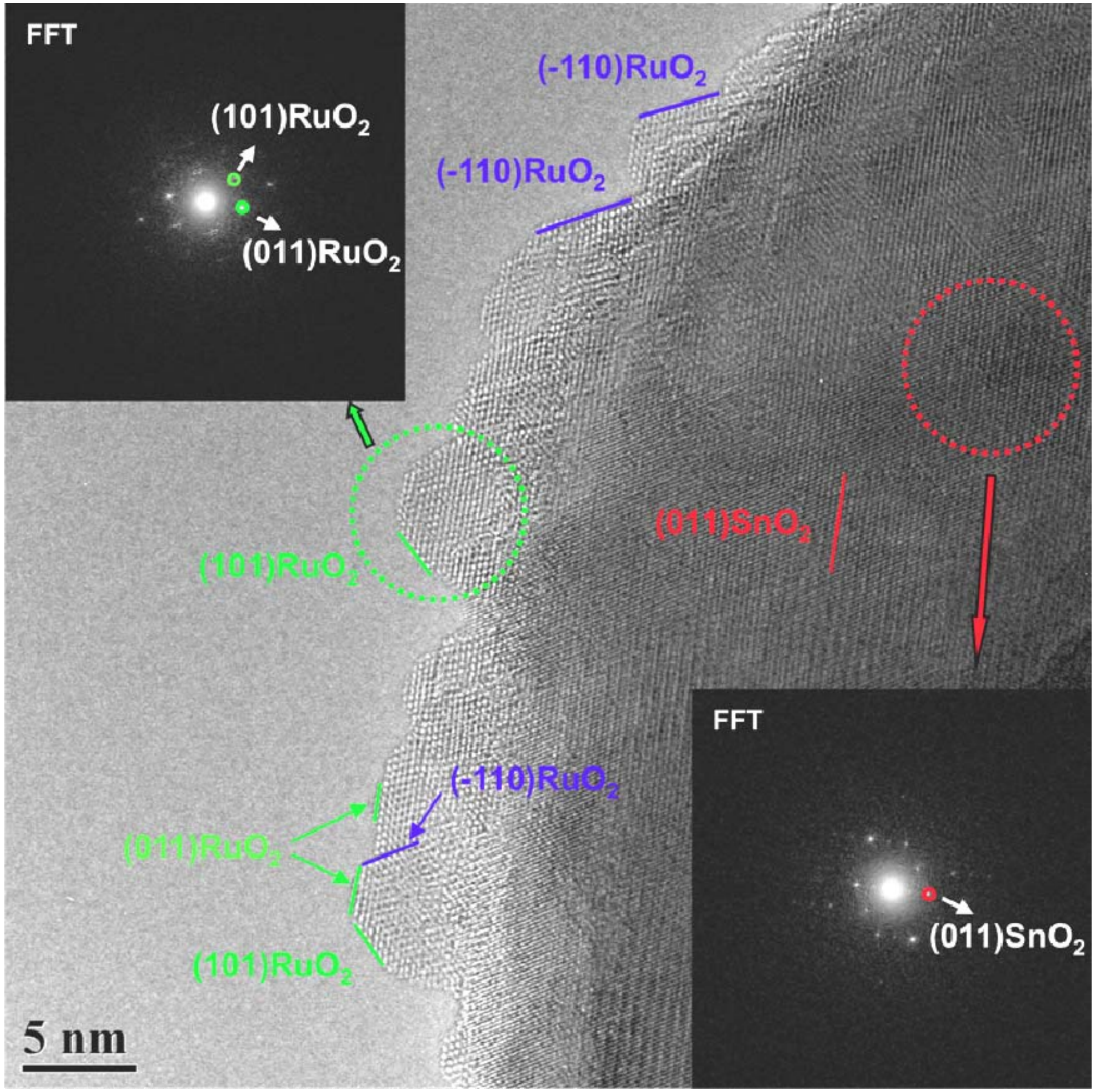
High efficiency potential (10 times that of a green leaf)
Combination with direct use of electricity

Water electrolysis: Theory and reality

M.A. Henderson / Surface Science Reports 46 (2002) 1–308



Water electrolysis: Theory and reality



Pd/CNT in H_2O_2 synthesis also a test reaction for water splitting

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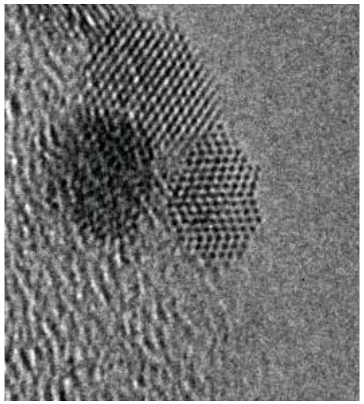
Pd nanoparticles supported on N-doped nanocarbon for the direct synthesis of H_2O_2 from H_2 and O_2

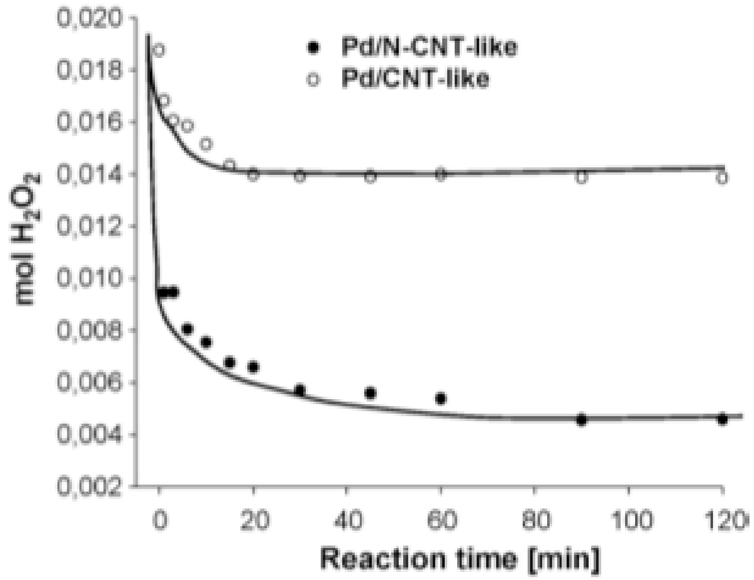
Catal. Today, 2010

S. Abate [a], R. Arrigo [b], M.E. Schuster [b], S. Perathoner [a,*], G. Centi [a], A. Villa [b], D. Su [b], R. Schlögl [b]

[a] Dipartimento di Chimica Industriale ed Ingegneria dei Materiali (INSTM, UdR Messina, CASPE), University of Messina, Salita Sperone 31, 98166 Messina, Italy
[b] Department of Inorganic Chemistry, Fritz-Haber Institut der Max Planck Gesellschaft, Berlin, Germany

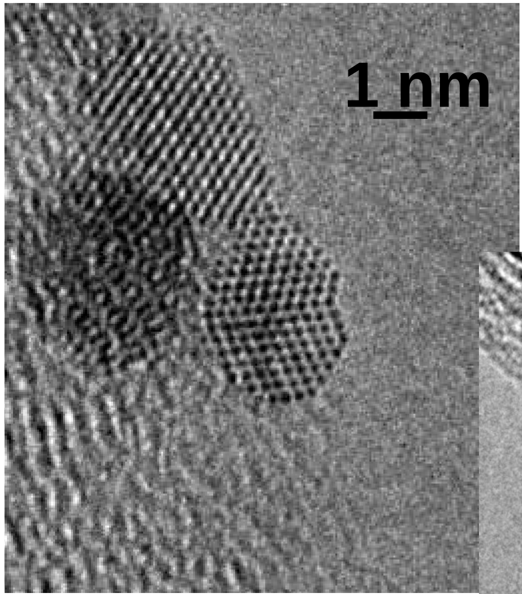
Catalyst	Mol $H_2O_2/(kg_{cat}\,h)$	Selectivity H_2O_2, %
0.9% Pd/N-CNT-like	128	45
0.9% Pd/CNT-like	98	35
3% Pd/C	112	43
2.5% Pd/C	42	–
2.5% Au/2.5% Pd/C	110	–
1.5% Pd on sulphonic acid polystyrene resins	70	77
0.6% Pd/carbon black	49	99
2.4% Pd/0.1% Au/Al_2O_3	12	–
0.9% Pd/0.1% Pt/carbon	8	83

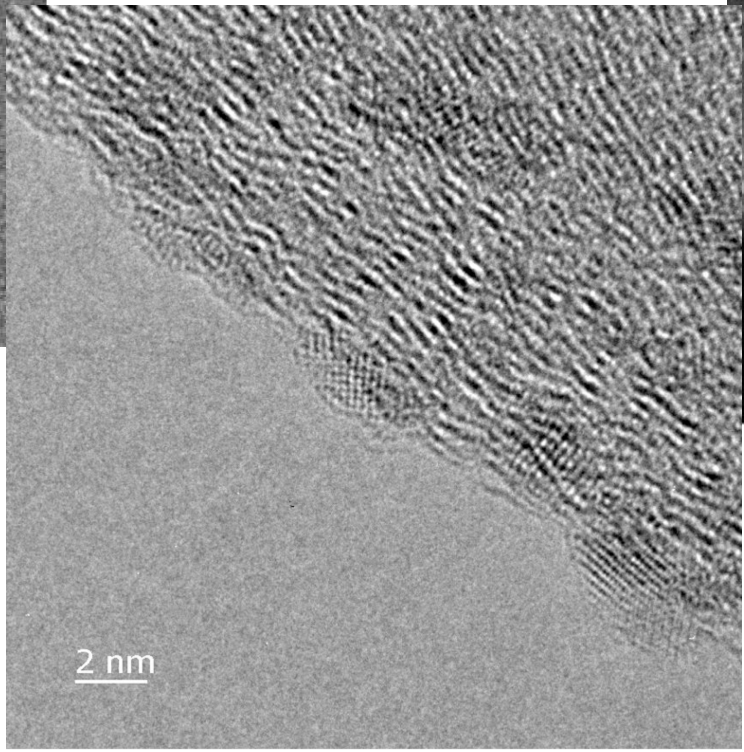


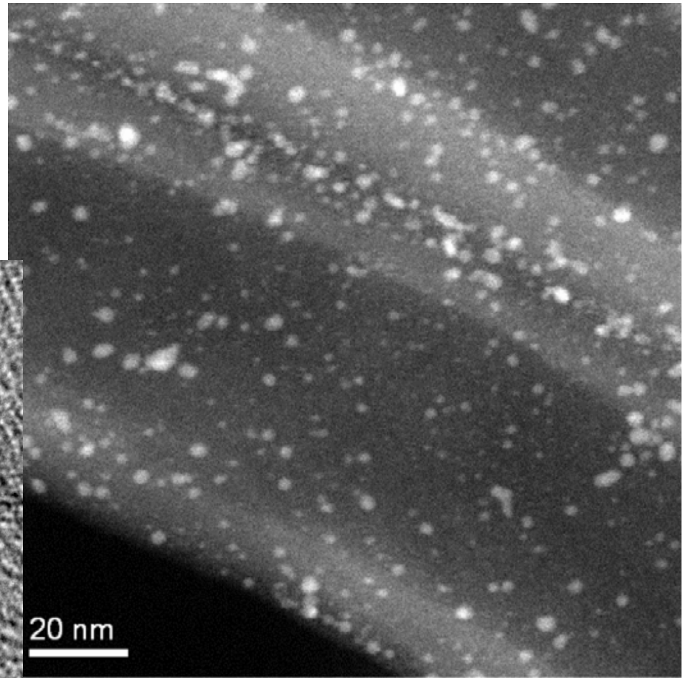


Principle of microscopic reversibility: control by chemical potential

Pd/CNT in H_2O_2 synthesis also a test reaction for water splitting

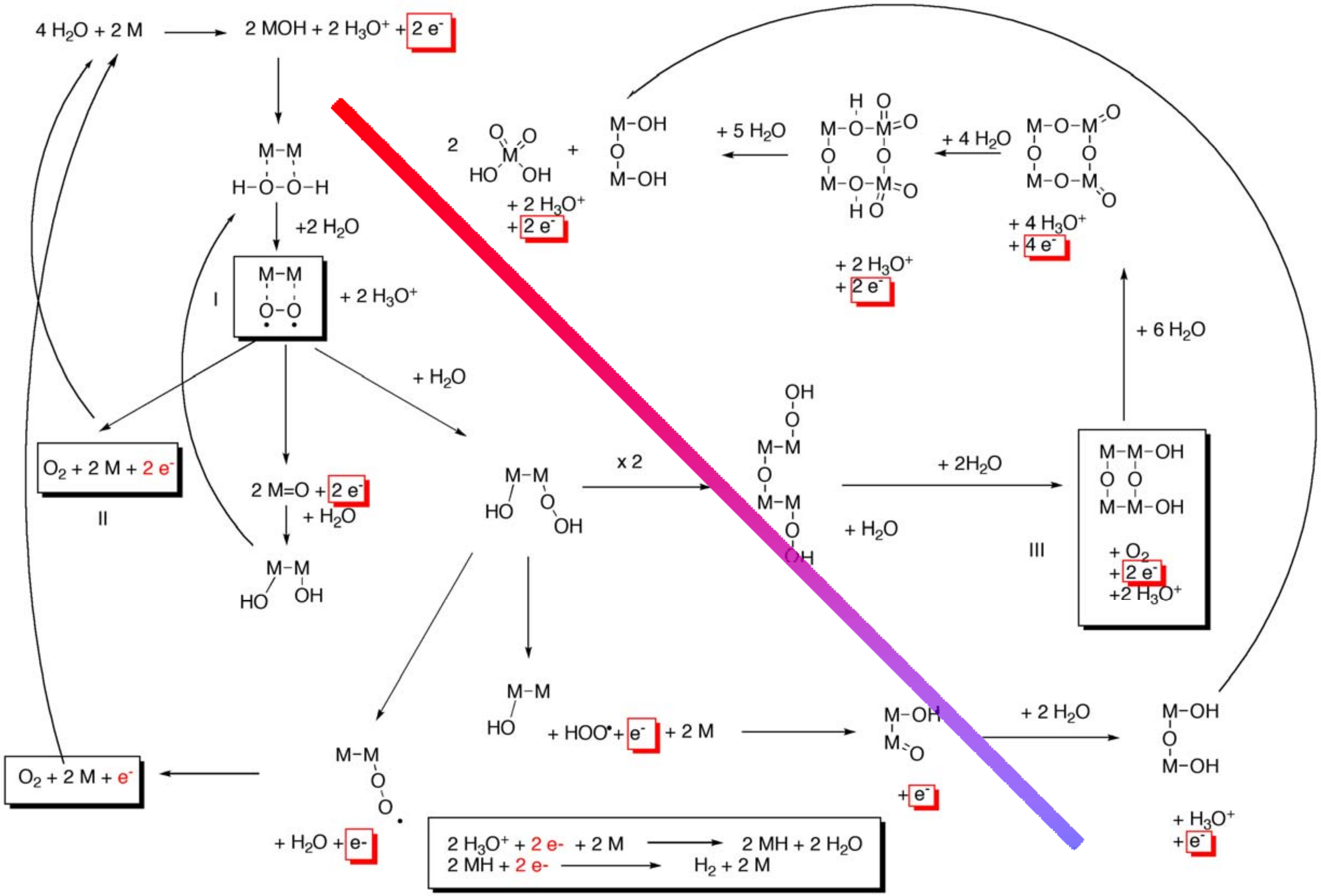




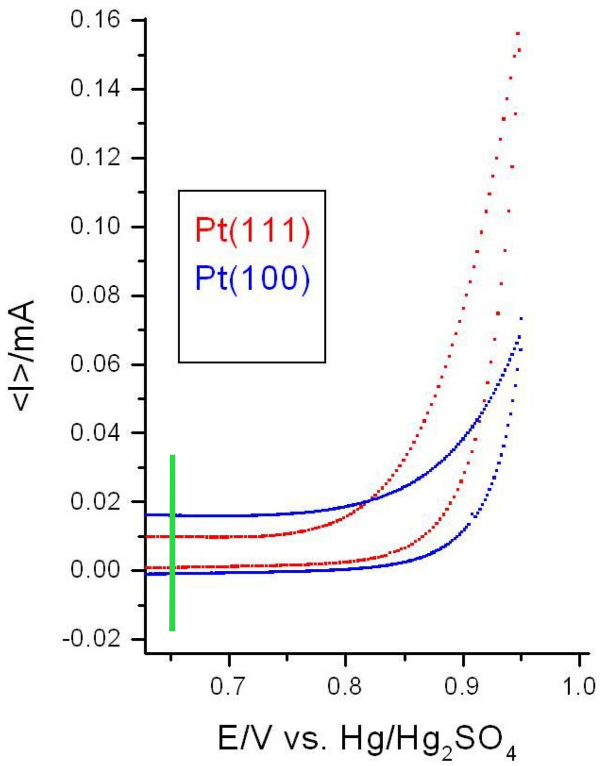


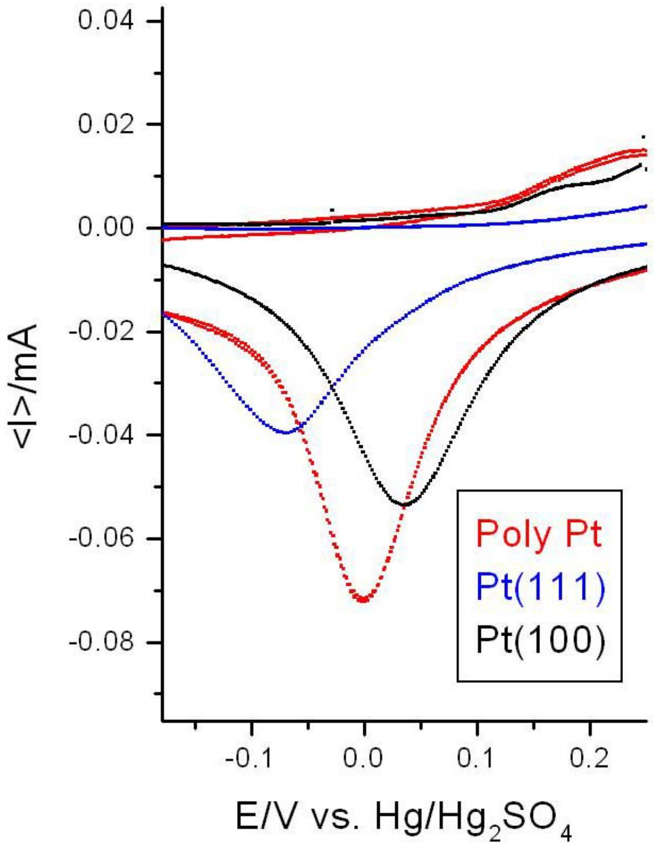
Principle of microscopic reversibility: control by chemical potential

A scenario for a simple reaction: "OER" electron flow not characteristic



“Reality” over Pt





Rusting of Pt on its way to oxygen evolution

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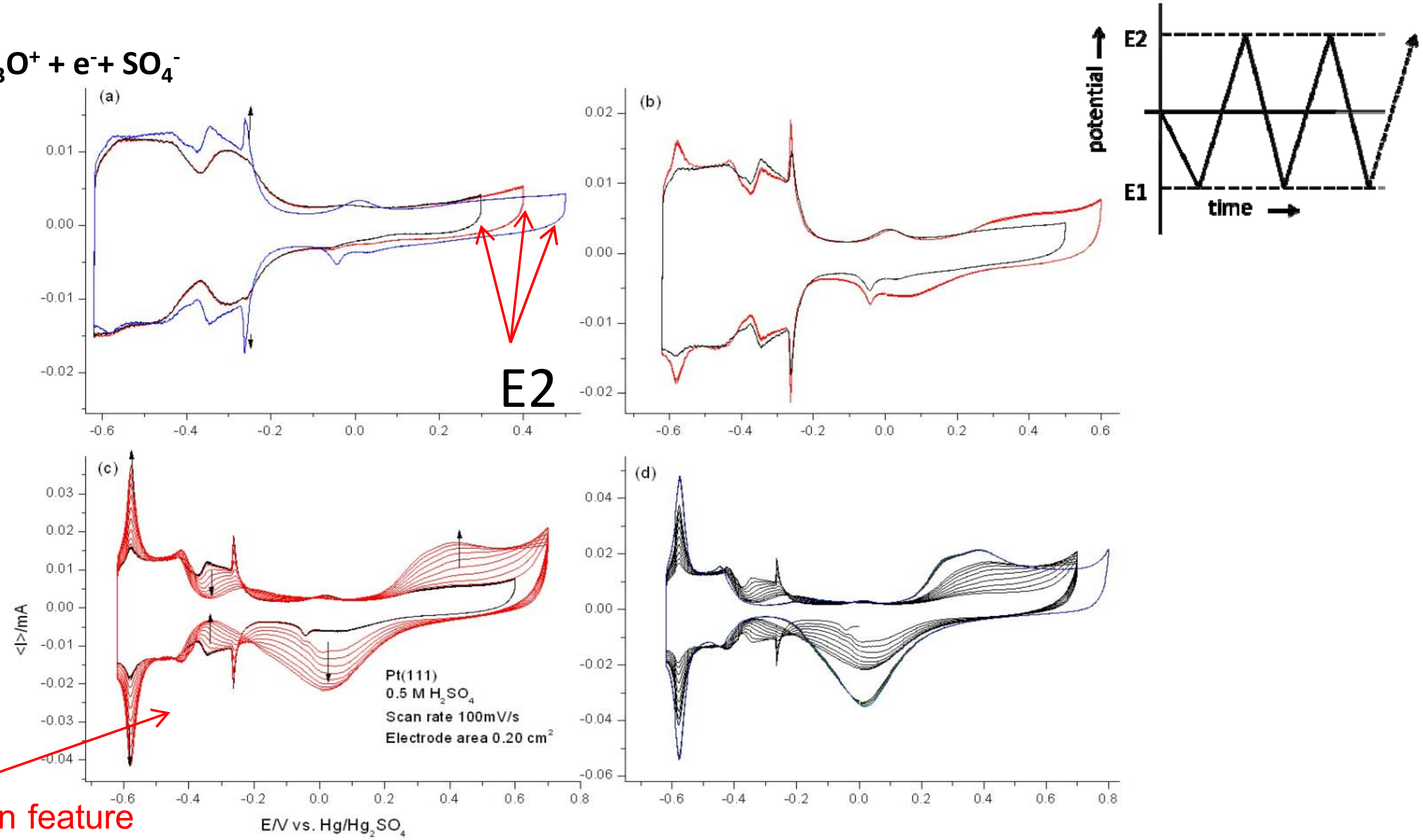
$H_2O + HSO_4^- \rightarrow H_3O^+ + e^- + SO_4^-$



Anion adsorption feature breaks down at E2 = 0.7V

The evolution of Pt(111) CV as the E2 is varied from 0.3V to 0.8V slowly in 0.5M H_2SO_4

Dynamics of Pt in OER

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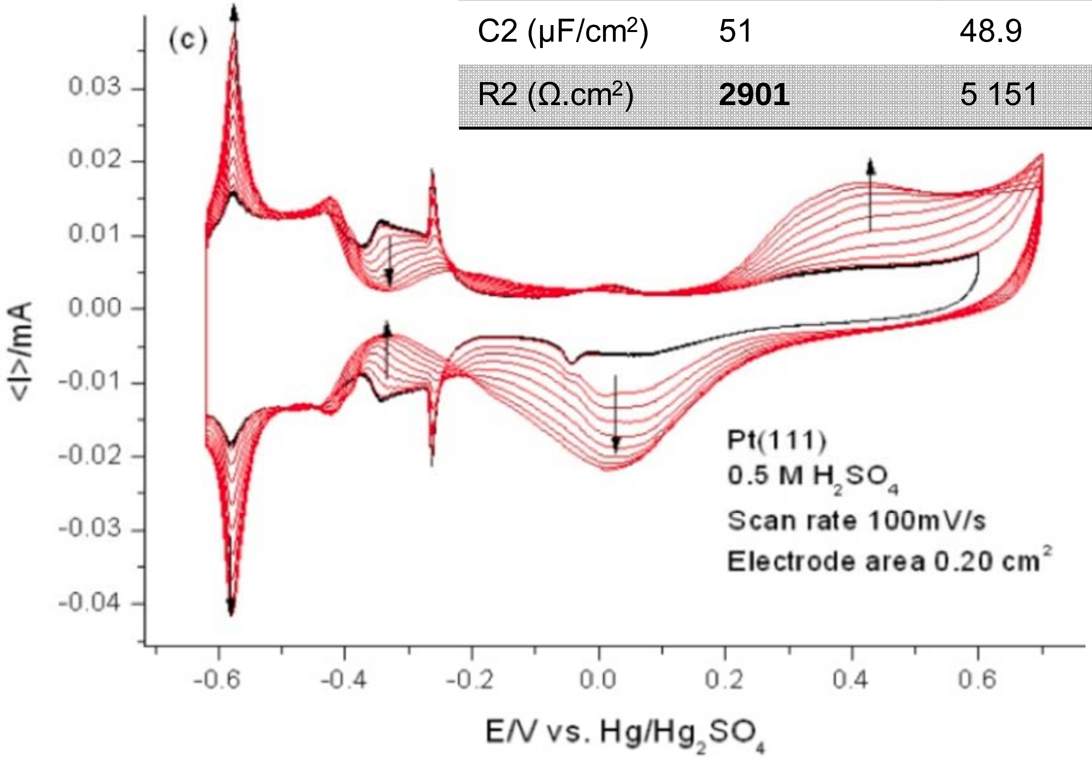
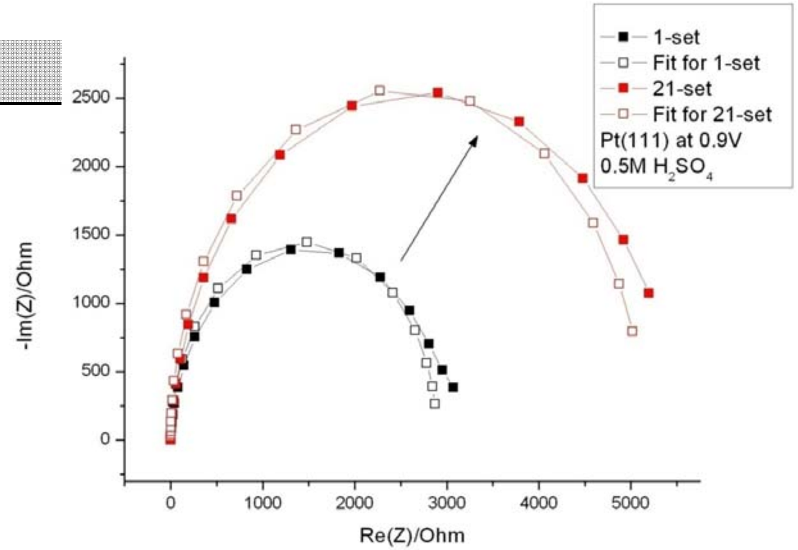
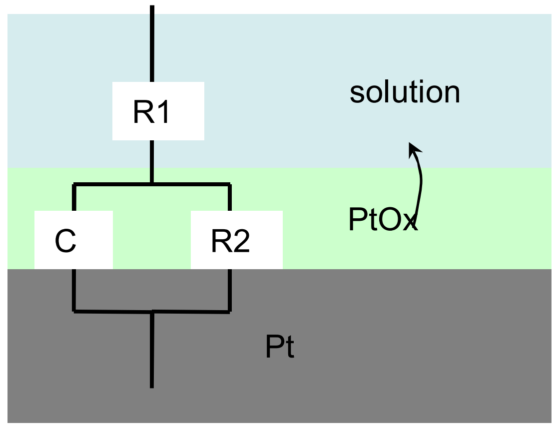
R1+C2/R2	1-Set	21-set
R1 ($\Omega.cm^2$)	1.68	1.69
C2 ($\mu F/cm^2$)	51	48.9
R2 ($\Omega.cm^2$)	**2901**	5 151







Irreversible roughening
Enhanced hydrogen production
Oxidic overlayer pre-requisite for OER

Excursion: about in-situ environments

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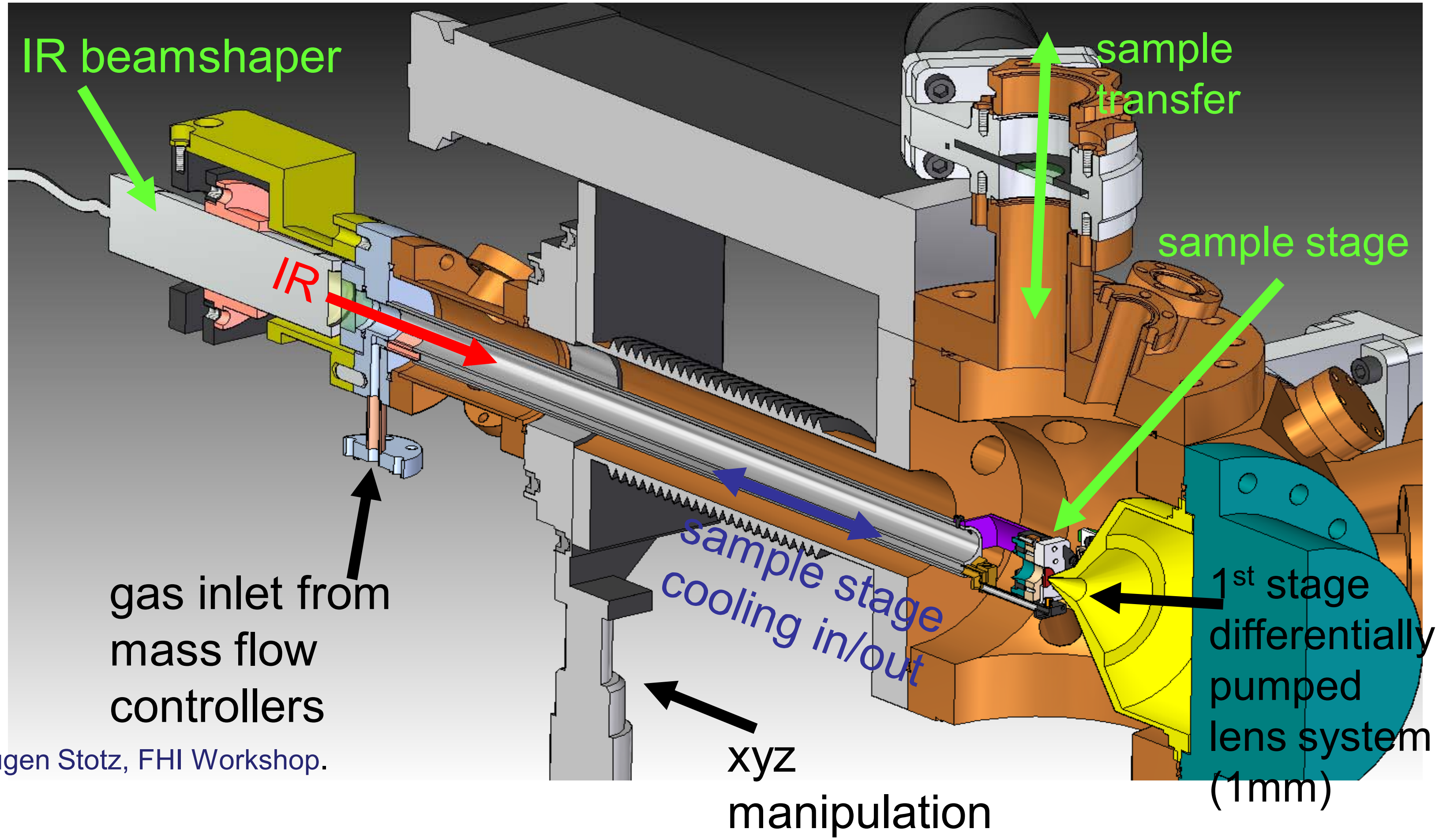
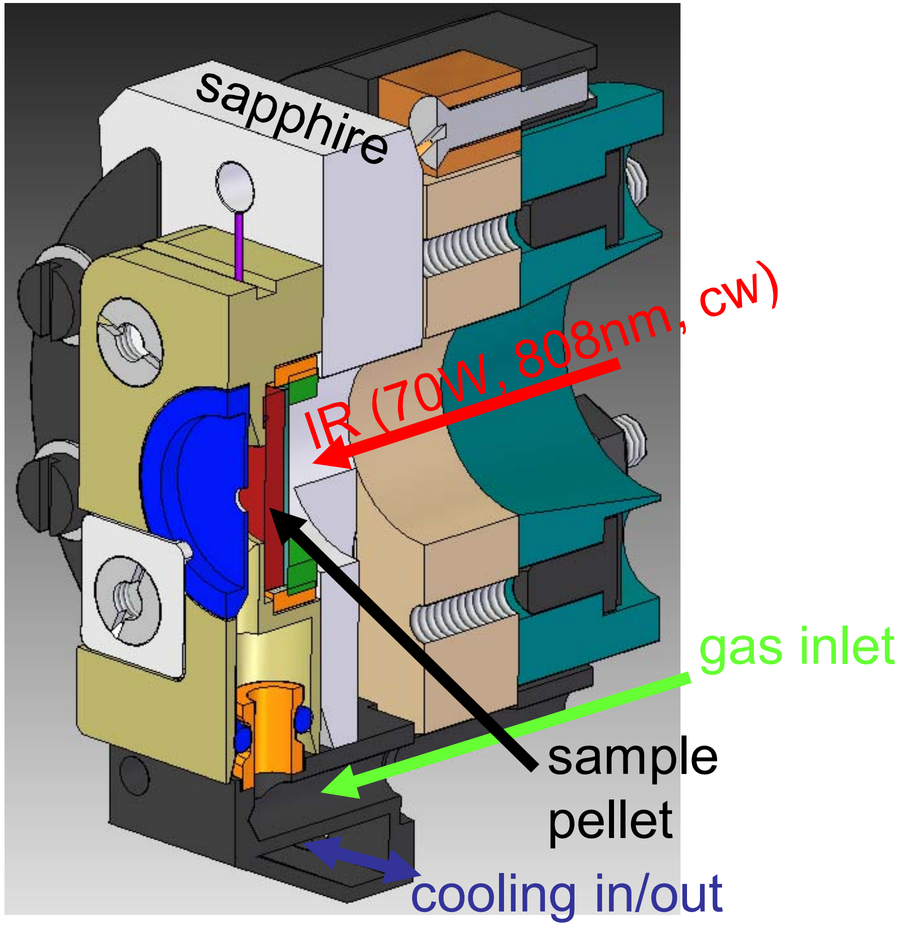


Eugen Stotz, FHI Workshop.

Excursion: about in-situ environments



Rusting platinum

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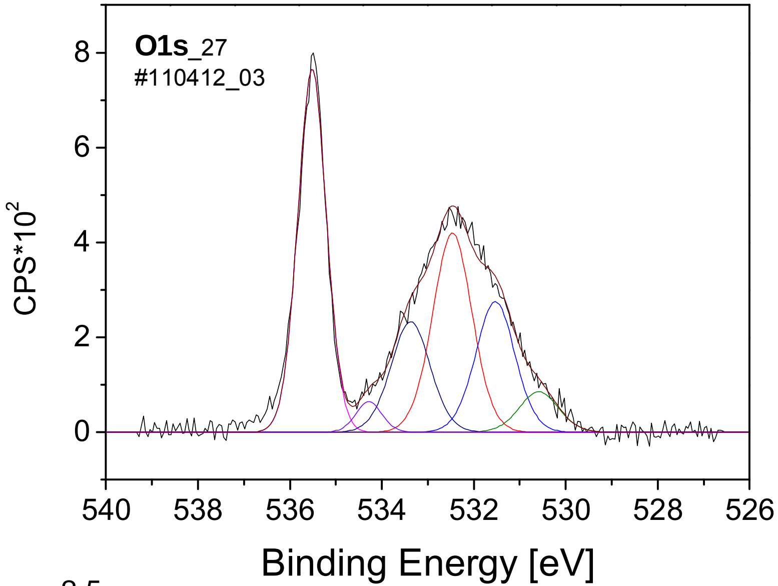
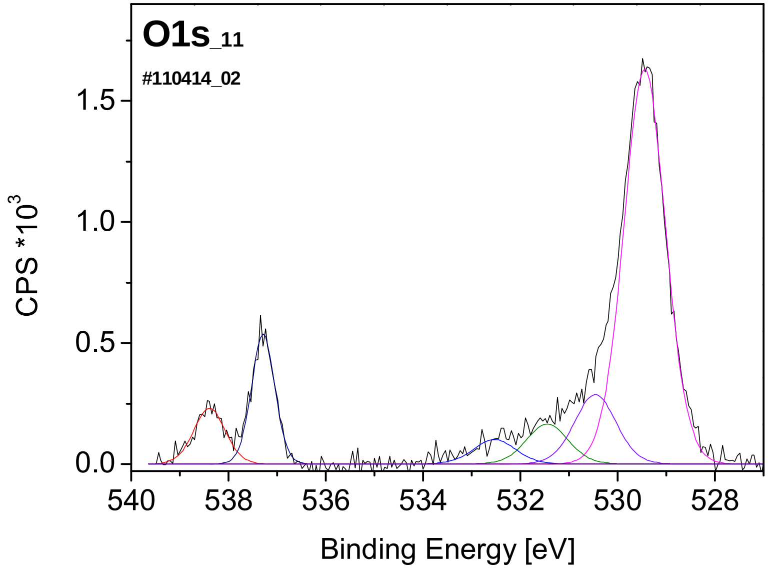
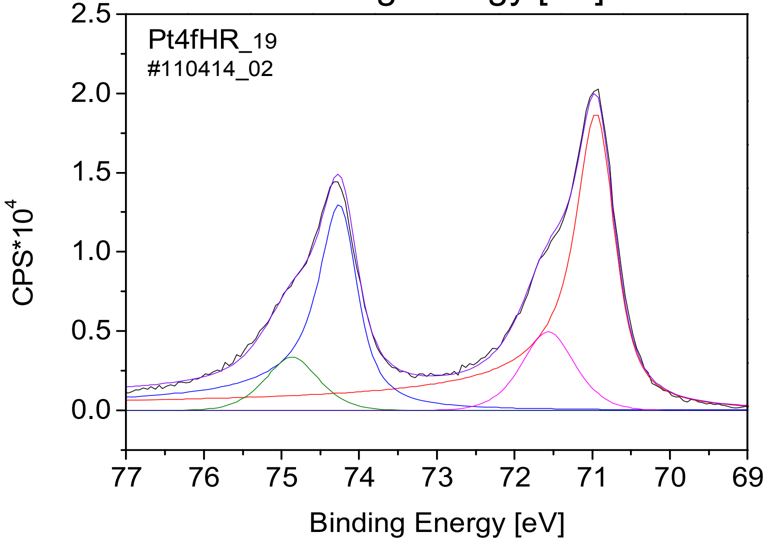
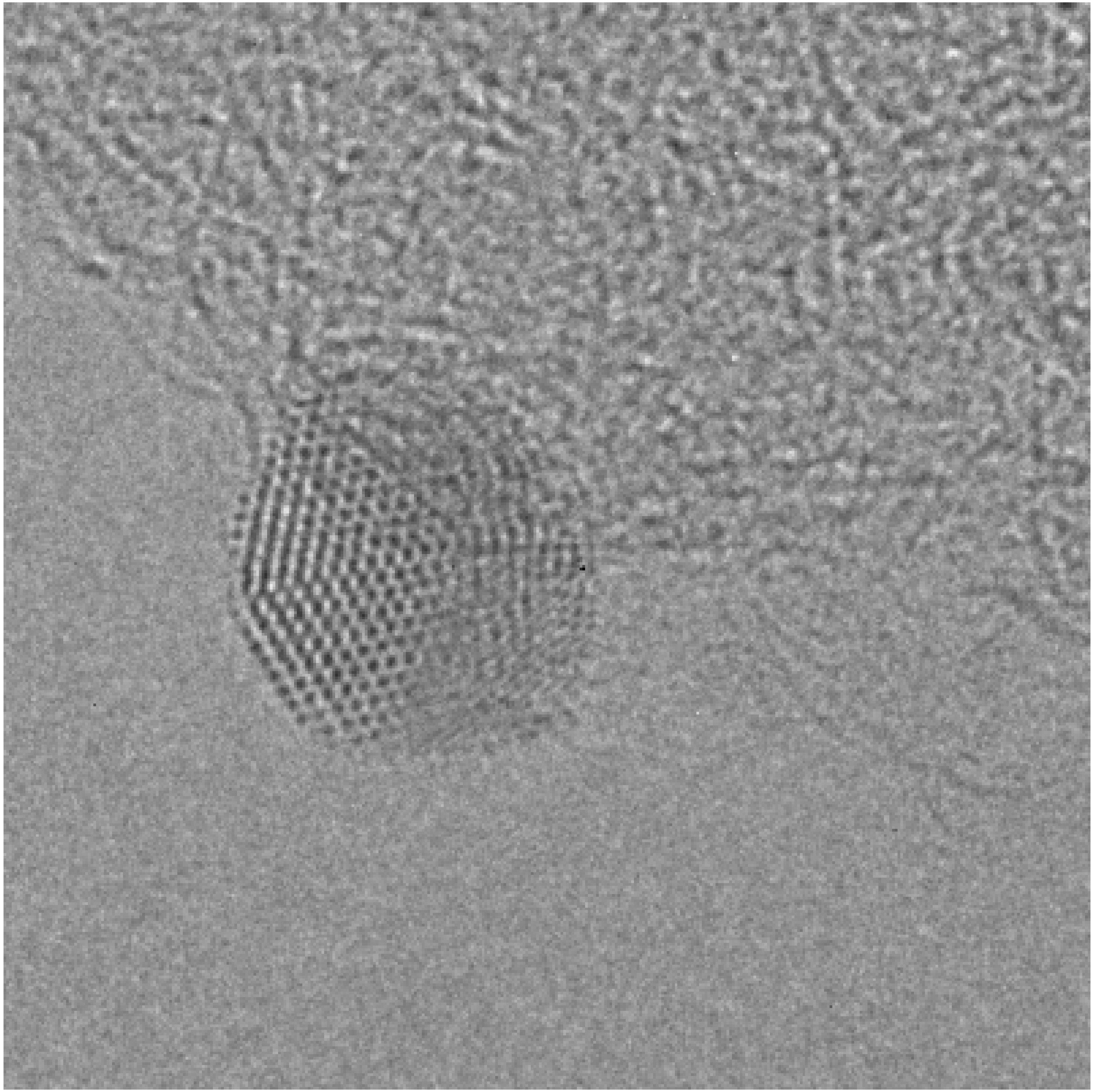




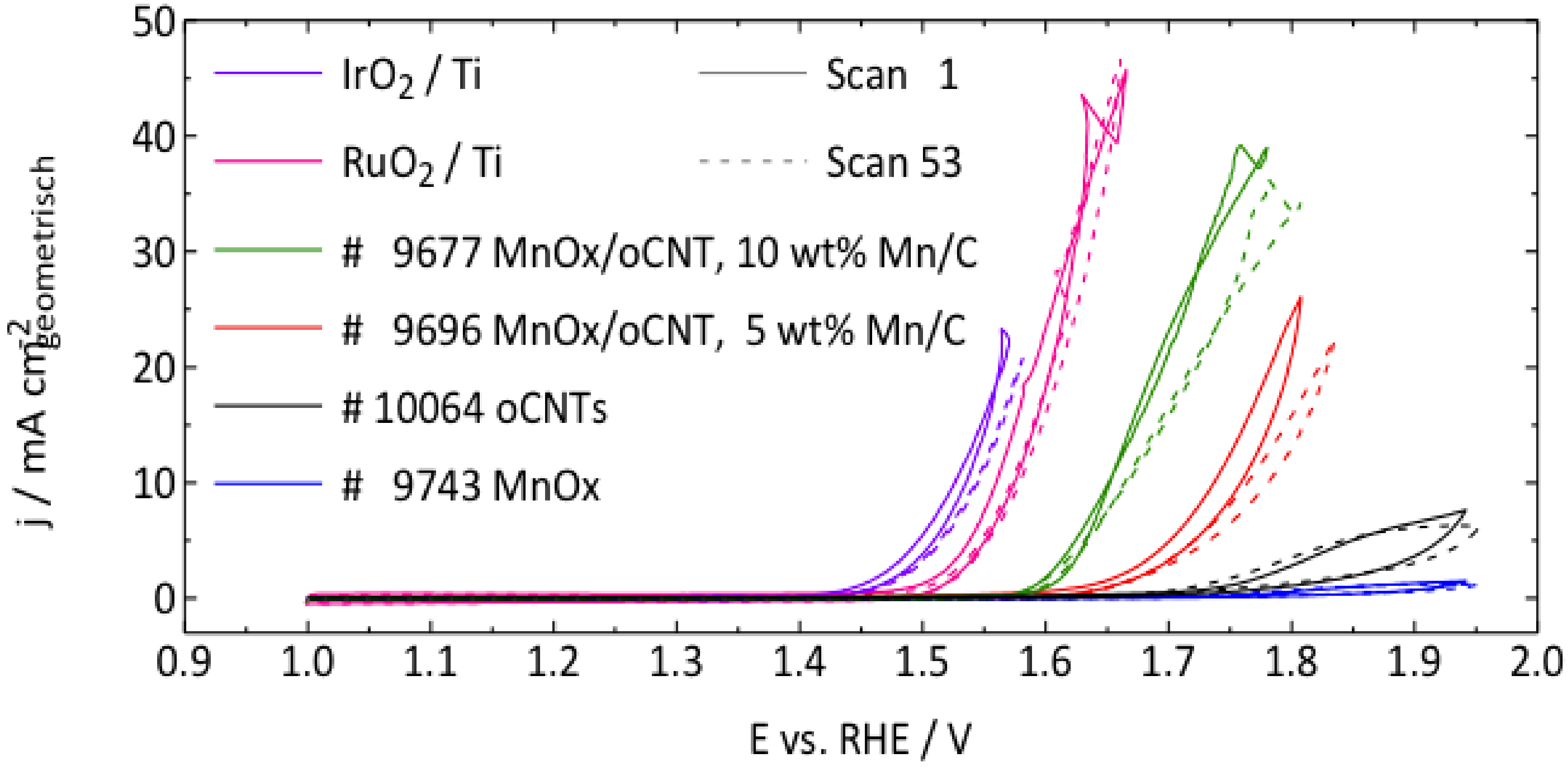


In-situ oxidation and detection at 150 eV kinetic energy reveals water and hydroxide at low T different from oxide. Pt is divalent.

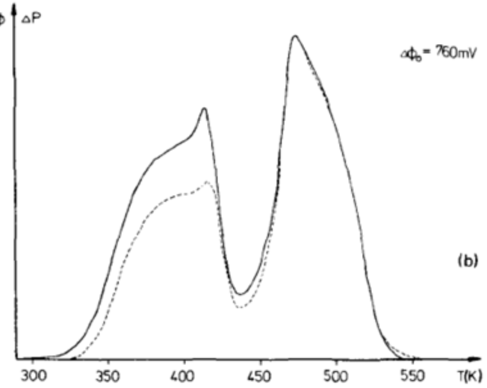
Contamination and carbon protection issues

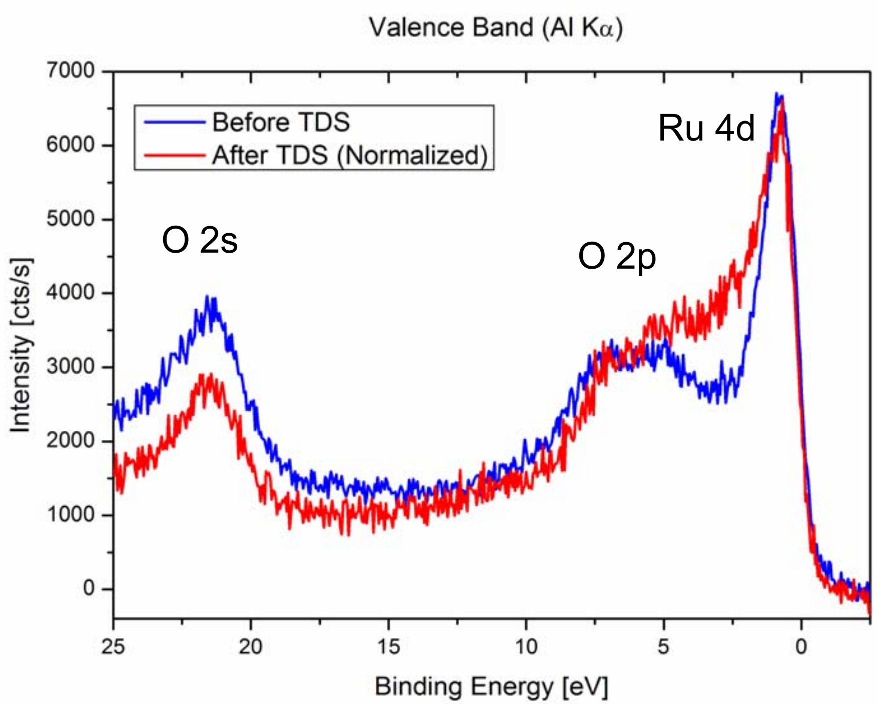


Then we take oxides….
(electrically conducting)

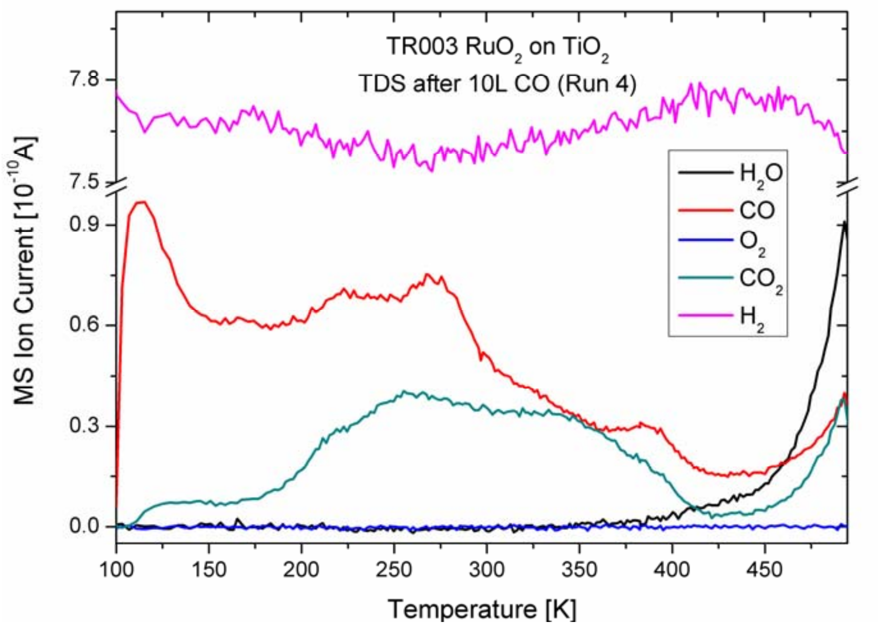


Properties of RuO_x electrodes: a challenge for characterization





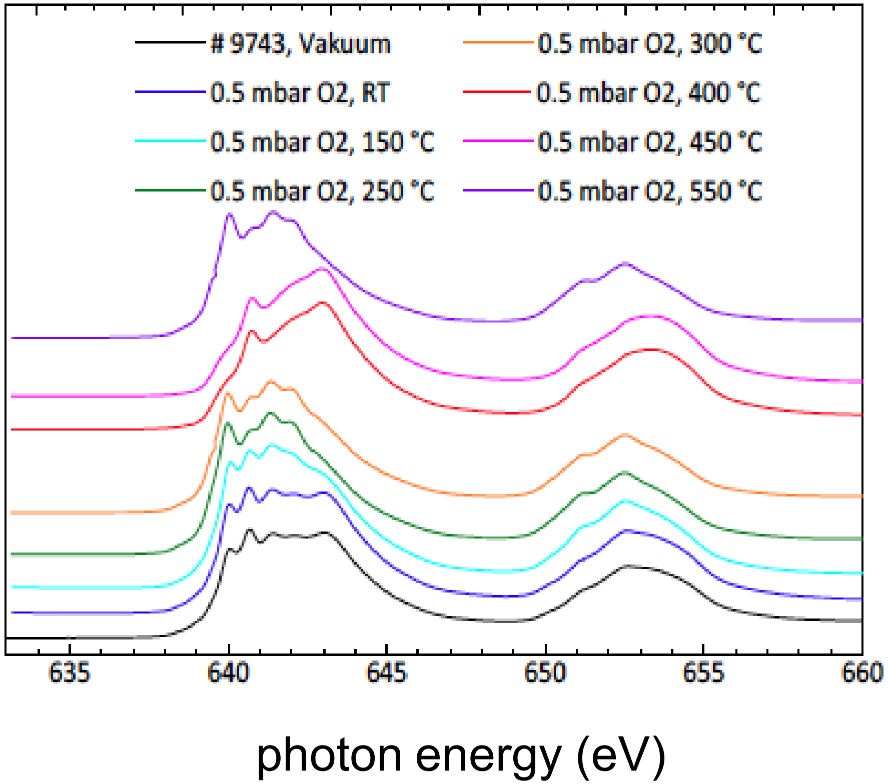
D. Menzel et al.

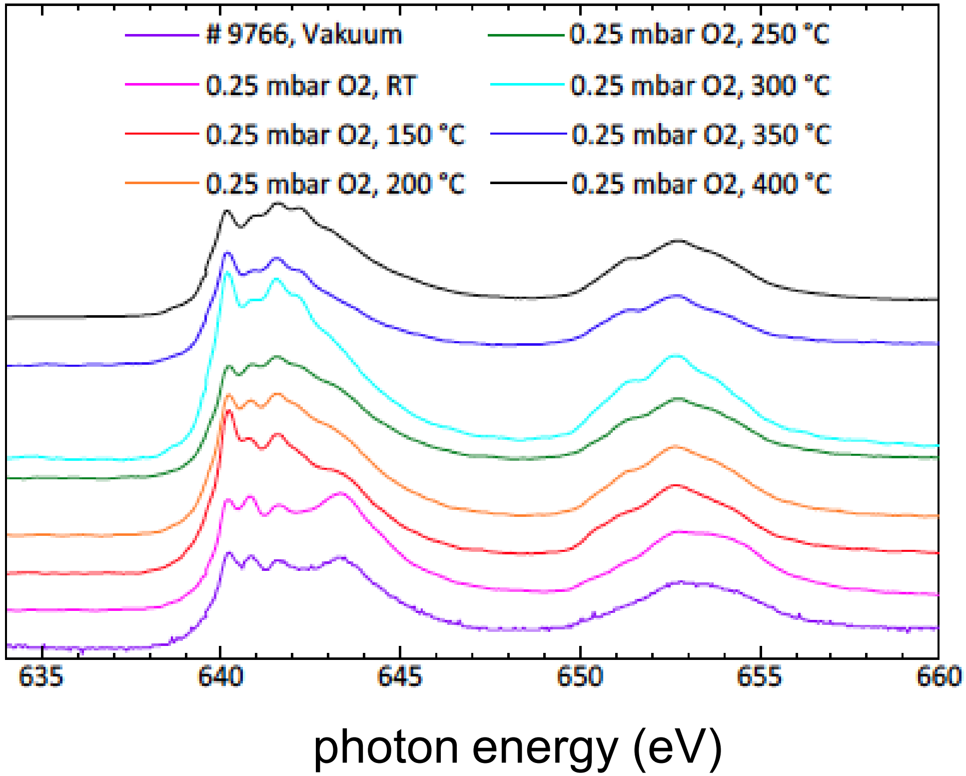


The electrode is a conducting oxide.
CO TDS up to 550 K causes reduction: no $RuO_{2,}$ suboxide

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

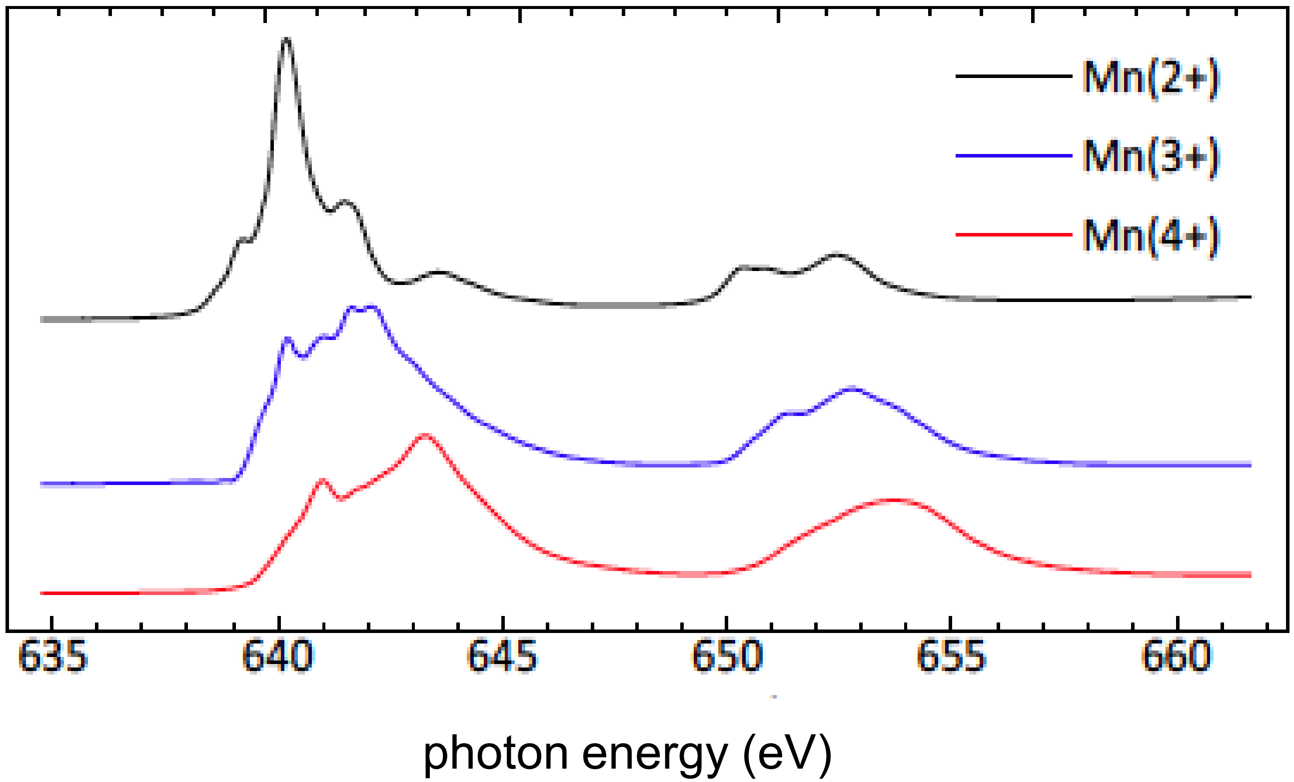
Ambient pressure NEXAFS for reactivity





The CNT nanoparticles are well reducible, the bulk oxide gets fully oxidized

Ambient pressure NEXAFS for reactivity



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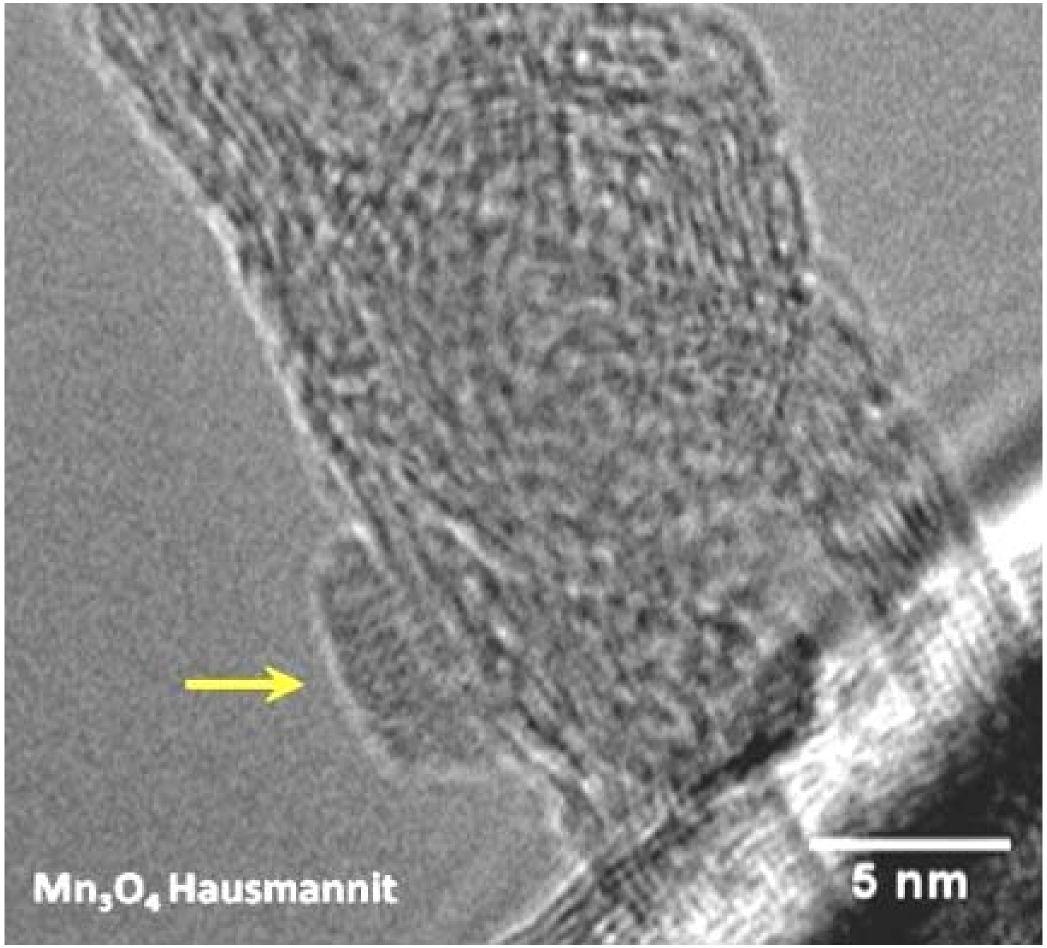
Ambient pressure NEXAFS for reactivity



The CNT nanoparticles are well reducible, the bulk oxide gets fully oxidized

Batteries

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There are several battery concepts besides the popular Li ion systems

State of the art:

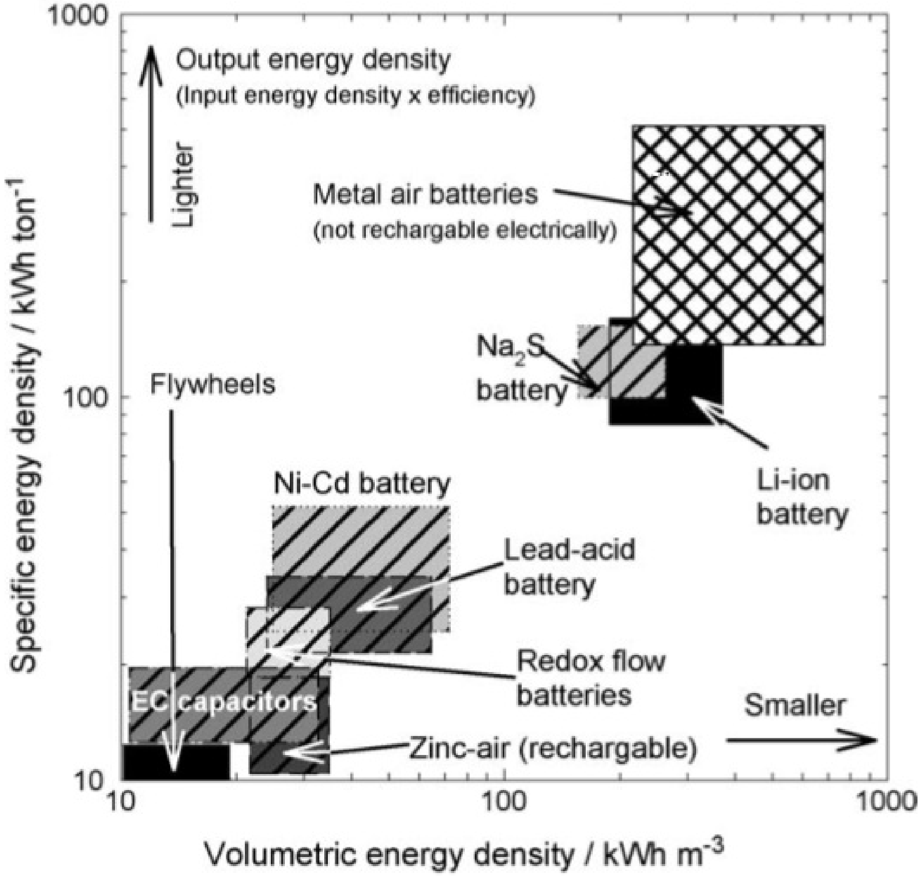
At the lower edge of capacity range

Many unsolved fundamental questions such as

:

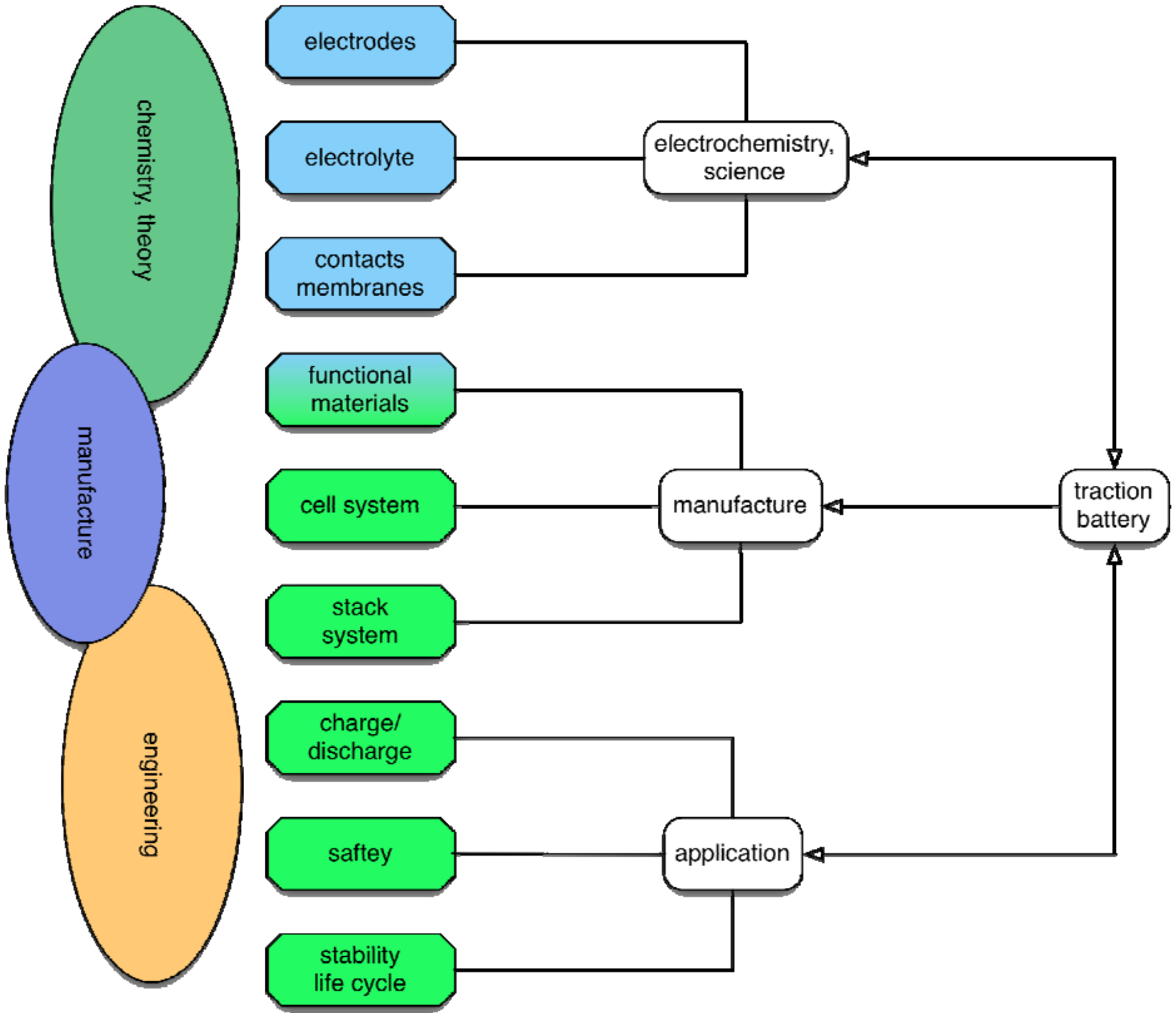
- storage mechanism
- solid electrolyte interface
- transport mechanisms

Empirical evolution impressive but still insufficient for world-scale electro-motion



Another catalytic system with even unknown reactions involved

Science of systems



Electrode materials of interest

unicat
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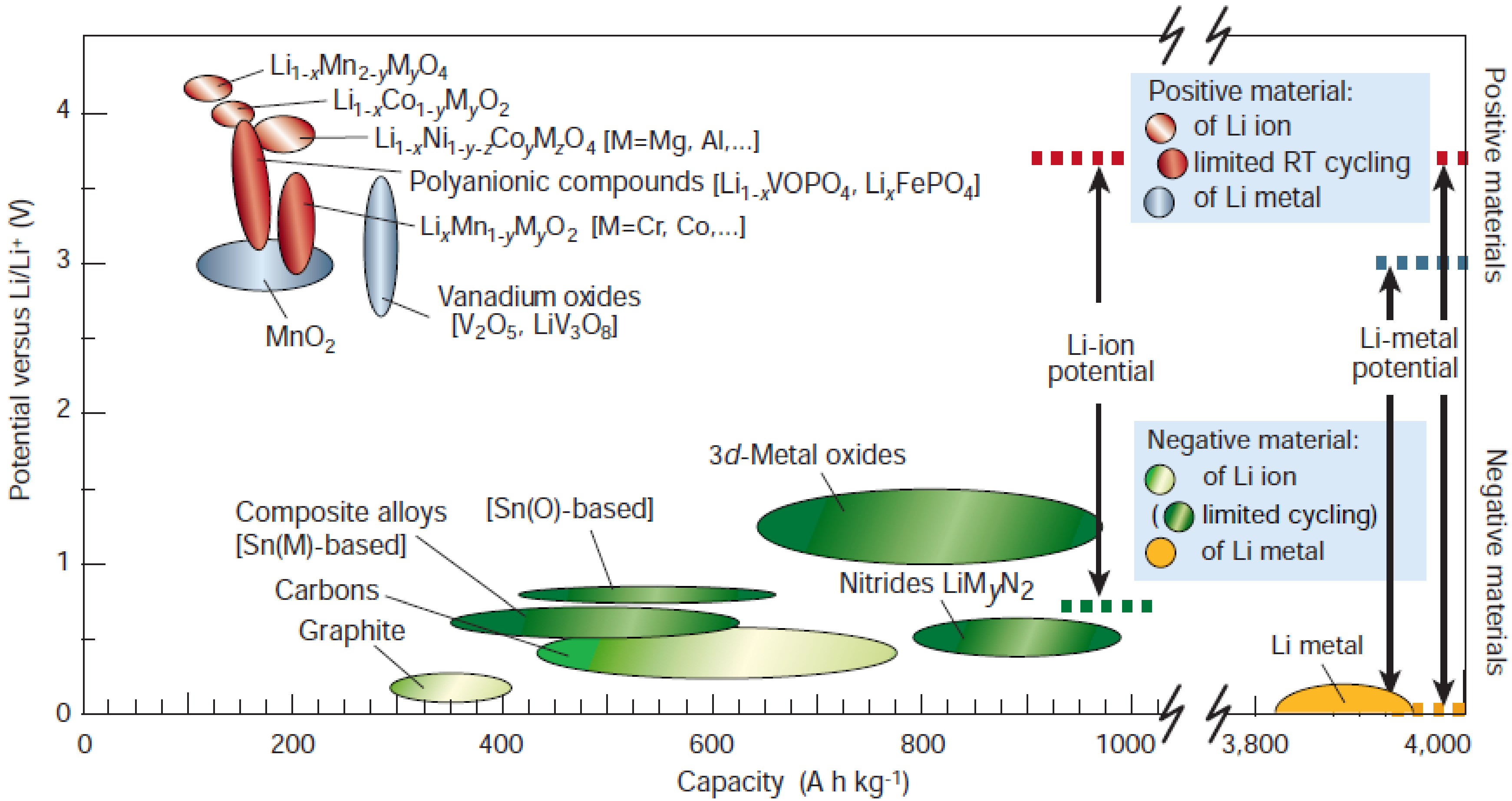

Tarascon et al., Nature 1414 (2001) 359

Electrode materials of interest
(cycling cathodes)

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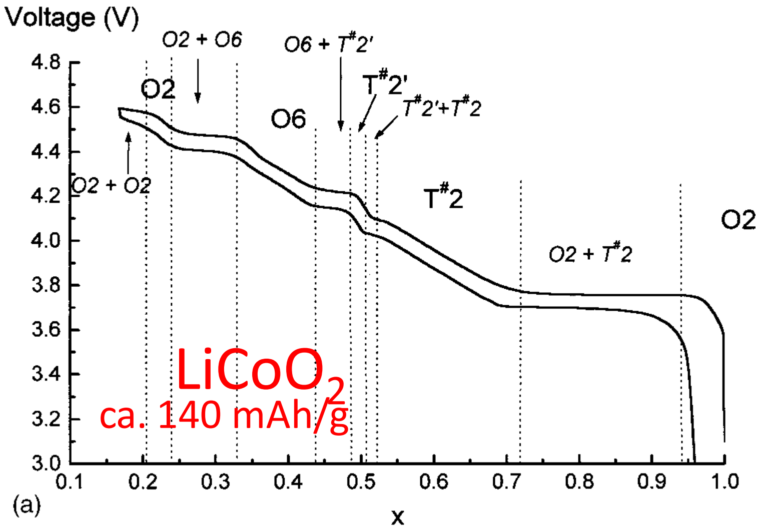
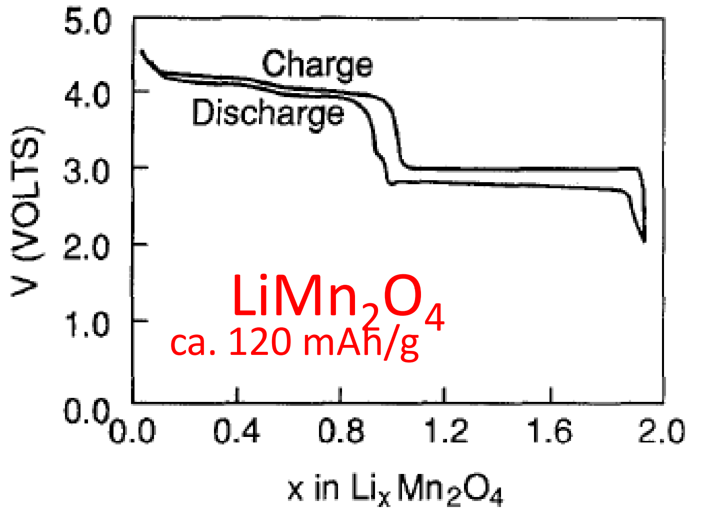
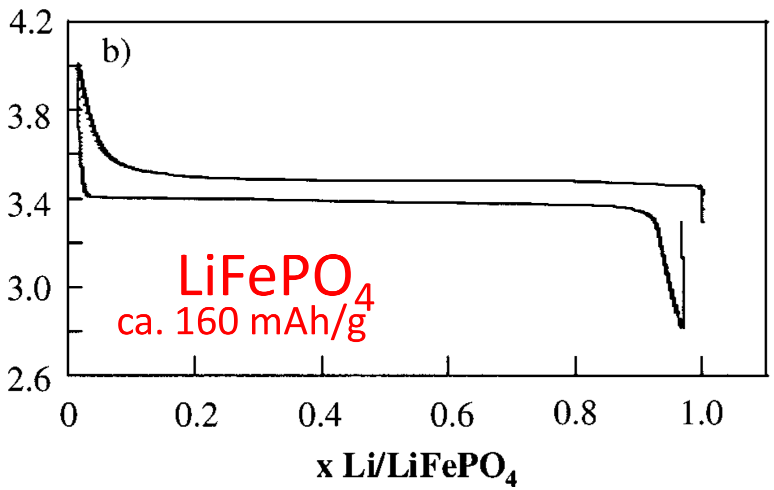


Carlier et al., J. Electrochem. Soc. 149 (2002) A1310



Tarascon et al., J Electrochem. Soc. 138 (1991) 2859

Analogy: Elucidate the reaction mechanism in catalysis from a macrokinetic experiment: impossible



Huang et al., Electrochem. Solid- State Lett., 4 (2001) A170

Predominant open questions

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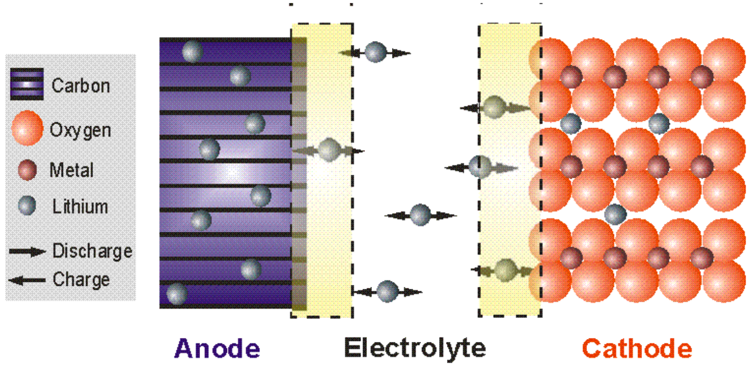
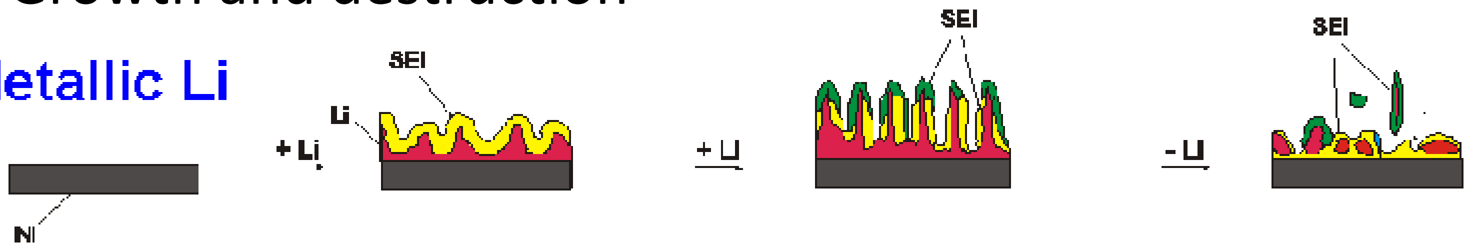
1. Ion transport and intercalation



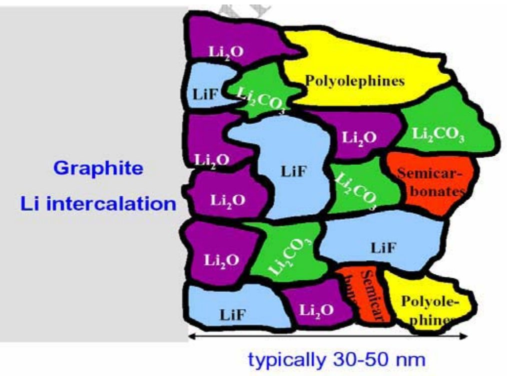
2. Solid-Electrolyte-Interface

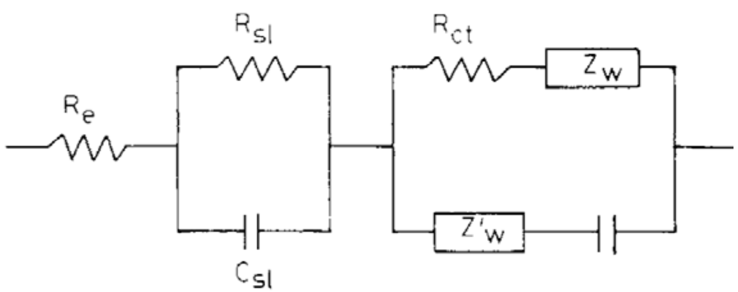
a) Growth and destruction

Metallic Li



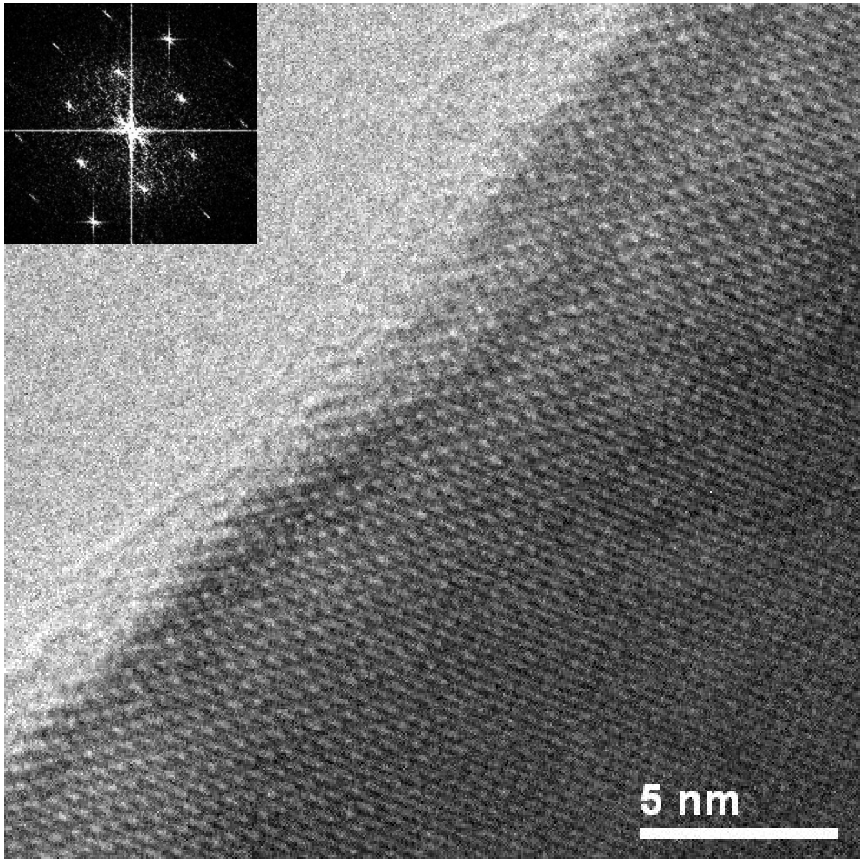
b) Phase composition and transport properties

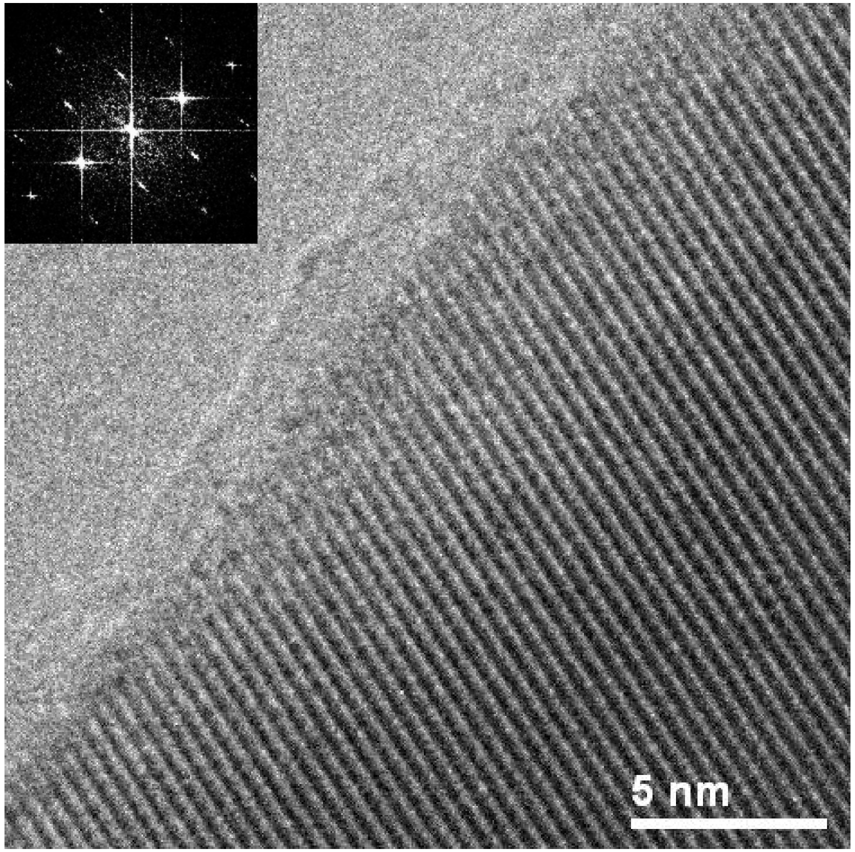




electrical equivalent cirquit

$LiCoO_2$ (Aldrich) before cycling





0 min beam exposure

15 min beam exposure

$LiMn_2O_4$ (Aldrich) before cycling

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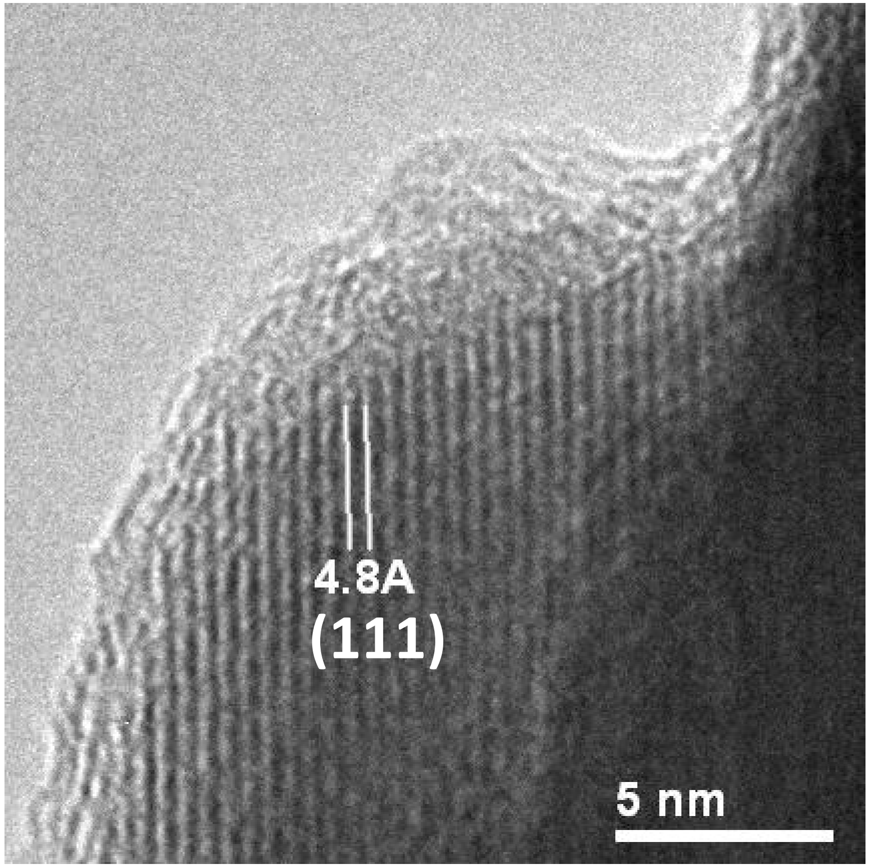
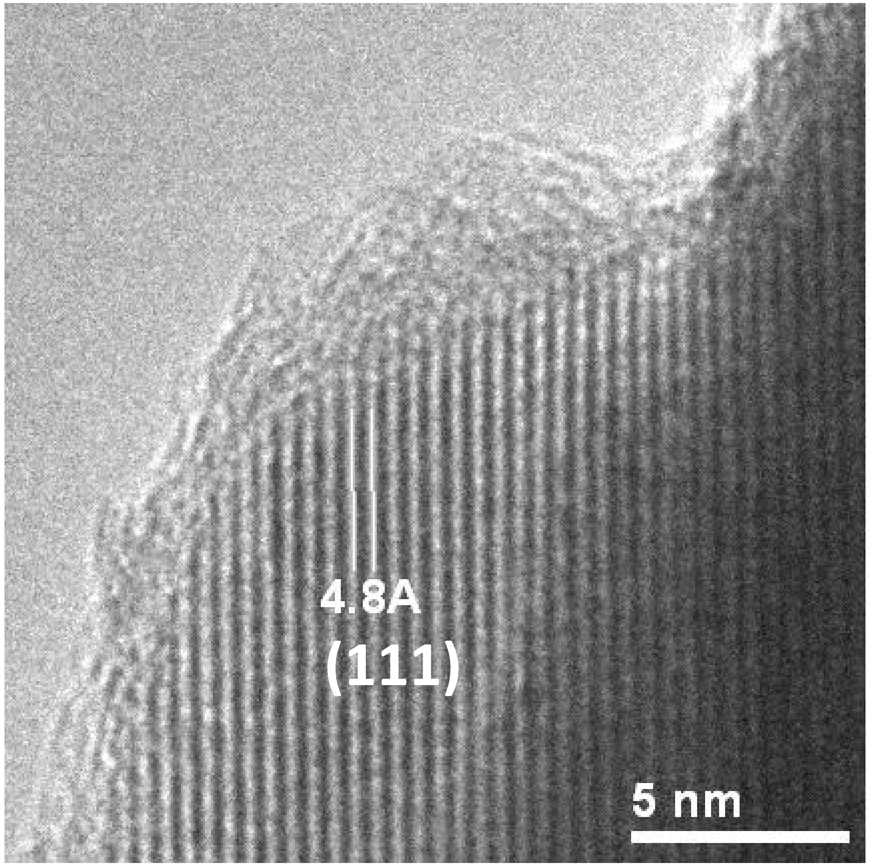


0 min beam exposure



15 min beam exposure

Li battery cathodes: electrical conductivity with chemical storage

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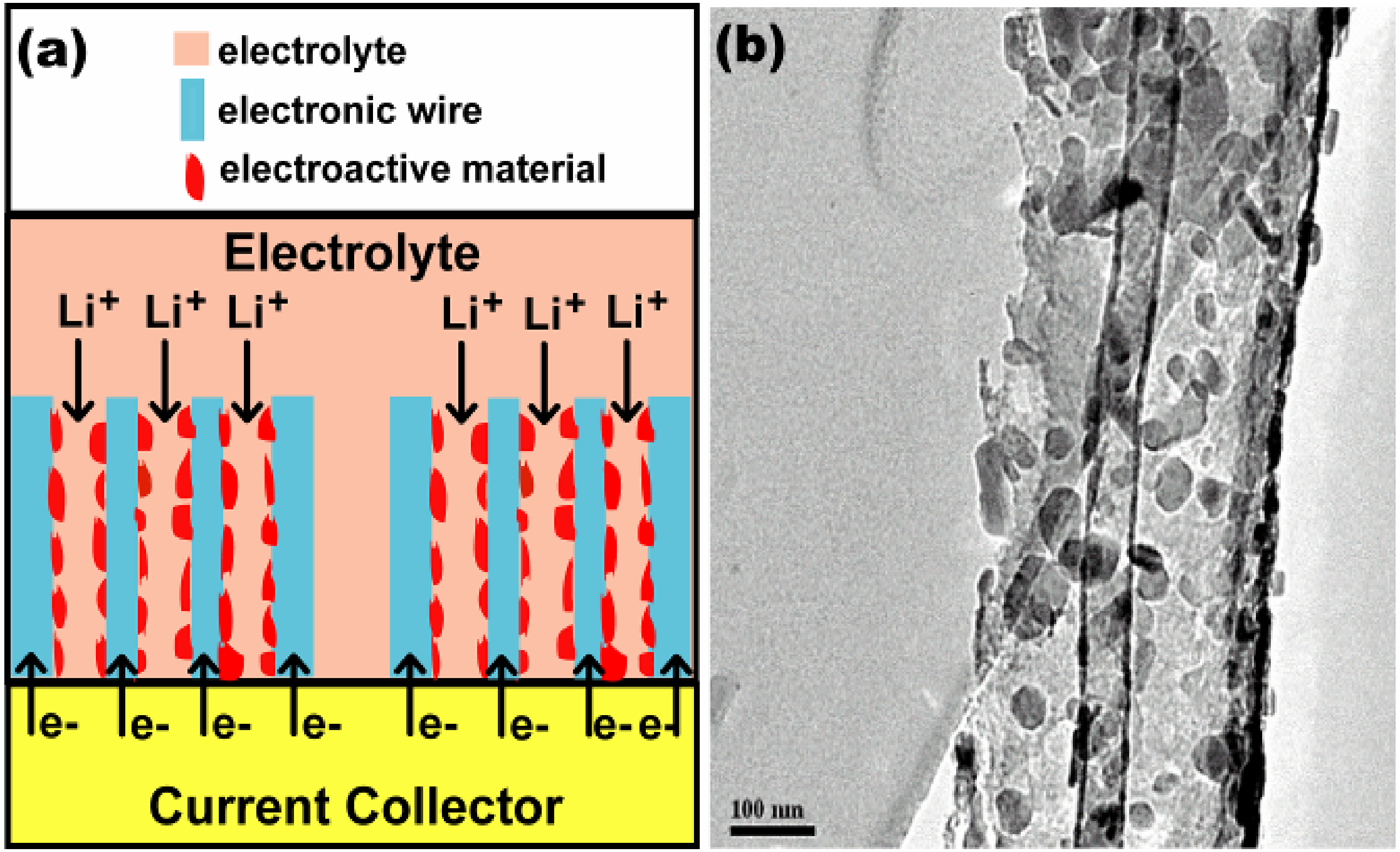
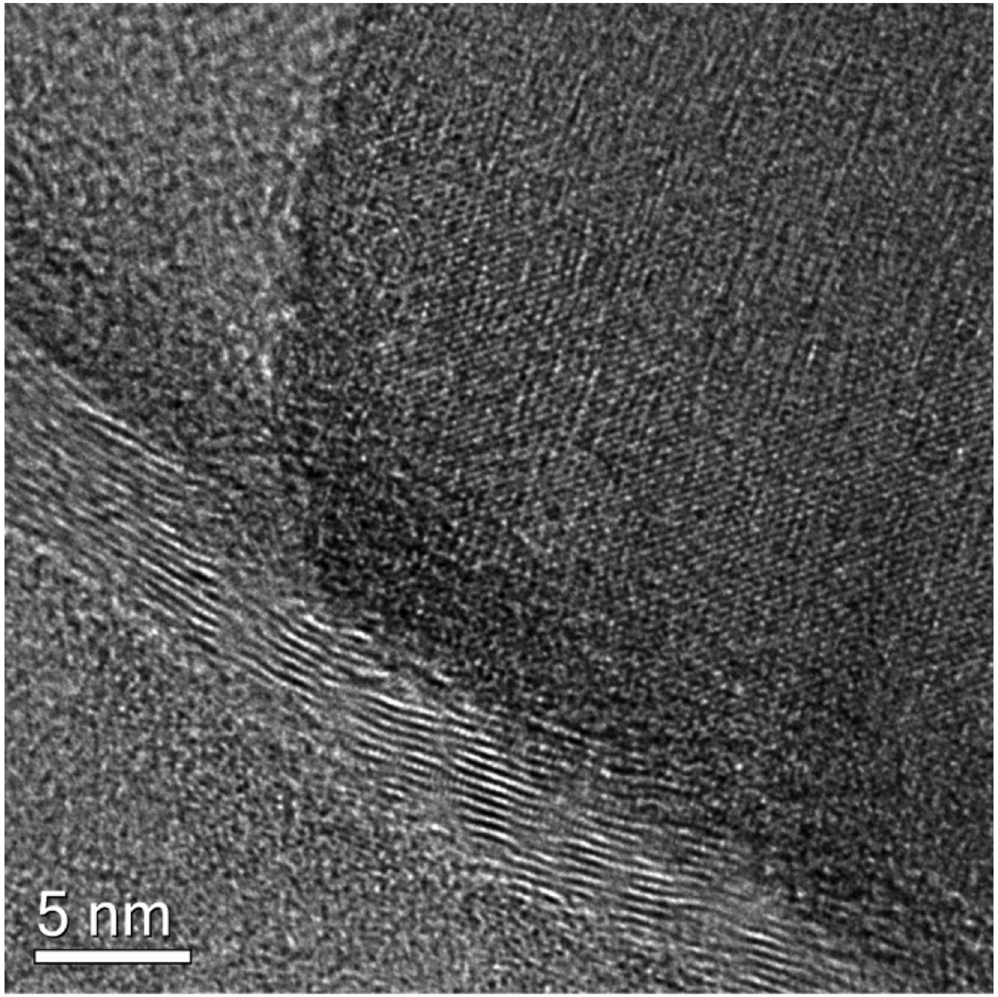


Li battery cathodes: electrical conductivity with chemical storage



Li battery cathodes: electrical conductivity with chemical storage

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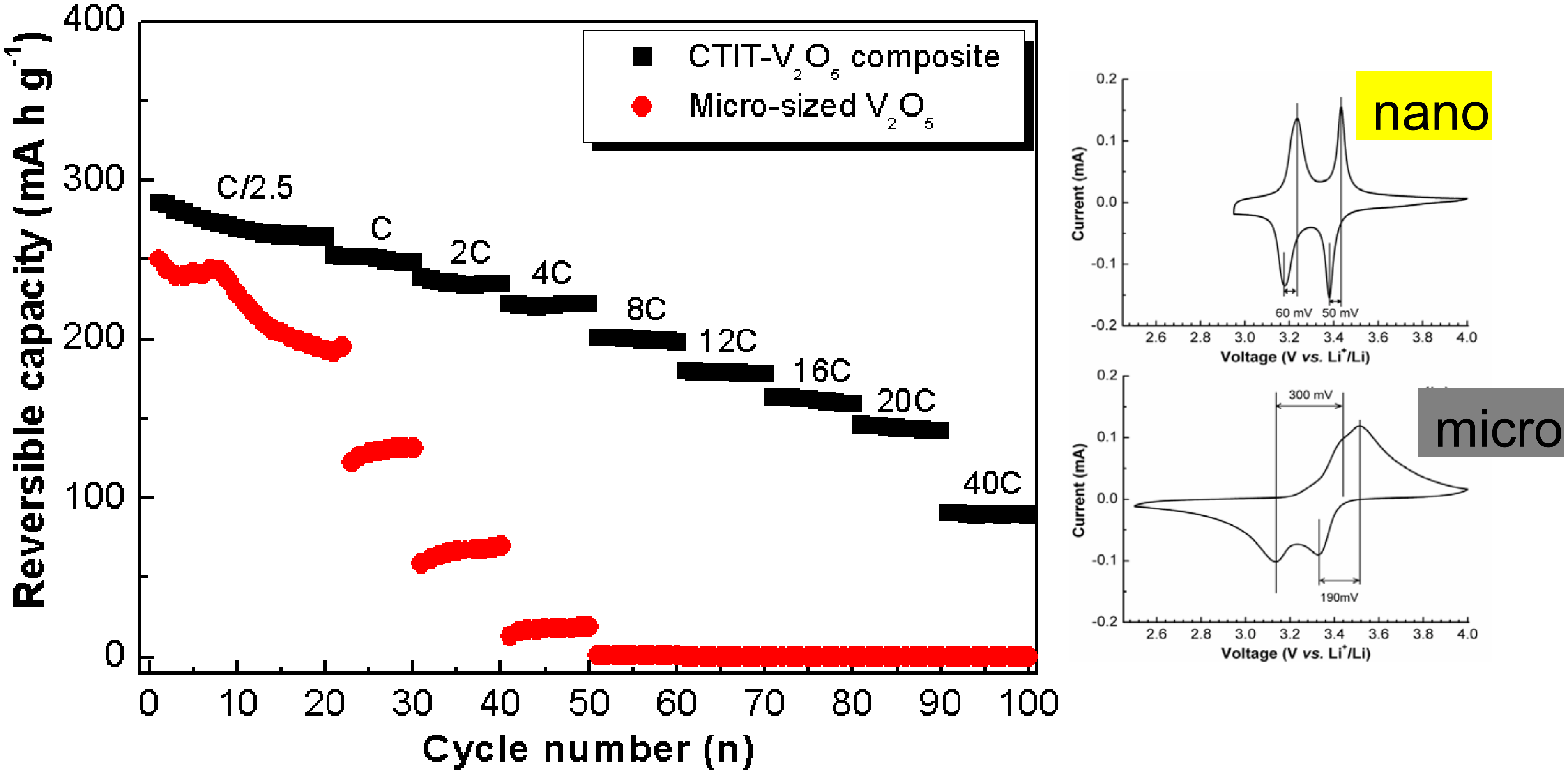
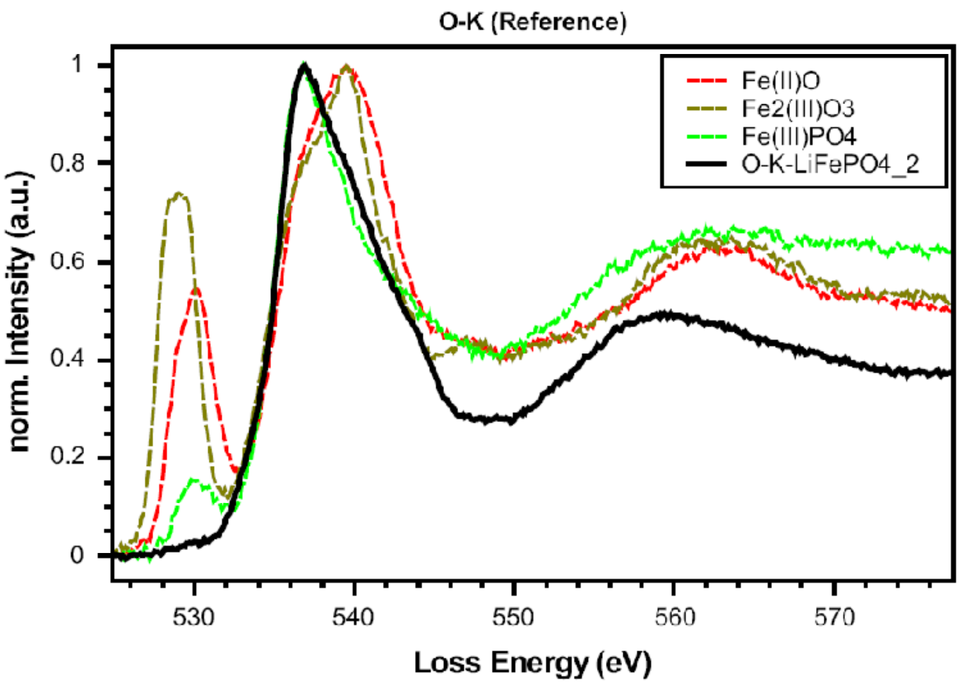
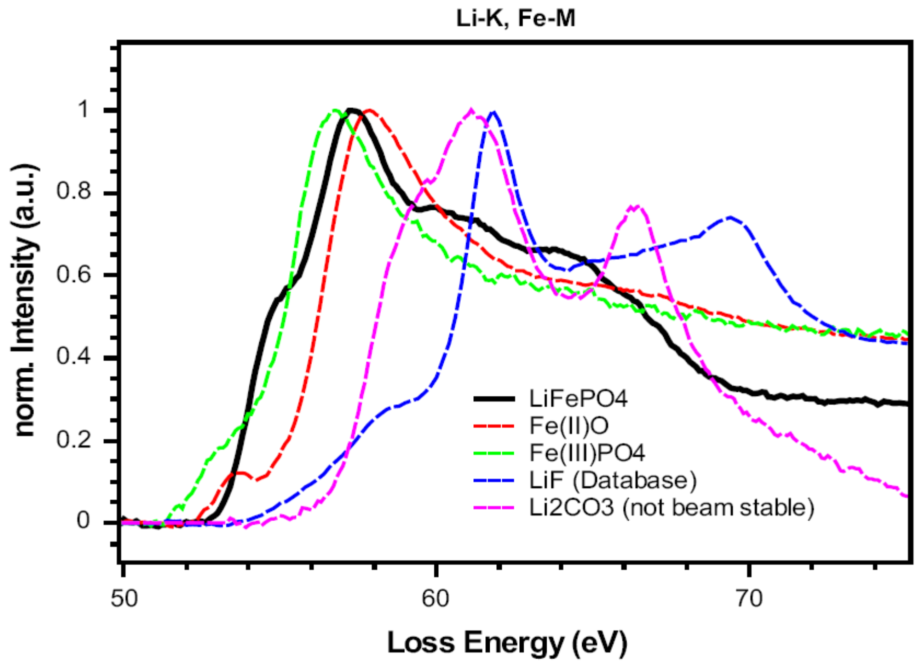


Chemical bonding in Li-ion systems



Note loss of pre-edge



Superposition of Li K edge with Fe M edge
Missing white line Li^+

EELS recorded in diffraction mode at authentic structures of $LiFe(PO_4)_2$

To take home: energy technology is a long-term activity

- Energy storage through chemical bonds is pre-requisite for the sustainable use of regenerative energy at global grid scale.
- We need all technologies that we can think of; before deciding on pathways explore the potentials on scientific insight and not on economic or engineering arguments.
- Heterogeneous catalysis and electrocatalysis are very similar phenomena with much synergy but some distinct differences (such as temperature effects).
- The way forward is to advance fundamental insight (models) simultaneously with phenomenological knowledge.
- We have the theoretical and experimental tools and the insight, let it get to work now for the benefit of our succeeding generations.

Grazie!

Water to hydrogen: the key

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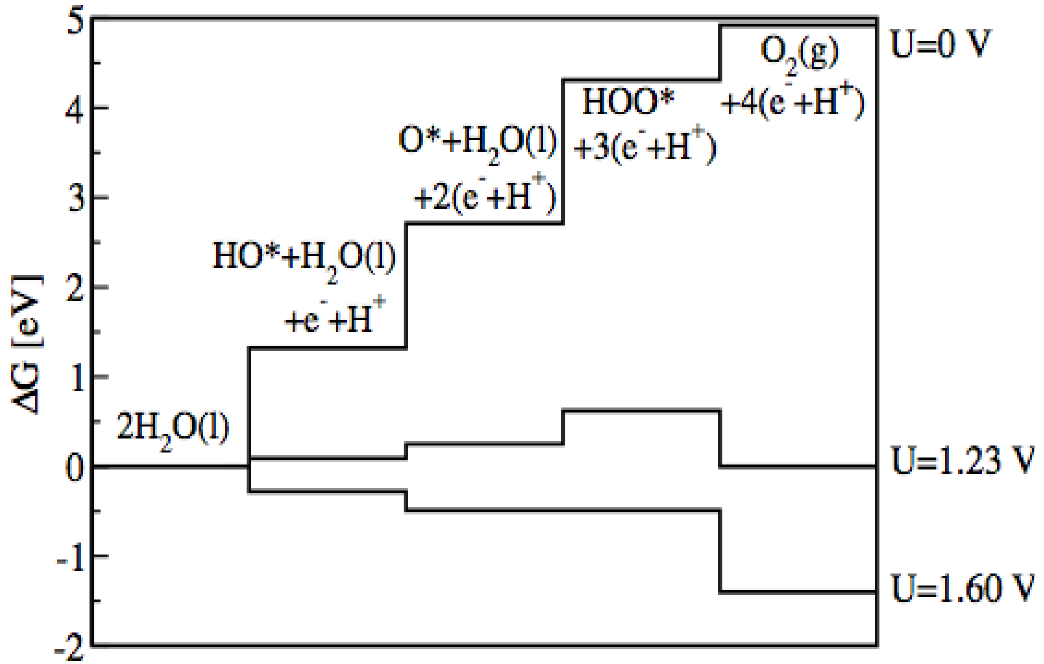
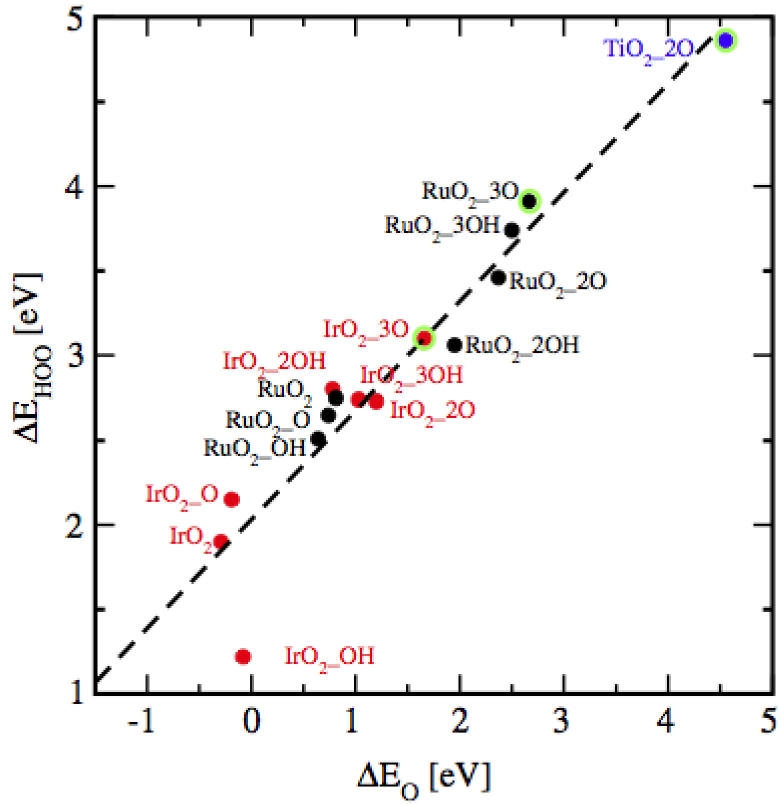
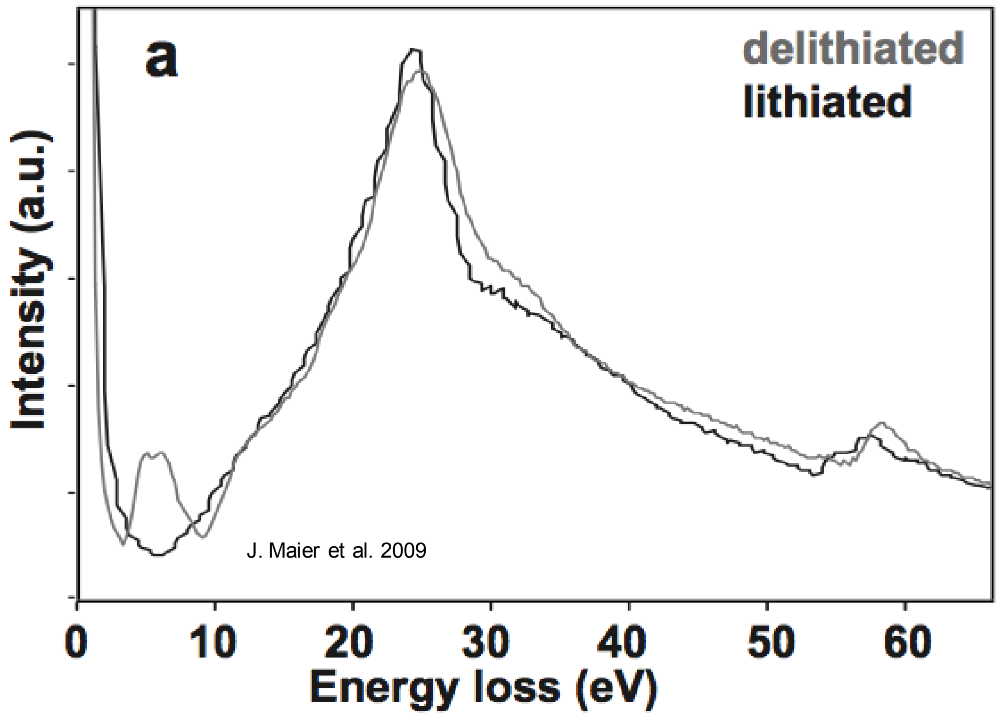


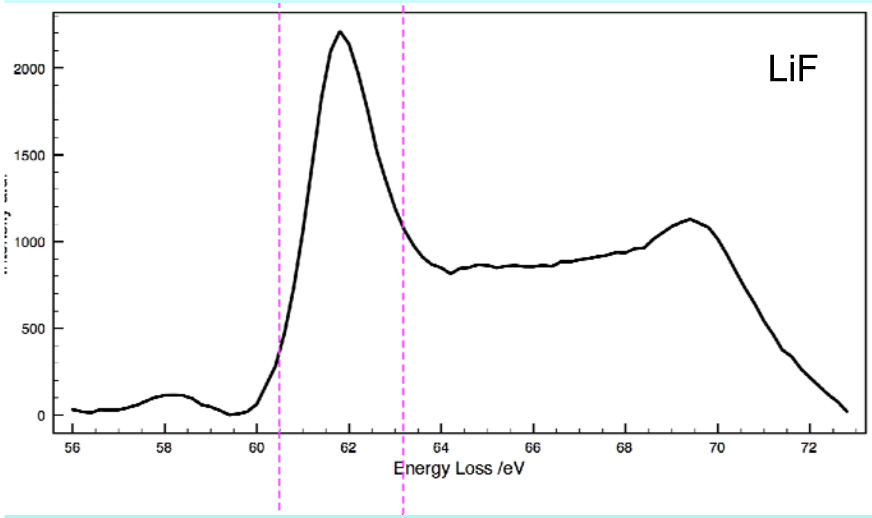
Norskov et al. 2008



Electrocatalysis: a poorly understood field

Li battery cathodes: electrical conductivity with chemical storage





Li-iron phosphate (?)

Understanding of storage and transport mechanisms is critical

Electrocatalytic reduction?

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Fe and Pt carbon nanotubes for the electrocatalytic conversion of carbon dioxide to oxygenates

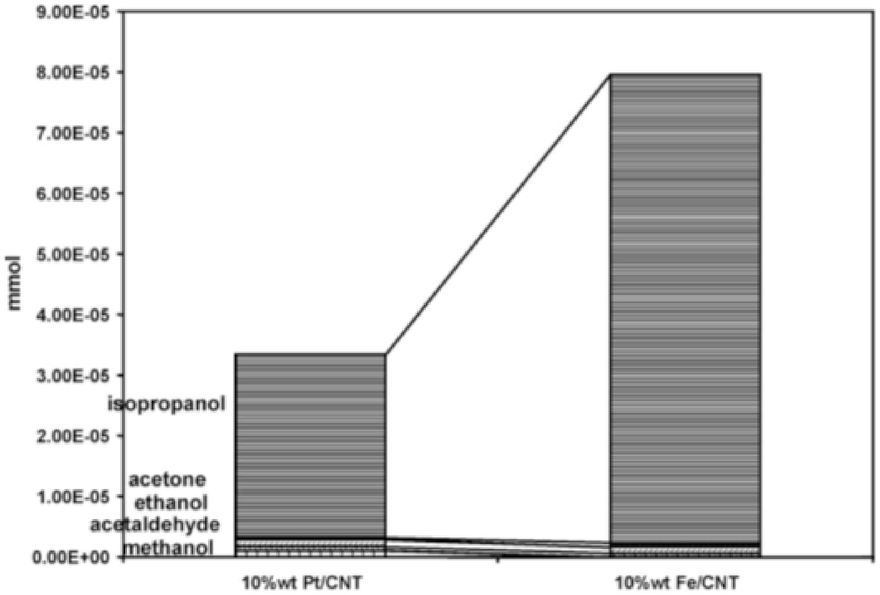
M. Gangeri [a], S. Perathoner [a,*], S. Caudo [a], G. Centi [a], J. Amadou [b], D. Bégin [b], C. Pham-Huu [b], M.J. Ledoux [b], J.-P. Tessonnier [c], D.S. Su [c], R. Schlögl [c]

[a] *Dept. of Industrial Chemistry and Materials Engineering, University of Messina, Salita Sperone 31, Messina, Italy*
[b] *Lab. Des Matériaux, Surface at Procédés pour la Catalyse, CNRS & ULP, Strasbourg, France*
[c] *Fritz Haber Institut der M.P.G., Berlin, Germany*

Catal. Today, 2009

Convert CO_2 in an electrocatalytic cell with (solar) hydrogen to solar fuel in one step

Electrocatalytic reduction?



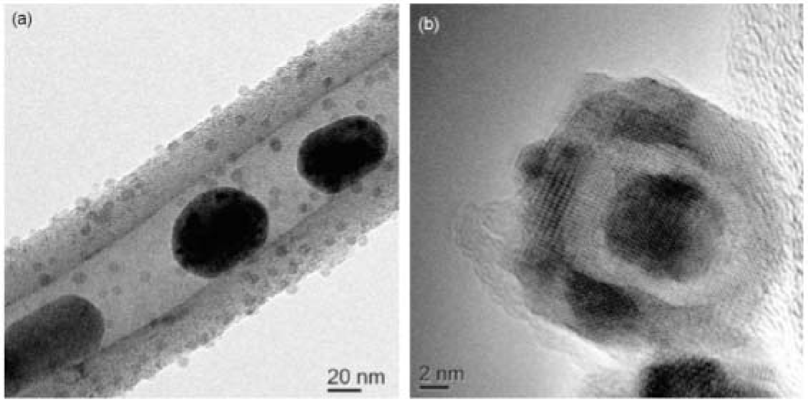
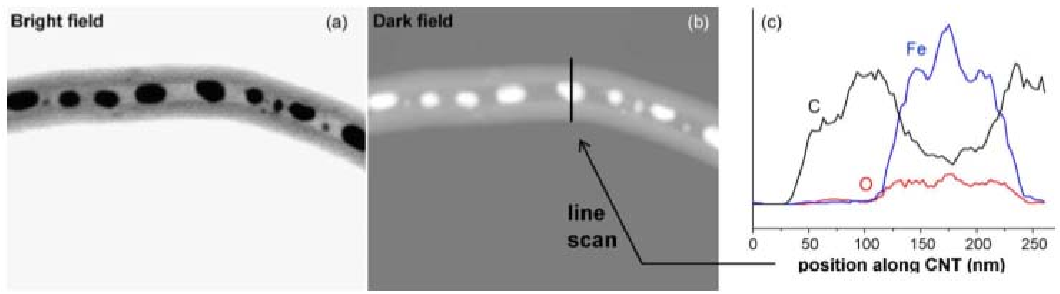


Fig. 3. (a) TEM and (b) HRTEM images of Fe/CNT electrocatalyst.



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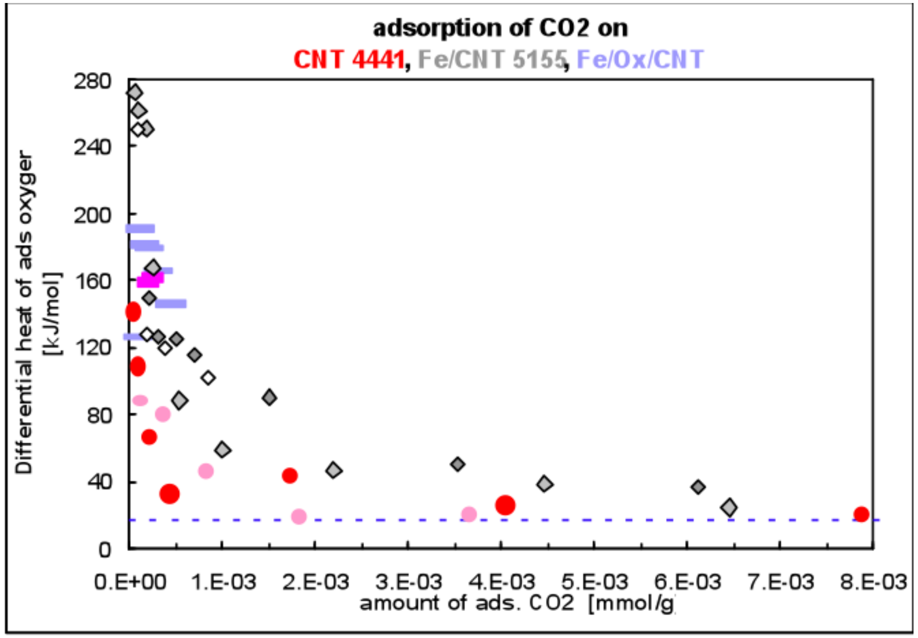


Challenges:

Remove bimodal distribution

Control sub-surface chemistry of Fe

Convert CO_2 in an electrocatalytic cell with (solar) hydrogen to solar fuel in one step

Finale
Energy is not only a science-technology issue

- The prize! (is cheap energy social?)
- If economy is the benchmark politics should
  - Stop hidden subsidies
  - Impose full cost on energy conversion
  - Impose tight rules of sustainability
  - Stop micro-management
- If society is the benchmark politics should
  - Care for information and education
  - Understand systemic character of challenge
  - Impose the principle: decision-responsibility
  - Care for a educated dialogue across society

One bottleneck: hydrogen

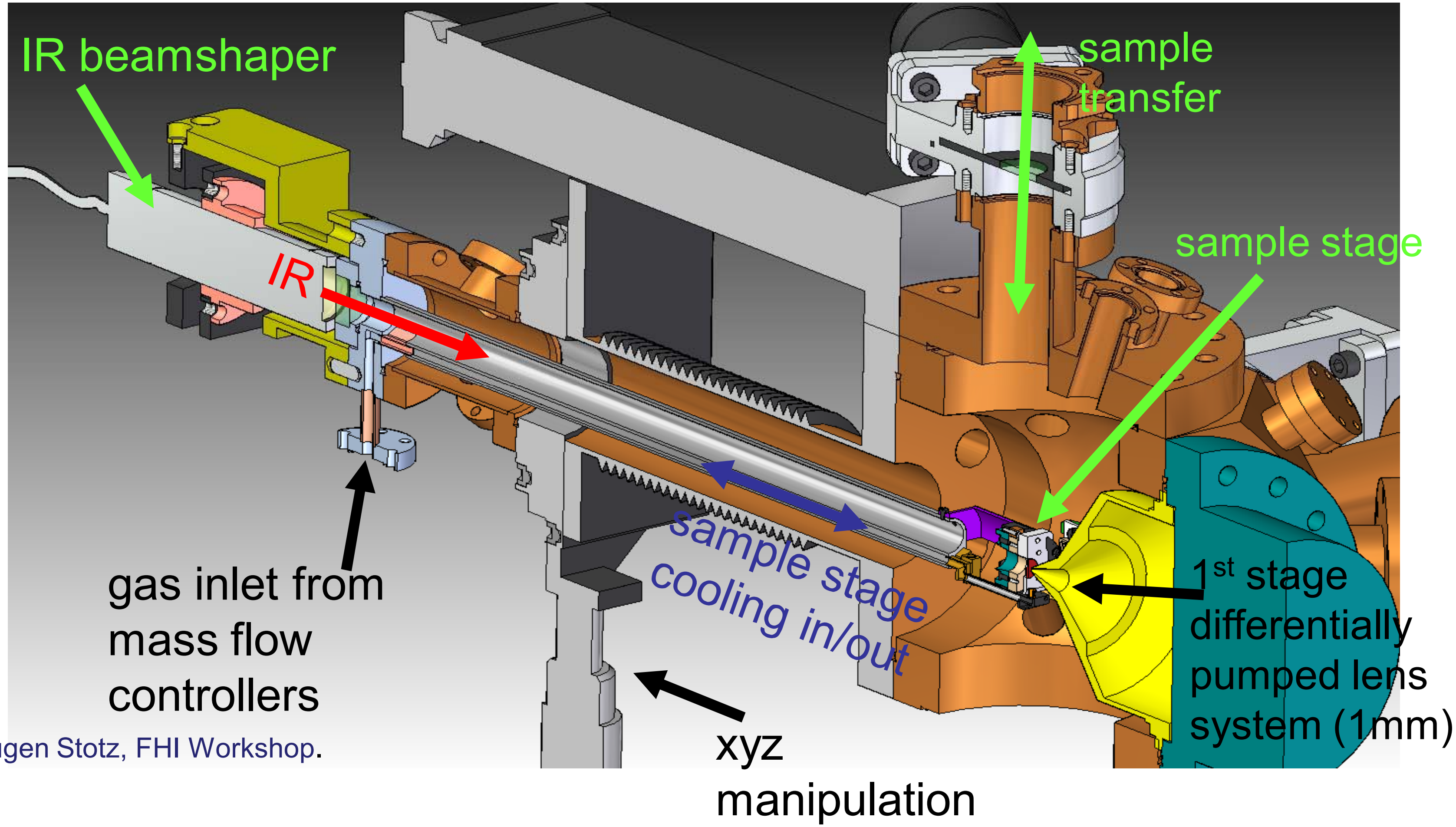
- Converting water to hydrogen and oxygen is today not possible for large-scale energy storage.

$$2\ H_2O \leftrightarrow 2\ H_2 + O_2$$

- Solar hydrogen as platform storage system.
- No interferences with the biosphere.
- Critical process for “solar refinery”.
- Missing basic knowledge about controlling energy barriers of the reactions of the most simple molecules.

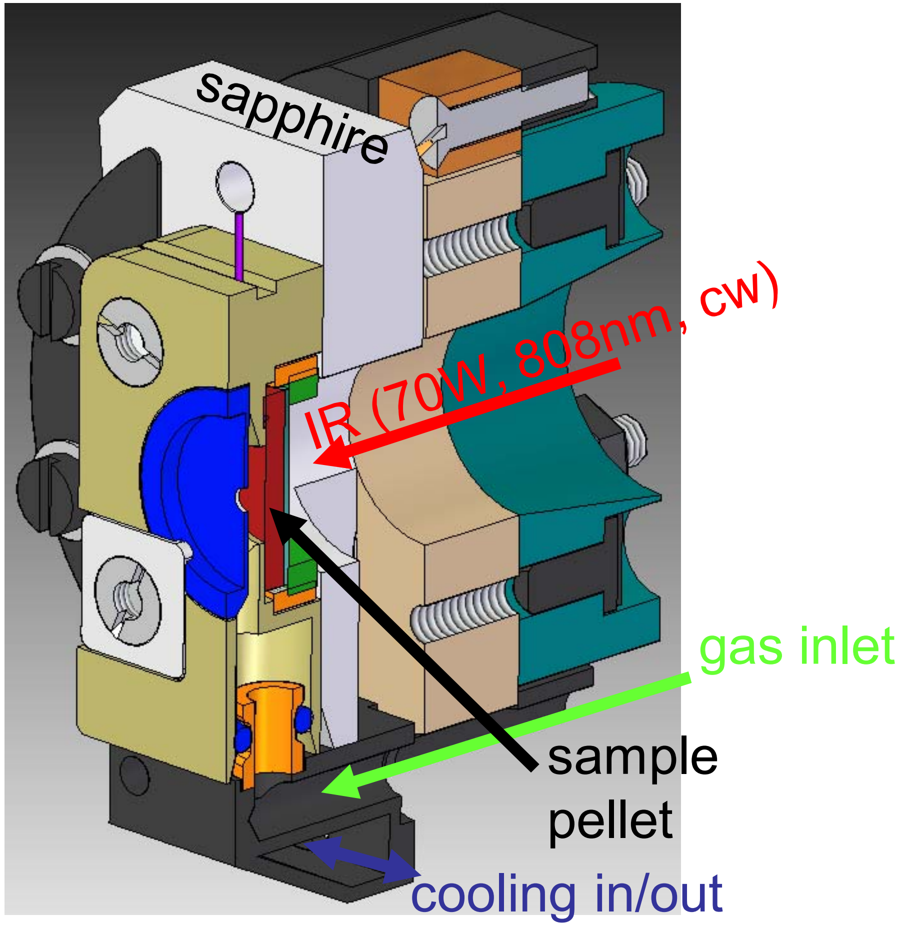
CEC: chemical energy conversion is a strategic solution from the “troublemaker” chemistry

Excursion: about in-situ environments

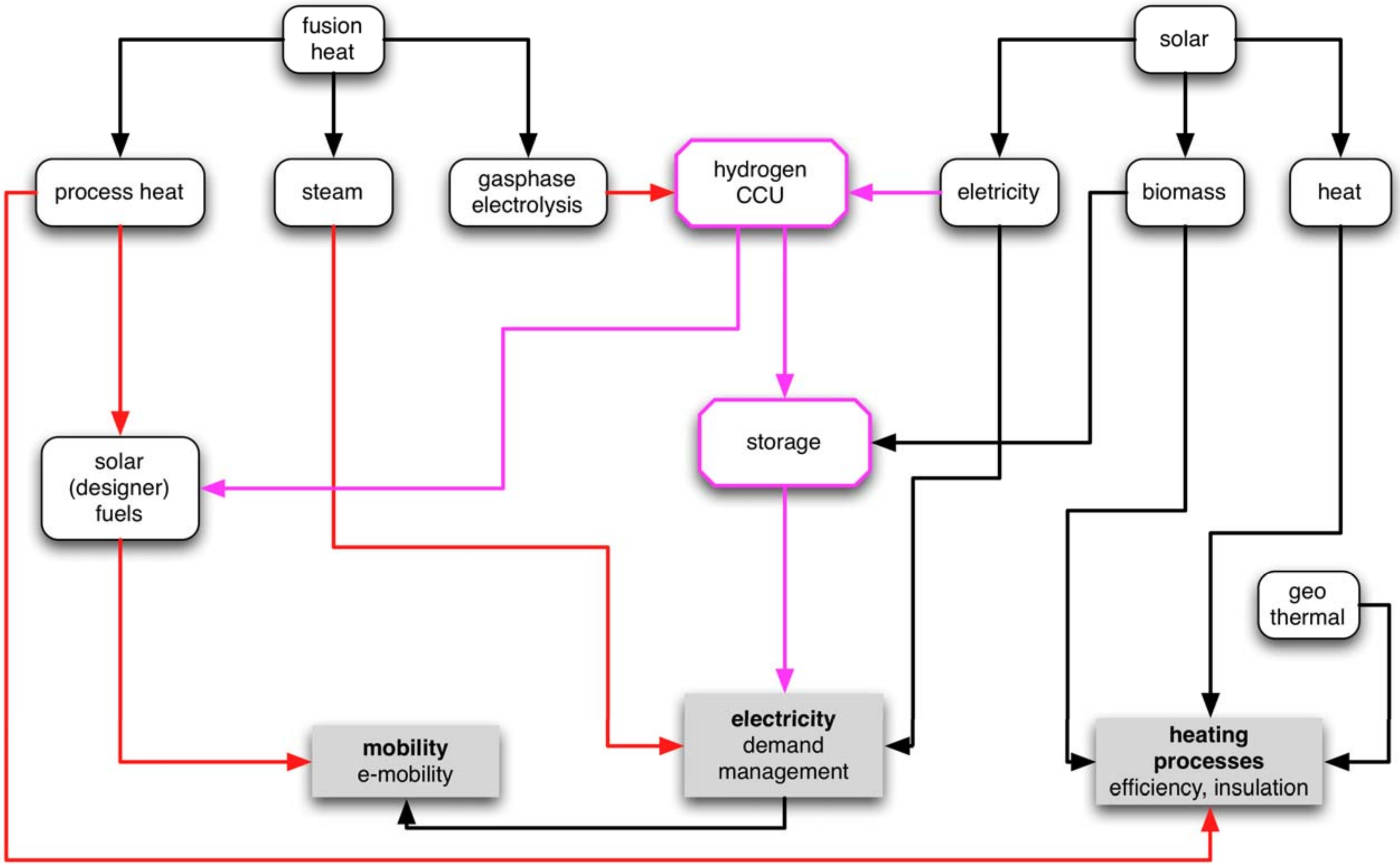


Eugen Stotz, FHI Workshop.

Excursion: about in-situ environments



Fusion and regenerative: a useful couple



Nature of the “rust” film

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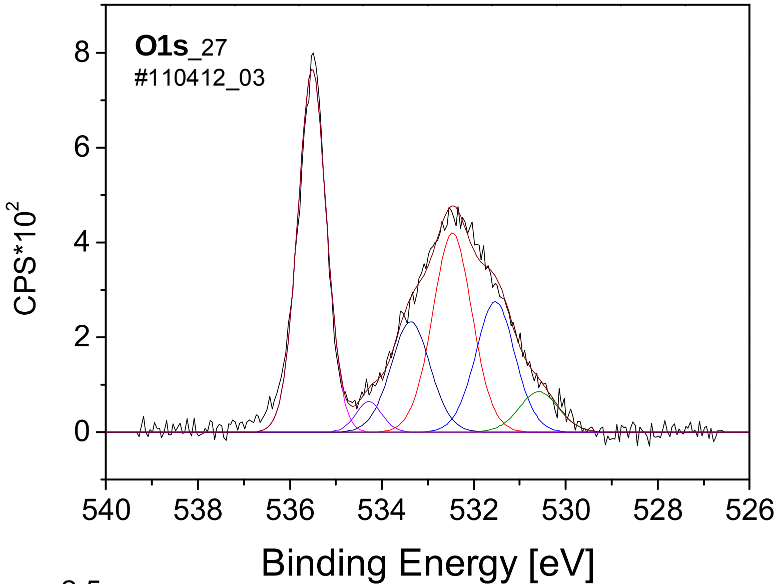
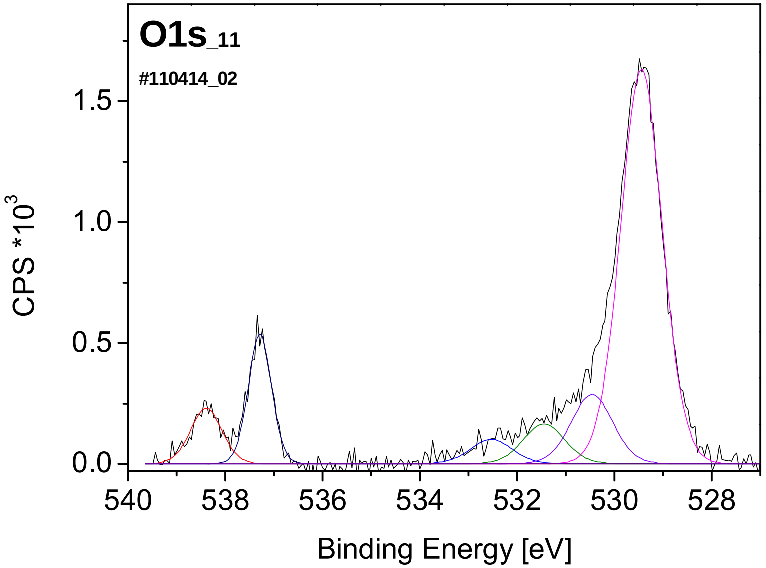
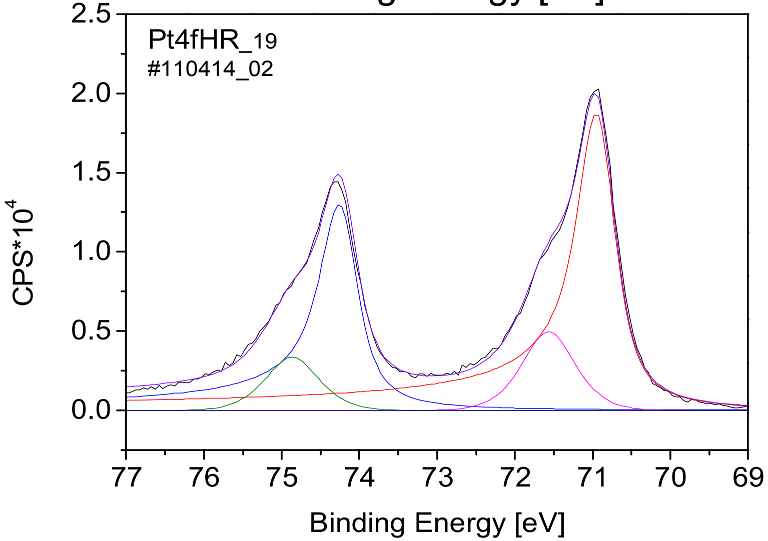


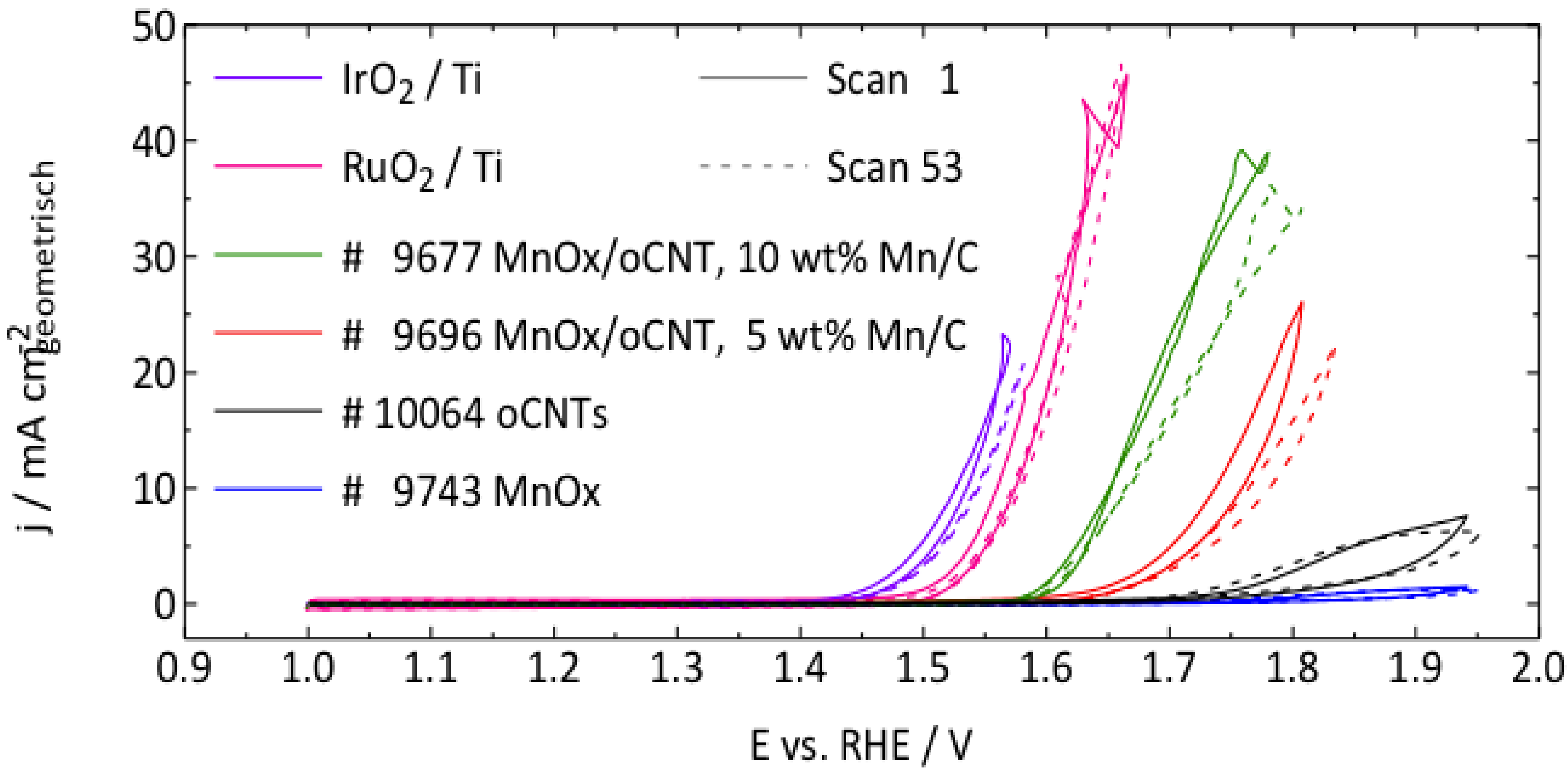




In-situ oxidation and detection at 150 eV kinetic energy reveals water and hydroxide at low T different from oxide. Pt is divalent.

Contamination and carbon protection issues

OER: “Reality” over Pt and alternatives



Ambient pressure NEXAFS for reactivity

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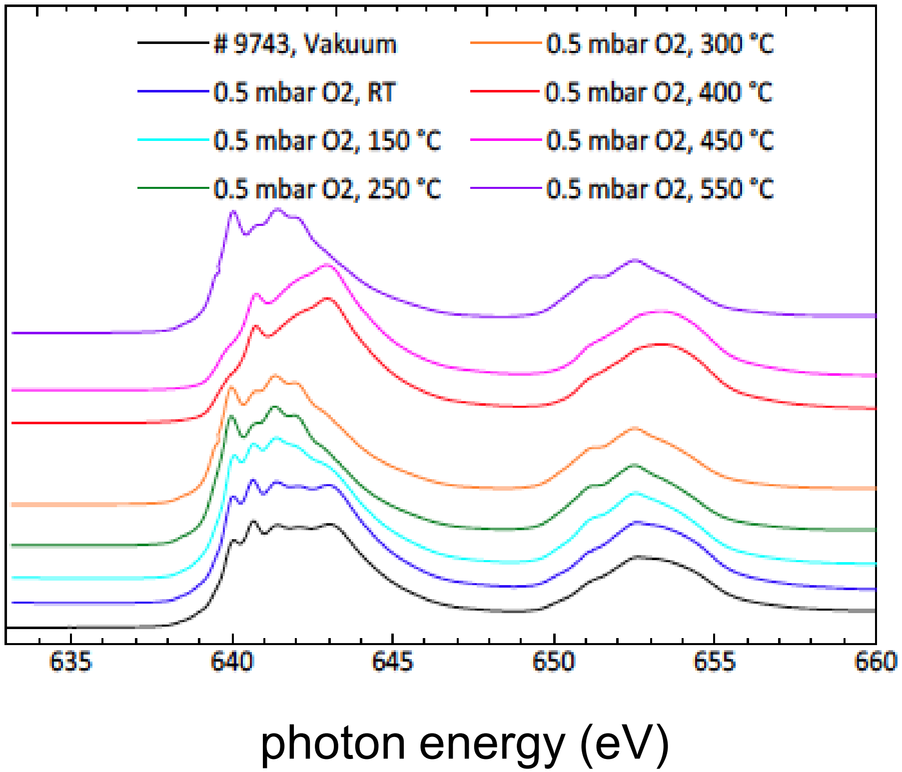
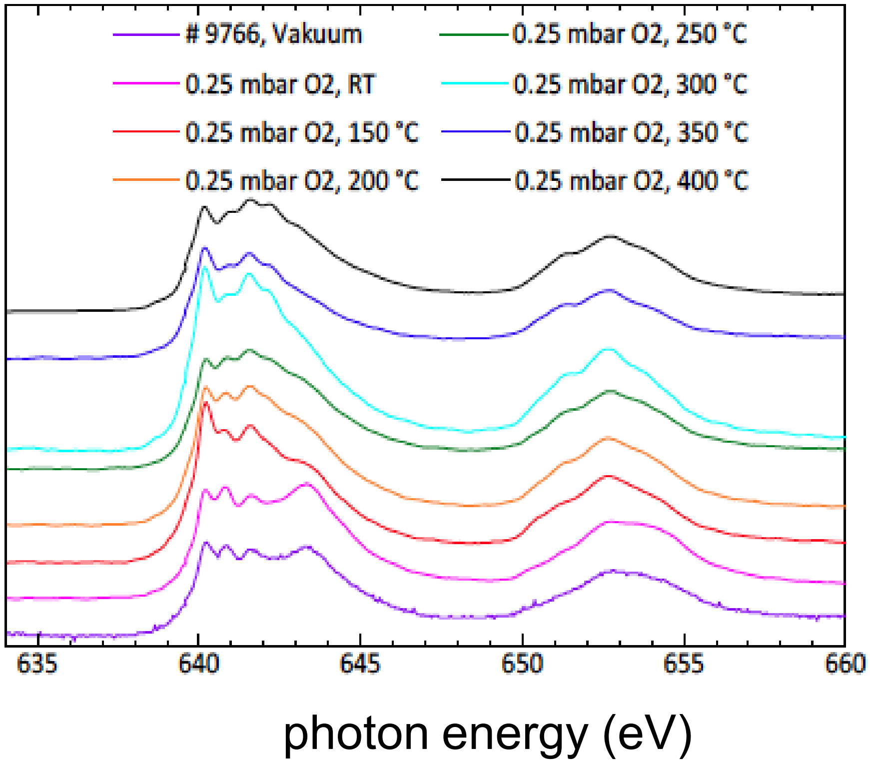
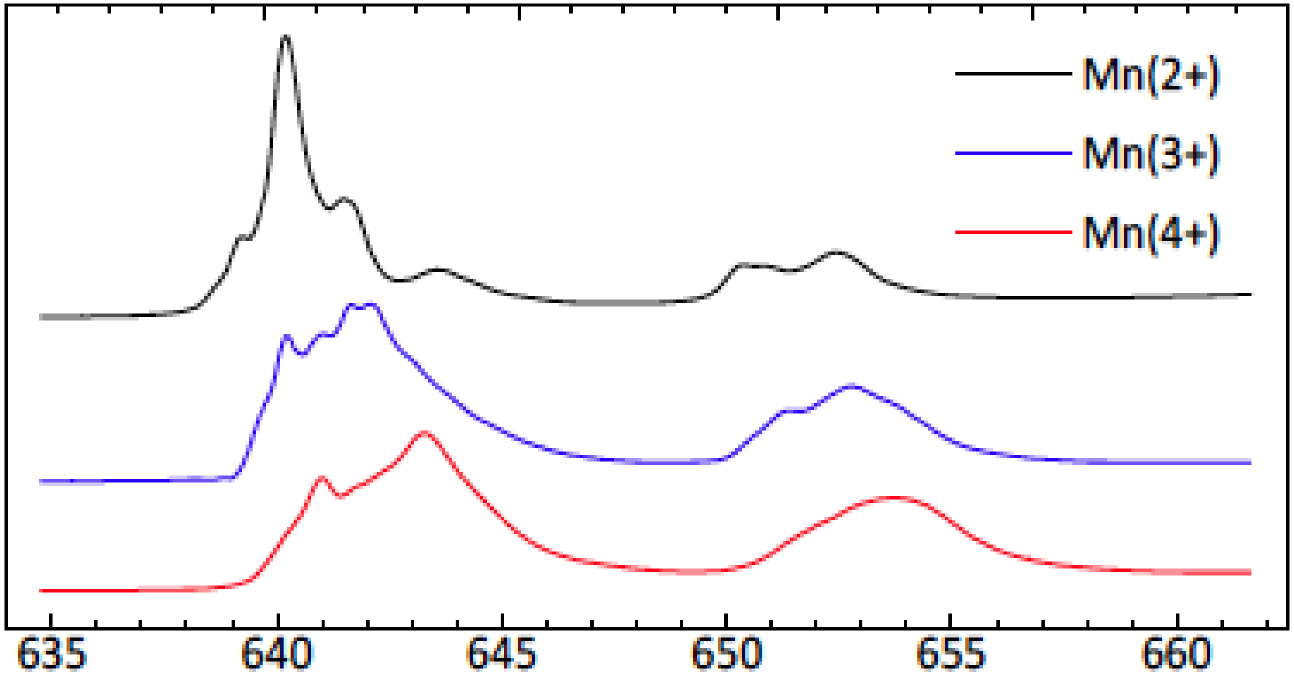




The CNT nanoparticles are well reducible, the bulk oxide gets fully oxidized

Ambient pressure NEXAFS for reactivity



photon energy (eV)

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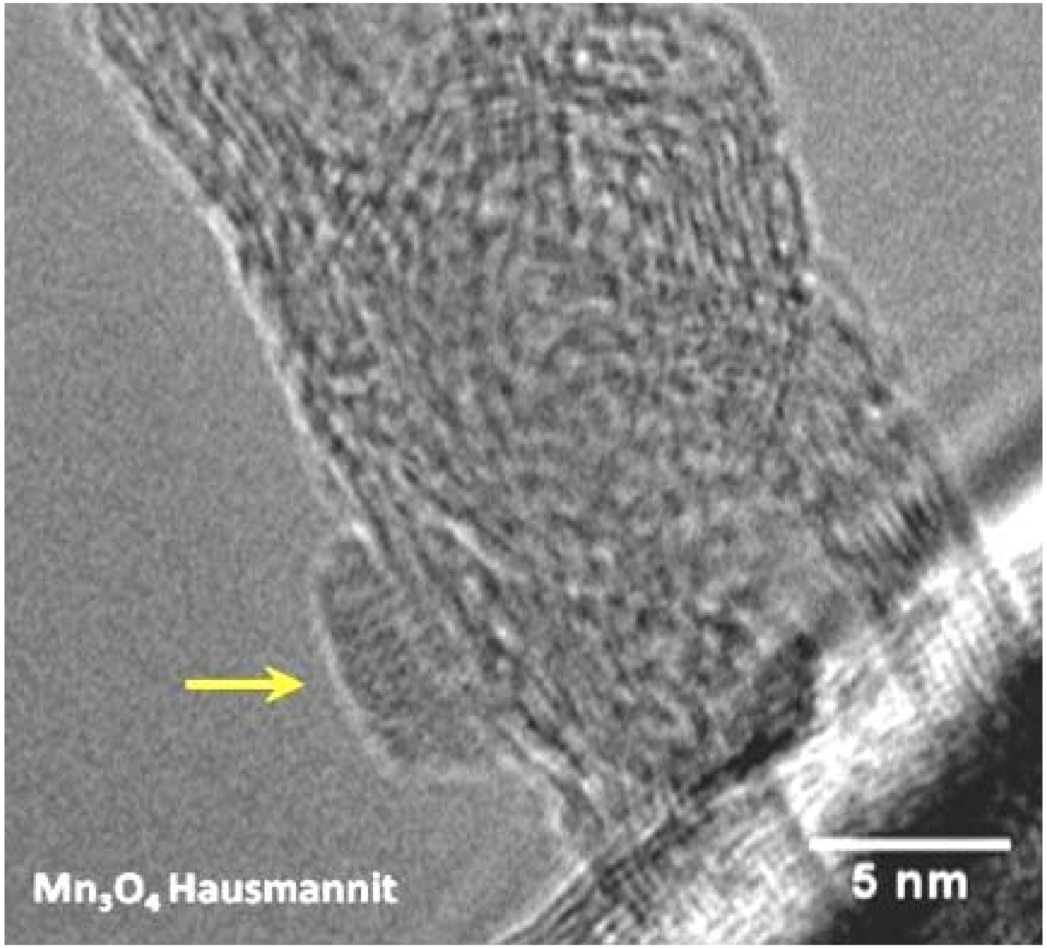
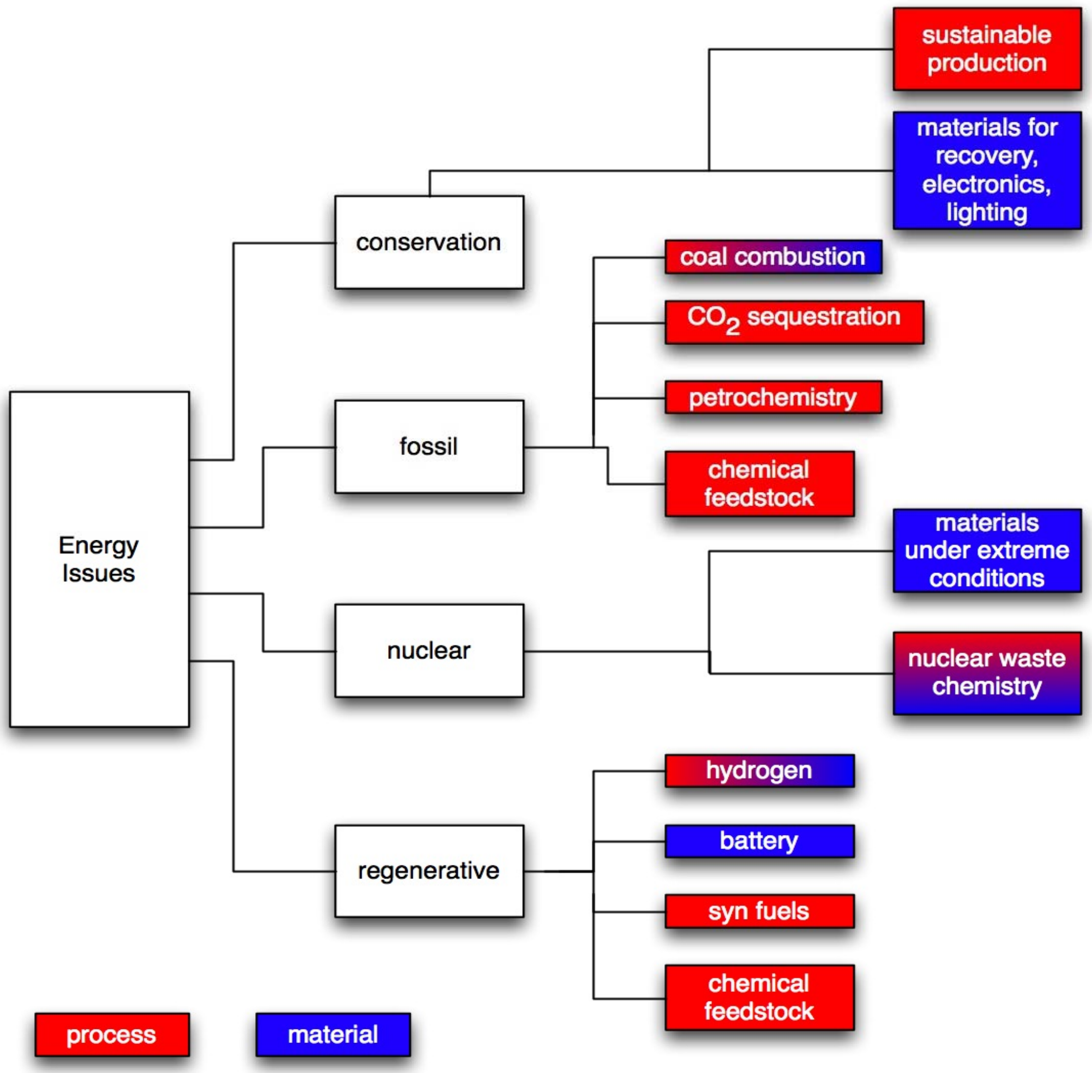
Ambient pressure NEXAFS for reactivity



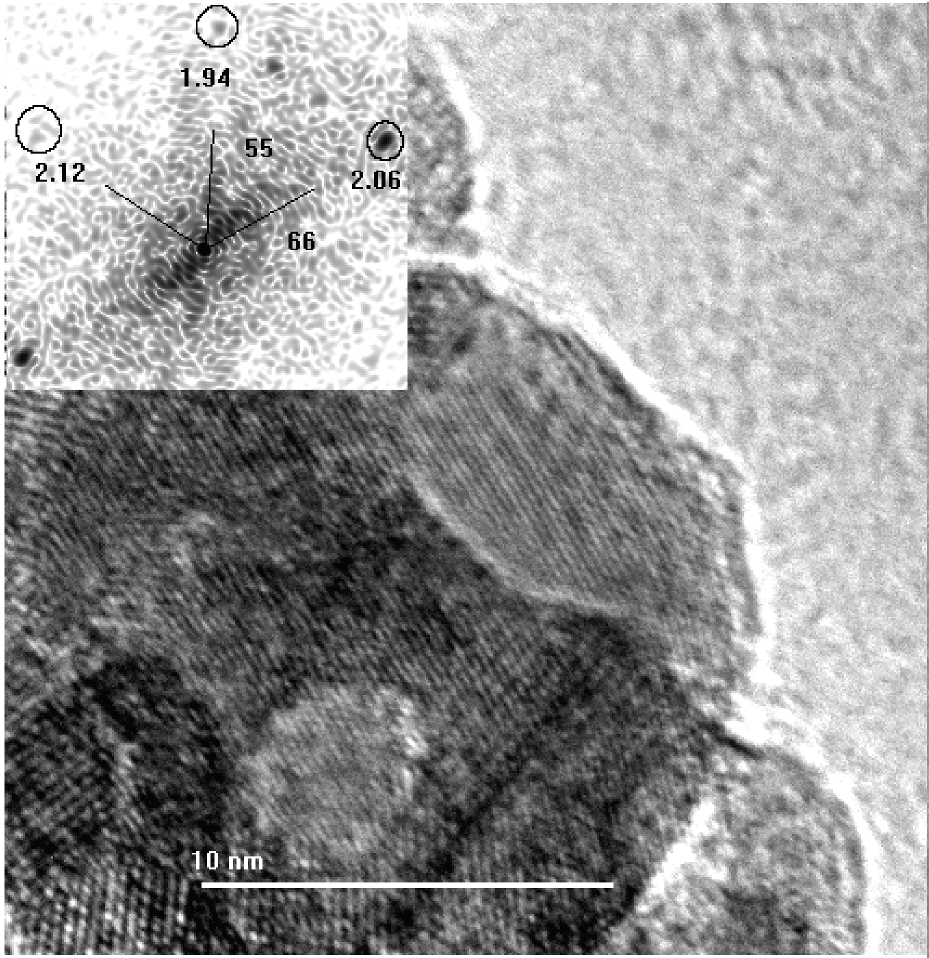
The CNT nanoparticles are well reducible, the bulk oxide gets fully oxidized

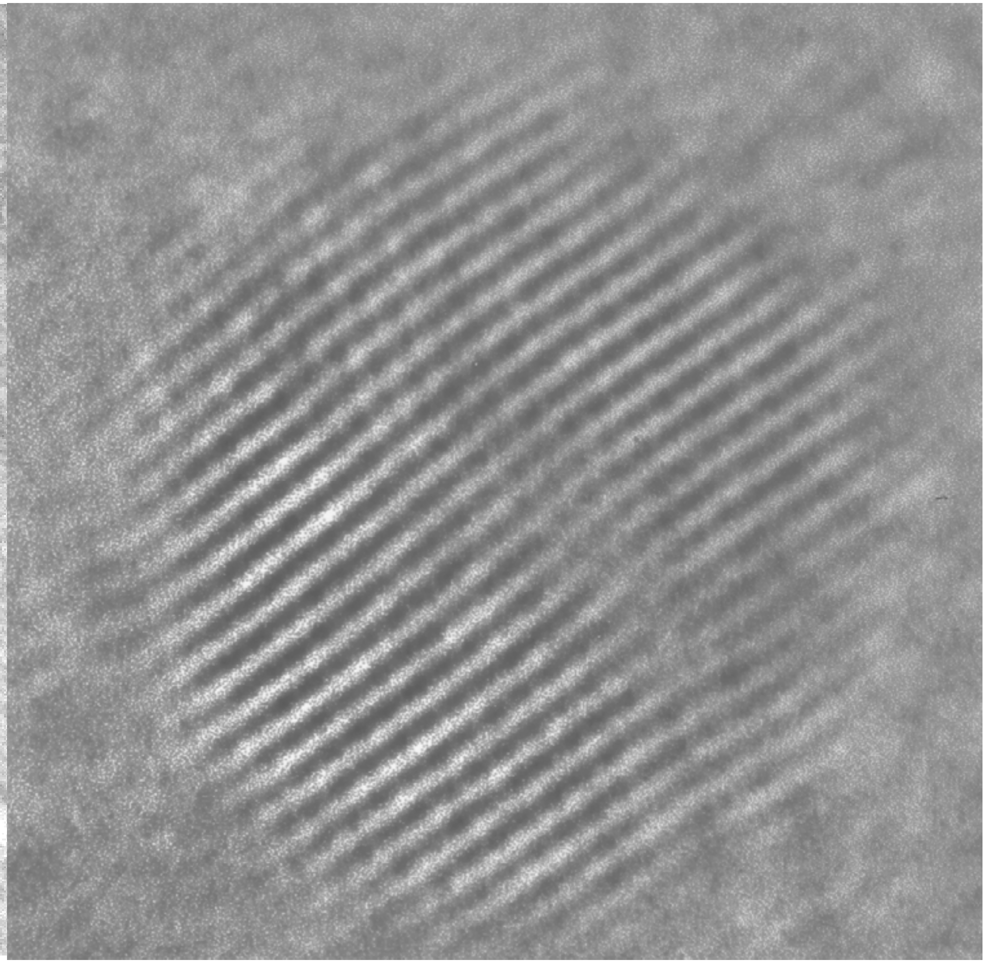
Chemistry: strategic for energy



- In energy science chemistry plays a multiple indispensable role;
- Efforts to save energy carriers (partly by chemistry) are most important now
- But cannot solve the issue fundamentally

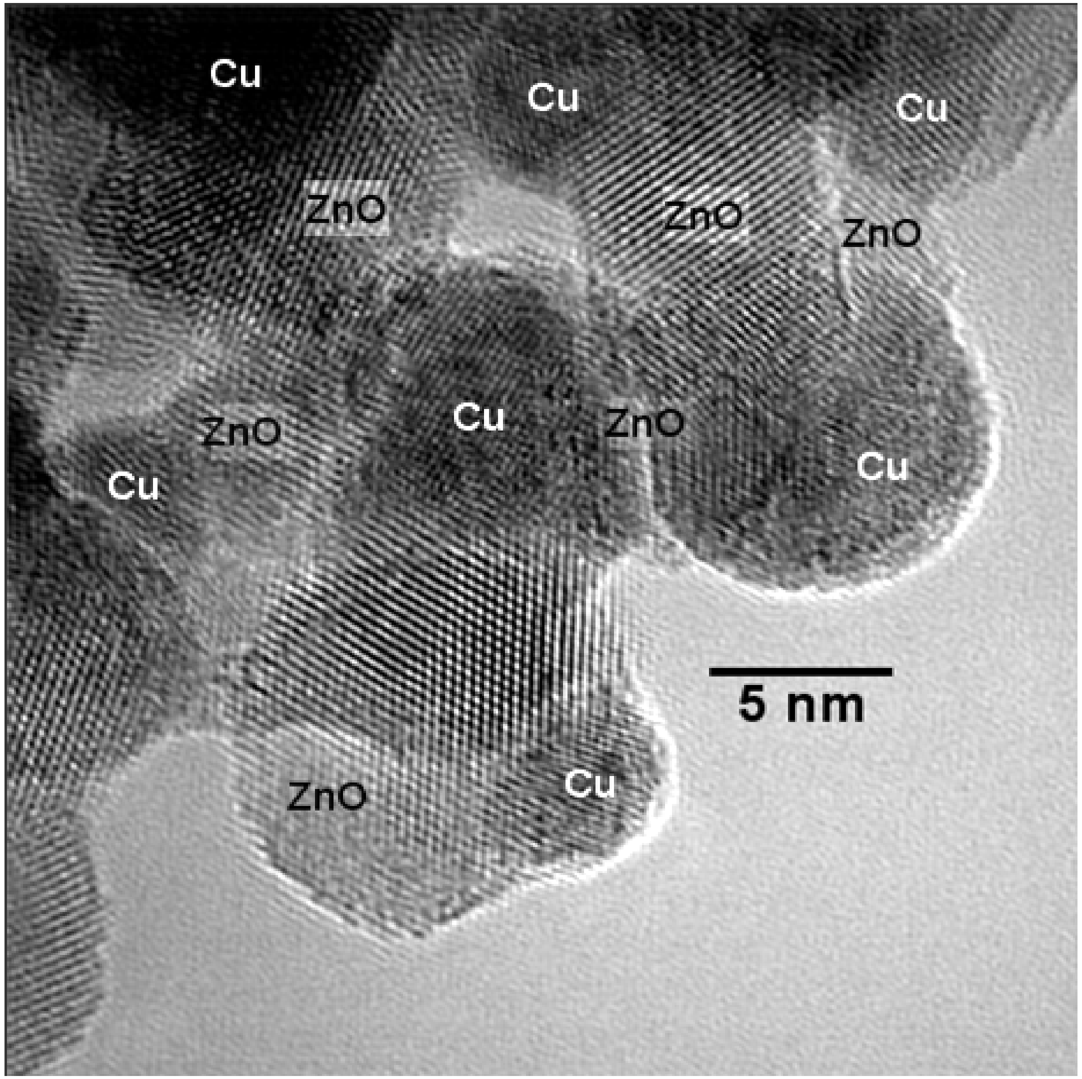
Structural "plasticity"





Cu can incorporate small amounts of oxygen without forming an oxide

Structural “plasticity”



To do list

- Stay realistic about technology potentials.
- Keep using existing technologies in energy use (e.g. synthetic methane as fuel).
- Forward effectively science and technology of all regenerative energies including chemical storage.
- Deploy decentralized hierarchical energy supply chains in Germany: use opportunity to renew, stop impeding the change!
- Promote science of fusion energy and of nuclear fission treatment plus potential alternatives.

Li battery cathodes: electrical conductivity with chemical storage

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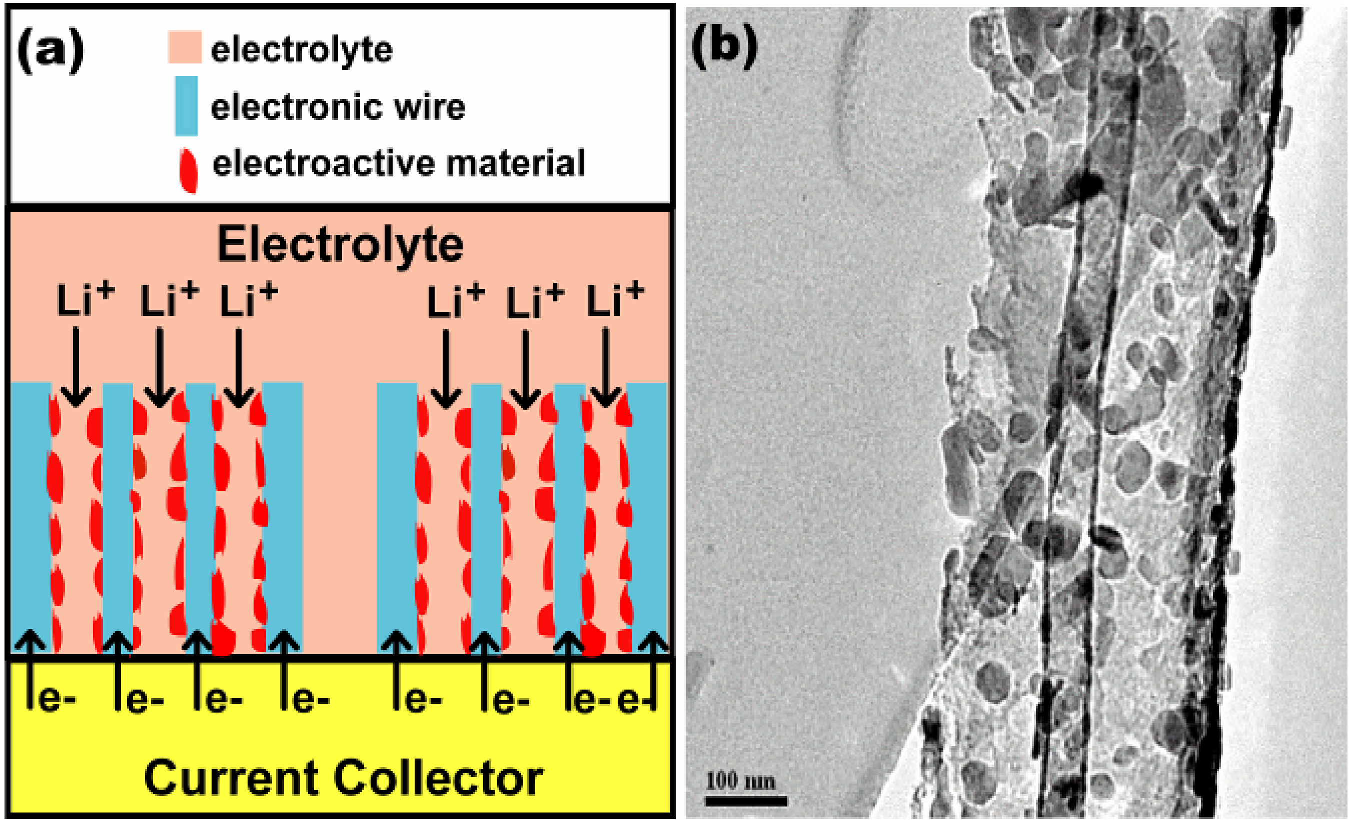
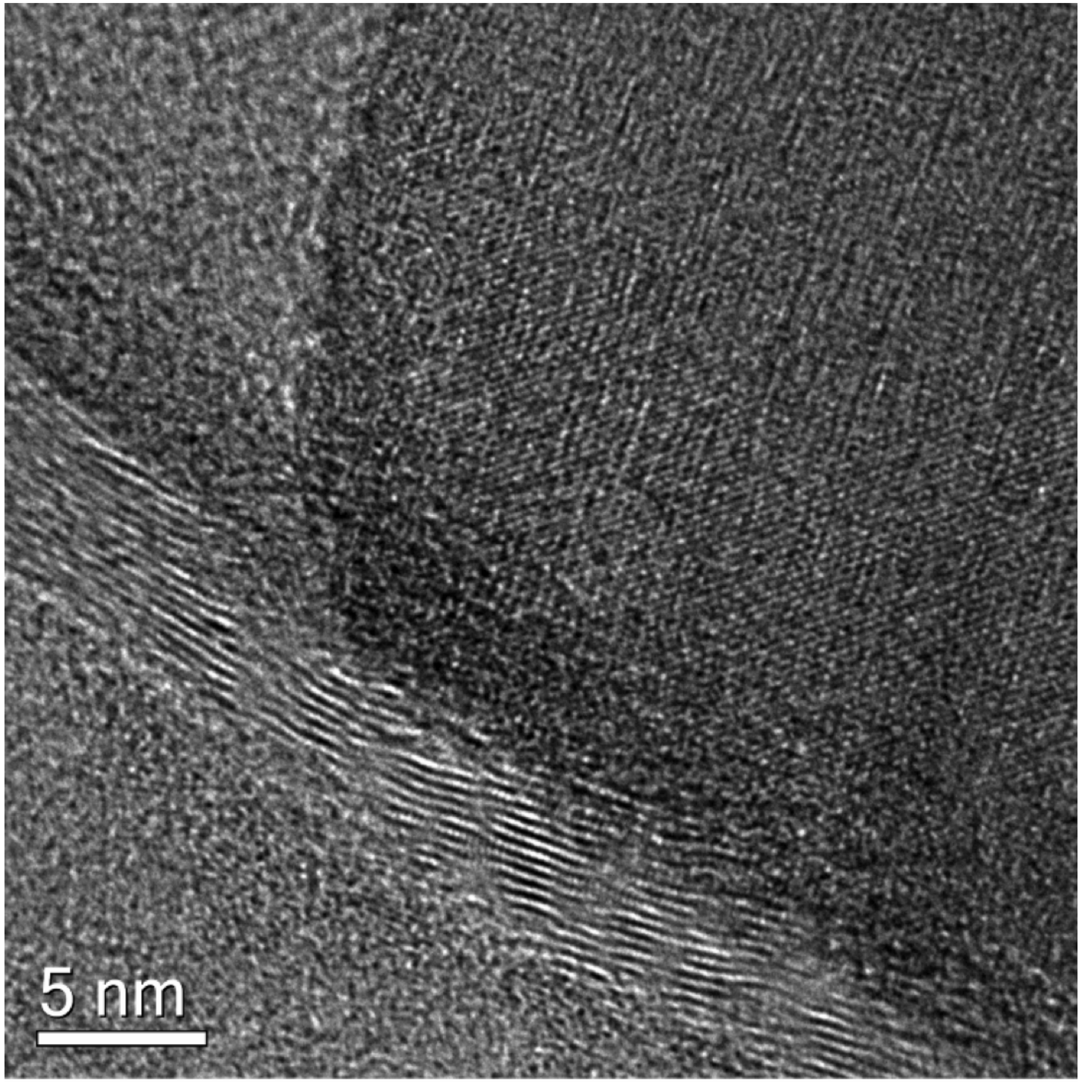
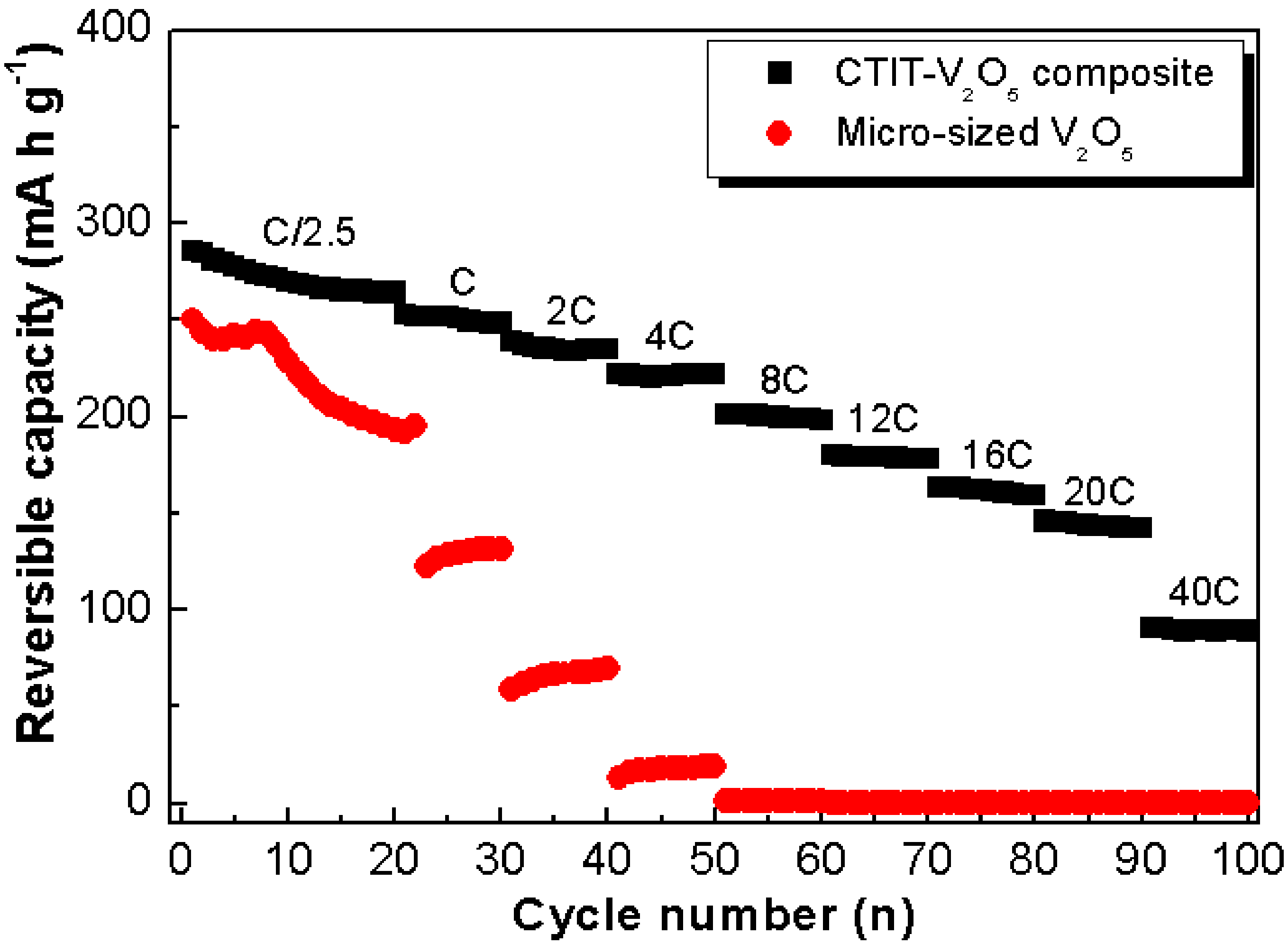


with J.Maier

Li battery cathodes: electrical conductivity with chemical storage



Li battery cathodes: electrical conductivity with chemical storage



Catalysis

- Catalysts are no static reactive surfaces.
- They exhibit a small number of active sites (high energy).
- These sites occur from reaction of the correctly designed catalyst precursor with its reactant environment.
- Catalysts have to be phase-defined materials to limit the solid state (surface) reactivity under operating conditions to the desired process.
- Surface solid state chemistry is the key to this class of functional materials.

What we have learned from the last decade of science