Effects of Catalytic Site Size on Activity of Model Electrodes Prepared By Mass-Selected Cluster Deposition

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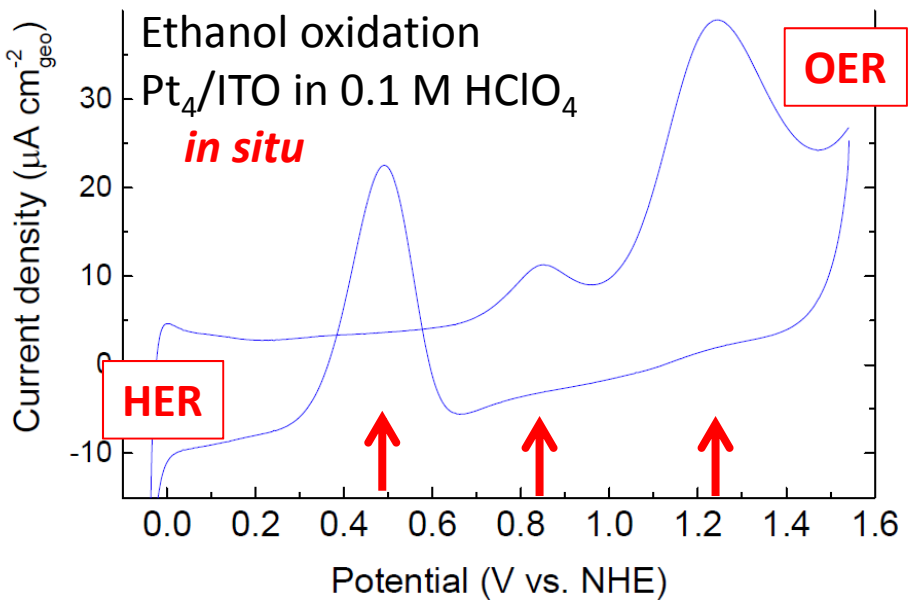
(Early work by Sebastian Proch, Mark Wirth, Michael Rosenfelder)

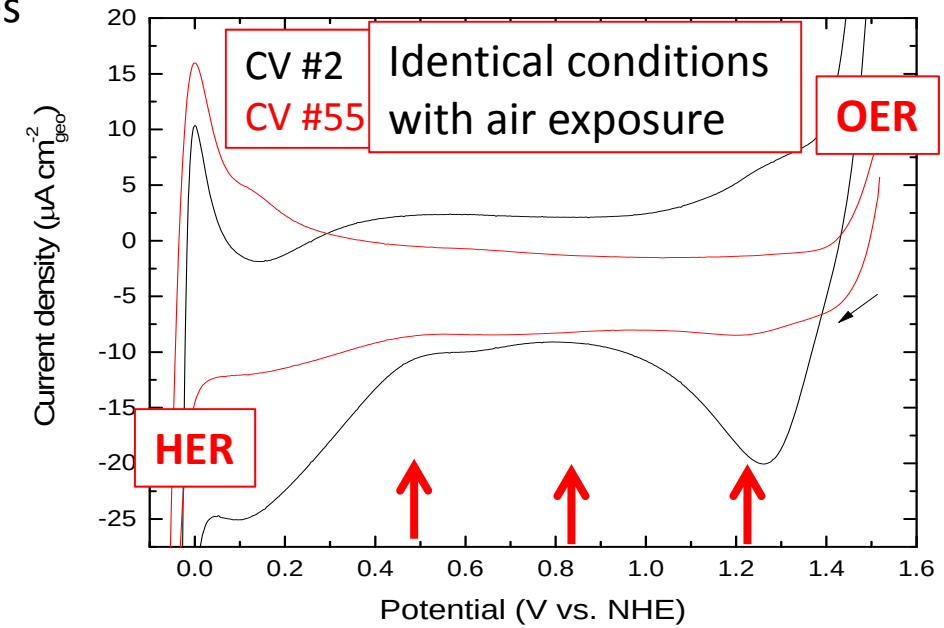
Electrochemistry: U.S. DEPARTMENT OF ENERGY Office of Science; DFG Deutsche Forschungsgemeinschaft

Related gas-surface chemistry: AFOSR AIR FORCE OFFICE OF SCIENTIFIC RESEARCH

In situ electrochemistry in a UHV system is hard – *Why bother?*

Avoid complications of adventitious adsorbates





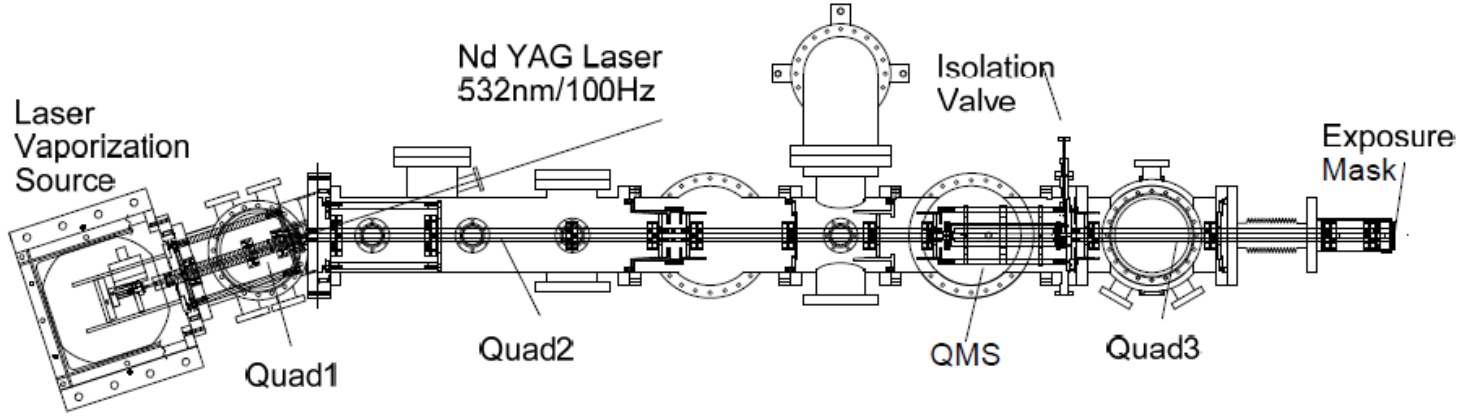
Electrochemical cleaning is fine for:

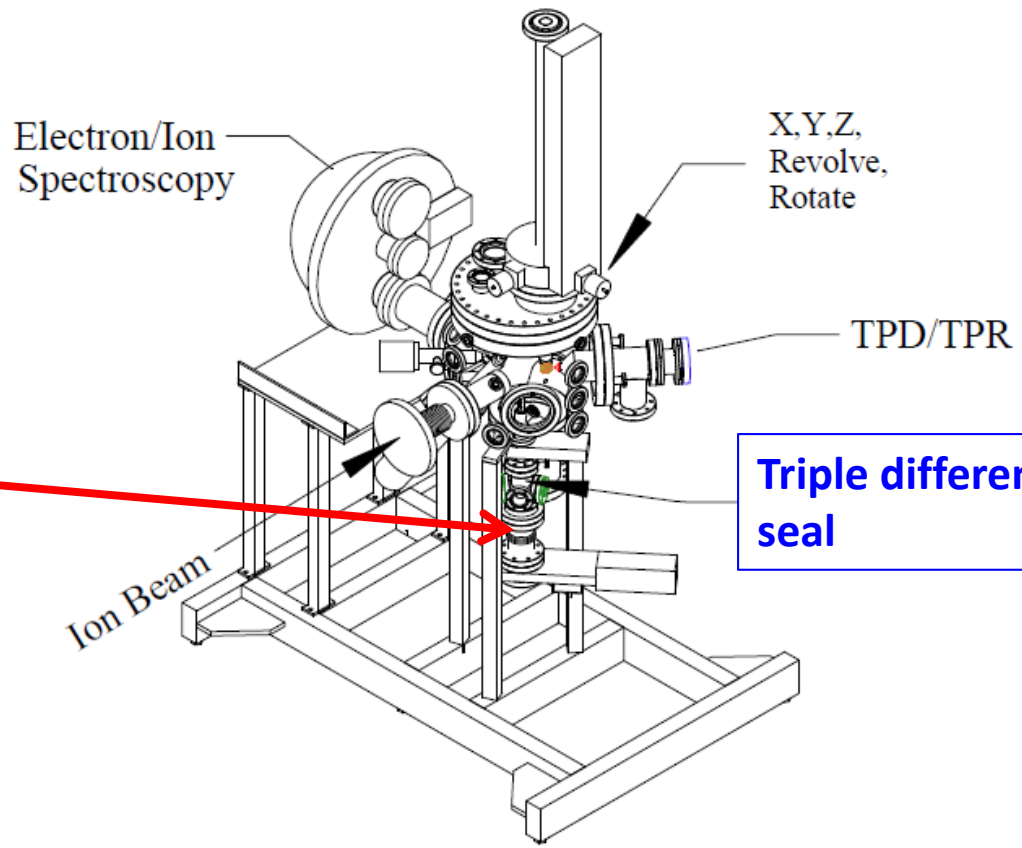
- Bulk/single crystals electrodes
- Large supported nanoparticles

Not for small, size-selected clusters!

Potential cycling may change the size by etching or potential-induced diffusion

Size-Selected Electrochemistry Without Air Exposure



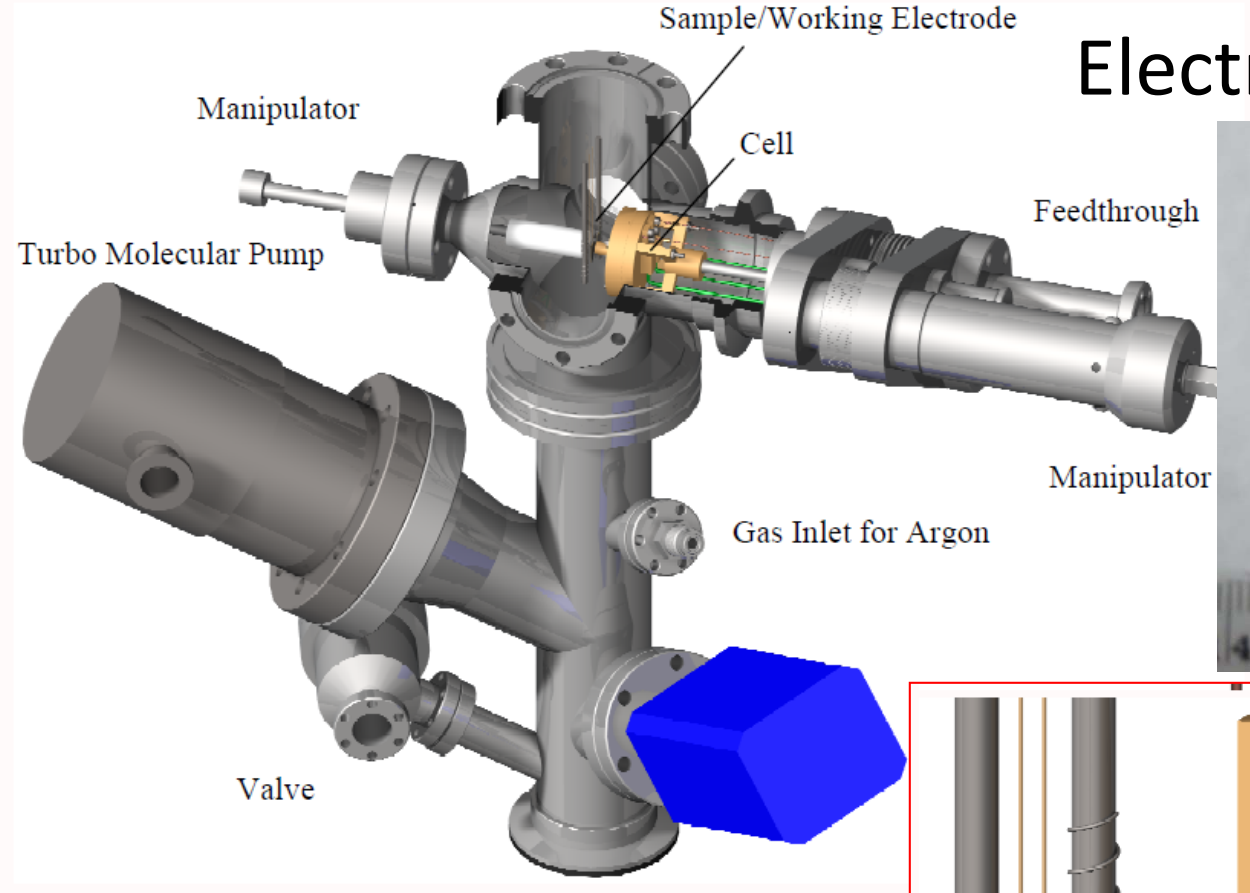


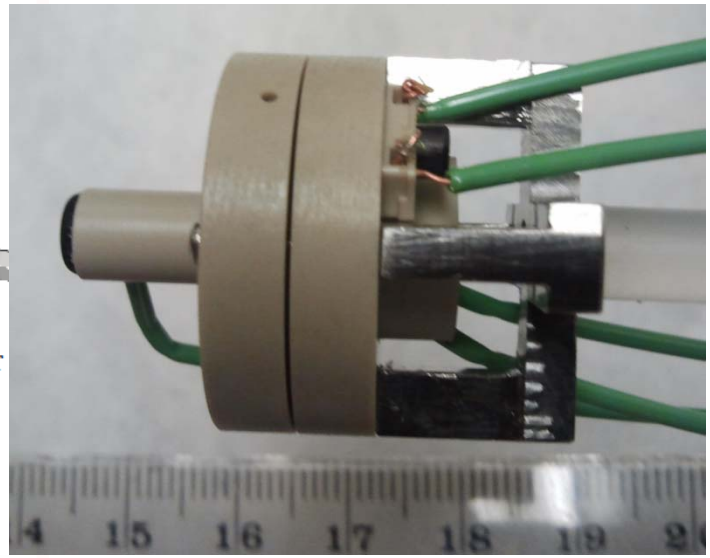
Electrochemistry Antechamber

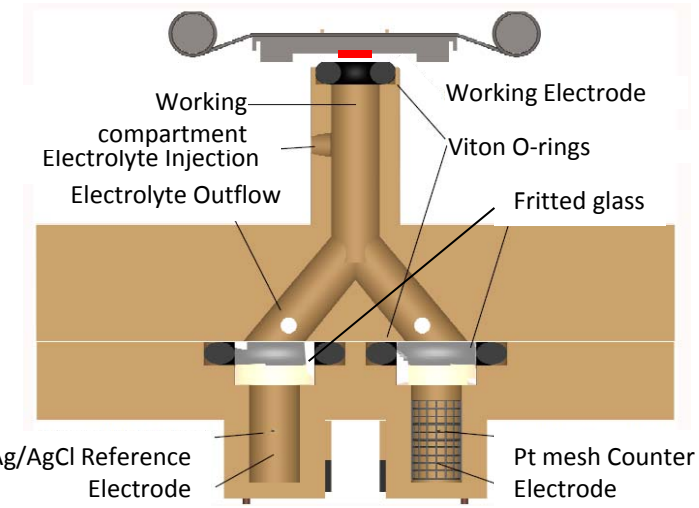
- Separately pumped UHV chamber
- Can be vented without affecting main chamber UHV

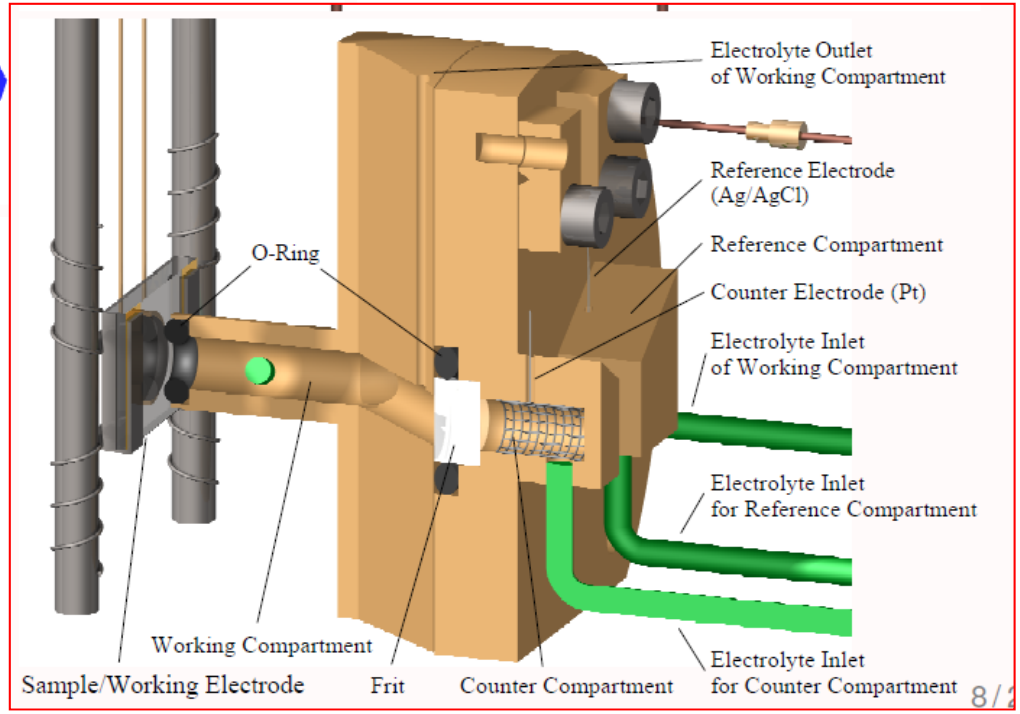
Triple differential seal

Electrochemistry Setup

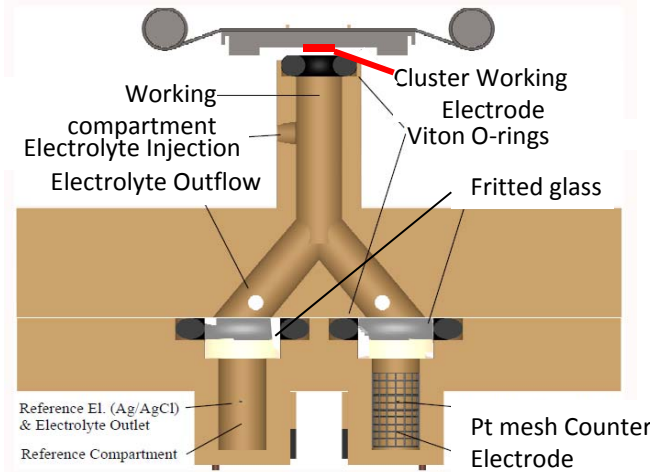








Protocol



- Clean/characterize electrode substrate in UHV
- Deposit 1.5 x 10^{14} Pt atoms/cm^2 as Pt_n^+
  - Equivalent to 0.1 ML Pt
- XPS characterization
- Lower into antechamber, pressurize with argon
- Seal to electrochemical cell
- Pump in electrolytes, do series of cyclic voltammograms (CVs)

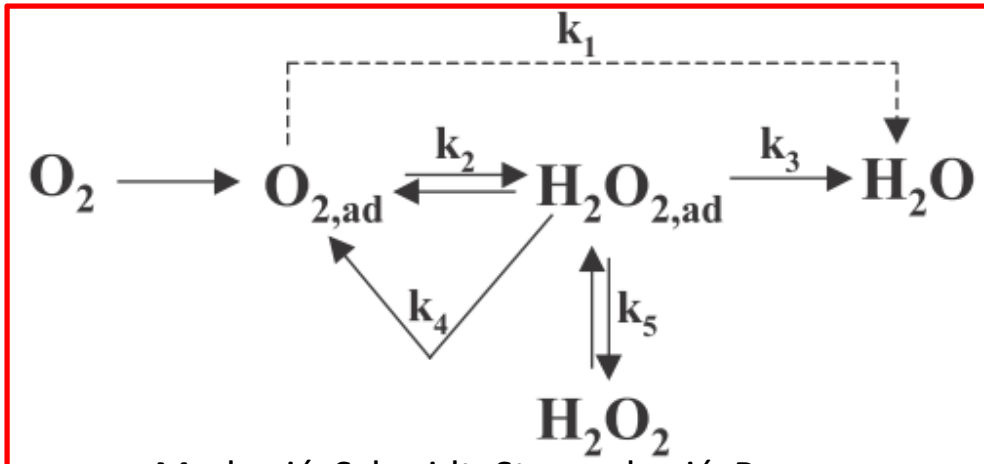
Problems

- *In situ* requirement → static experiments only
- Need for a dry, bakeable reference electrode
  - Ag/AgCl, reproducible to ~15 meV from day to day
- Limited working time due to Cl^- diffusion/poisoning.
- Cell alignment to cluster spot

Oxygen Reduction Reaction (ORR)

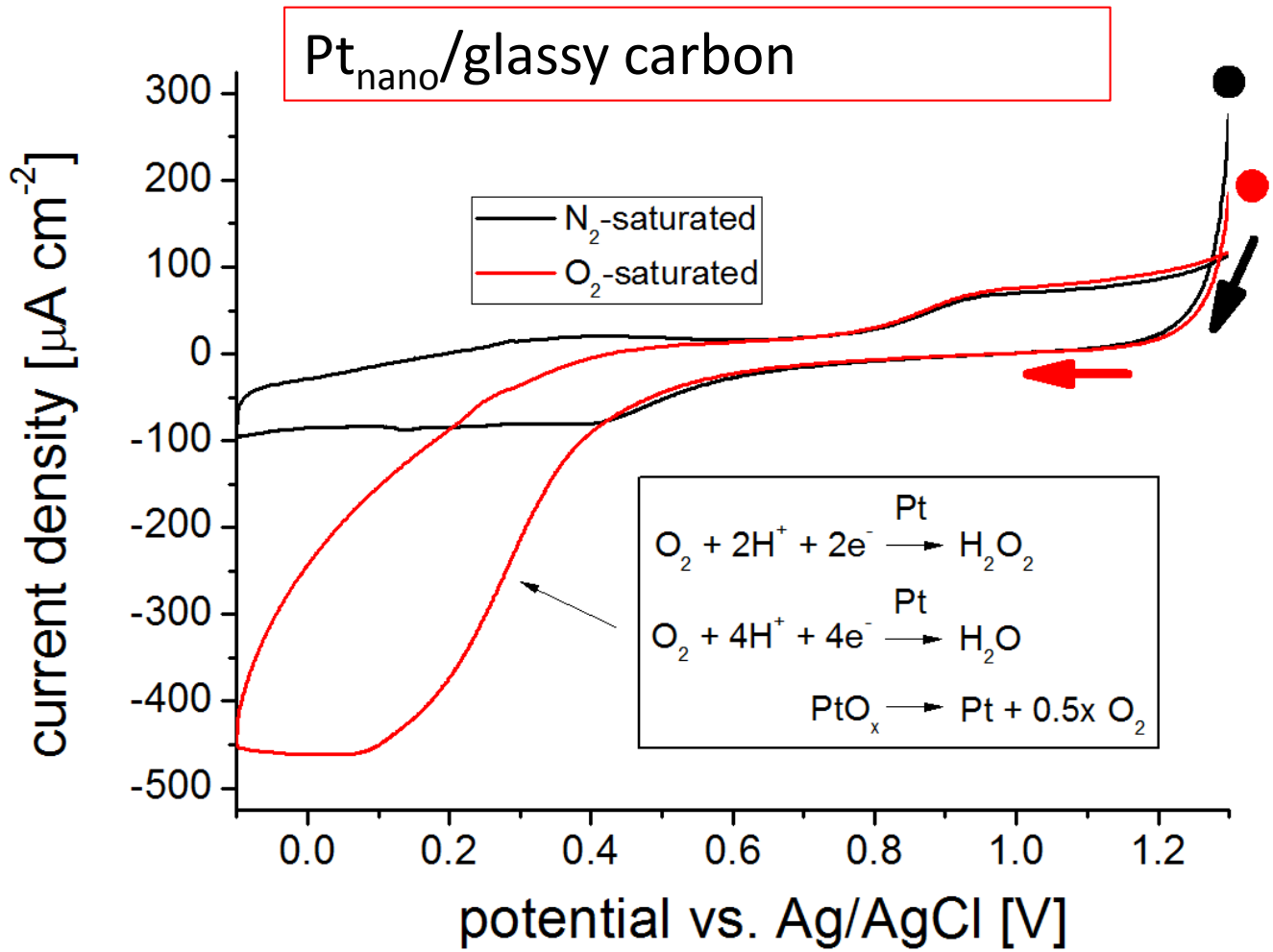
- Limiting factor in fuel cell efficiency
  - Need better catalysts to reduce overpotential
  - Reduce amount of Pt required
- $O_2 + 4\ e^- + 4\ H^+ \rightarrow 2\ H_2O$
- $O_2 + 2\ e^- + 2\ H^+ \rightarrow H_2O_2$

Start with Pt_n/glassy carbon
Electrolyte = 0.1 M $HClO_4$
O_2 saturated
N_2 sparged

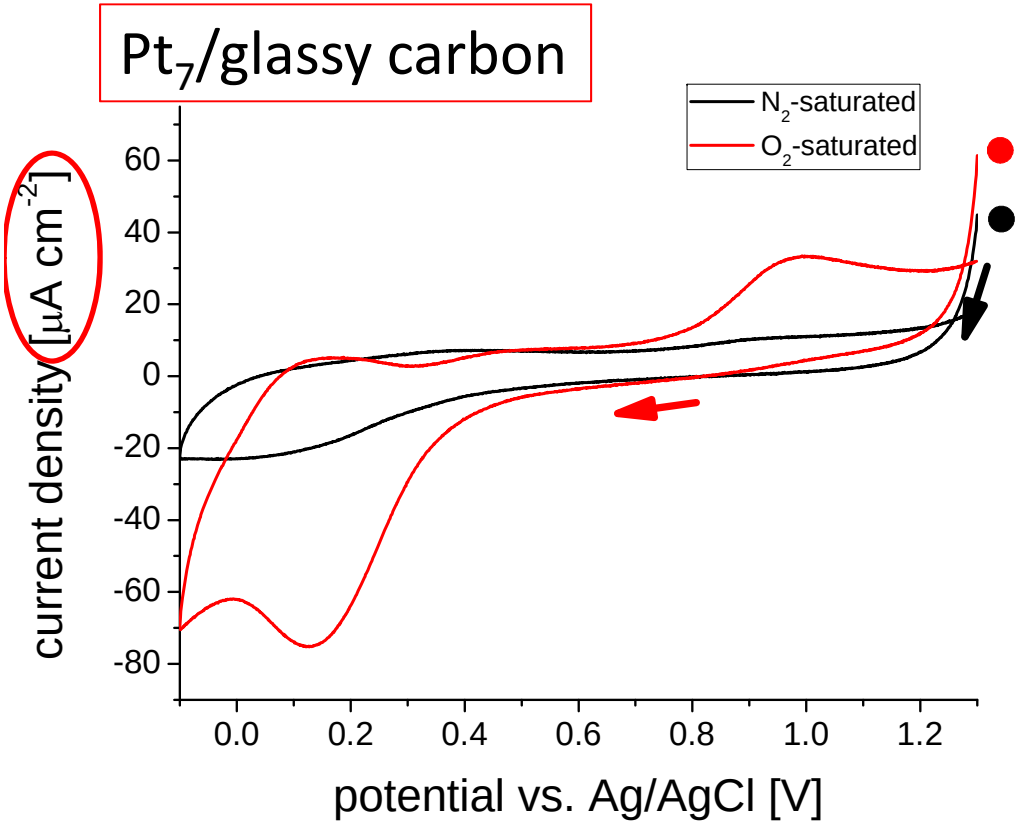


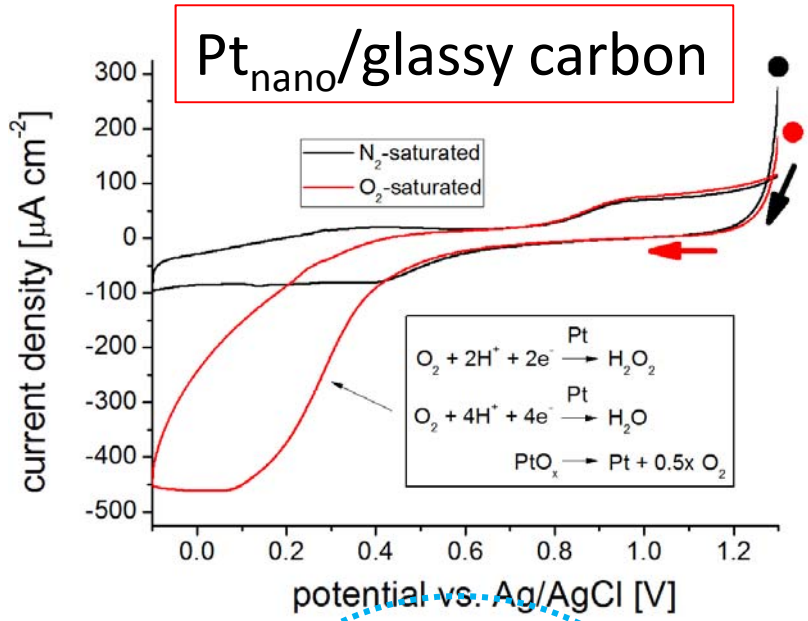
Marković, Schmidt, Stamenković, Ross, Fuel Cells **1**, 105 (2001)

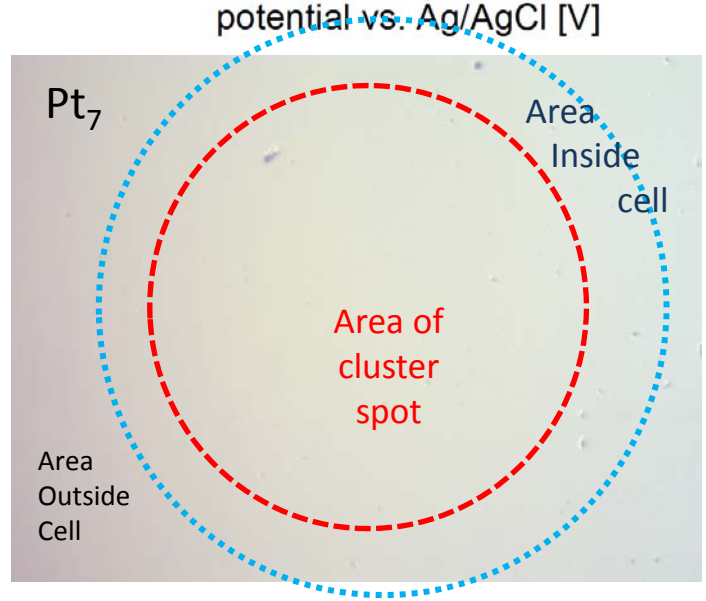
Size-selected ORR chemistry



Size-selected ORR chemistry

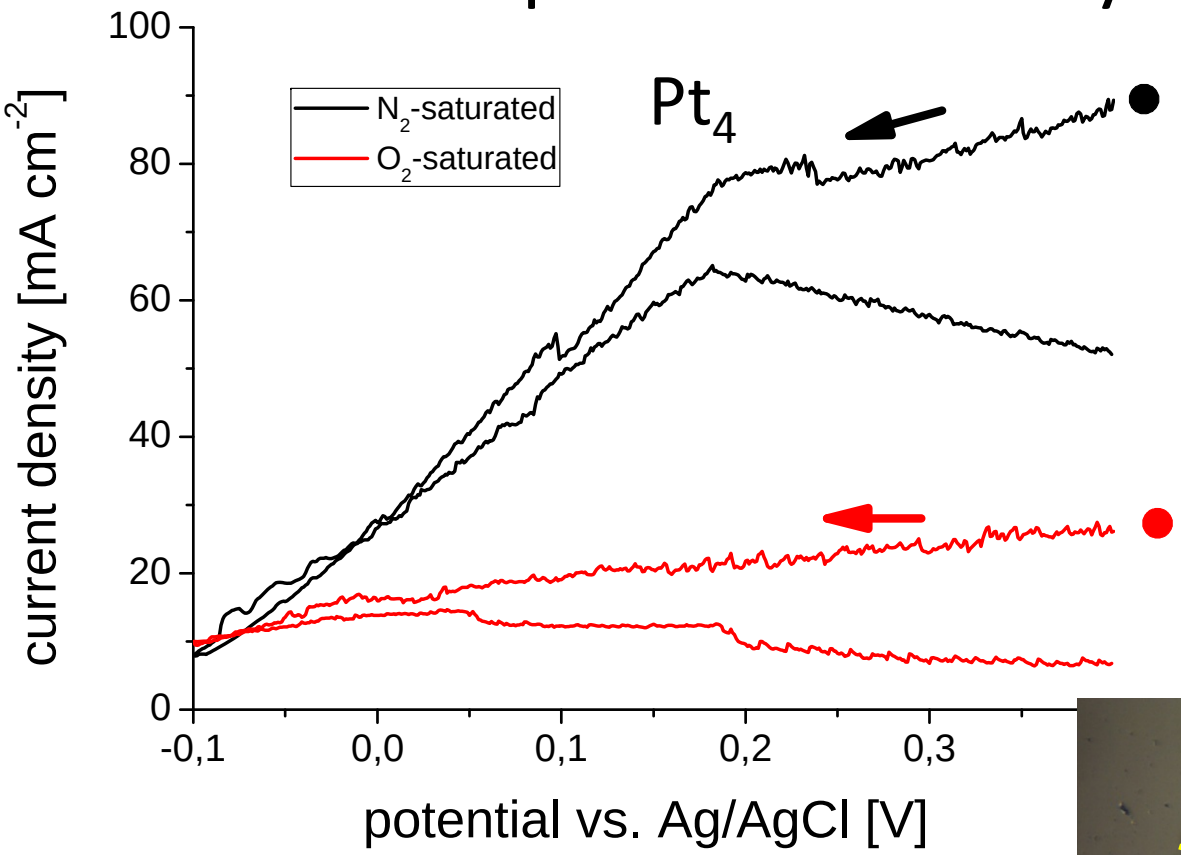




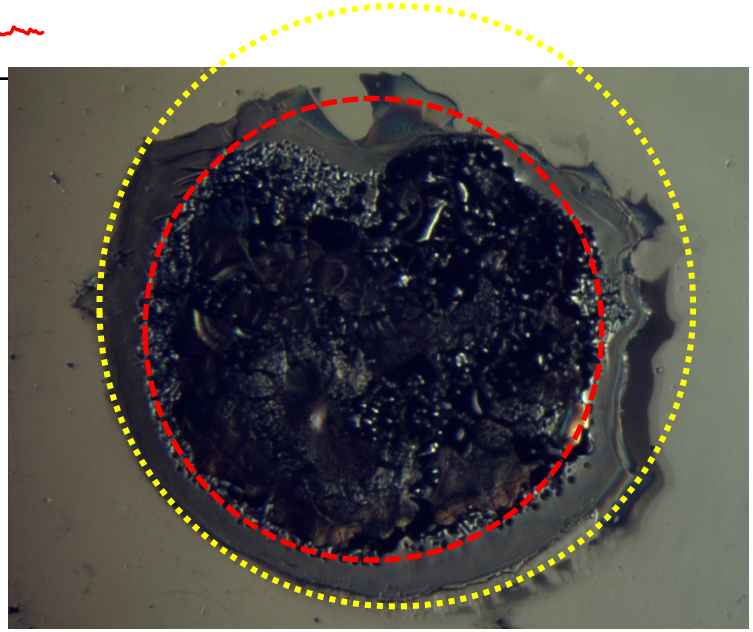


J. Am. Chem. Soc. 2013, 135, 3073−3086

Unexpected Chemistry



- Huge oxidation currents
- Lots of bubbles
- What is oxidizing what?



Many small Pt_n catalyze the reaction

$$C + 2\ H_2O \rightarrow CO_2 + 2\ H_2$$

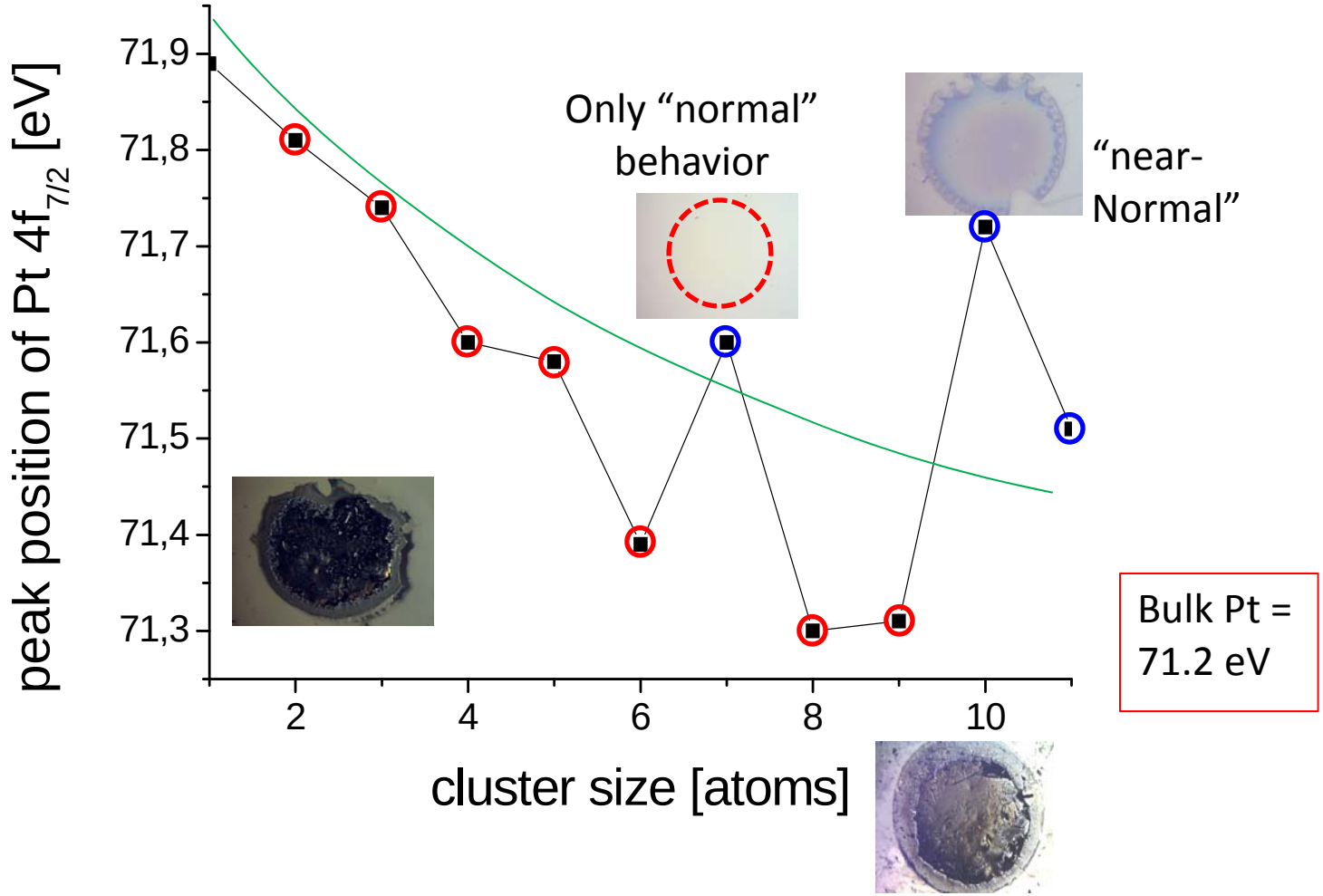
With essentially no overpotential and high efficiency: J. Am. Chem. Soc. 2013, 135, 3073−3086

Interesting result, but it prevents study of ORR or other reactions

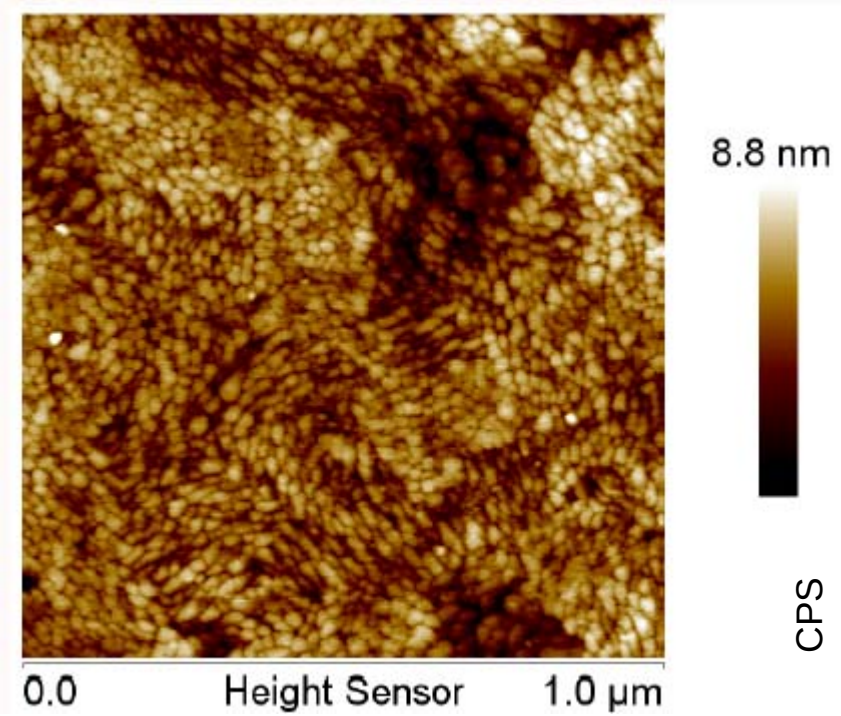
Anti-correlations between Pt 4f binding energy and ORR catalysis

Glassy carbon oxidation by water, catalyzed by Pt_n

High Pt 4f BE is associated with no carbon oxidation "normal ORR"



Switch to an electrode support than can't be oxidized: Indium Tin Oxide (ITO).



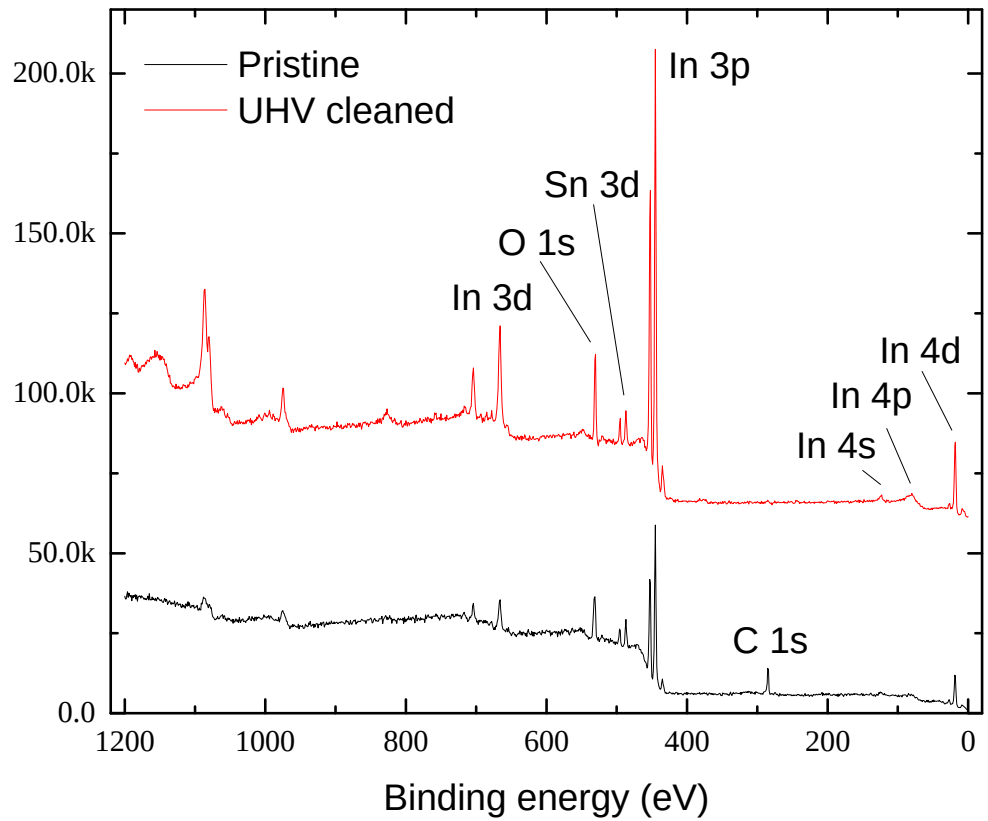
Polycrystalline with 15 – 20 nm domain size

- AFM R_a = 1.1 nm
- Roughness may be good
  - Help stabilize clusters?

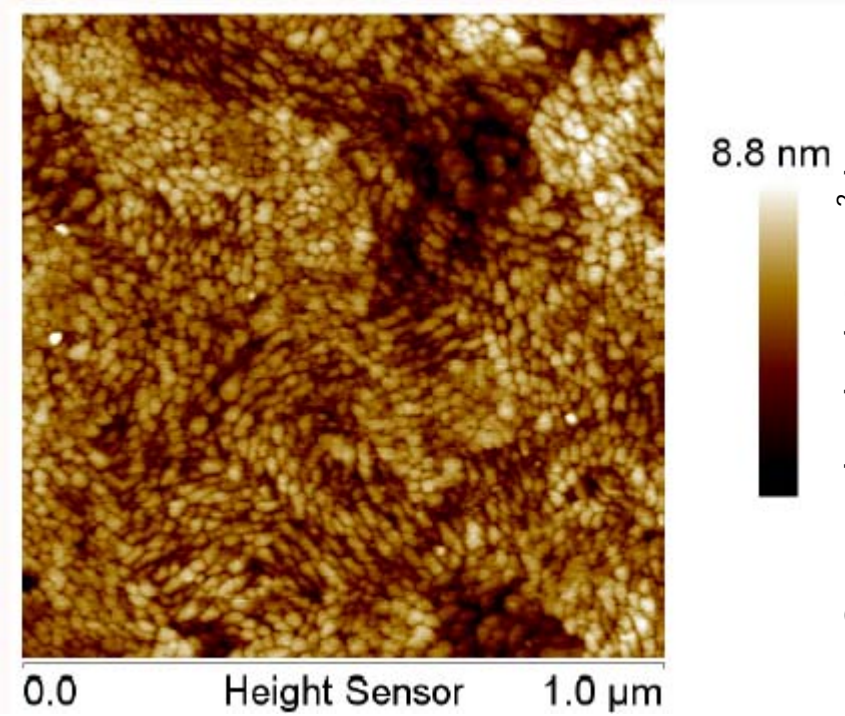
Adventitious carbonaceous adsorbates

- Cannot be eliminated by heating in UHV or in O_2
- Do affect chemistry

Sputter/anneal in O_2



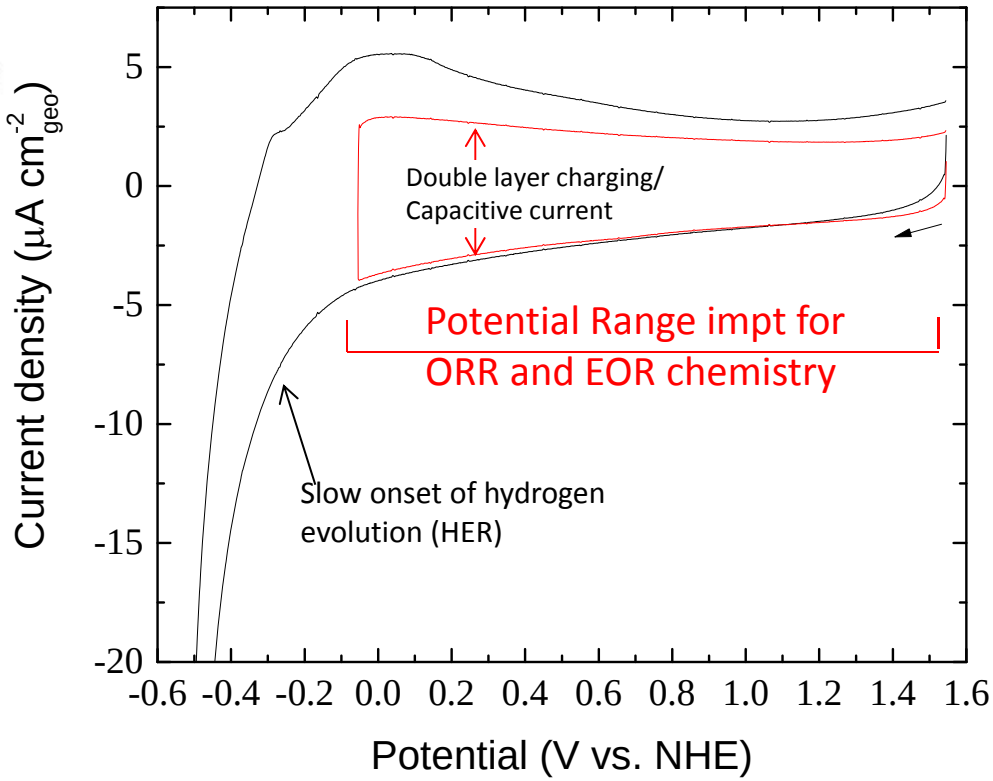
Avoid carbon oxidation: ITO electrode substrates



Polycrystalline with 15 – 20 nm domain size

- AFM R_a = 1.1 nm
- Roughness may be good
  - Help stabilize clusters?

Most important point: UHV-cleaned ITO is quite inert in the potential range of interest -0.1 to 1.5 V vs. NHE



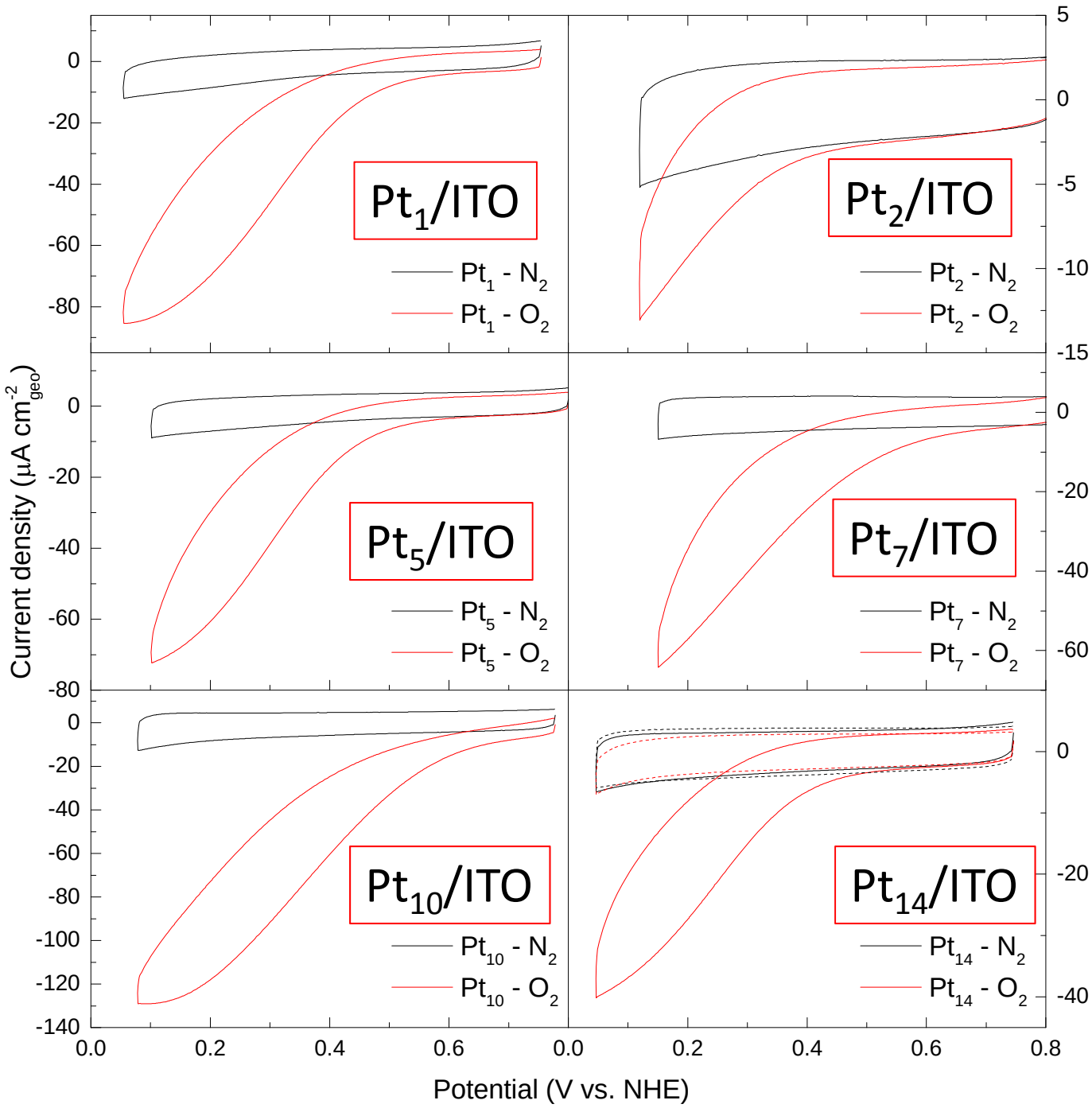
ORR over Pt_n/ITO electrodes

Start with narrow range CVs to avoid Pt redox chem

ORR is clearly seen even for Pt_1

NOTE alignment problem
Currents are lower limits

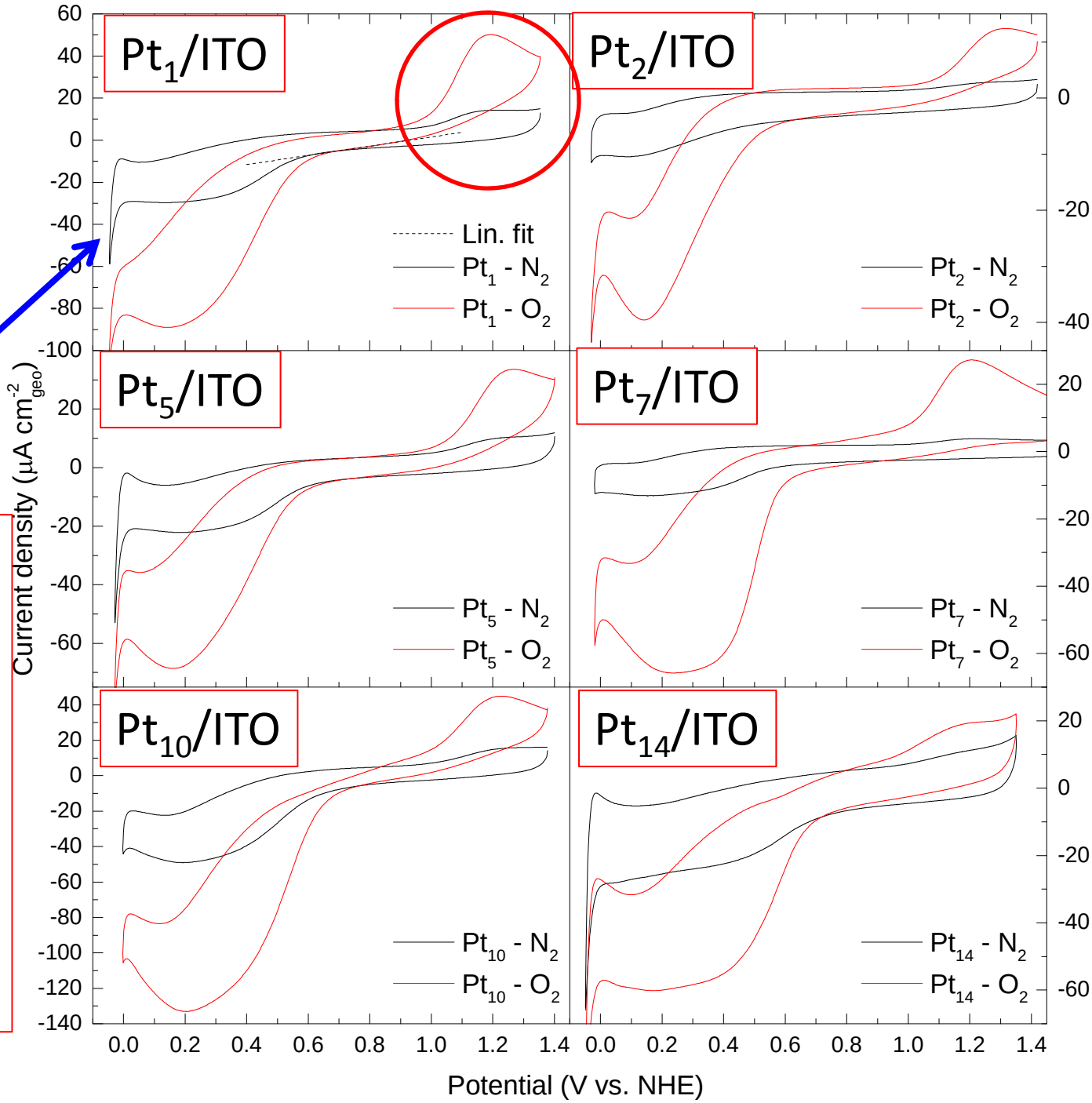
Mass activity is at least ~10 times higher than for Pt_{nano}/ITO under same conditions.



Cluster – containing electrodes

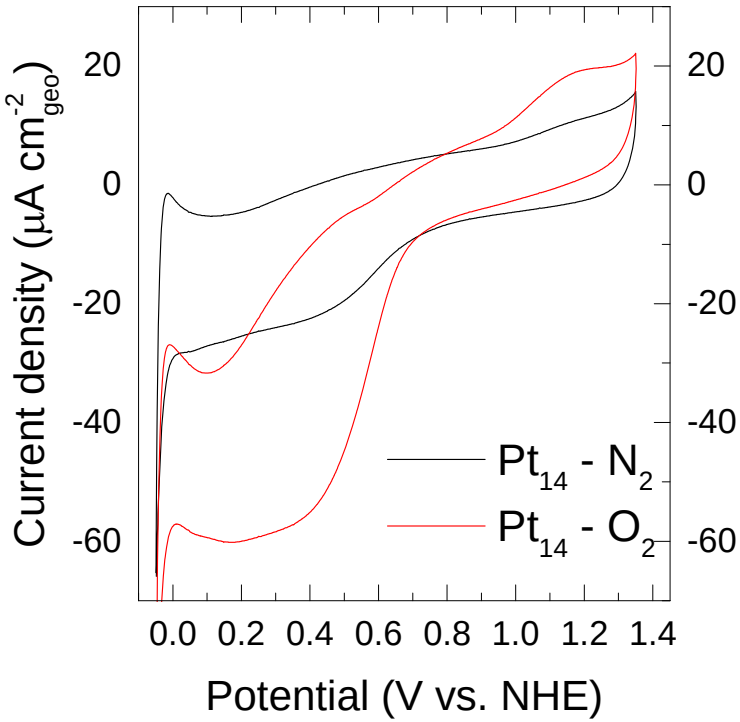
Full range CVs
All sizes active for HER and ORR

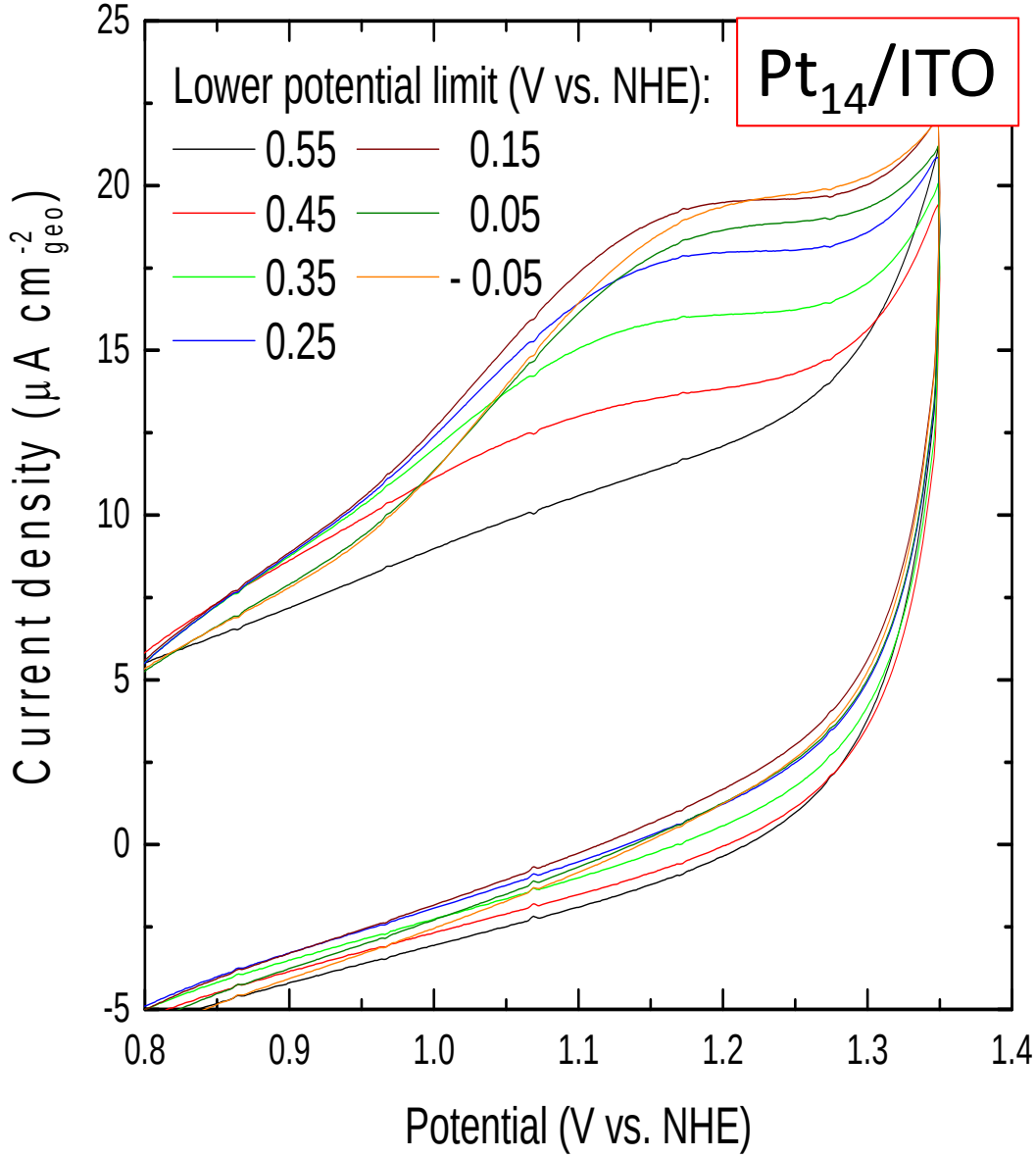
- ~1.2 V Oxidation peak cannot be Pt oxidation
  - too large
- Only seen after sweeping through the ORR wave
  - oxidation of ORR products
  - H_2O_2 oxidation (HPOR)

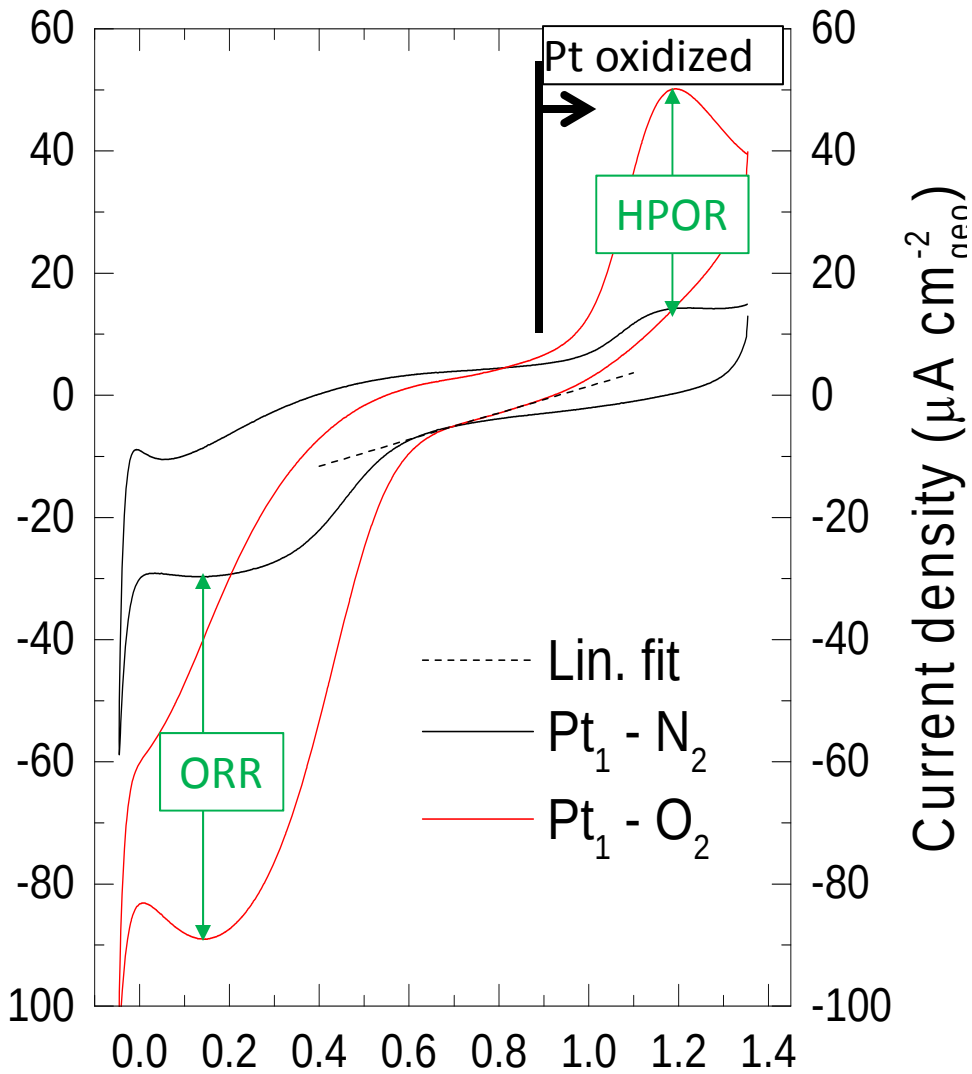


Hydrogen Peroxide Oxidation Rxn (HPOR)

We can vary the amount of H_2O_2 produced by changing the lower potential limit. HPOR peak should increase as we go further into the ORR wave.







Katsounaros, I.; Schneider, W. B.; Meier, J. C.; Benedikt, U.; Biedermann, P. U.; Auer, A. A.; Mayrhofer, K. J. J. Phys. Chem. Chem. Phys. 2012, 14, 7384–7391.

H_2O_2 is created during ORR at low potentials

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

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

React catalytically on the oxidized Pt surface at high potentials

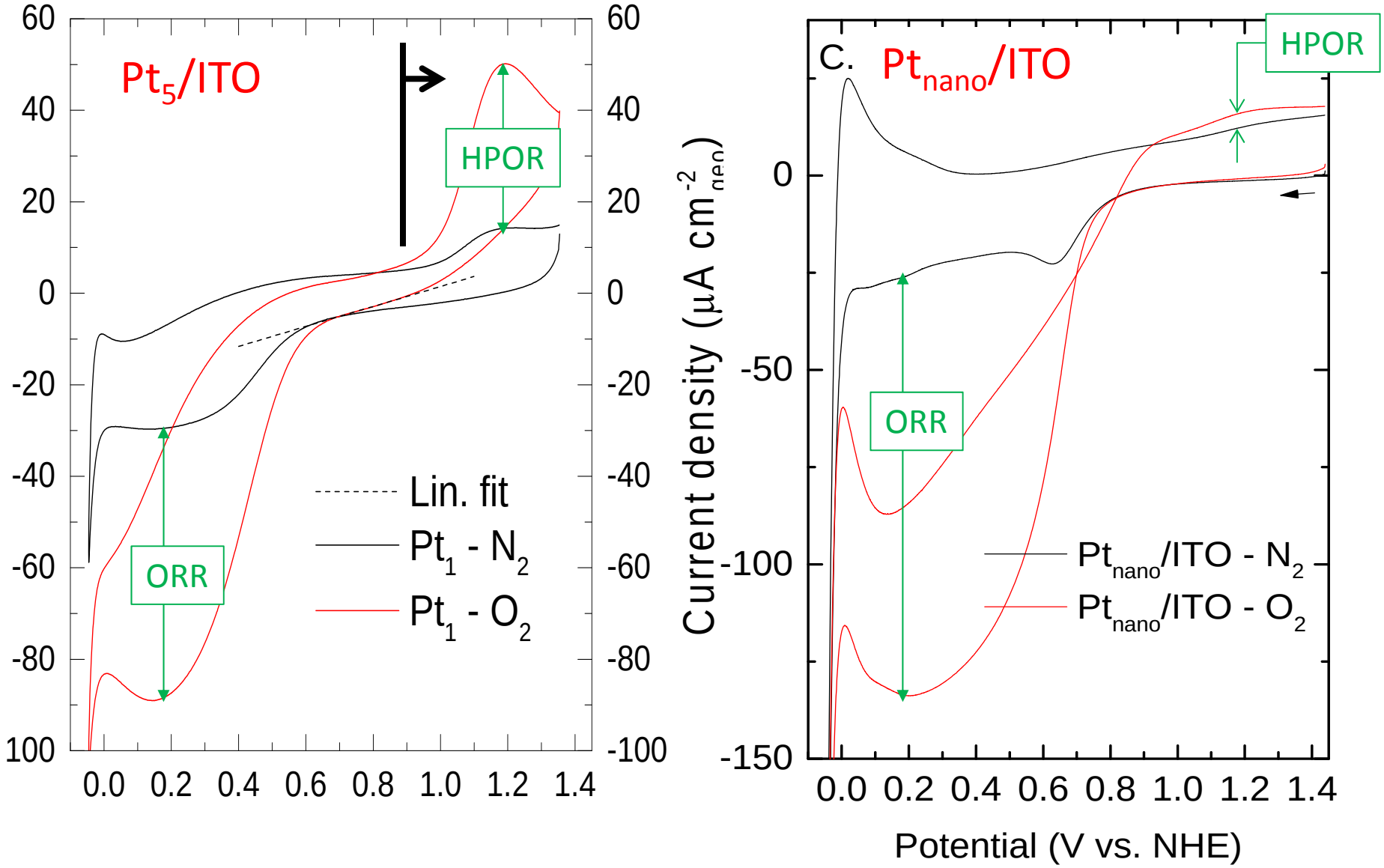
$2\,Pt(OH) + H_2O_2 \rightarrow 2\,Pt(H_2O) + O_2,$

$2\,Pt(H_2O) \rightarrow 2\,Pt(OH) + 2\,H^+ + 2\,e^-$

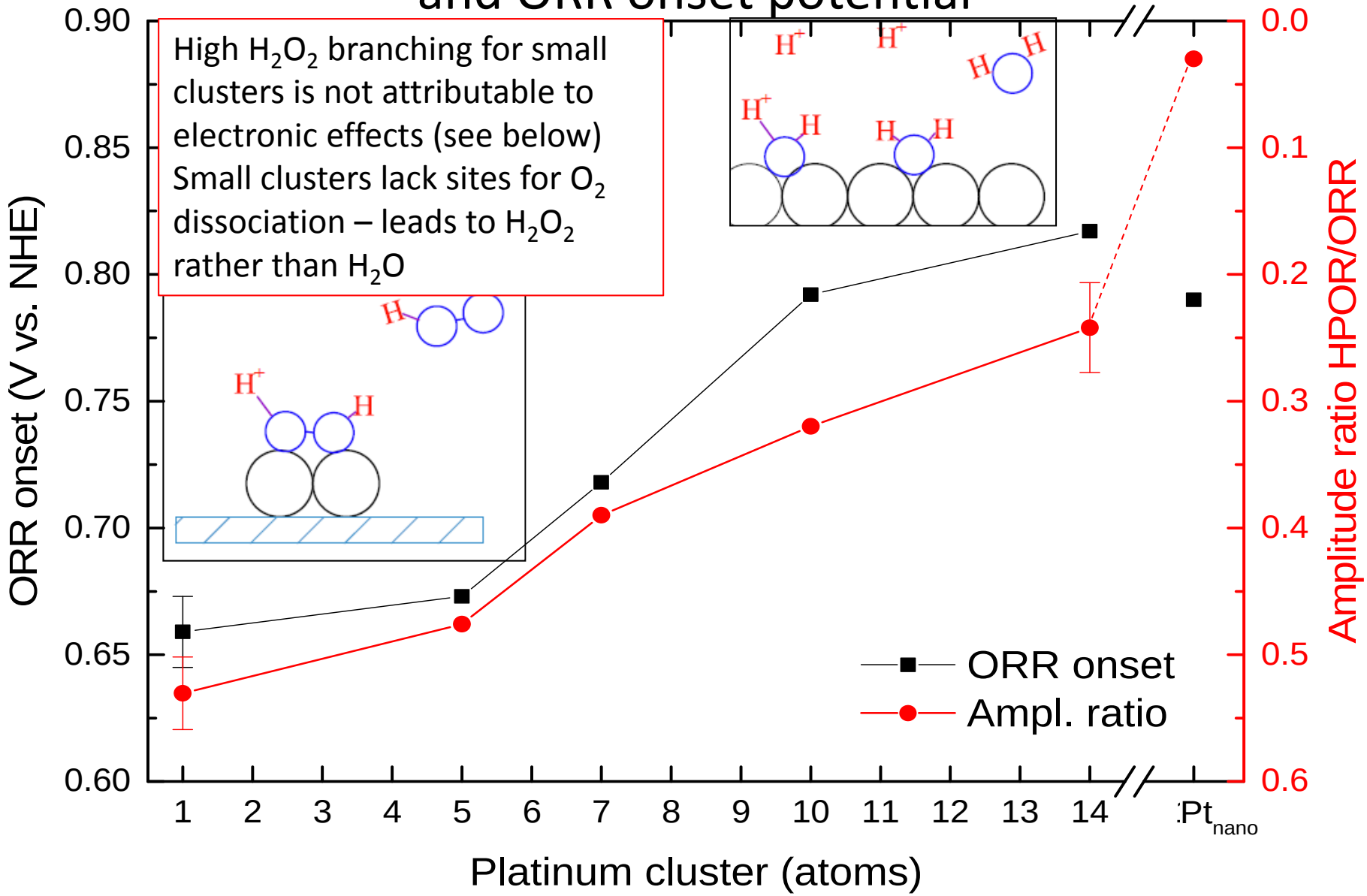
$H_2O_2 \rightarrow 2\,H^+ + O_2 + 2\,e^-$

HPOR = hydrogen peroxide oxidation reaction

MUCH more HPOR for small clusters than for Pt_{nano} or Pt_{poly}



Cluster size dependence of HPOR branching and ORR onset potential

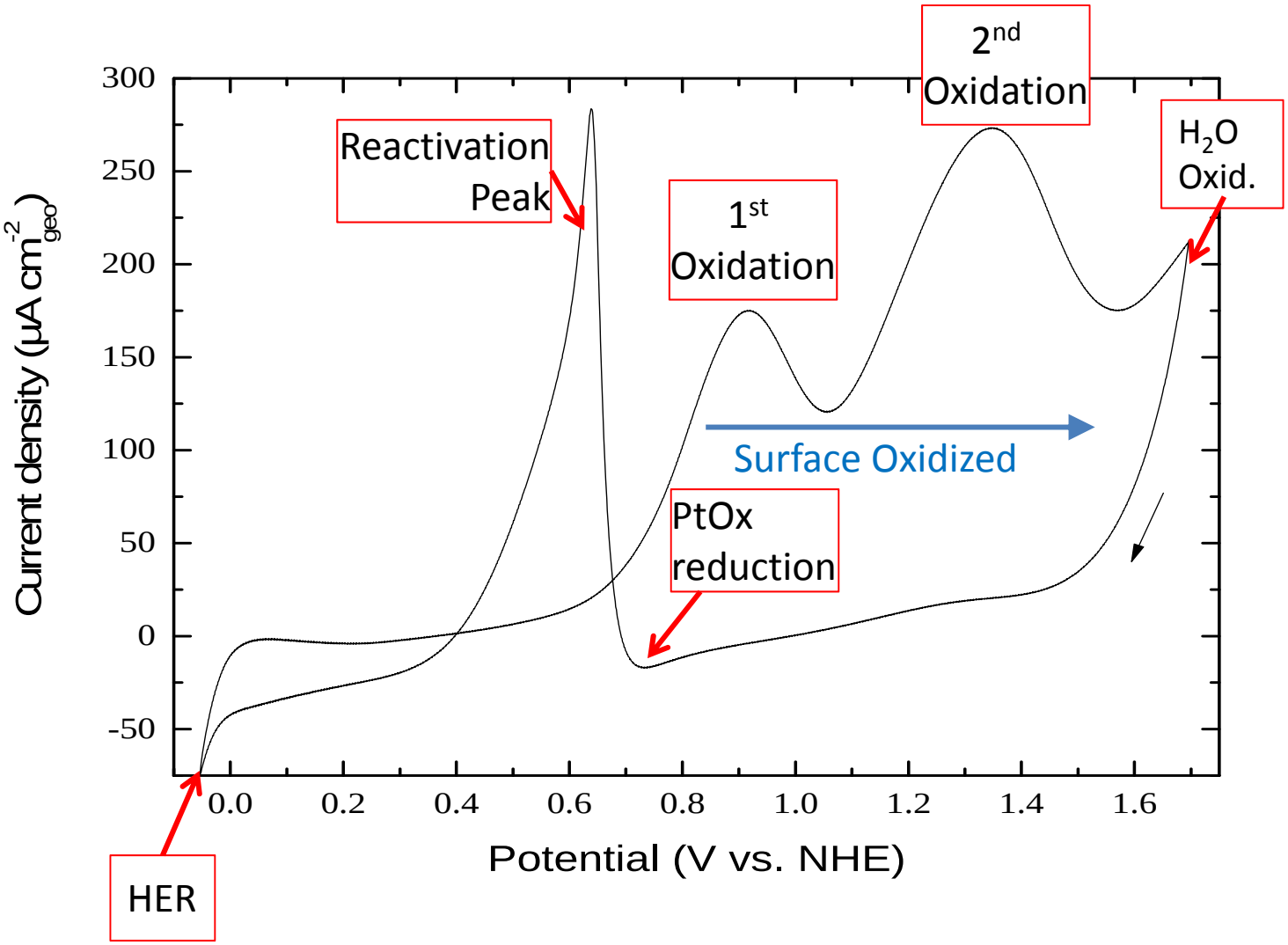


Ethanol Oxidation

- Direct Ethanol Fuel Cells
  - Would like to produce CO_2 but it is hard to break the C-C bond
  - Mostly produce acetaldehyde and acetic acid
- Very complex chemistry
  - DEMS
  - Vibrational spectroscopy
  - And all kinds of electrochemical tricks
  - Mechanism is still not completely understood
- We will focus on effects of Pt site size

Ethanol oxidation on Pt_{nano}/ITO

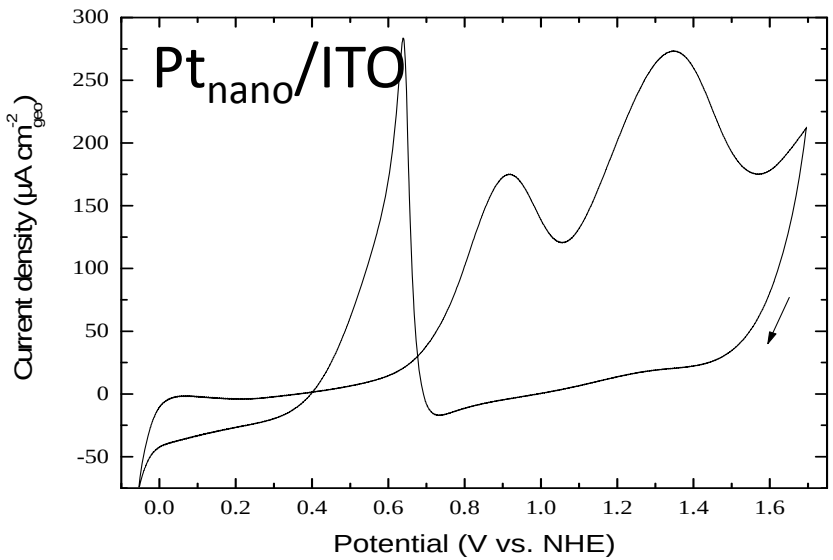
Pt_{nano} 1 vol% EtOH in 0.1 M $HClO_4$

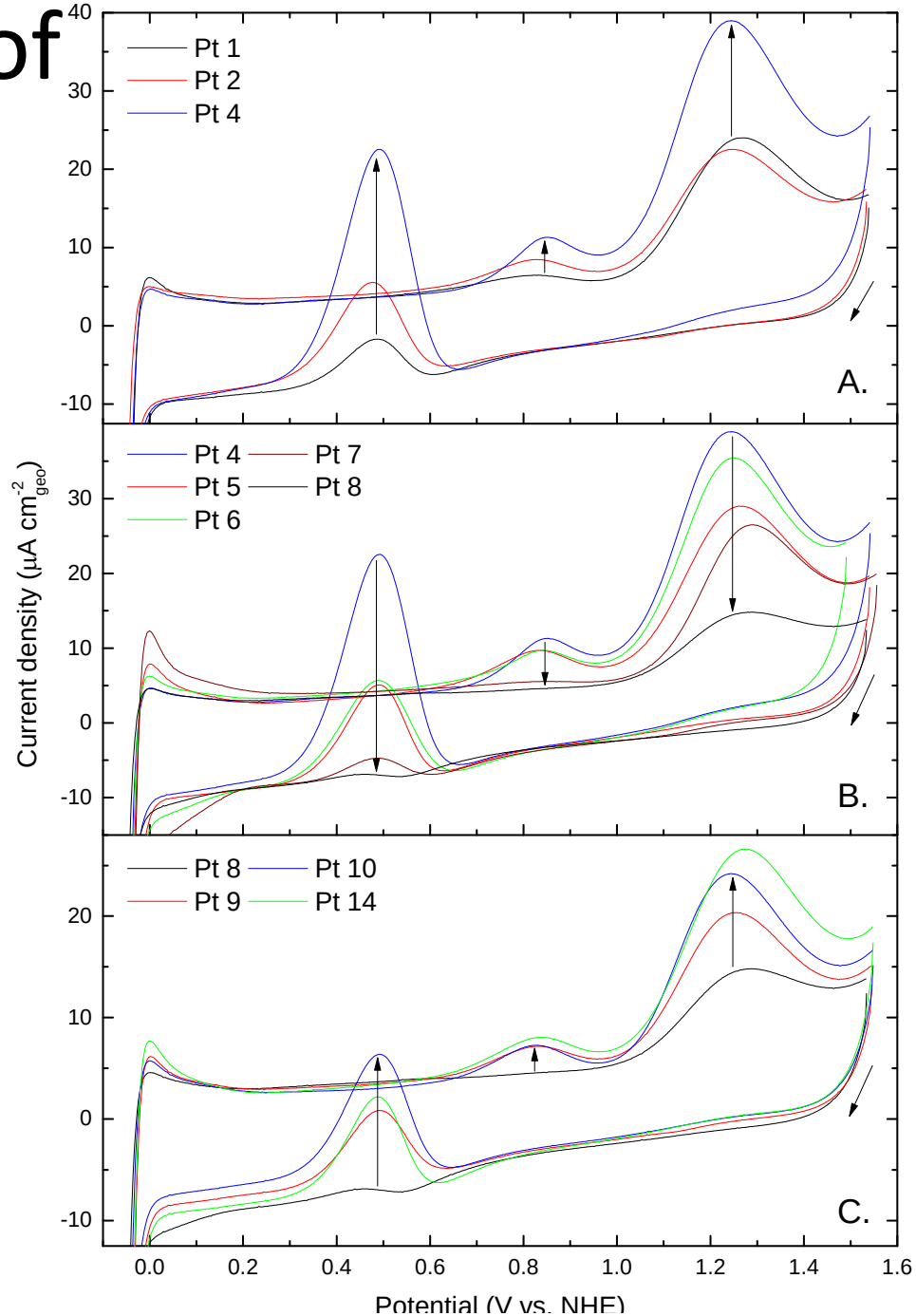


Size dependence of EOR activity

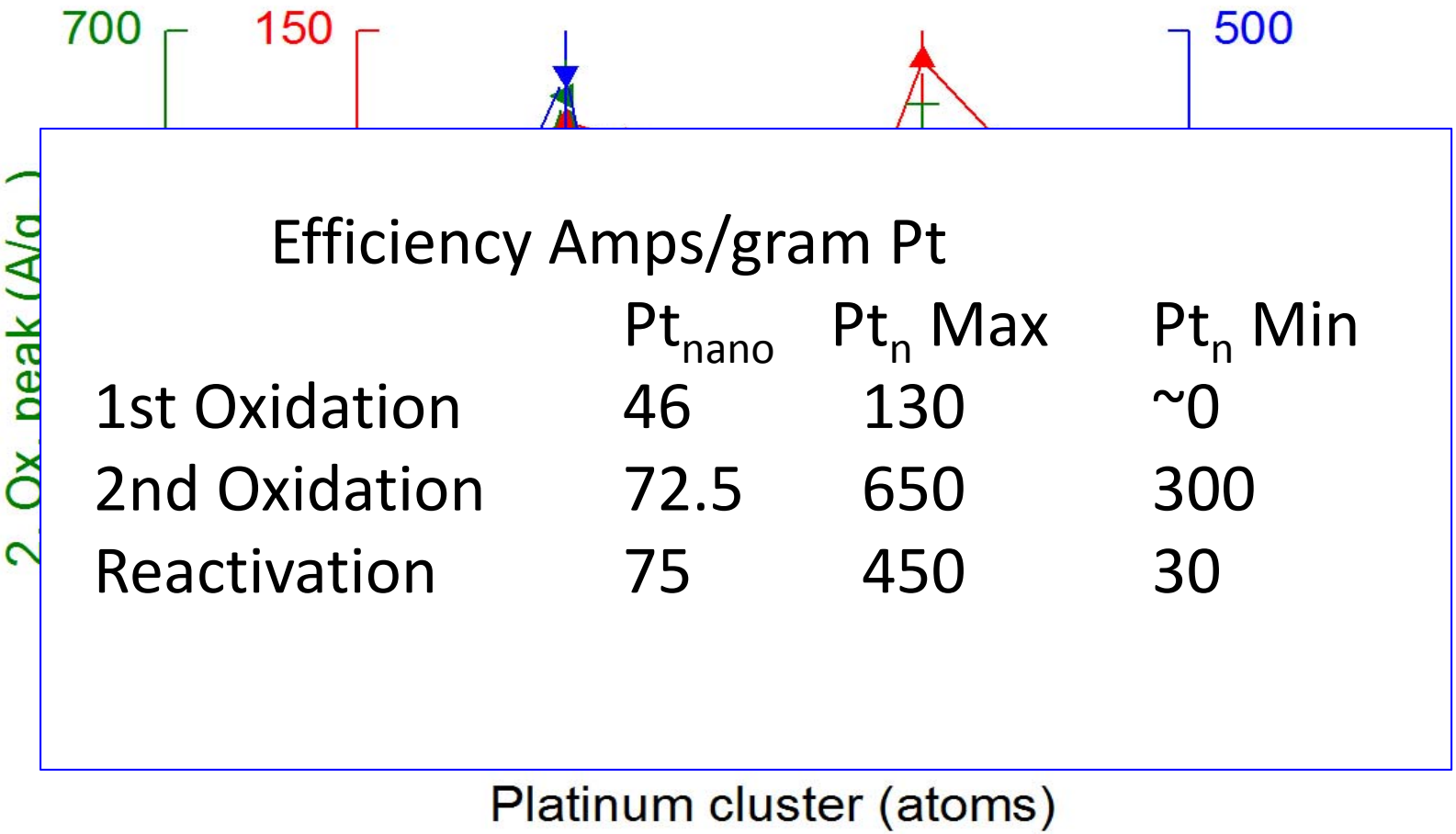
CVs for EOR on 0.1 ML Pt_n/ITO in 0.1 M $HClO_4$ + 1 % EtOH; scan rate: 0.1 V/s.

Strong oscillations of activity with size.





Activity vs. Size in CV #13 on each sample

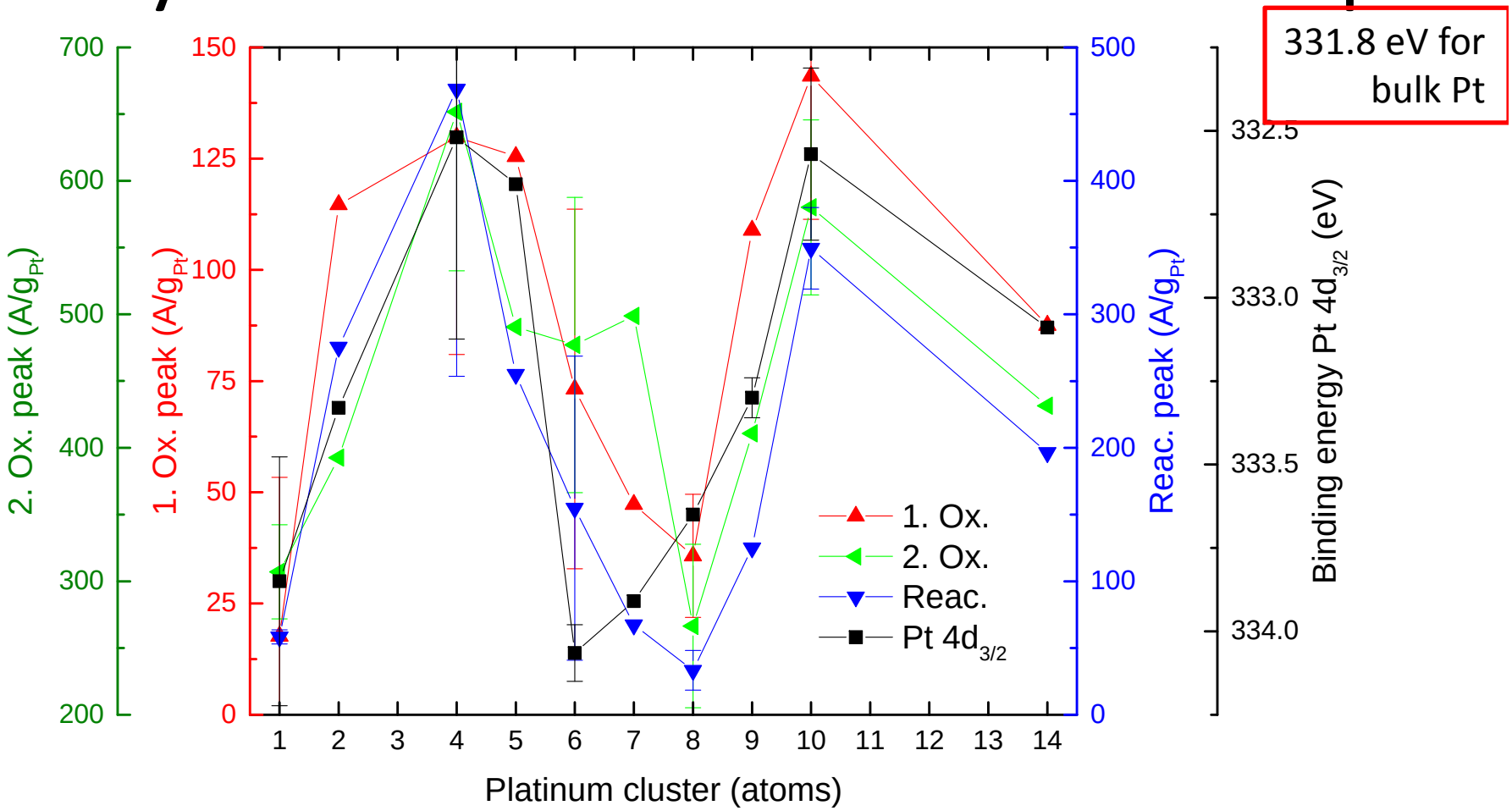


Efficiency Amps/gram Pt

	Pt_{nano}	Pt_n Max	Pt_n Min
1st Oxidation	46	130	~0
2nd Oxidation	72.5	650	300
Reactivation	75	450	30

1. Relative intensity of the 3 EOR peaks varies with cycling
2. Size dependence is preserved for at least 30 CVs, implying that the clusters remain intact.

Activity vs. Size in CV #13 on each sample

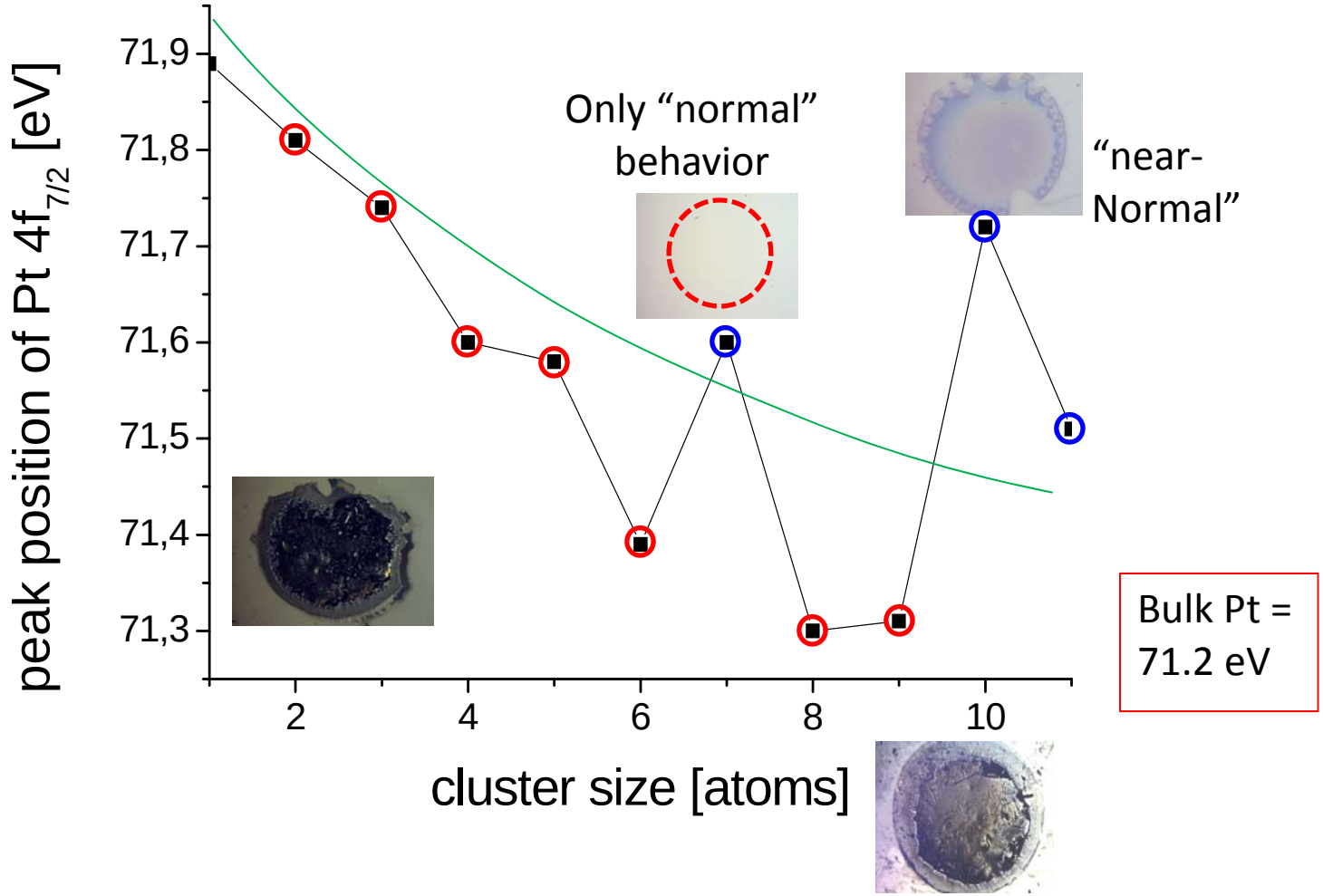


1. Strong fluctuations show that the clusters remain intact.
2. **Anti-correlation with Pt 4d core level binding energy**
3. **No sign of covergence toward bulk-like properties**

Anti-correlations between Pt 4f binding energy and ORR catalysis

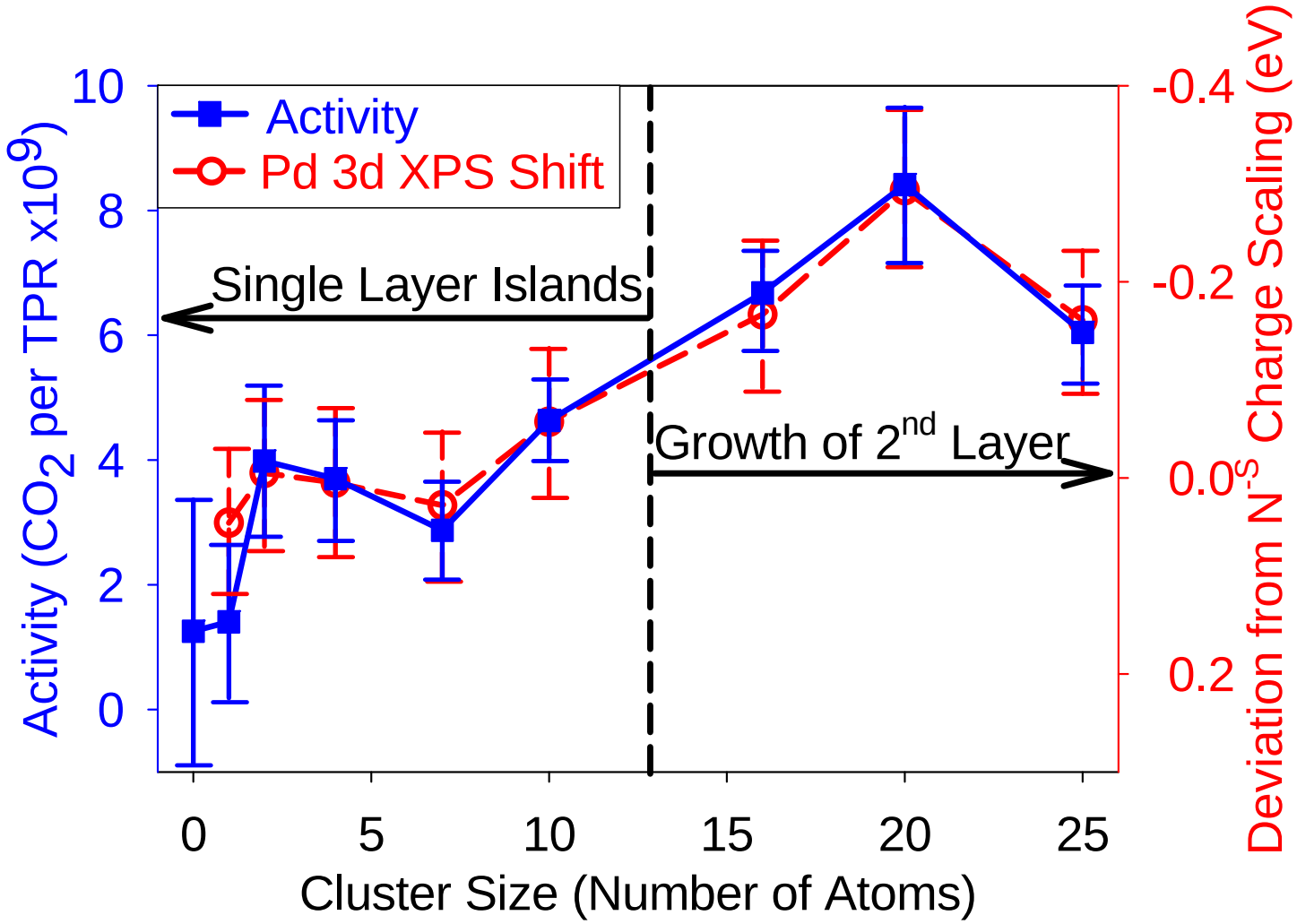
Glassy carbon oxidation by water, catalyzed by Pt_n

High Pt 4f BE is associated with no carbon oxidation "normal ORR"



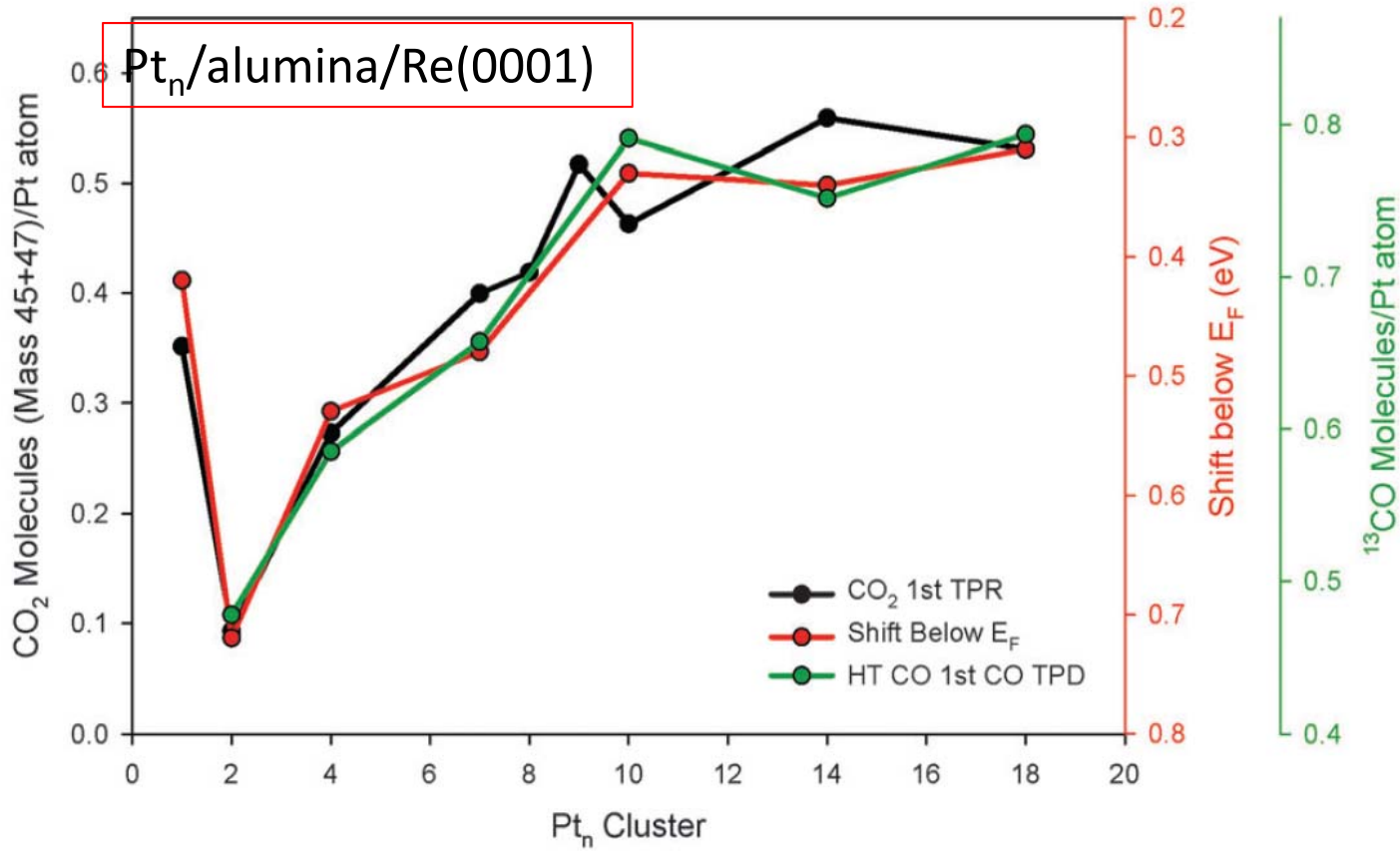
Other examples of anticorrelations between XPS BEs and Oxidation catalysis

CO oxidation over $Pd_n/TiO_2(110)$ under gas-surface conditions



Other examples of anticorrelations between XPS BEs and Oxidation catalysis

CO oxidation under gas-surface conditions Anticorrelation with Valence band onset and with a particular type of binding site.



What causes the Anticorrelations?

Two perspectives on core level shifts:

Initial State

High BE means that Pt or Pd is in an electron-poor (positively charged) state which stabilizes all the electronic orbitals.

Low BE means that Pt or Pd is electron rich, which increases electronic energy due to e^--e^- repulsion

Final State

High BEs result from poor screening of the final state core hole. Means that Pt or Pd are electron poor.

Low BE means that core hole is well screened and delocalized. Pt or Pd must have electron rich and polarizable valence shells

Conclusions

- Small, monodisperse clusters can have strongly size-dependent chemistry
  - Activities (currents) are strongly size dependent
  - Peak or onset potentials are weakly size dependent
- Oxidation catalysis activity is dependent on electron rich clusters
  - rate limiting step is bond activation in water, EtOH
- H_2O_2/H_2O branching in ORR may be controlled by the size of the available sites for O_2 binding/dissociation
- Can see ORR, OER, HER, EOR, HPOR even on very small clusters – one to two atoms!
- For small clusters – need to avoid adventitous adsorbates to see inherent size dependence
- Mass activities are substantially higher than for Pt_{nano}