Material Dynamics of OER Electrodes

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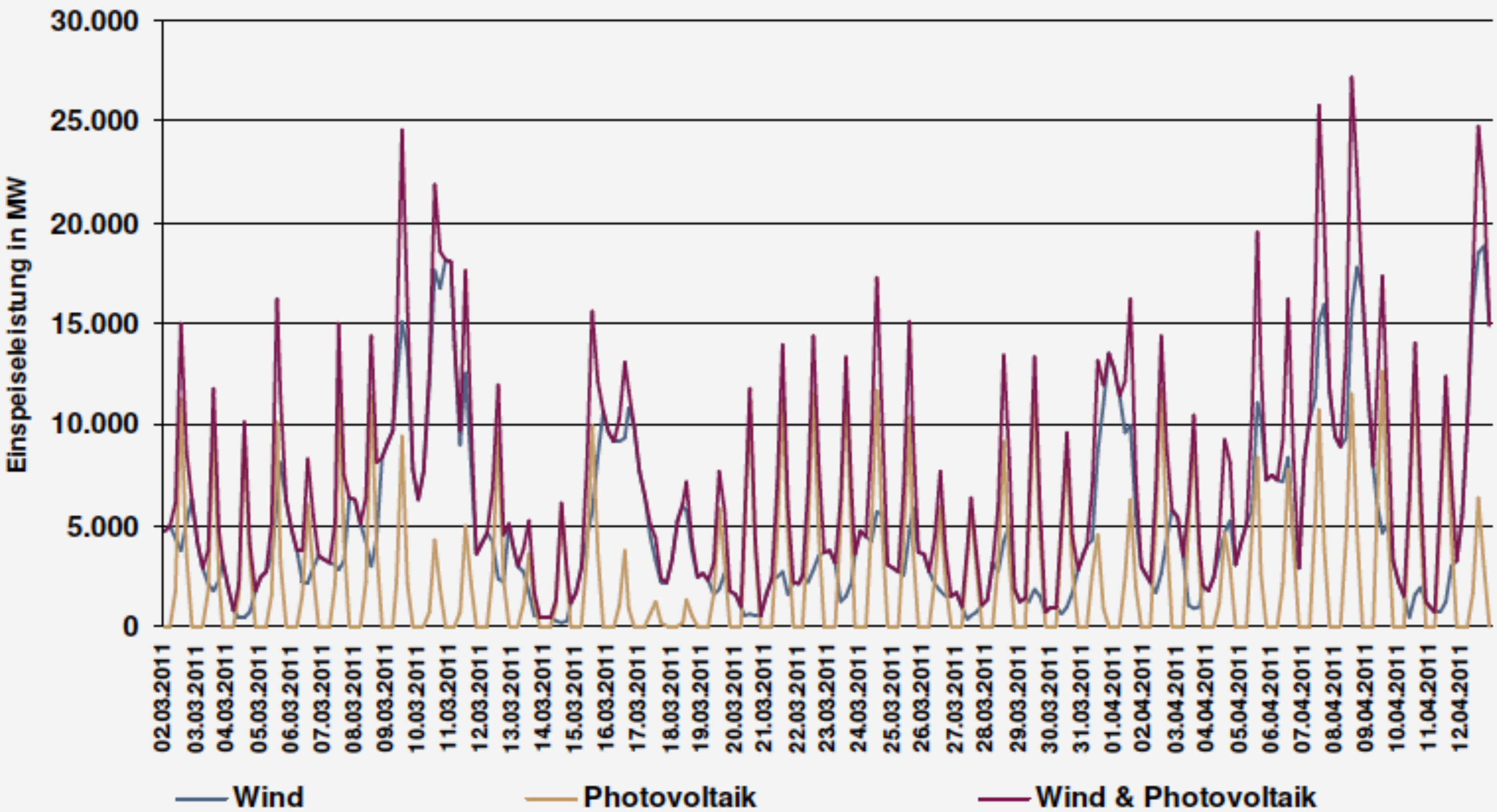
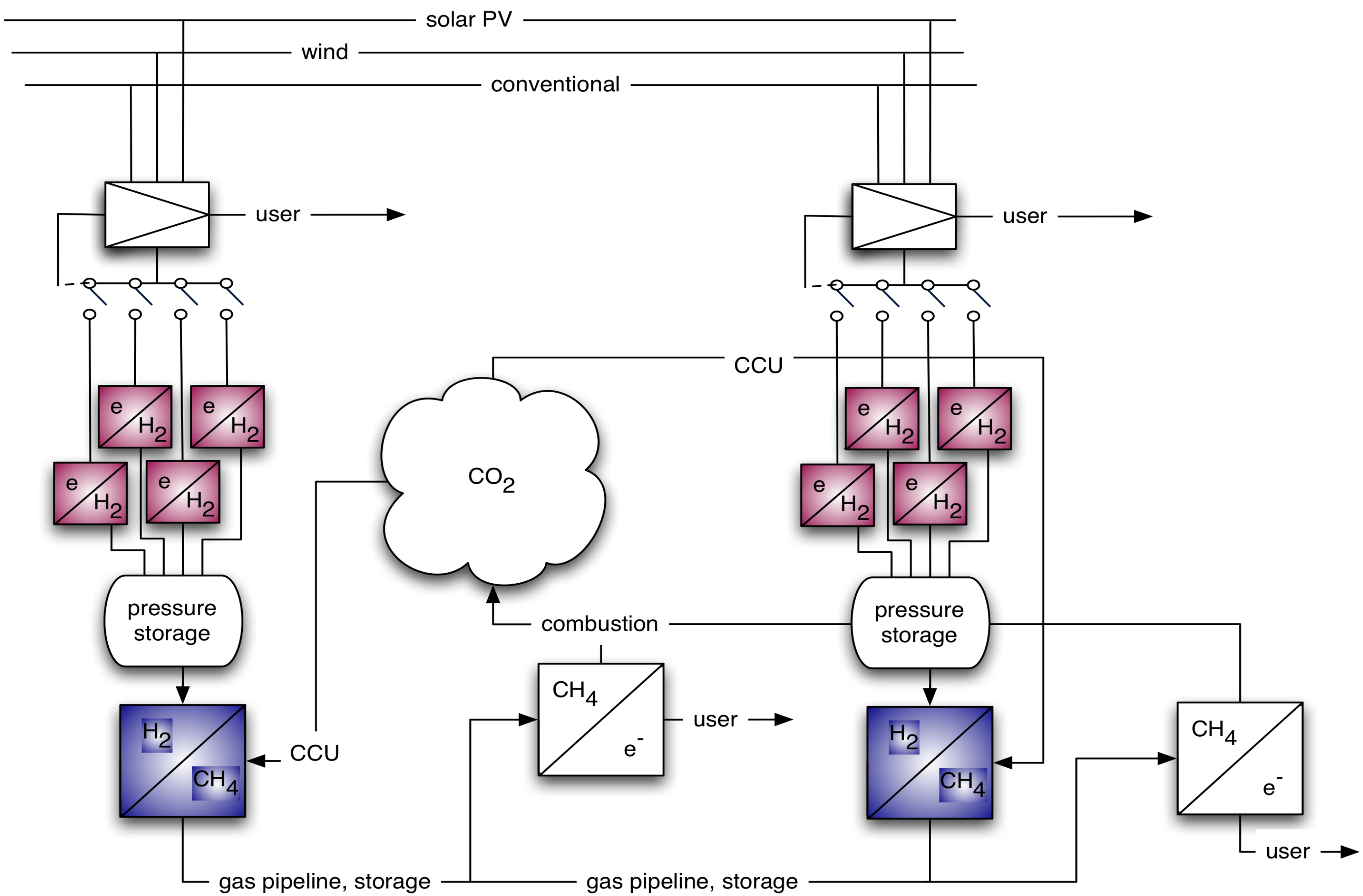
Energy storage

- Regenerative energy is presently “peak load” with limited predictability: fossil is base load.
- Cannot continue with the targets of the “Energie-konzept”.
- Saving is important but also not sufficient.
- Conversion of primary electricity into solar energy carriers is the critically missing technology.
- Chemical energy conversion using electro-photo-chemical devices and catalysis as core technology:
- Science of controlling chemical activation of small molecules.

Energy storage



Water splitting as load sink
Power-to-gas in addition to short-term storage



Water electrolysis

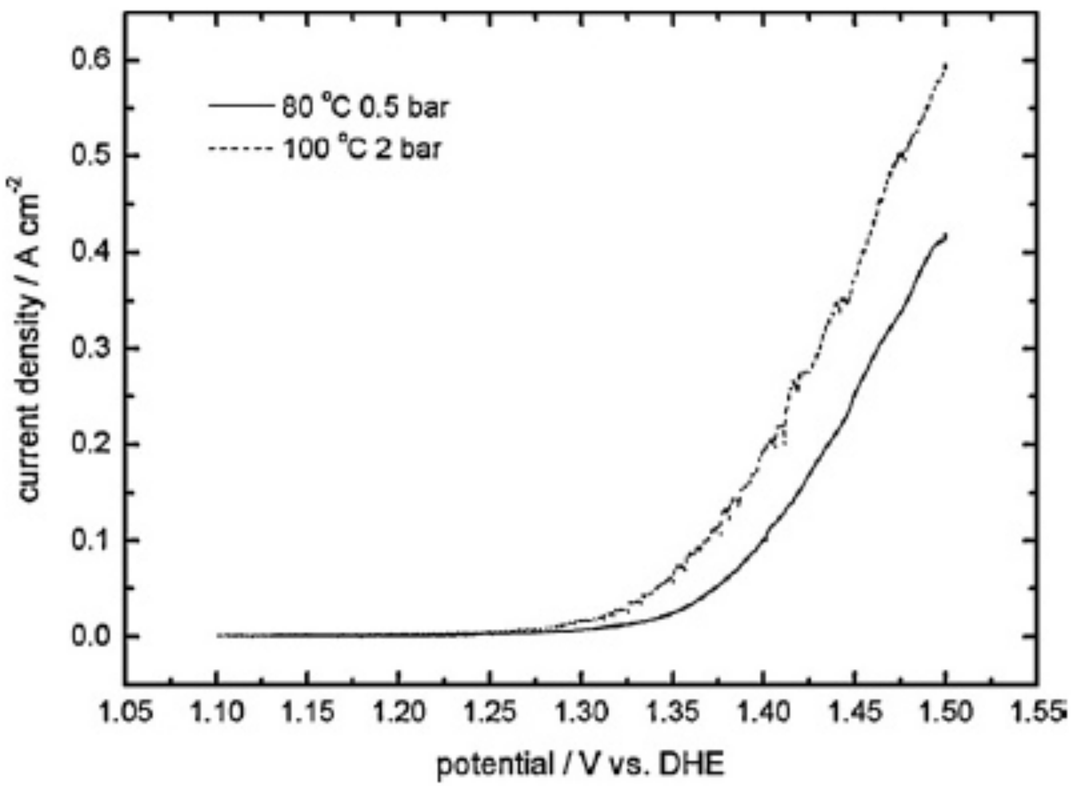


Fig. 11. Steady state polarization of $Ru_{0.7}Ir_{0.3}O_2$ electrode (1 mV s^{-1}).

Wu Xu et al J. Power Sources (2011)

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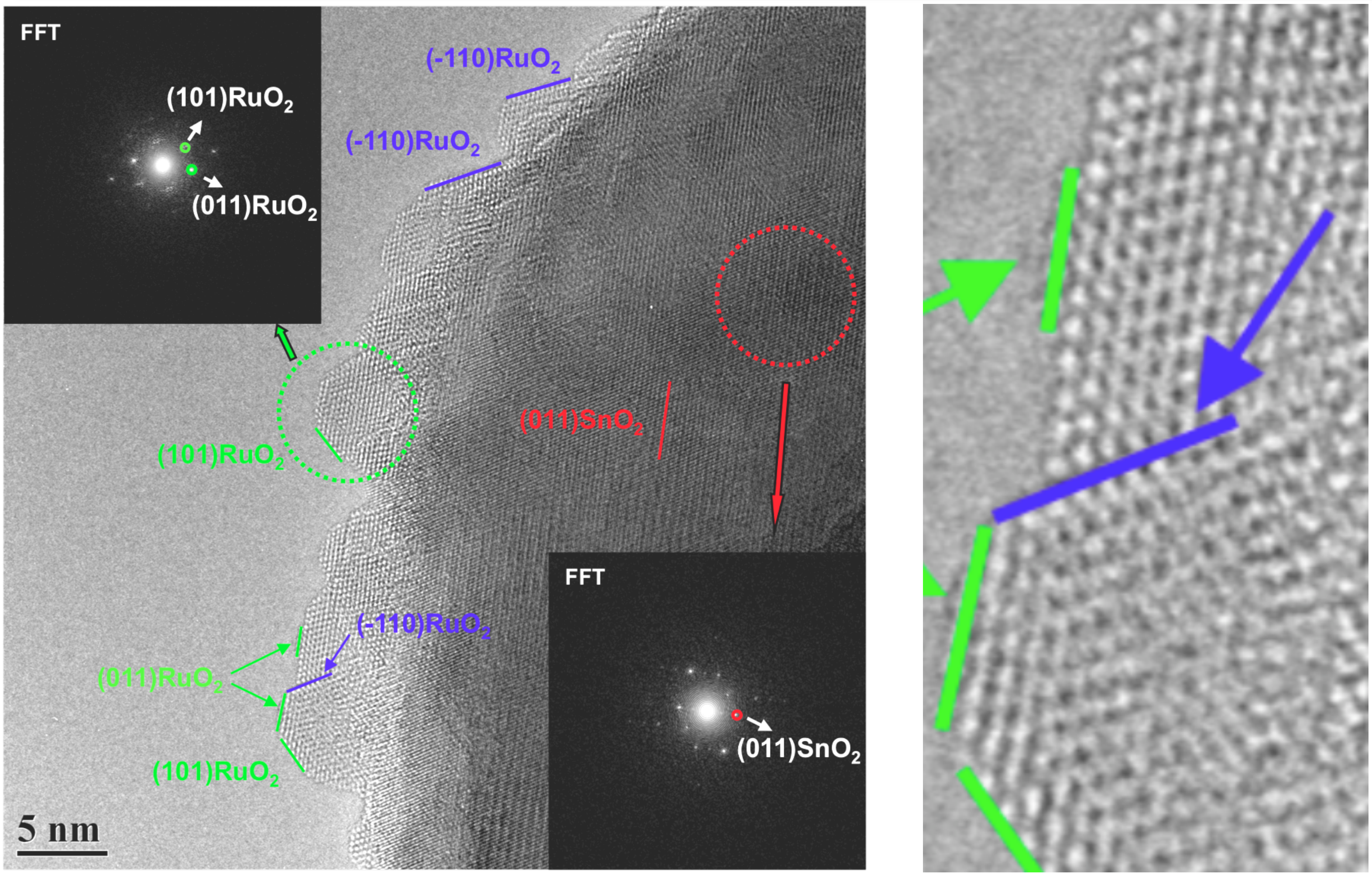
Water electrolysis

Table 1
Specifications of HOGEN®RE PEM electrolyzer by Proton Energy Systems

Hydrogen output	0.5 or 1.0 Nm^3/h
Max delivery pressure	200 bar
Hydrogen purity	>99.9% (optionally >99.999%)
Water usage	0.5 or 1.0 l/h
Water quality (min) required	deionized (ASTM Type II)
Power consumption	6.6 kWh/Nm^3
Electrical supply required	AC: 190–240 VAC, 1 phase, 50/60 Hz, 7.2 or 12 kVA DC: 60–200 VDC, 150 A (max)
Operating environment	Indoor (optionally outdoor)
Dimensions	97 × 105 × 106cm
Weight	220 kg
Installation	"Plug & play"
Controls and automation	Fully automatic and unattended

F. Barbir, Solar Energy (2005)

Oxidation electrodes
Nanotechnology provides kinetic stability



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Challenges for electrolysis

- Efficient operation under variable load.
- Stability against frequent power interruption.
- Better efficiency through lower OER overvoltage.
- No use of rare materials.
- Facile system design for mass production.

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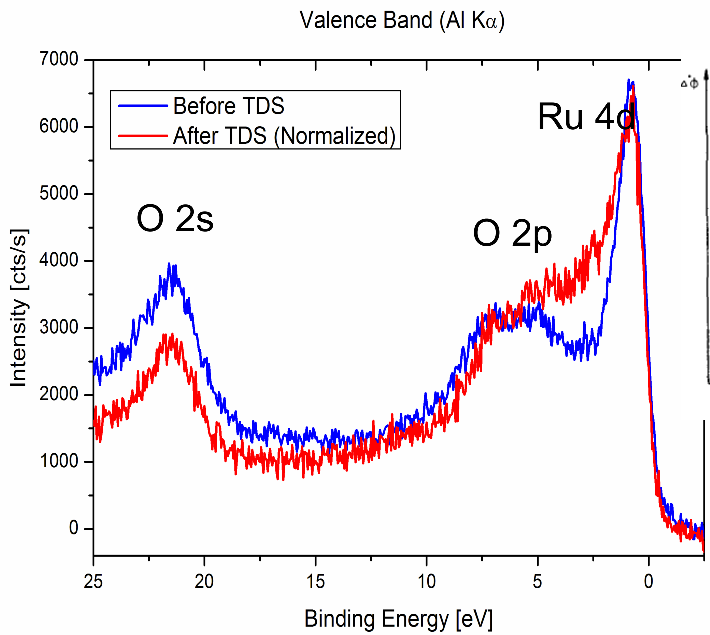
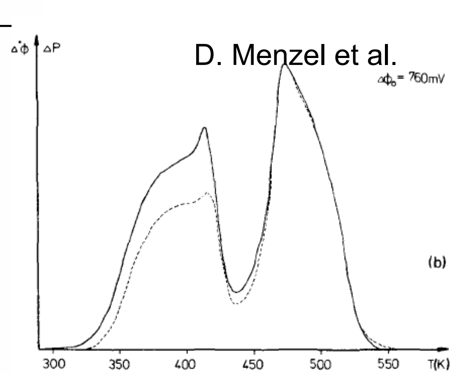
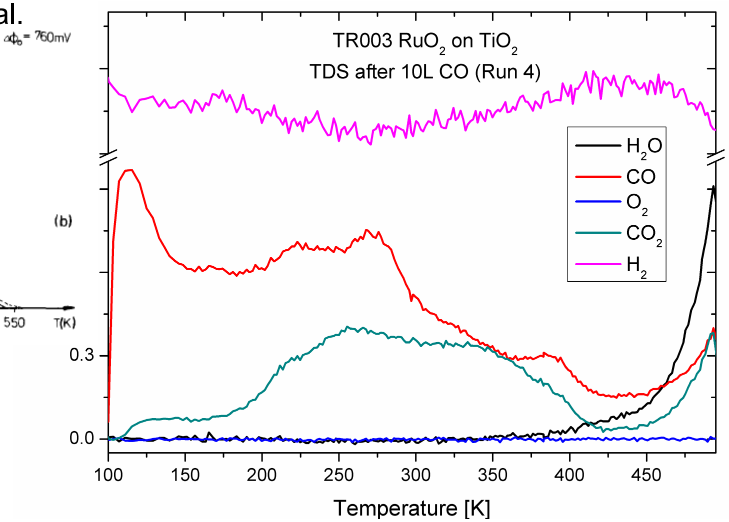
Properties of RuO_x electrodes: a challenge for characterization



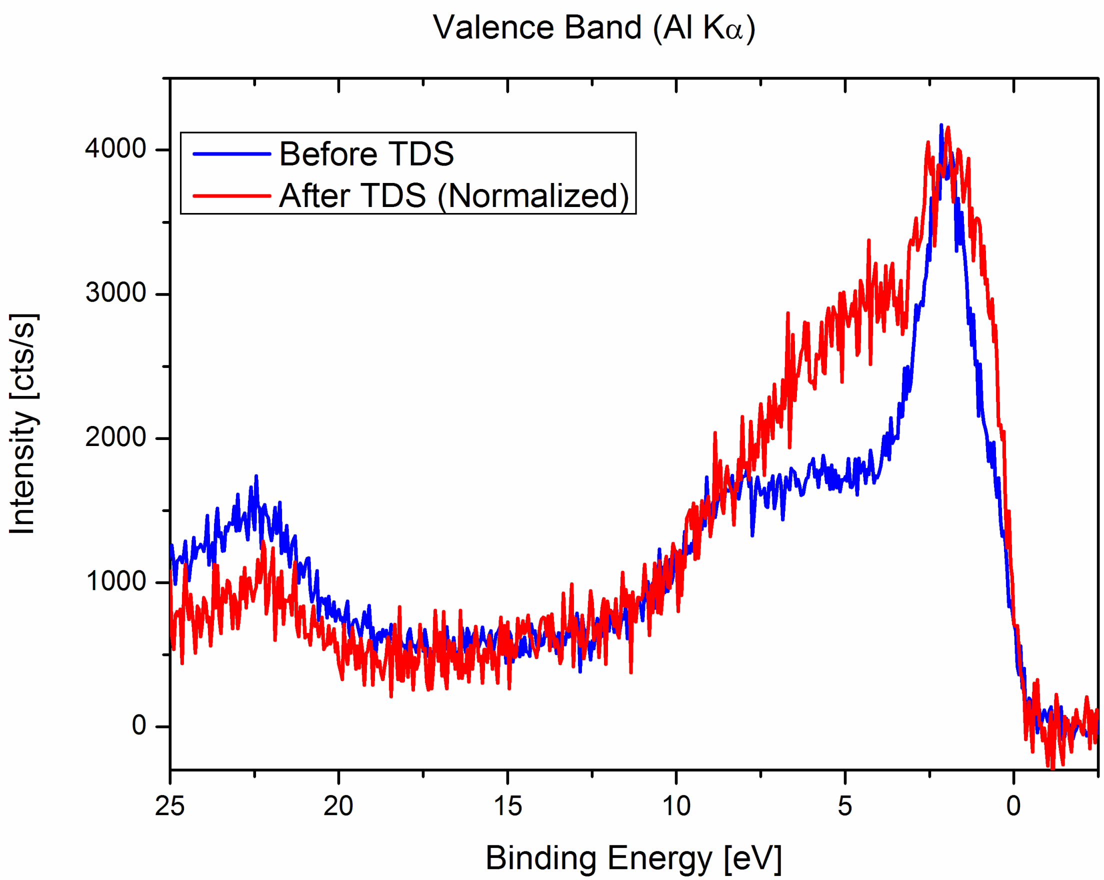


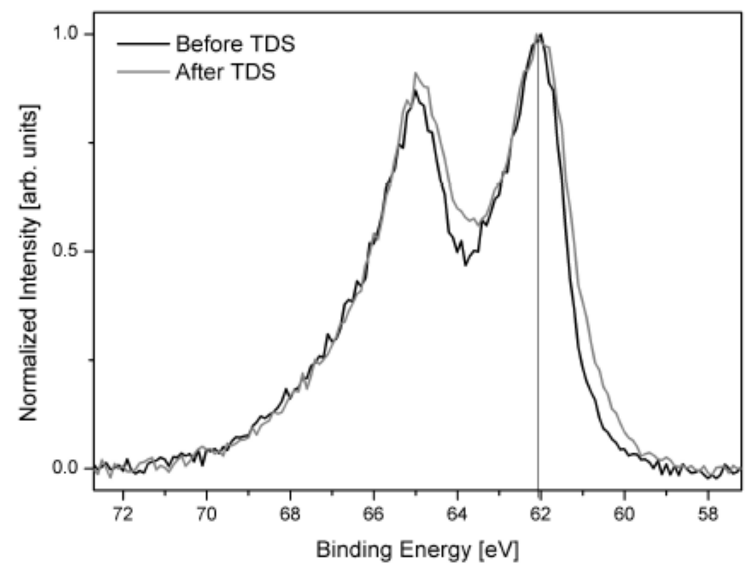


The electrode is a conducting oxide.
CO TDS up to 550 K causes reduction: no RuO_2, suboxide

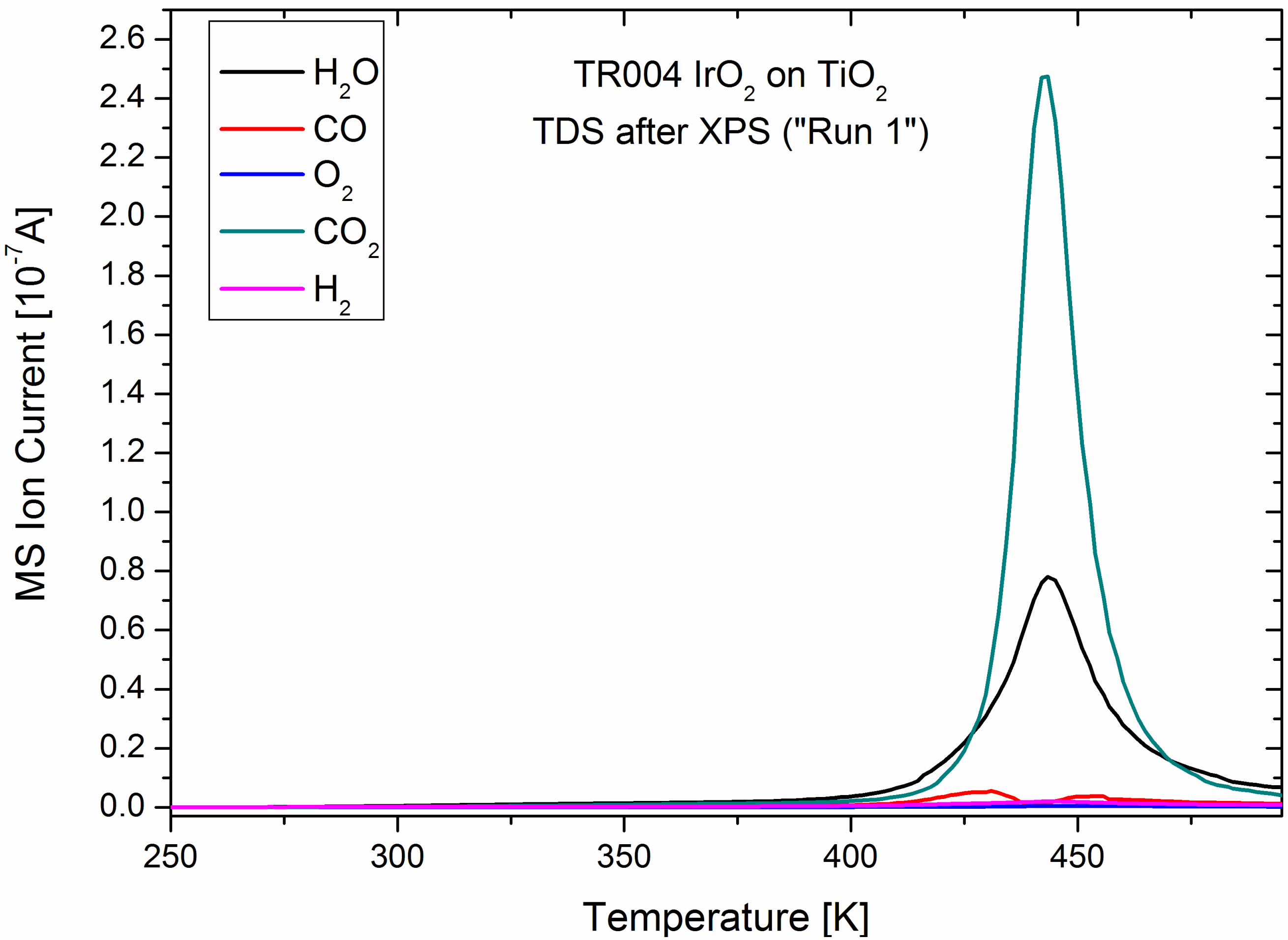
Equilibrated CO TDS senses oxidic sites with traces of metallic sites:
suboxide

IrOx: electronic structure





IrOx: TDS
Reaction dominates desorption



IrOx: TDS
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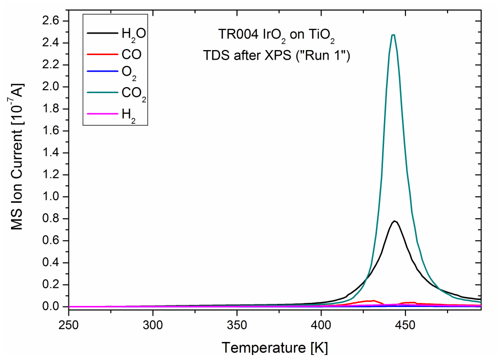
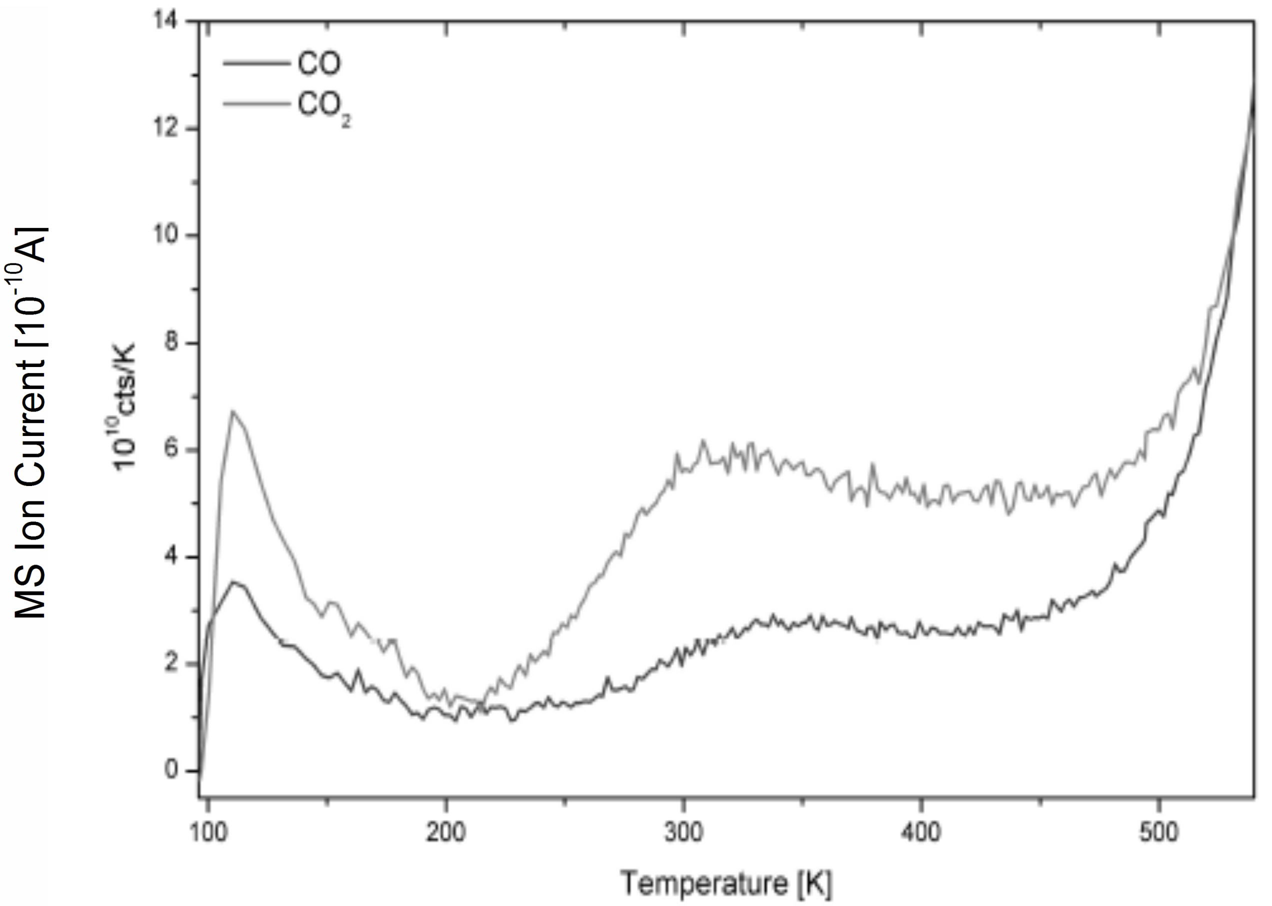
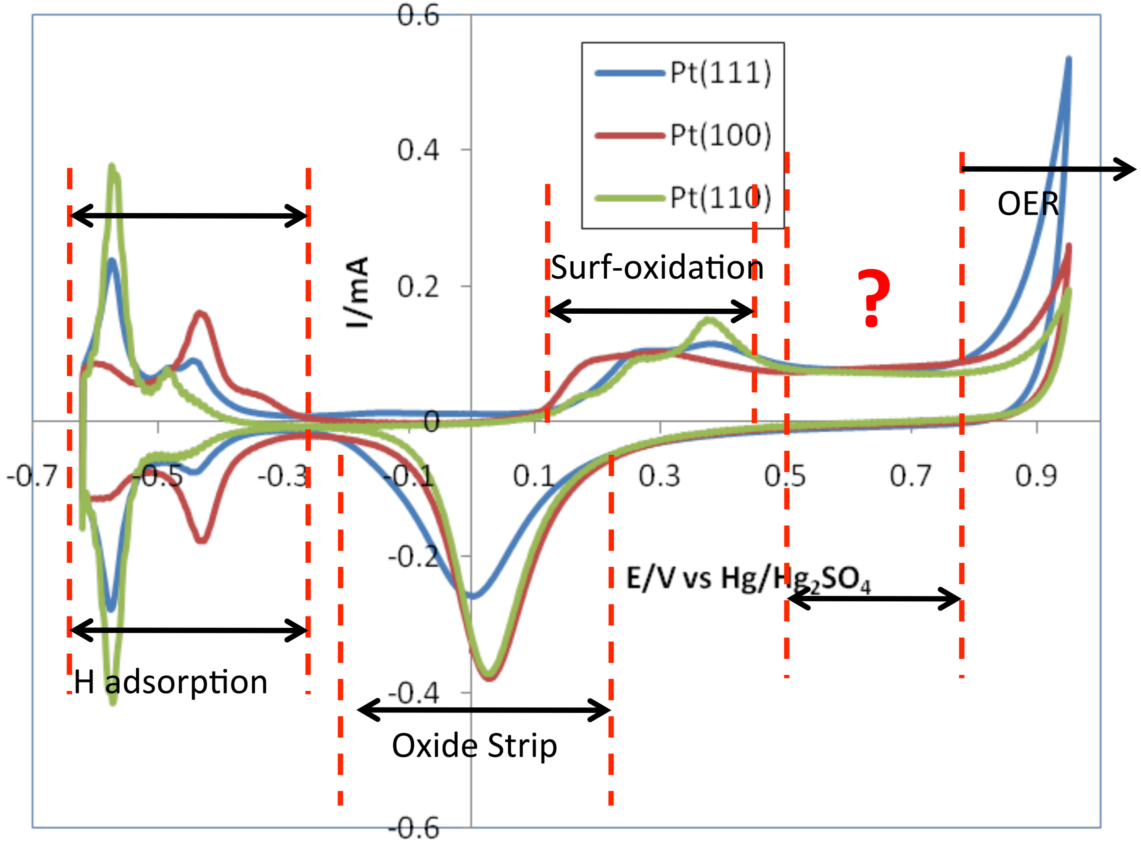
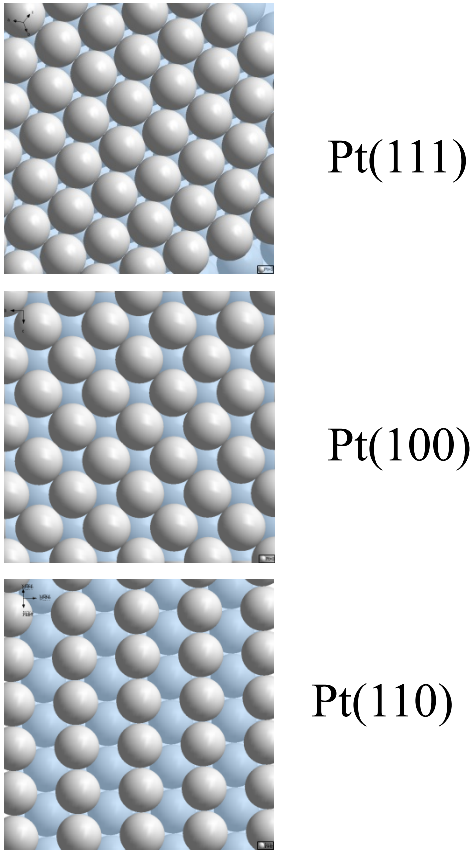


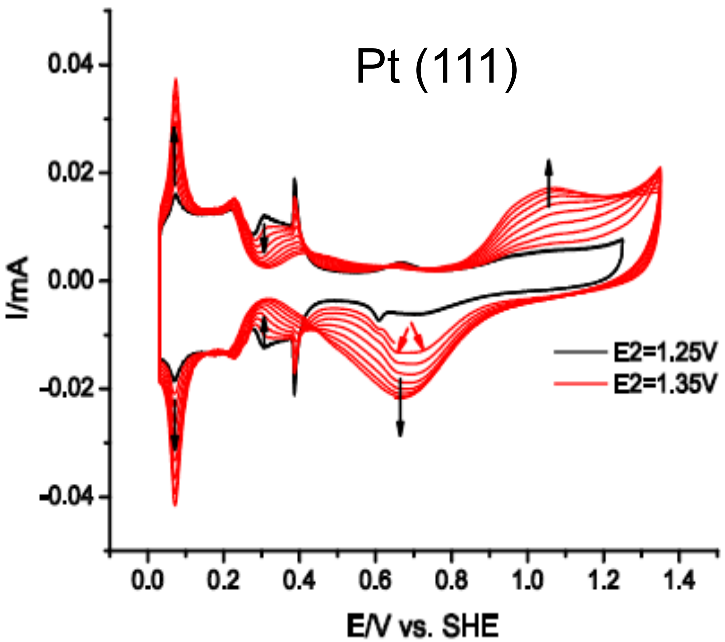


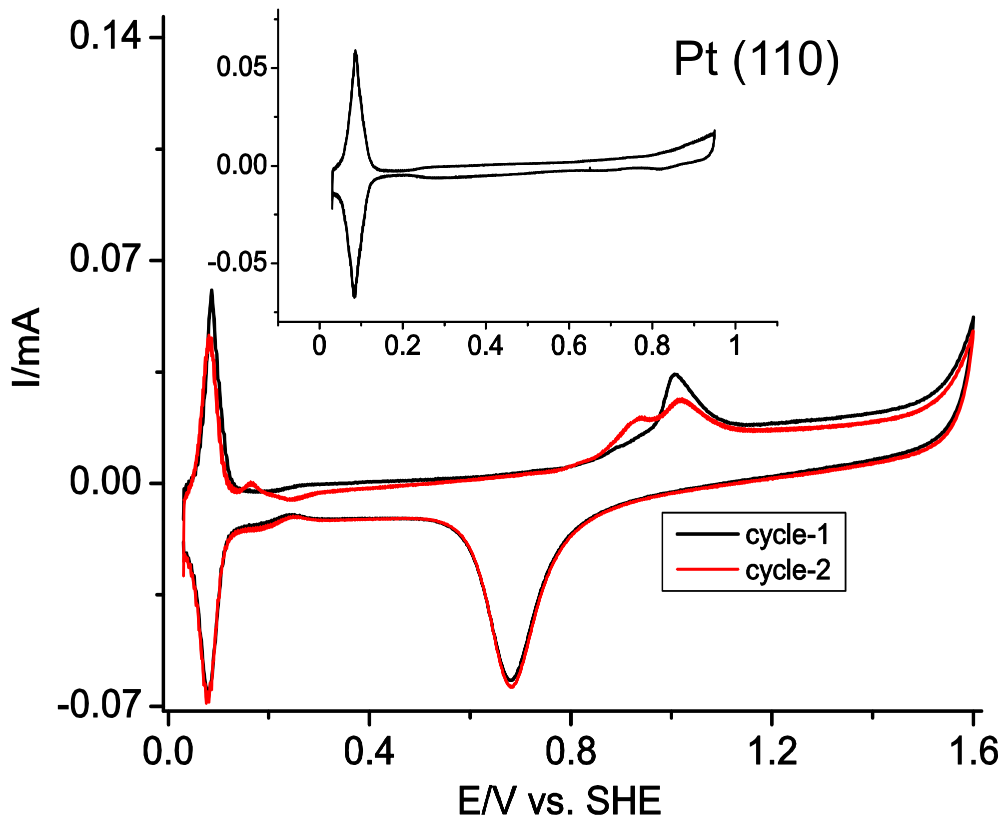
Pt: the archetype model



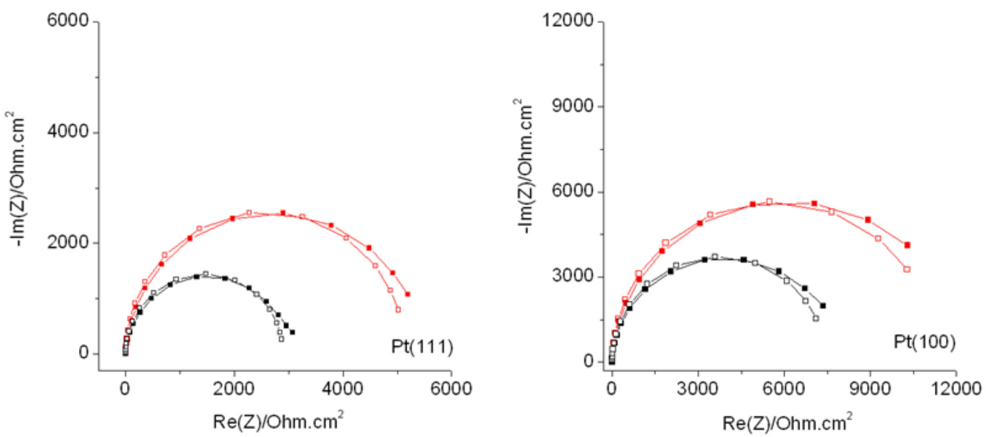


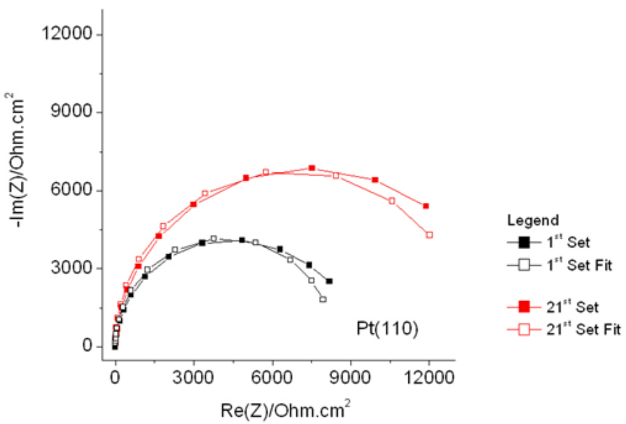
Pt electrodes at OER conditions
Structure sensitivity

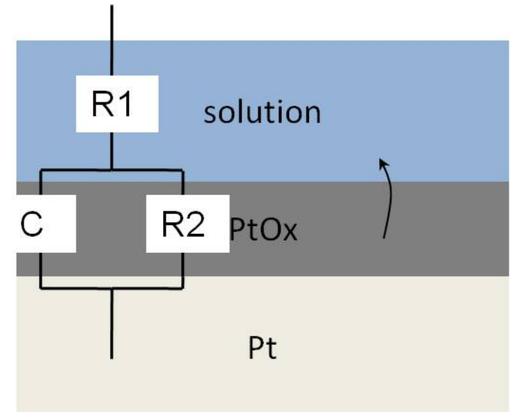




Impedance analysis:
Chemistry in the double layer







Parameters	Fitted value of parameters for various surfaces		
	Pt(111)	Pt(100)	Pt(110)
R1 ($\Omega.cm^2$)	1.68(1.69)	3.6(3.7)	2.0(2.1)
C2 ($\mu F/cm^2$)	51(48.9)	46(44.6)	44(42)
R2 ($\Omega.cm^2$)	2901 (5151)	7434(11307)	8351(13537)

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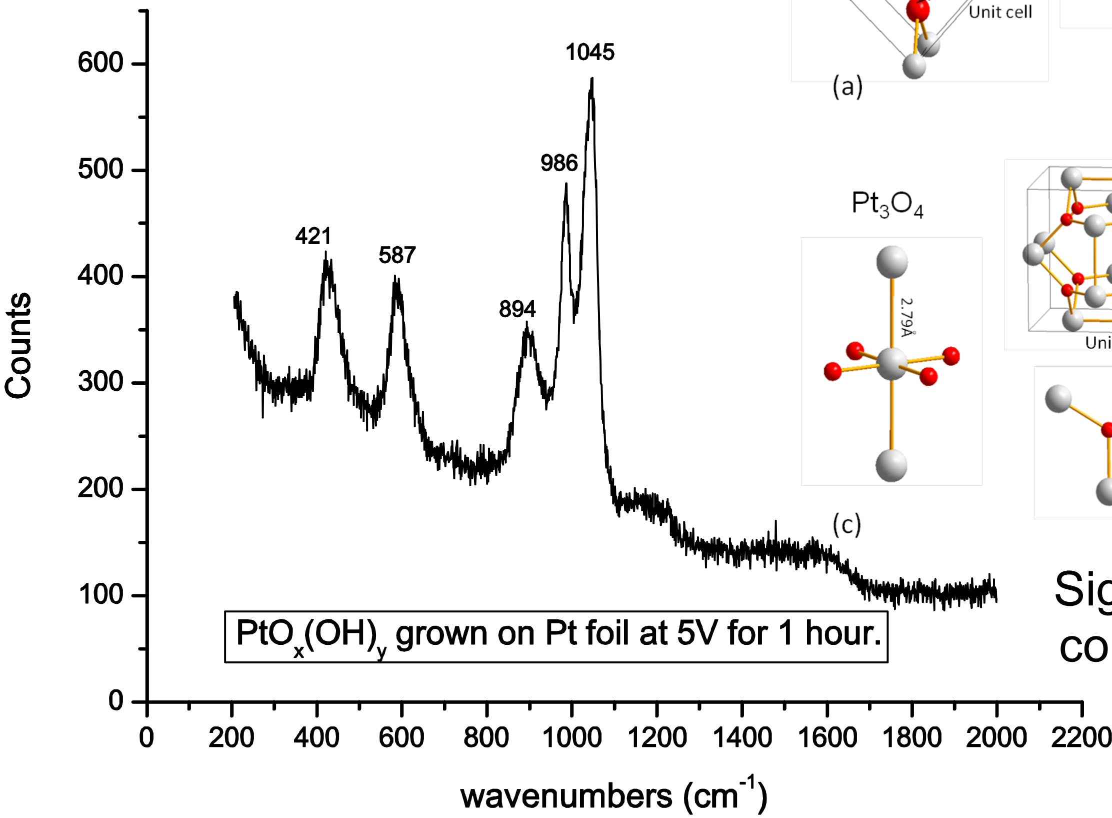
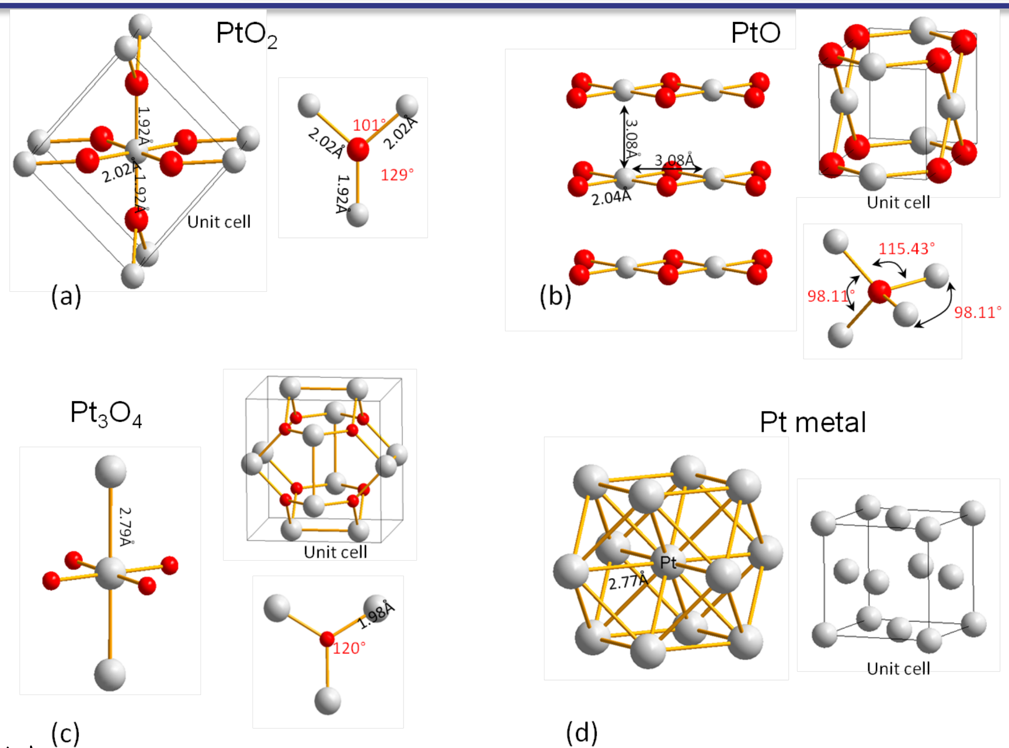
What Pt oxide?
By XRD no signature except textured Pt metal





Signature of a mixture with a dominant contribution form a tetrahedral oxygen coordination

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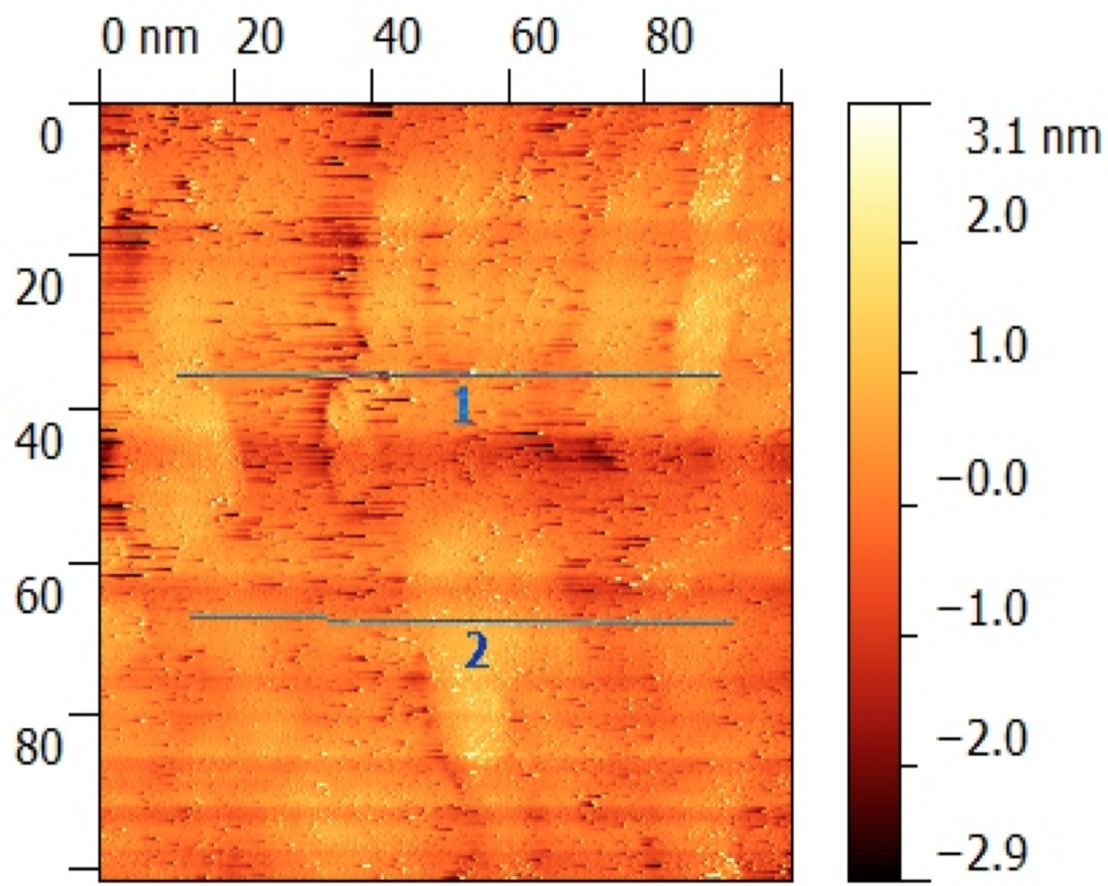
What Pt oxide?
By XRD no signature except textured Pt metal



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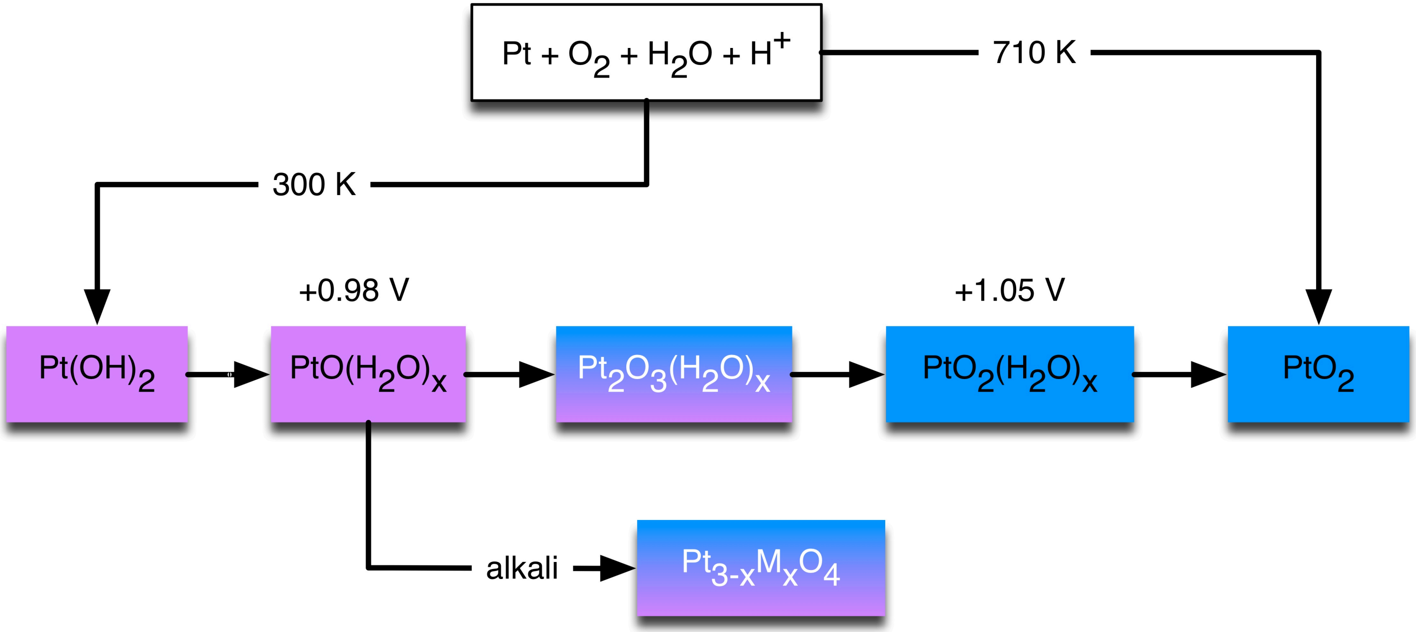
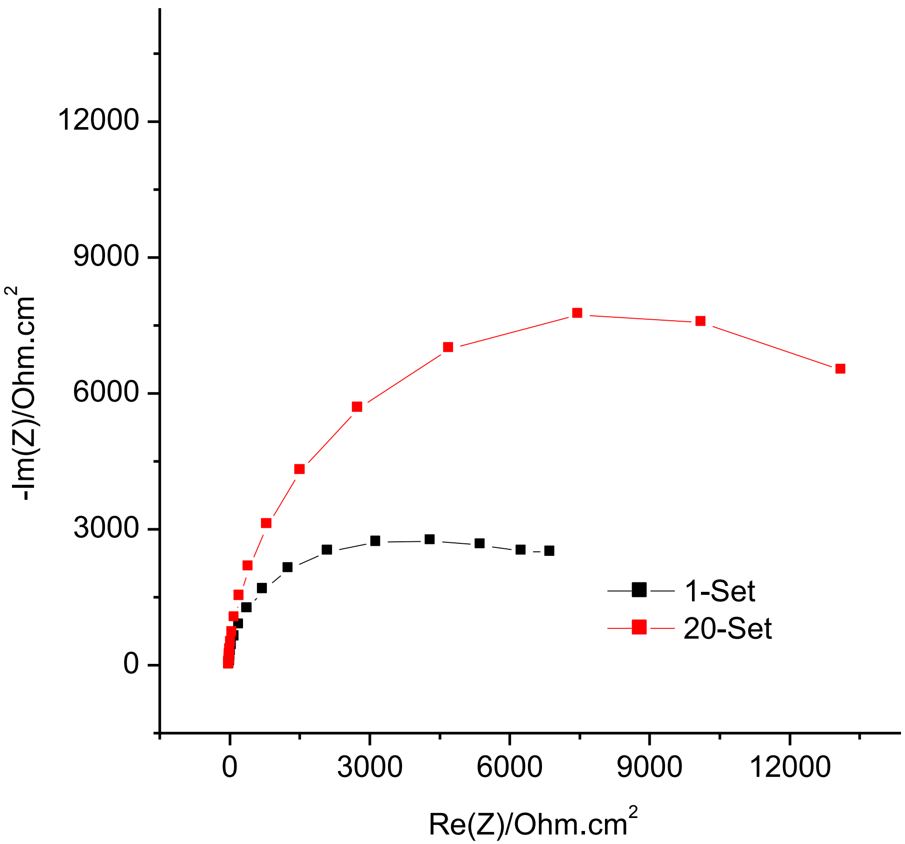
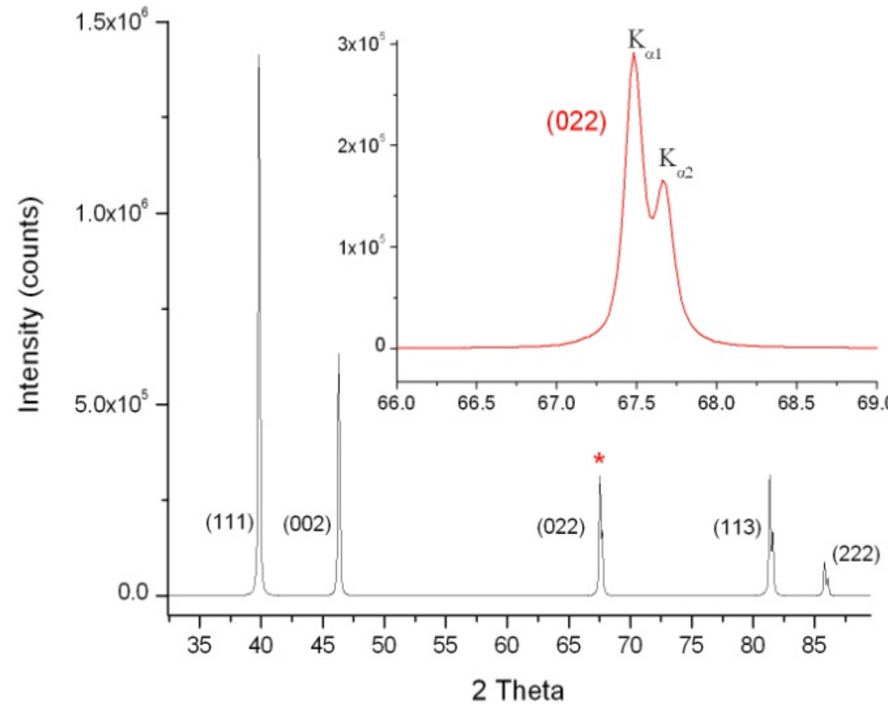
Oxolation chemistry

- Pt forms a series of hydrated oxides from divalent ions in solution.
- Gas phase oxidation impossible at ambient pressure (8 bar O_2).
- If dissolved either complexes with electrolyte (perchlorate) counter-ions or auto-condensation: in base hydroxo-ion (octahedral).



Pt foil as “real” electrode





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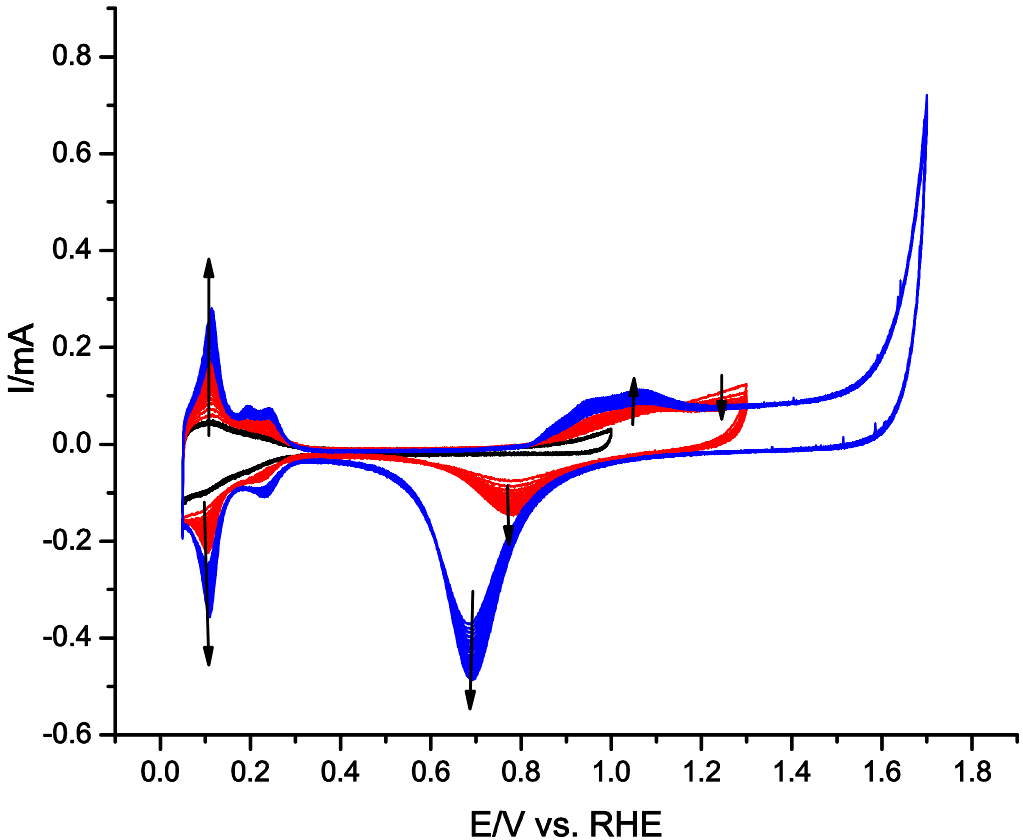
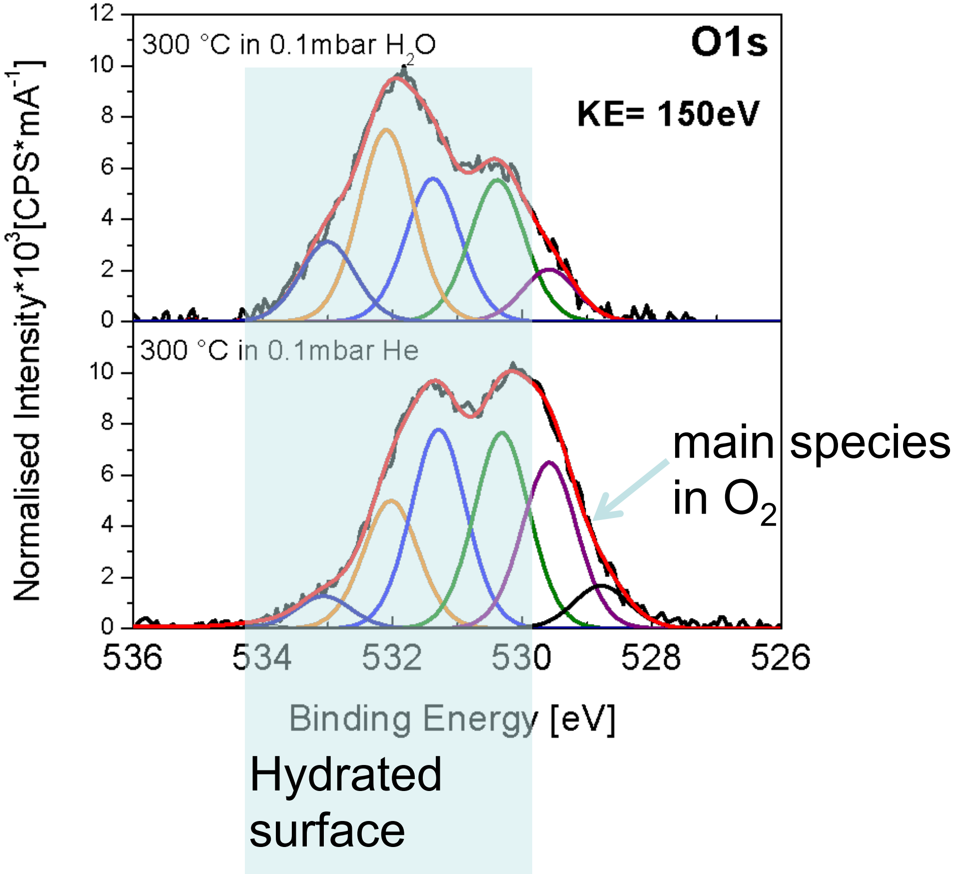
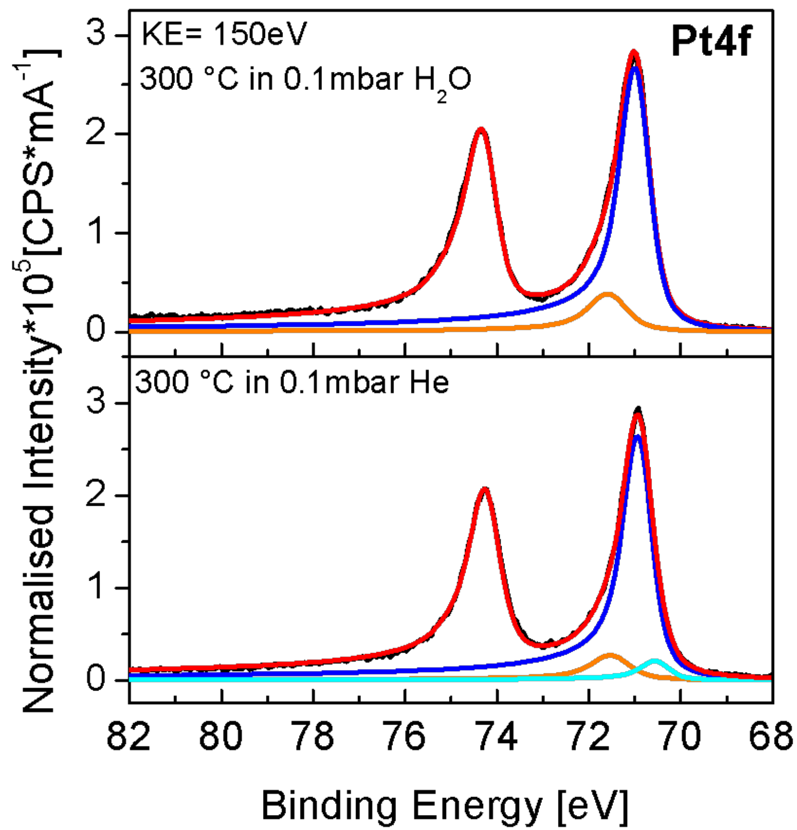


In situ observation under OER: Pt film on NAFION in liquid water

Polycrystalline Pt foil previously treated in O_2 at 250°C to remove the C





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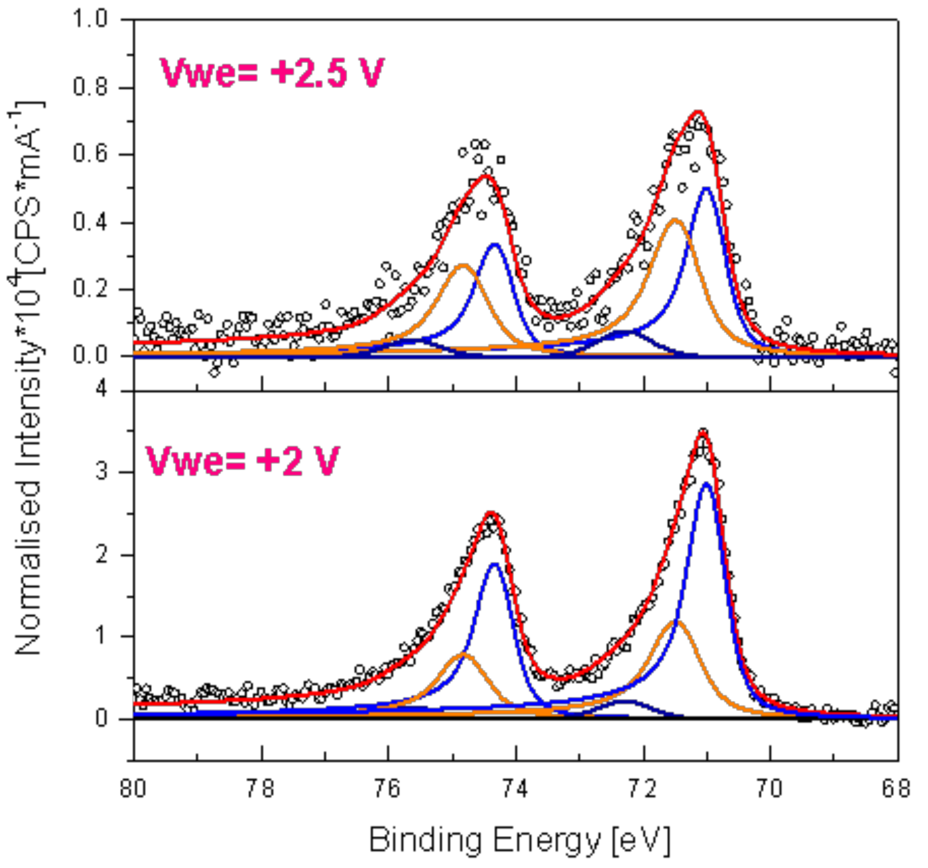

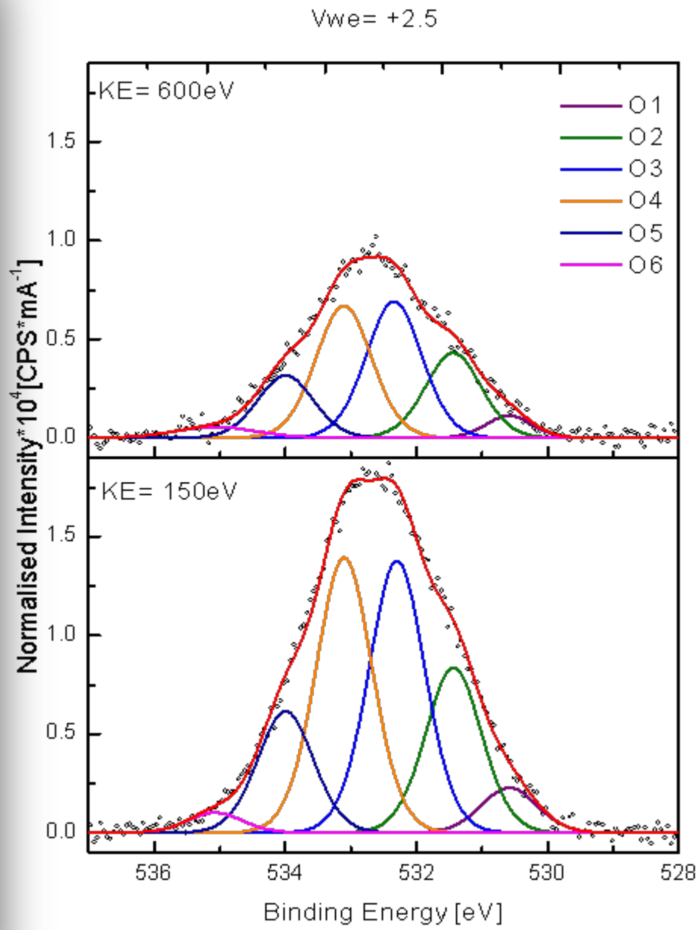

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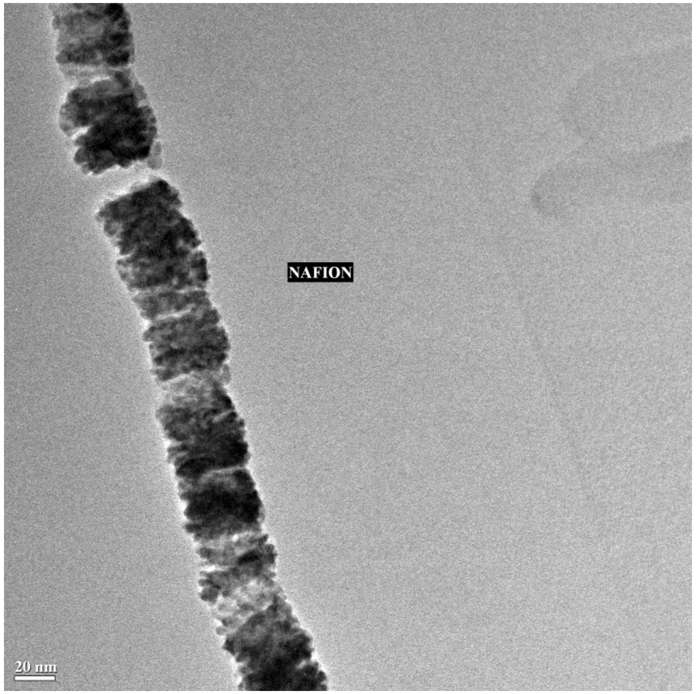

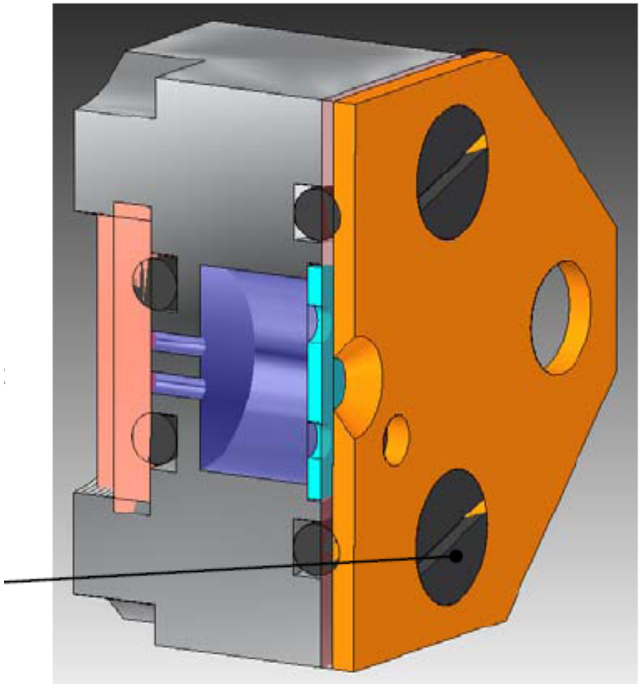

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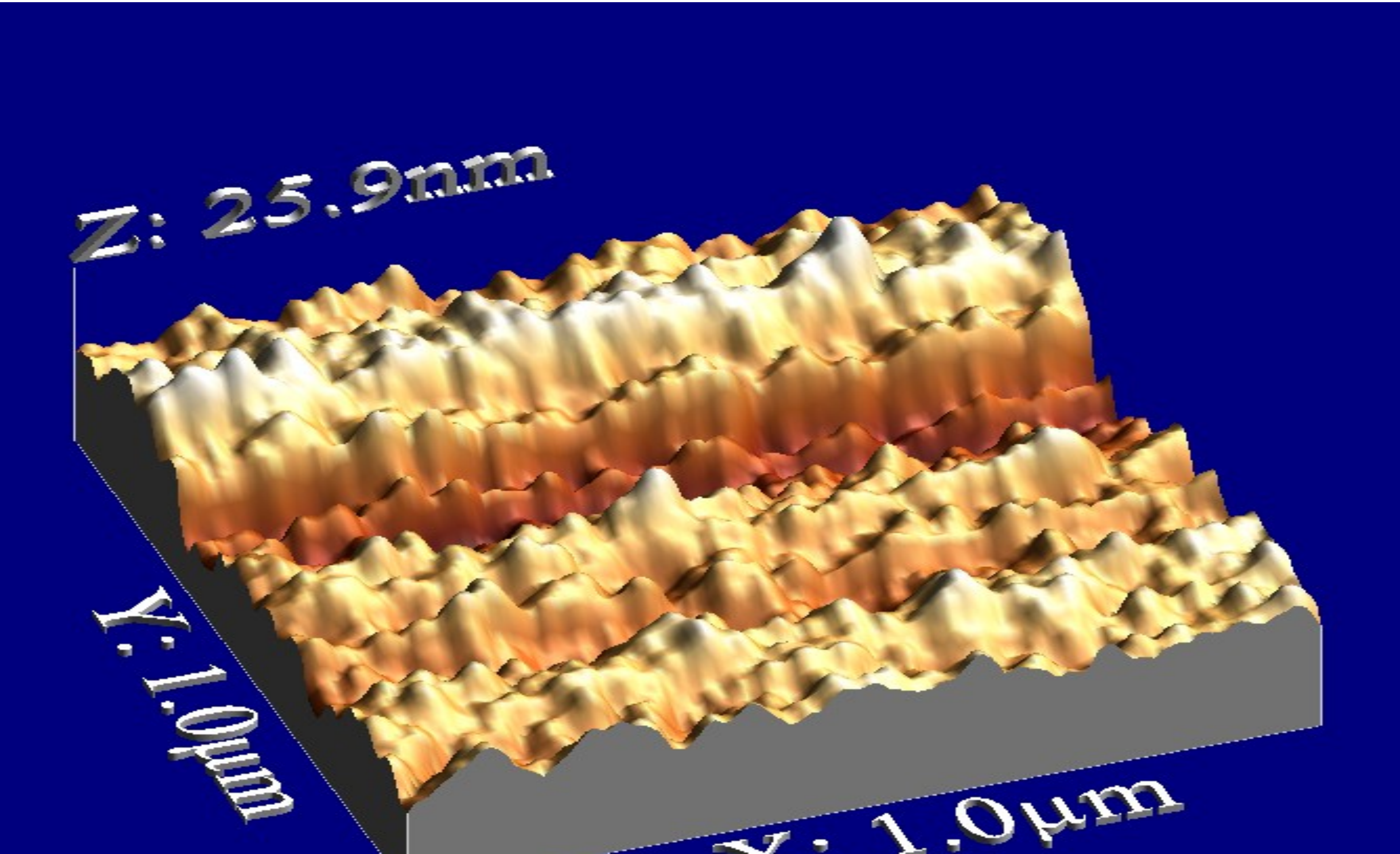
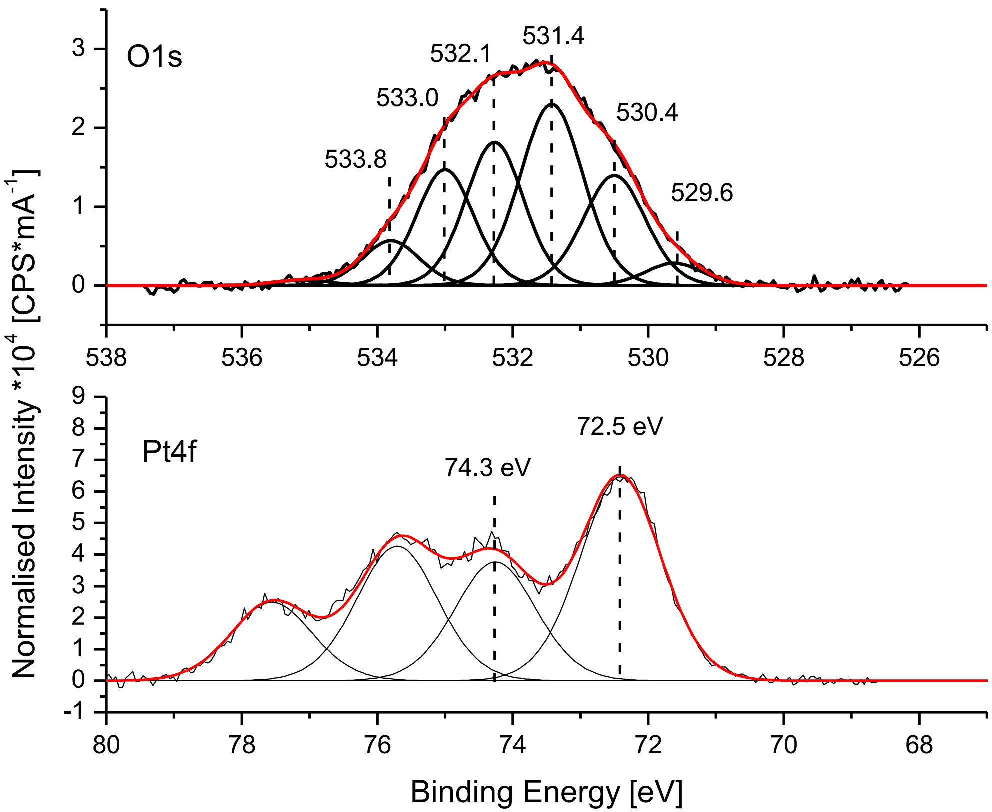
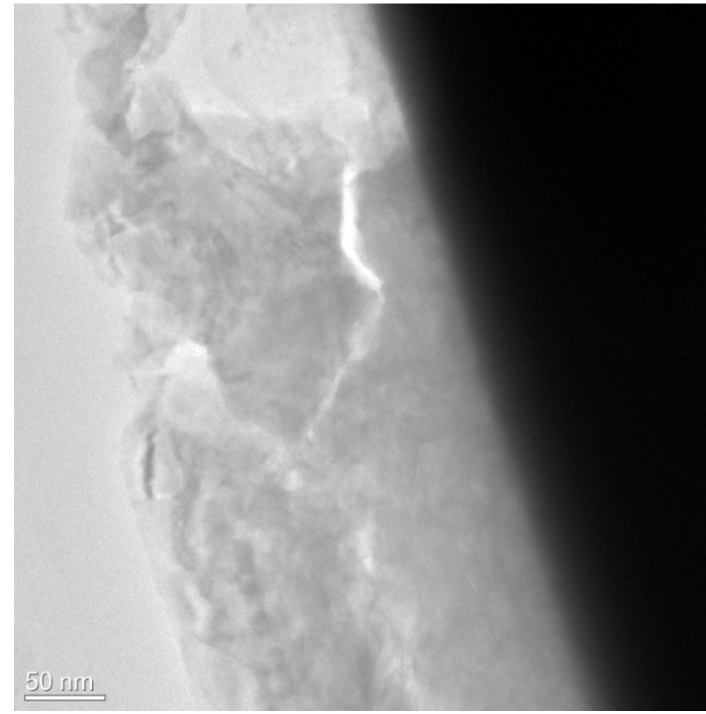


XPS and TEM of anodically oxidized Pt

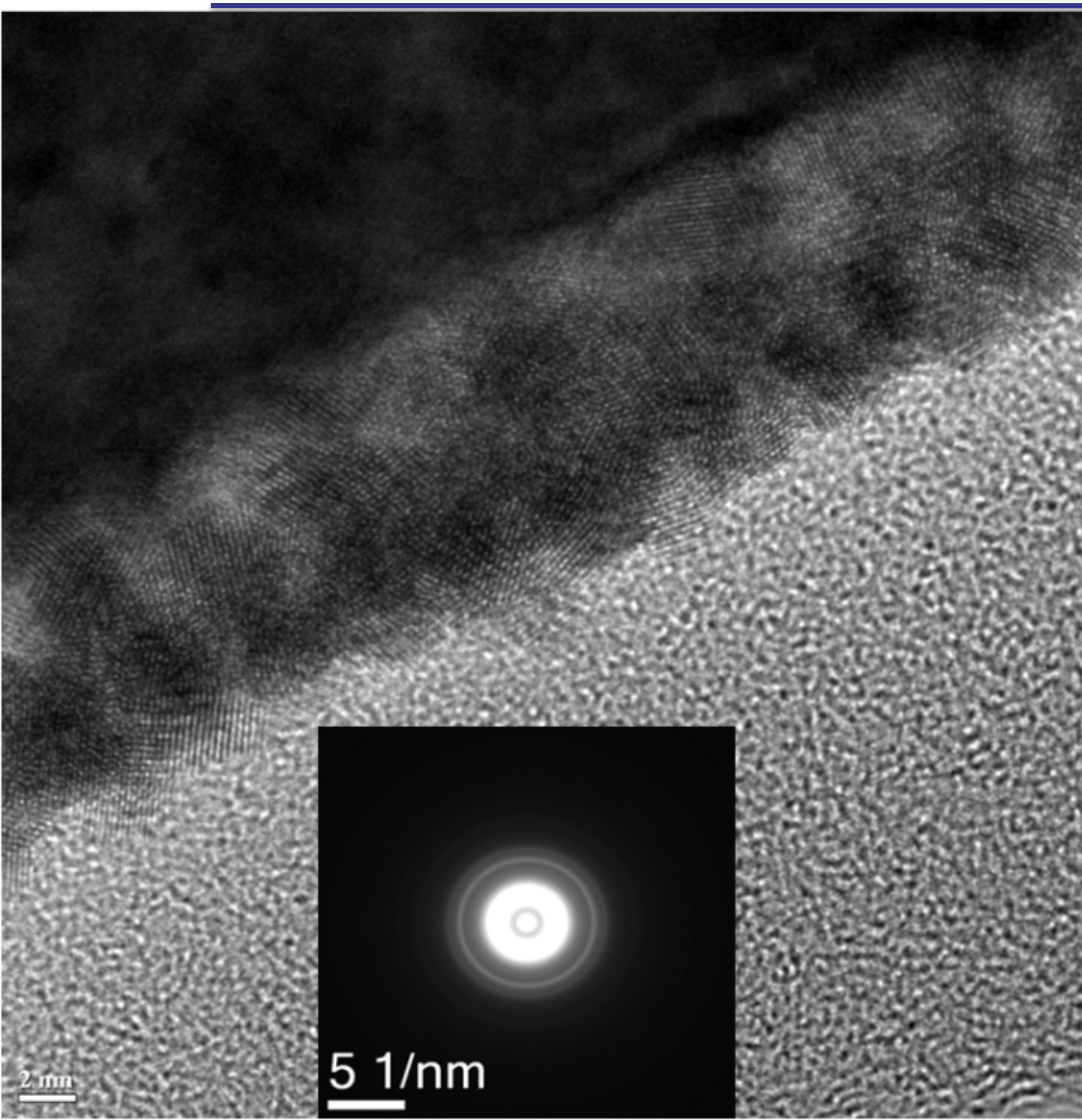


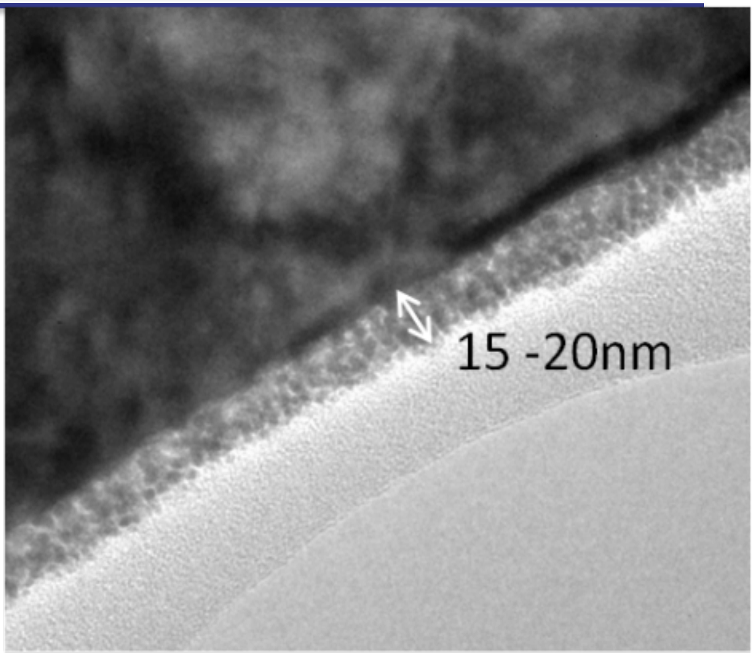


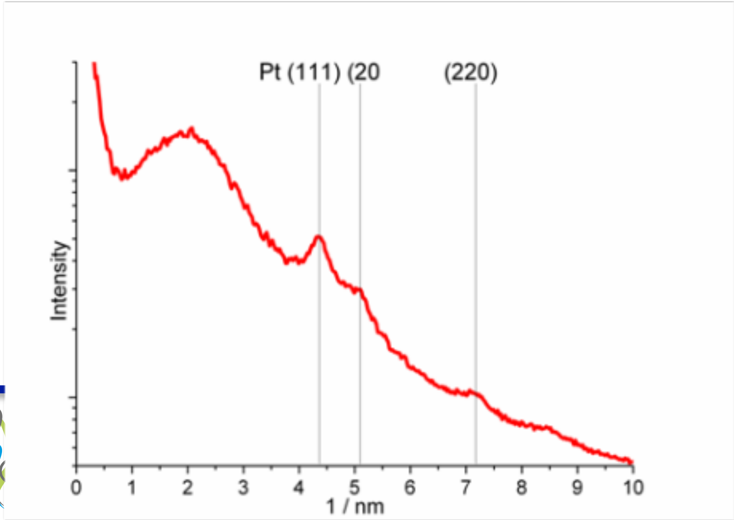
Anodically oxidized Pt-foil at 2.2 V vs. SHE

Formation of amorphous $PtO_x(OH)_y$ layer after anodic oxidation

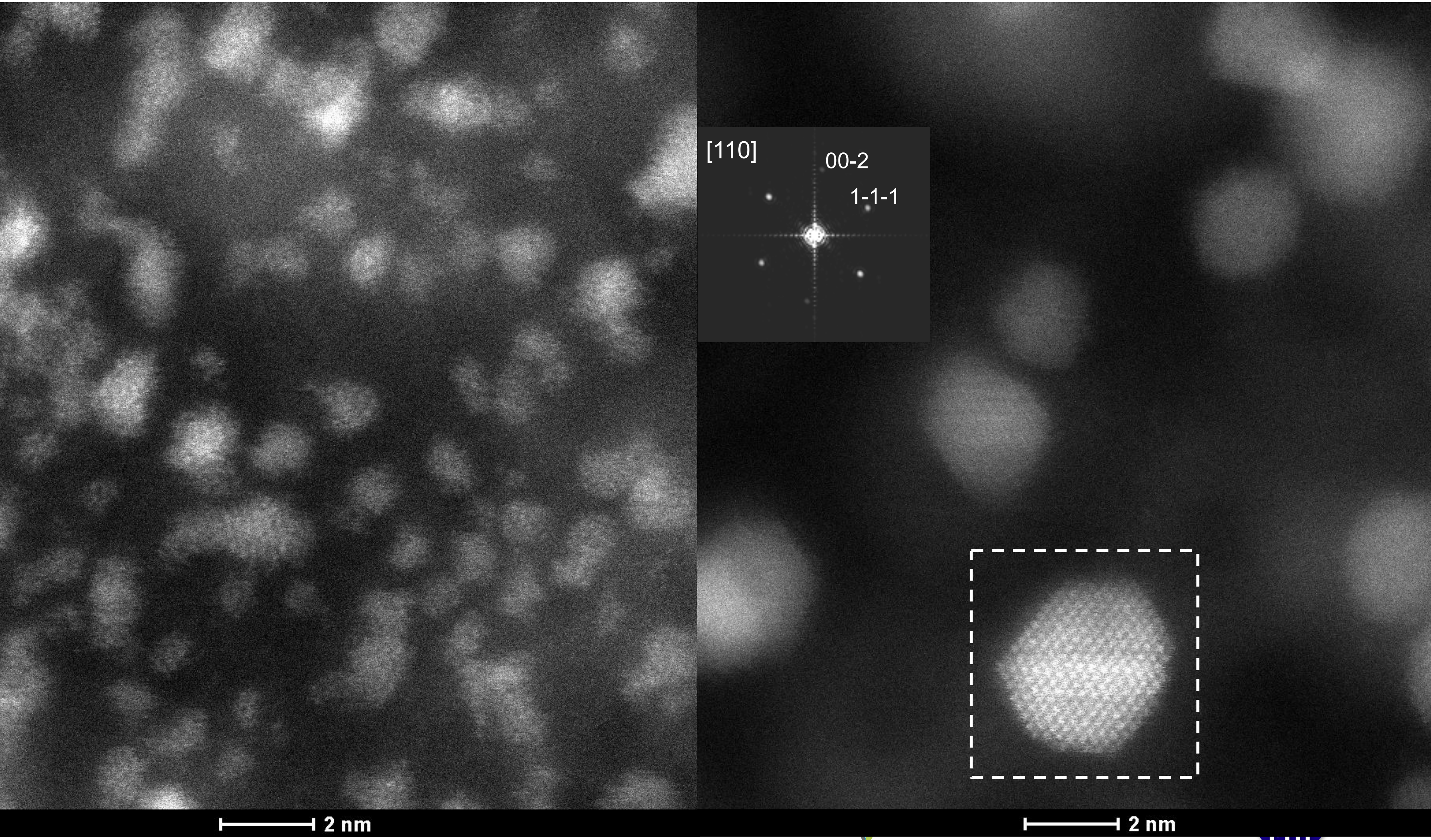
XPS and TEM of anodically oxidized Pt







Are NP of Pt enough?
Are they more stable?



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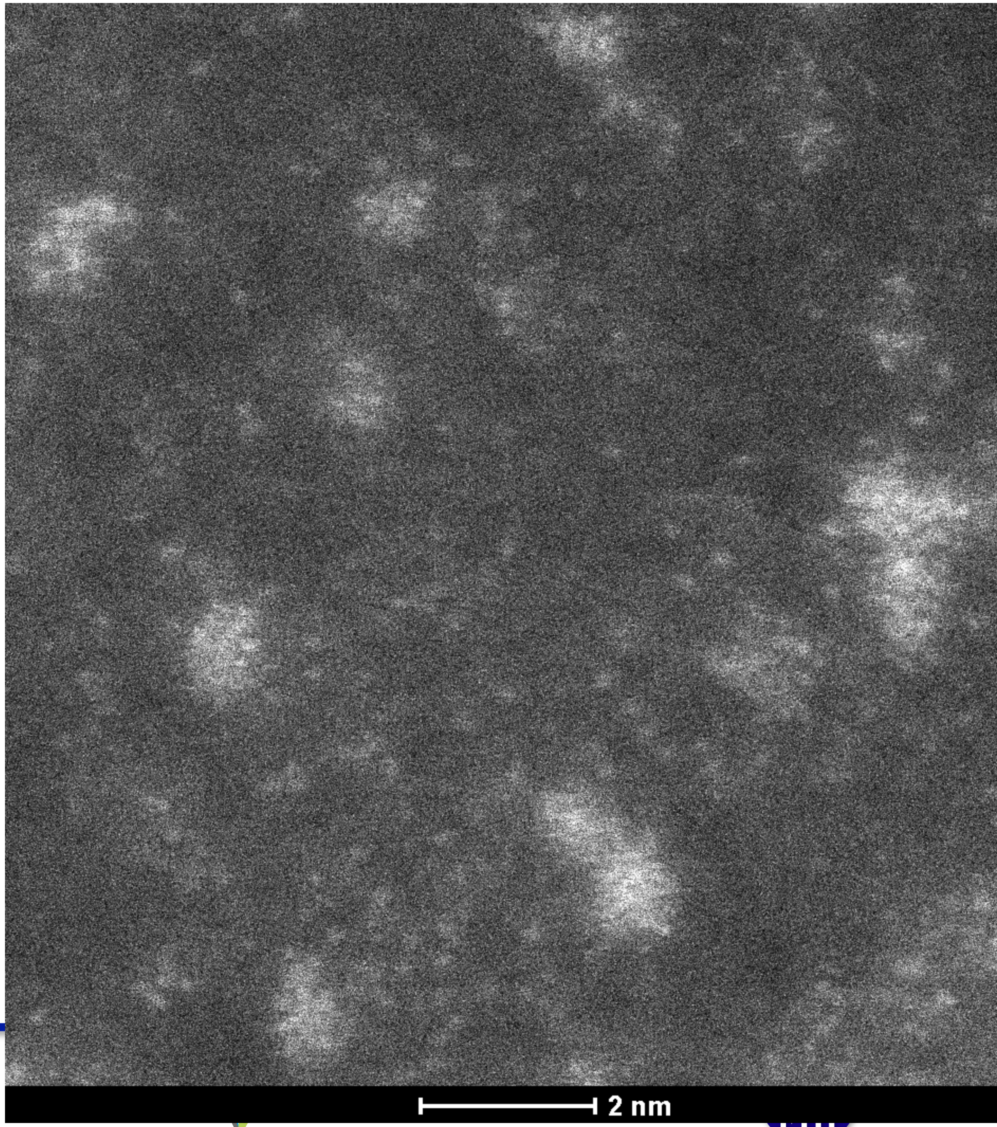
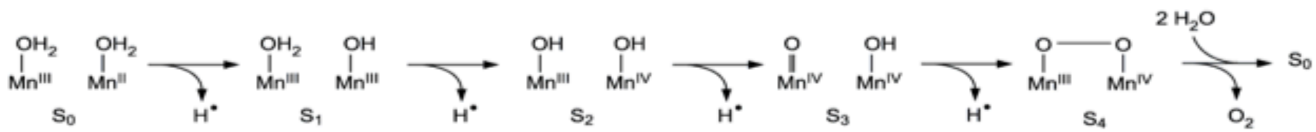


Summary: Pt (RuOx, IrOx) in water splitting

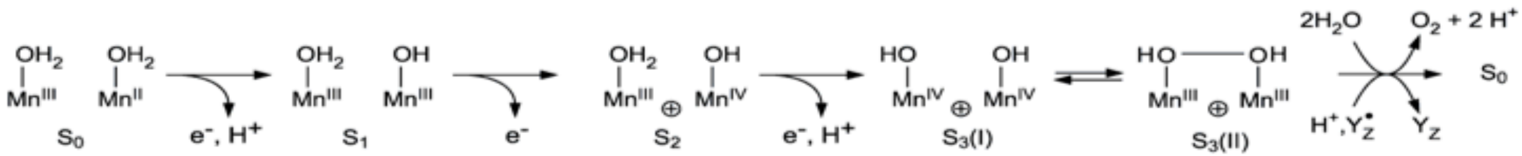
- In OER dimensional instability for large surfaces unavoidable (different extent and kinetics for orientation).
- Complex reaction sequence from sub-surface oxide, to divalent and at high load tetravalent species with a large number of coordinated water molecules:
- Product is a hydrated oxide mix “metal black”.
- Metastable with respect to re-formation of metal NP at open circuit conditions.
- Storage of peroxo-compounds in hydrated oxide.
- Operation above 373 K may stabilize electrode by avoiding formation of labile hydroxides (?).

A complex chemistry identical in green leafs and in electrolysis

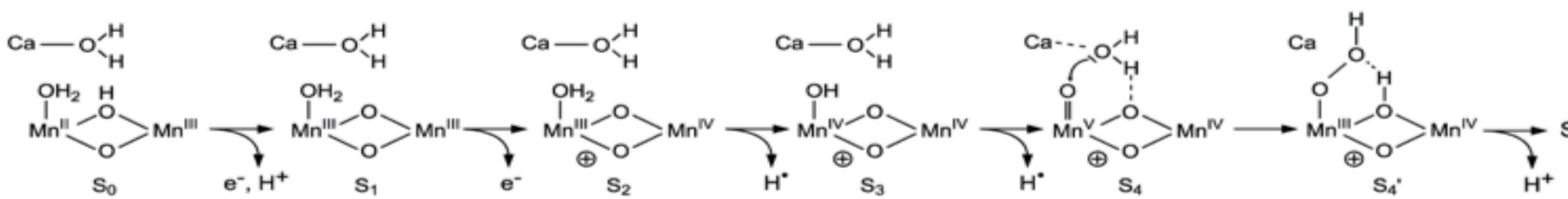
H-atom Abstraction (Hoganson and Babcock 1997)



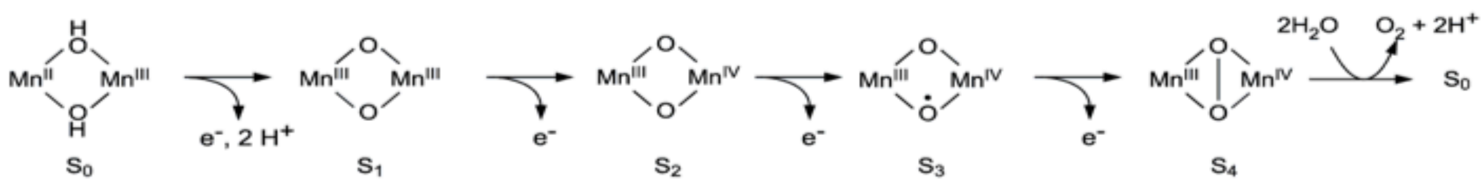
Peroxidic Intermediate in S_3 (Renger 1997; Haumann and Junge 1999; Siegbahn 2000)



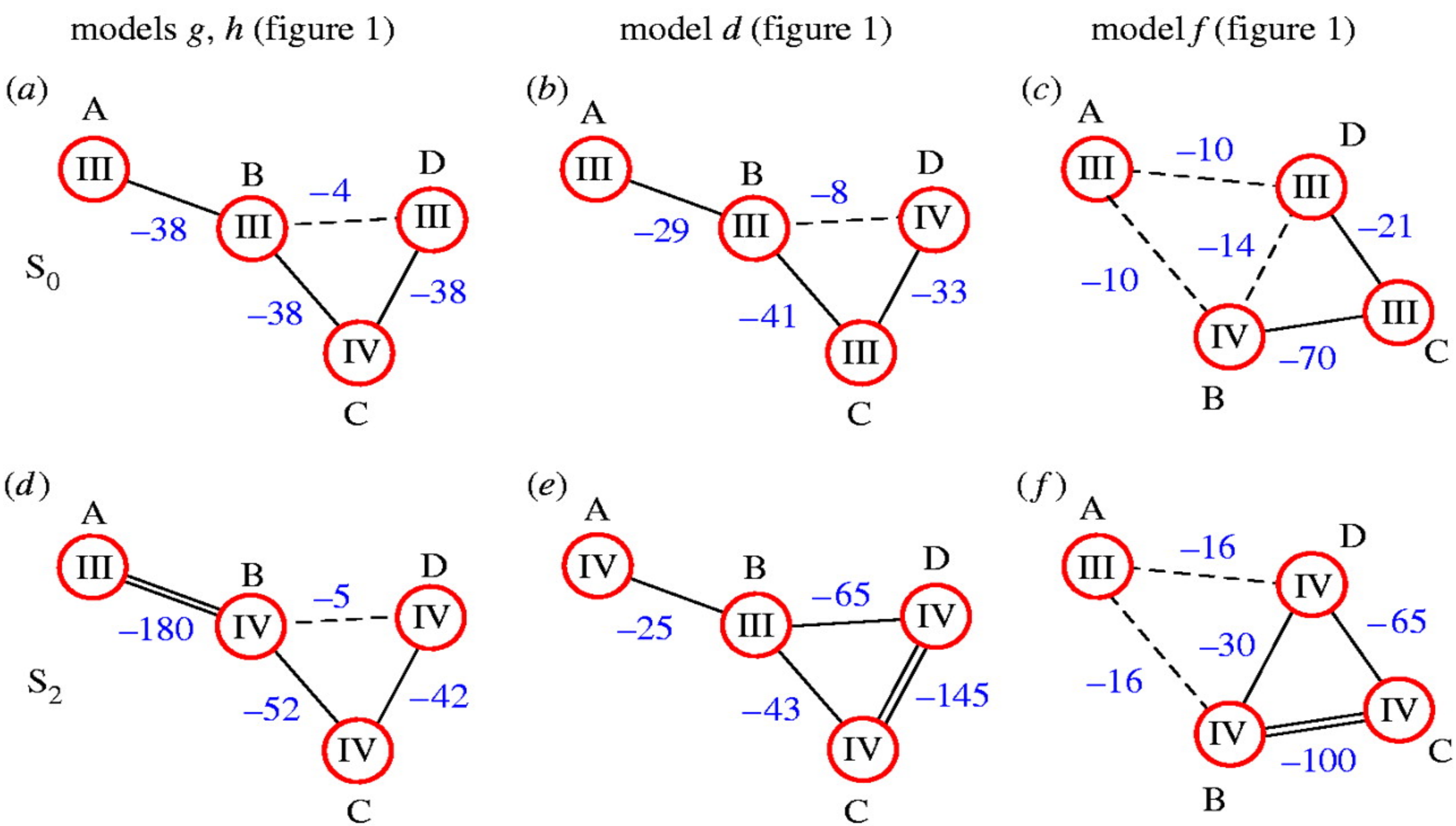
Nucleophilic Attack (Messinger et al. 1995; Pecoraro et al. 1998; Vrettos et al. 2001)



Radical in S_3 state (Yachandra et al. 1996; Haumann and Junge 1999; Siegbahn 2000, Messinger 2000)

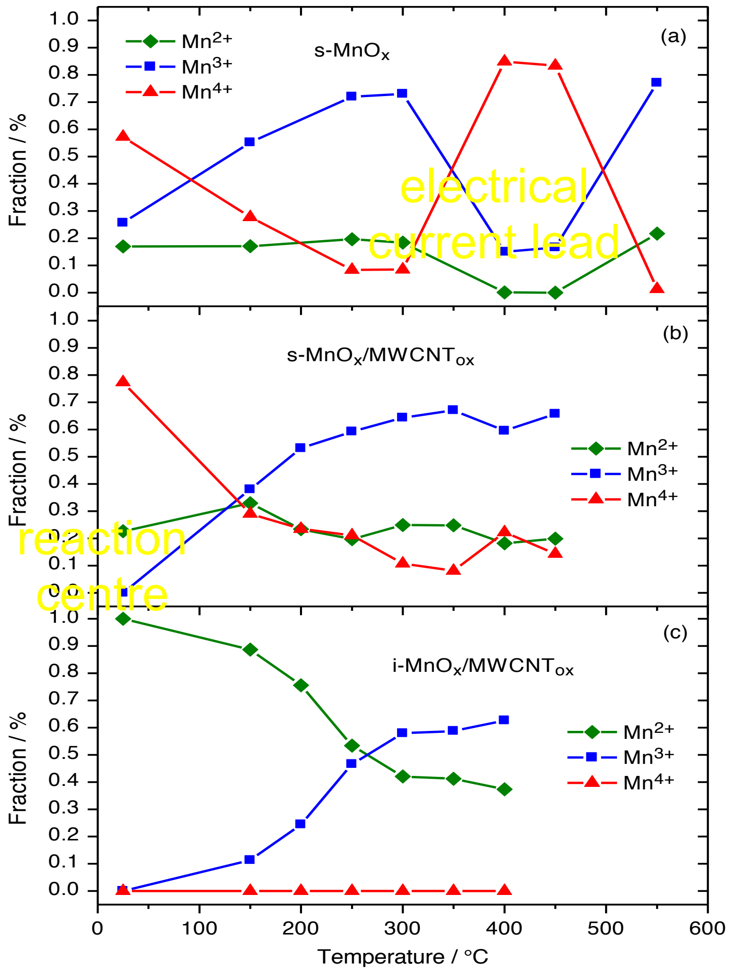


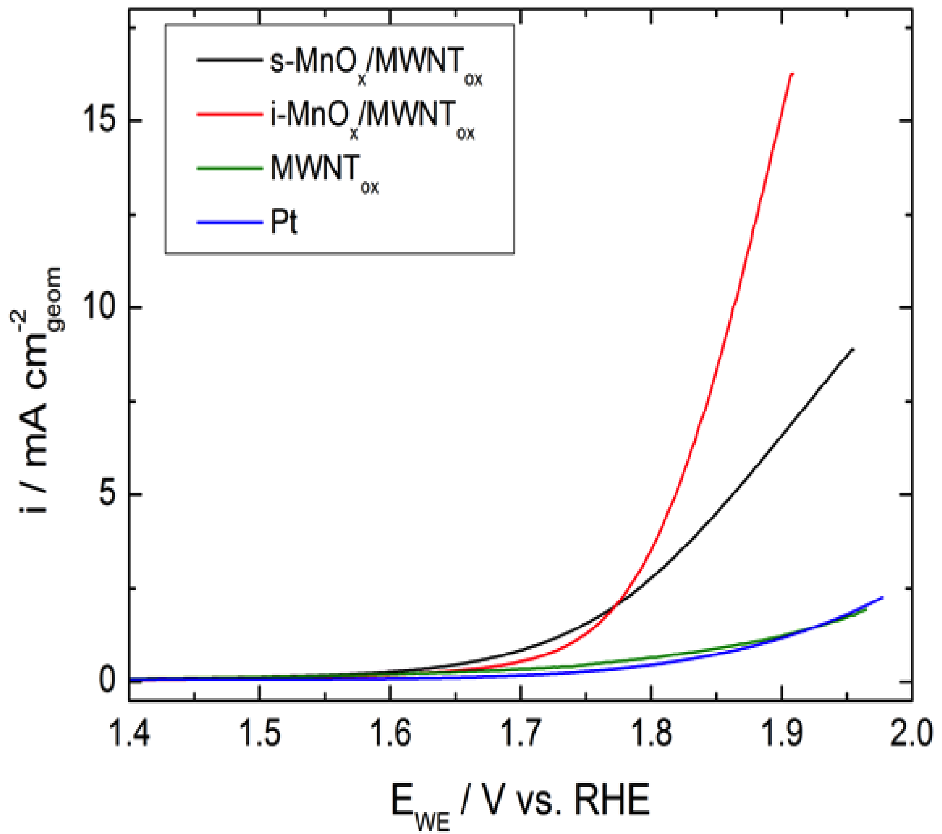
Redox dynamics seen by in-situ EPR



Zein S et al. Phil. Trans. R. Soc. B 2008;363:1167-1177

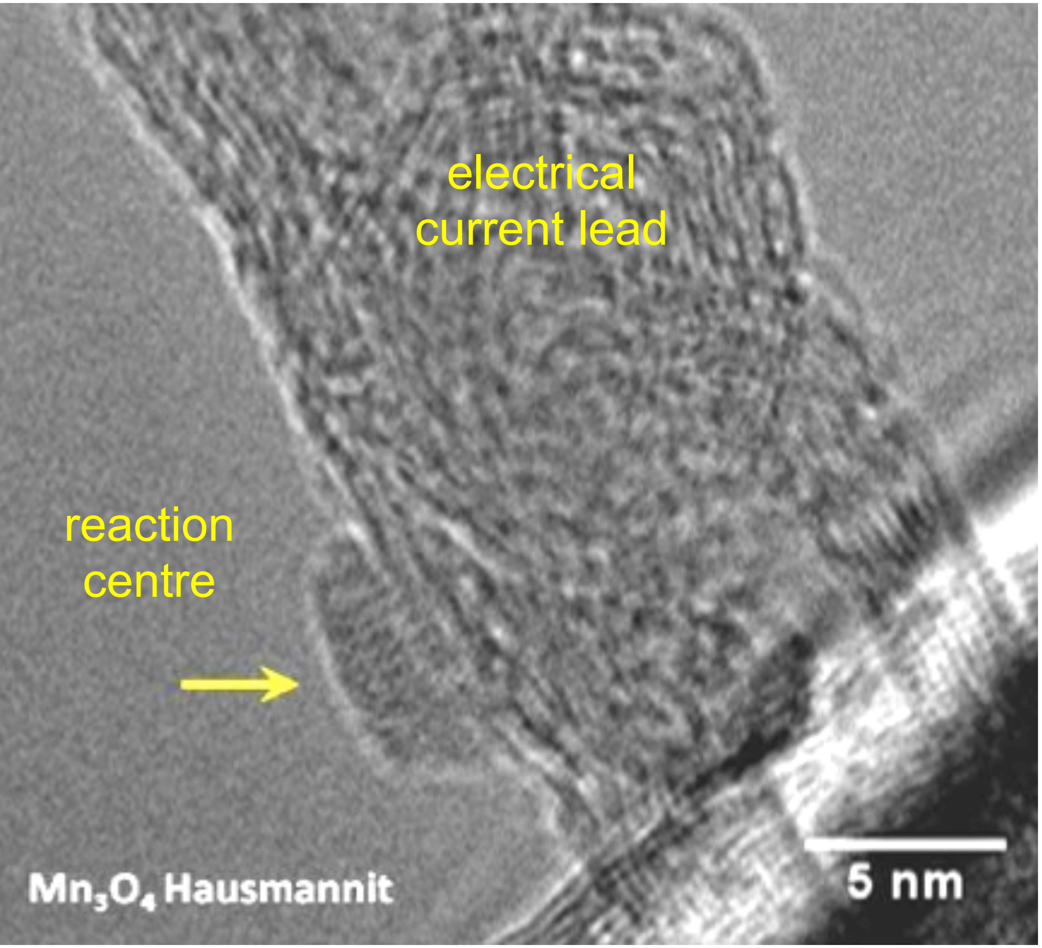
Electrolysis without noble metals: learning from nature





Nano- Mn_2O_3 made electrically contacted by functionalized CNT

Electrolysis without noble metals: learning from nature



Dem Anwenden muss das Erkennen vorausgehen

Max Planck

Thank You