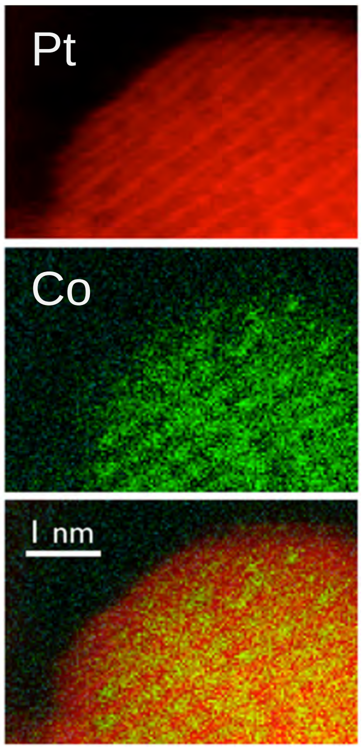
Seeing Electrochemistry Live at the Atomic Scale

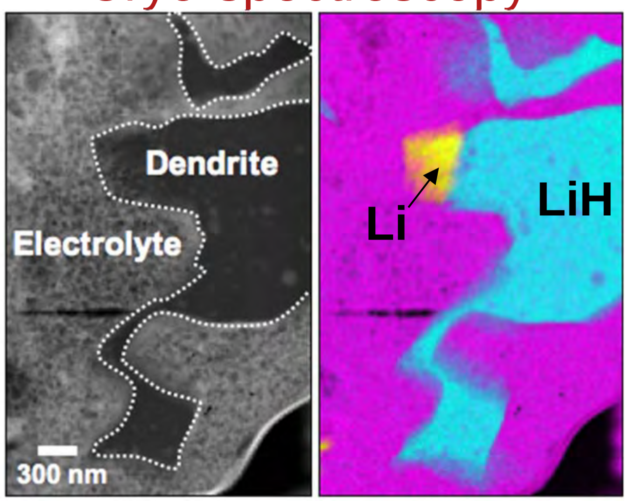
David A. Muller, Cornell University

Ex Situ → ***In Situ/Operando***

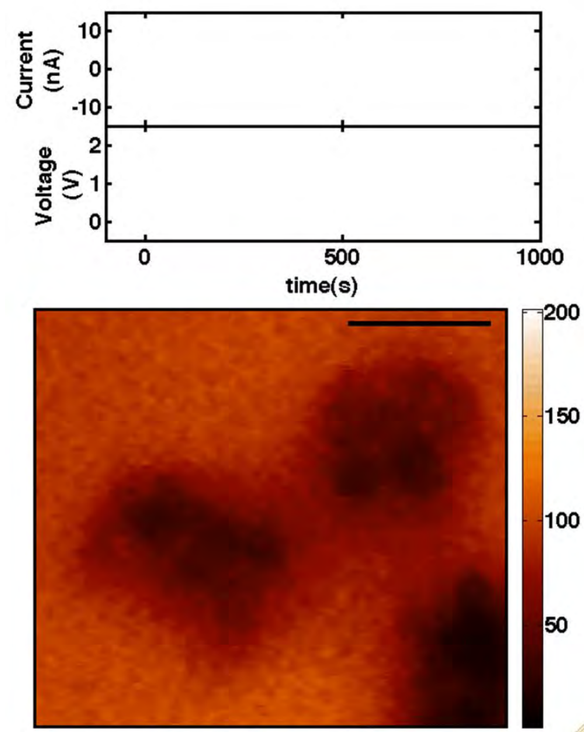


Atomic Resolution

Cryo-spectroscopy



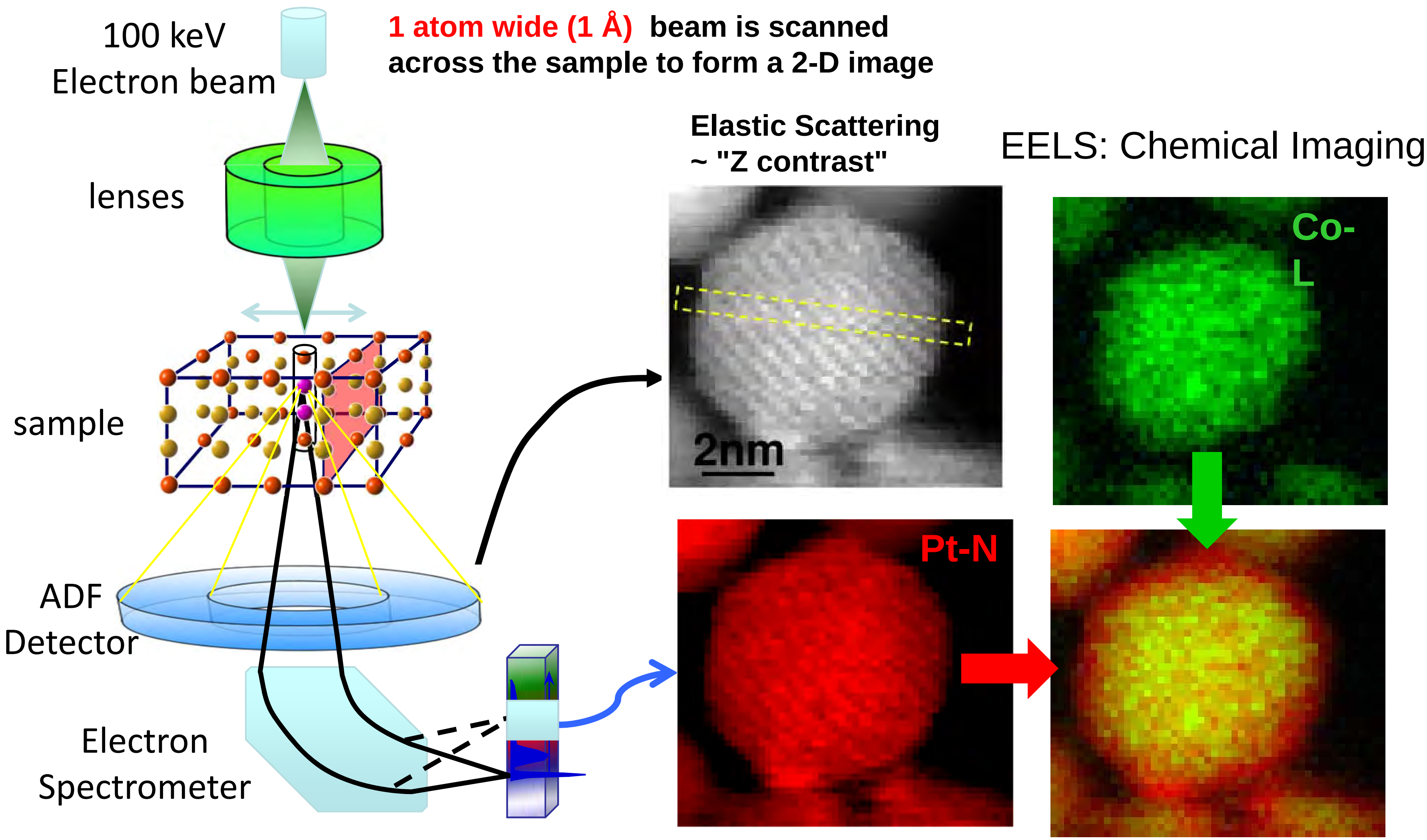
Tracking chemistry and bonding at liquid/solid interfaces



Electrochemistry in liquids

Scanning Transmission Electron Microscopy

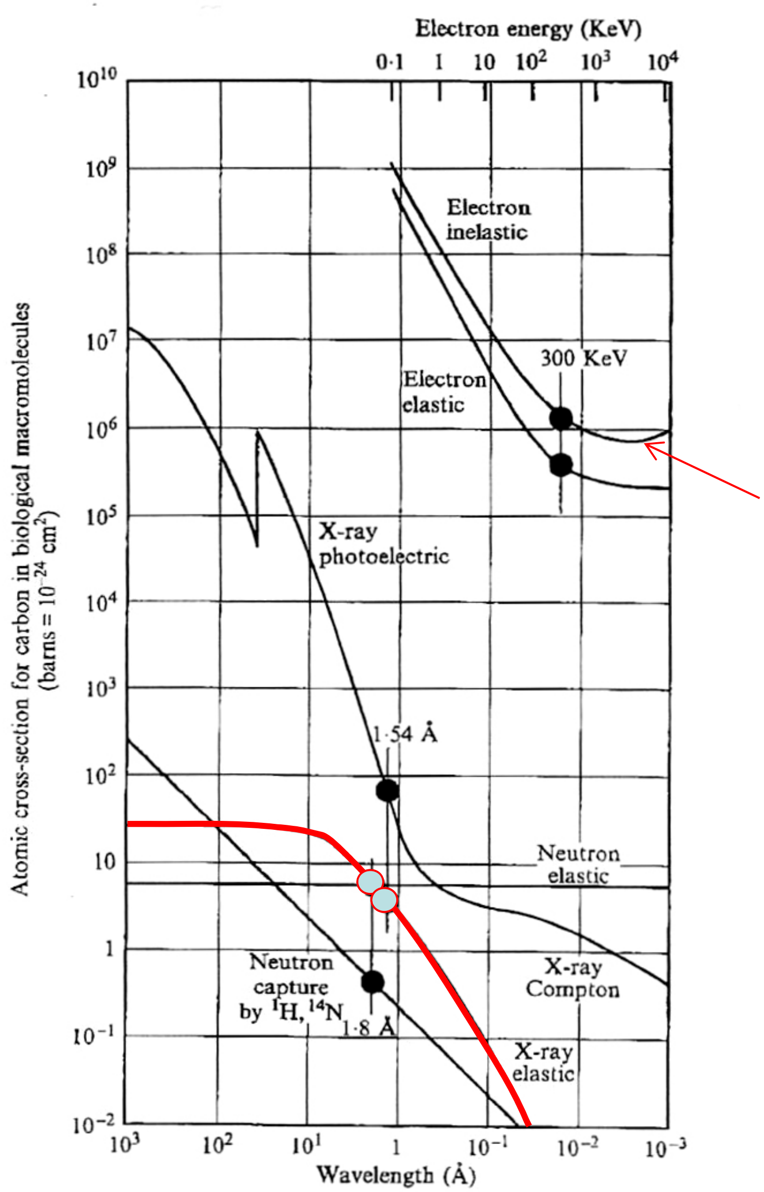
1 atom wide (1 Å) beam is scanned across the sample to form a 2-D image



Muller, Kourkoutis, Murfitt, Song, Hwang, Silcox, Dellby, Krivanek, *Science* **319**, 1073 (2008).

How Bad is Radiation Damage?

R. Henderson, Quarterly Reviews of Biophysics 28 (1995) 171-193.



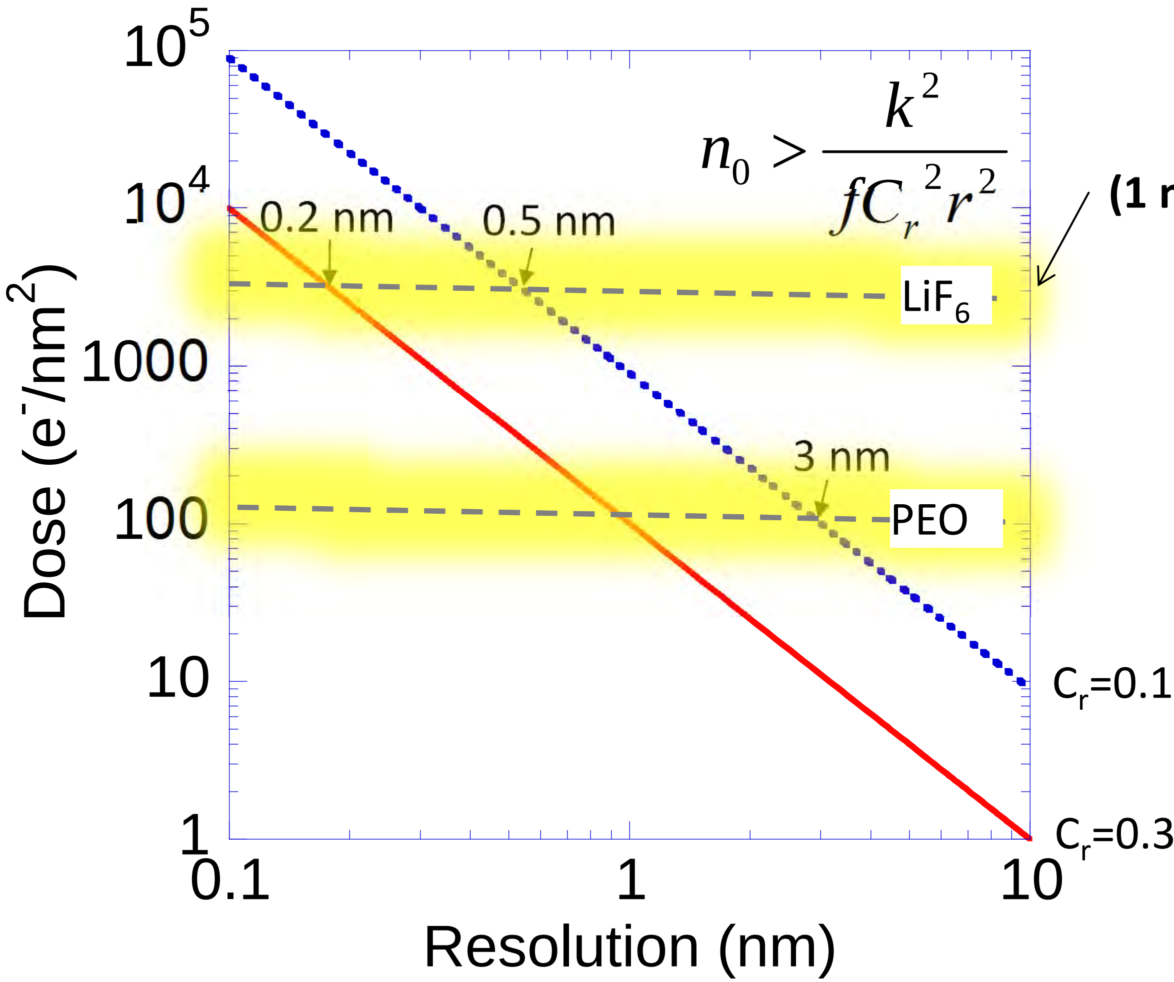
It's not the cross-section, but

How many damaging events per useful imaging event?

Least Damage:
Elastic imaging - Electrons wins
Inelastic imaging - Soft X-rays win

Dose Required for 2D-Imaging

Saxberg & Saxton, Ultramicroscopy **6**, 85–90 (1981)



(1 mM H_2 in H_2O)

Resolution ~ 1/(Dose)$^{1/2}$

Resolution ~ 1/(Contrast)

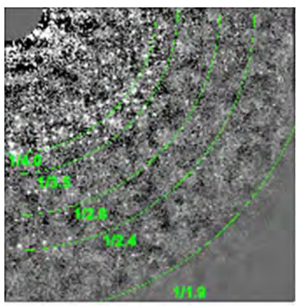
n_0 : dose
k : S/N = 3
f : fraction contributing to background = 1
C_r : contrast = 0.1-0.3
r: resolution

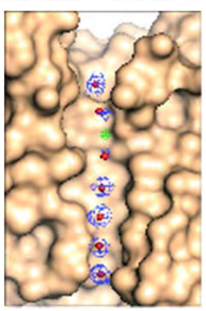
Maybe can do 1 atomic-resolution image in water, but not organic electrolyte
For 10-100 images, expect 1-10's of nm resolution

3D Cryo - Electron Microscopy

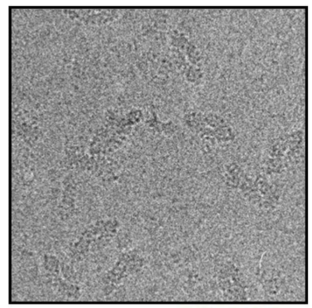
Biological structures are inherently 3D and require 3D techniques

Electron crystallography
2-D crystals of membrane proteins in their native environment
near-atomic resolution

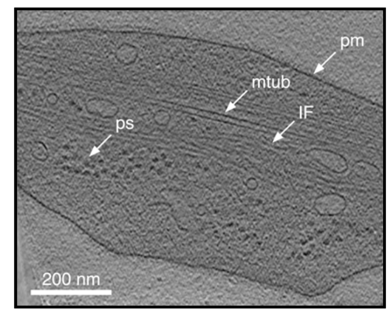


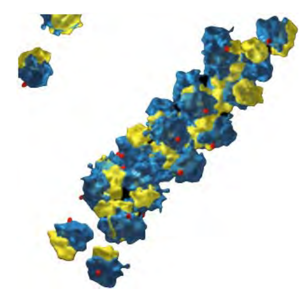


Single-particle analysis
Purified molecules in solution ~200-10 MDa
~2.2 Å resolution

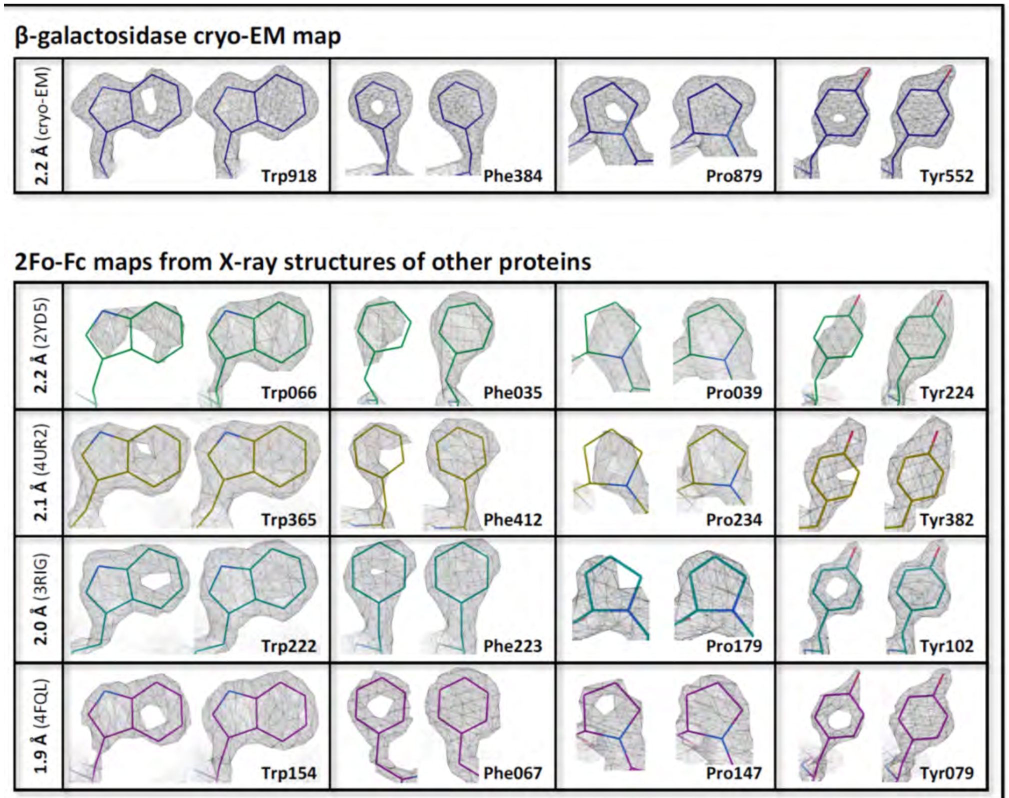


Electron tomography
Pleiomorphic samples, e.g., cells and organelles
~ 2-4 nm resolution

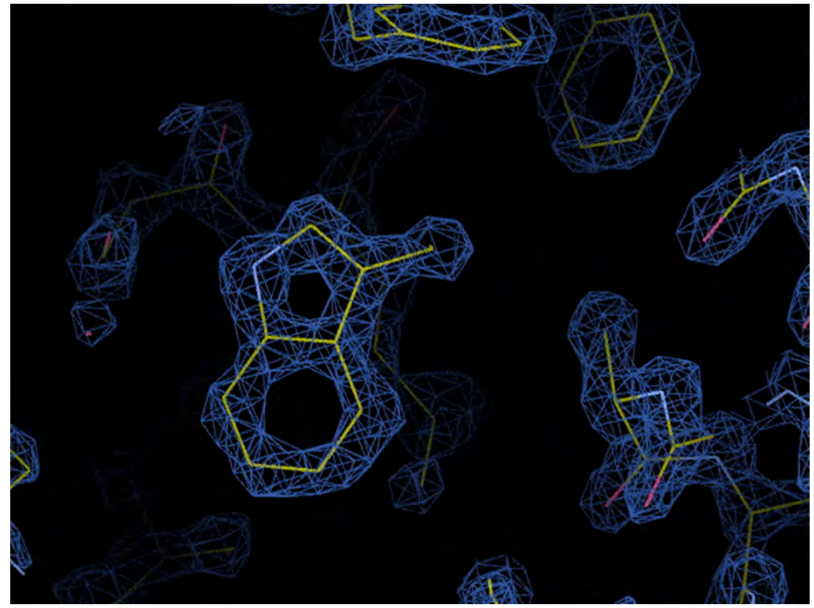




Single-Particle CryoEM vs X-ray



Bartesaghi, Science **348** (2015)

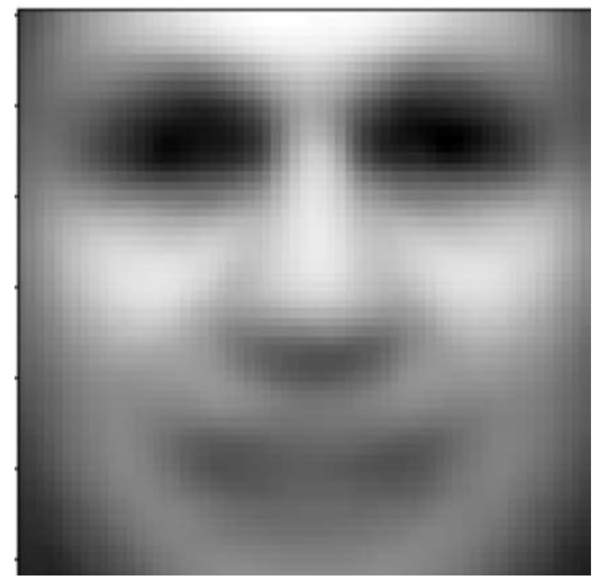


1.55 Å Cryo EM, Takayuki Kato, (2019)
24 hrs data collection, 120,000 particles

Single-Particle Methods should work for molecular and bio-Echem (Freeze at bias)
-needs similar molecules to work (so not so good for nanoparticle catalysts)

Imaging vs Diffraction/SPEM

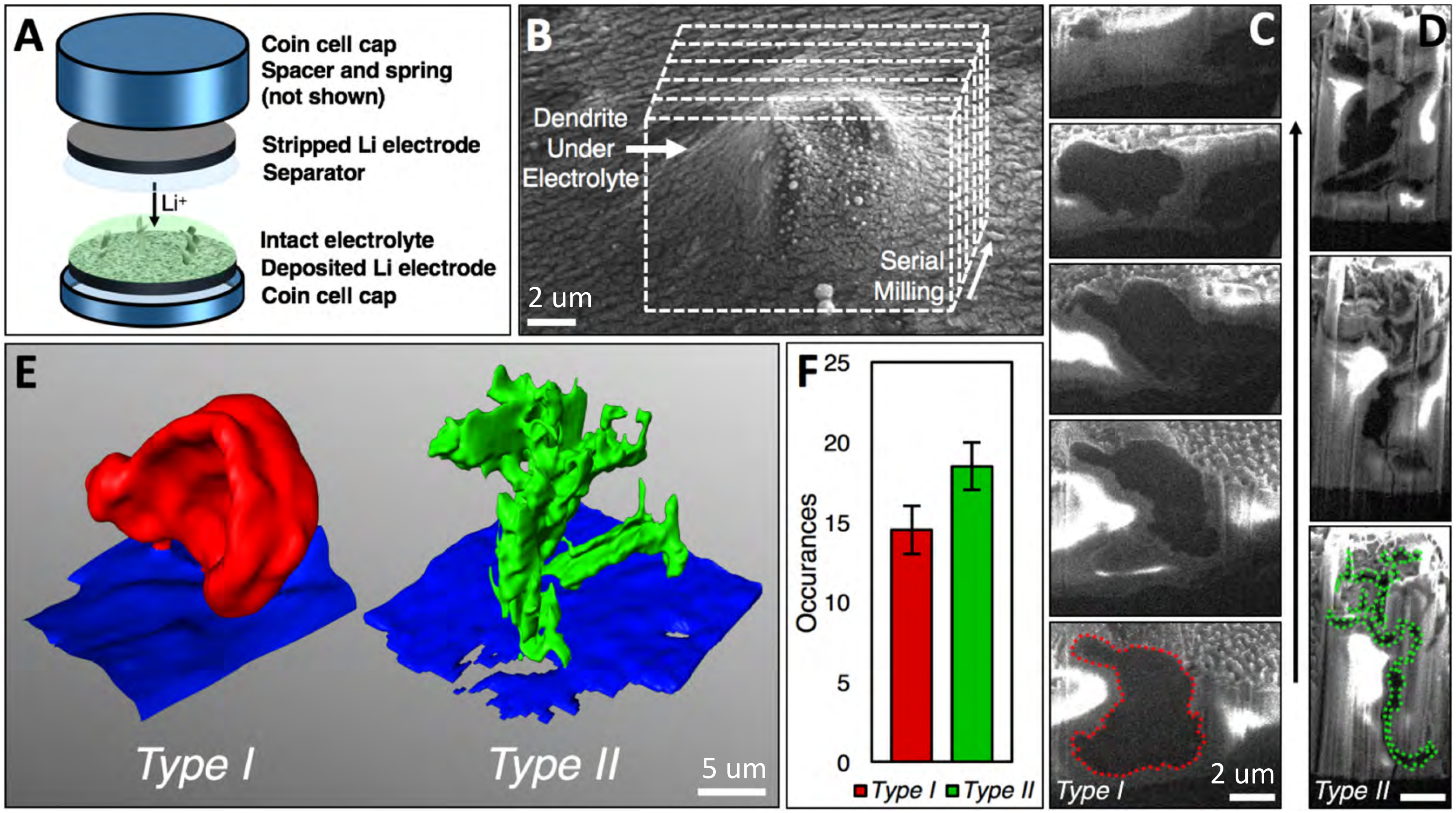
Ensemble - 1:1 mapping



Ensemble Average
Many:1 mapping

Catalysts, like people are inhomegenous

Dendrite morphology from cryo-FIB

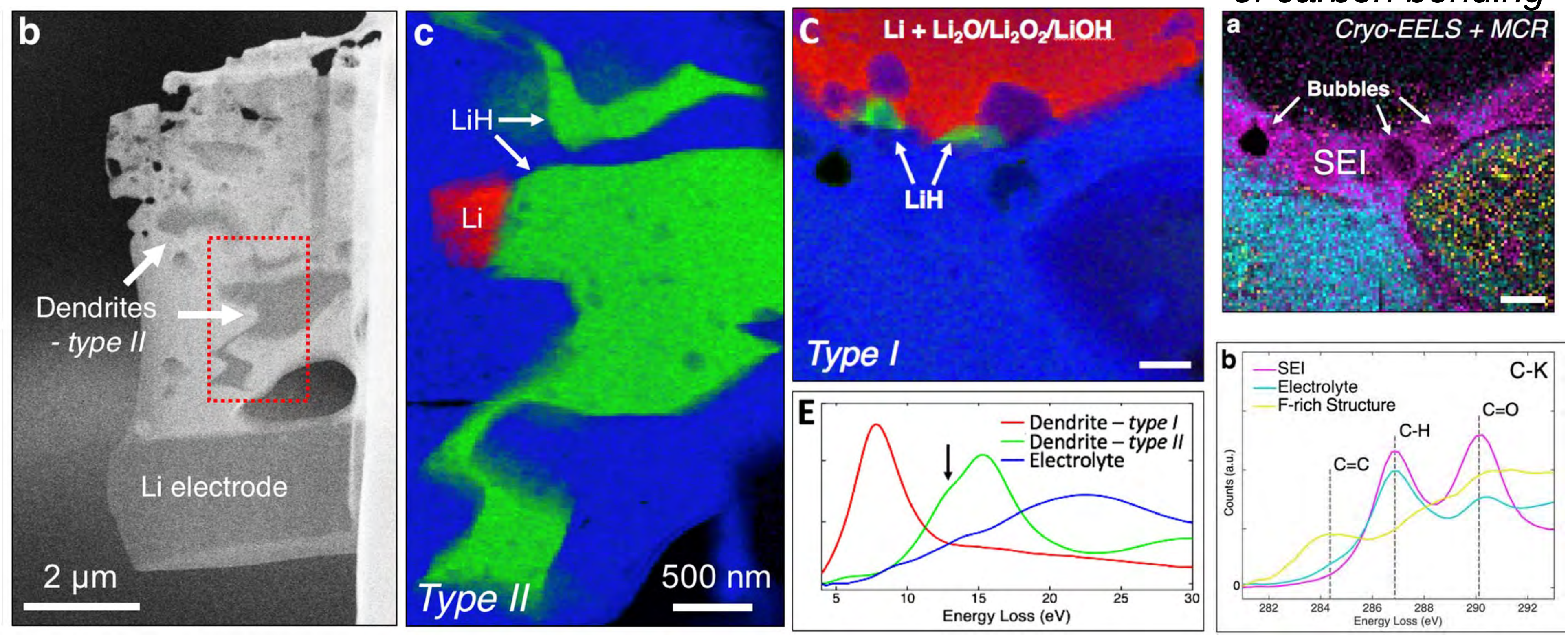


Serial cross-sectional cryo-FIB/SEM revealed two distinct dendrite morphologies
Narrow connection sites for Type II might give rise to “dead” Li

Zachman and Kourkoutis, *Nature*, (2018)

Two structurally and chemically distinct dentrite structures

Spatial variation of carbon bonding



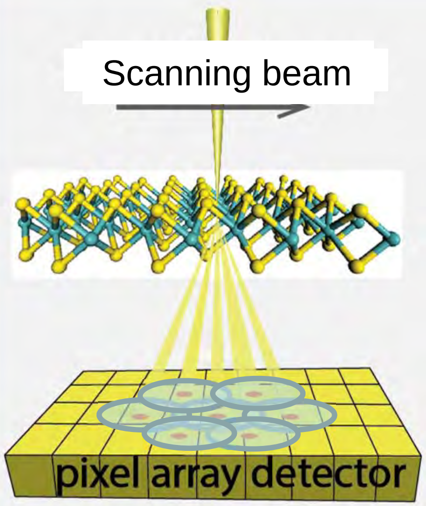
Type I dendrite:
- lithium metal, partially oxidized at its core
- transitioning to peroxide and hydroxides near the surface

Type II dendrite:
- uniform lithium hydride

Zachman and Kourkoutis, *Nature*, (2018)

Electron Microscopy for Catalyst Characterization

New Detector Records every electron that passes through the sample, at every probe position!



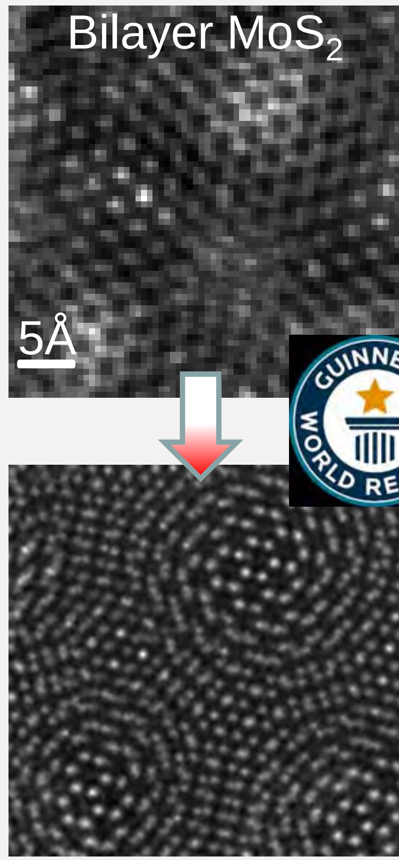
EMPAD:

High Speed: 0.86 ms/frame

Single Electron Sensitivity

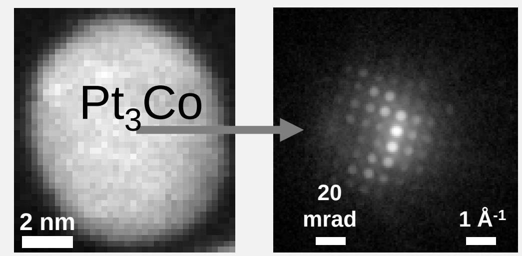
e^- Dynamic Range > 1,000,000:1

Microsc. & Microanal. **22**, 237 (2016)

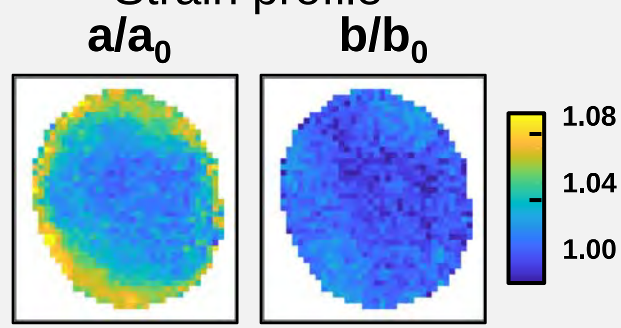


Nature **559**, 343 (2018)

Sub-nm Resolution,
pm-Precision Strain Mapping



Strain profile

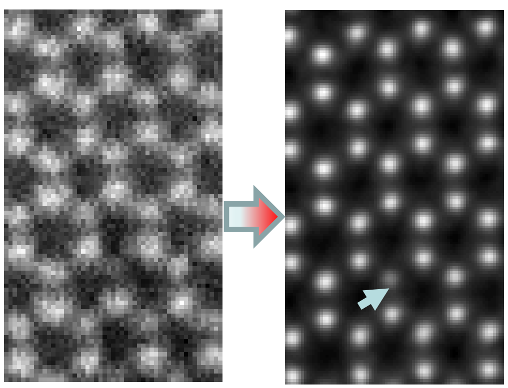


strain maps of core-shell nanoparticles with **1,000X less dose** than EELS or AC-STEM atom fitting & any orientation.

Electron Microscopy for Catalyst Characterization

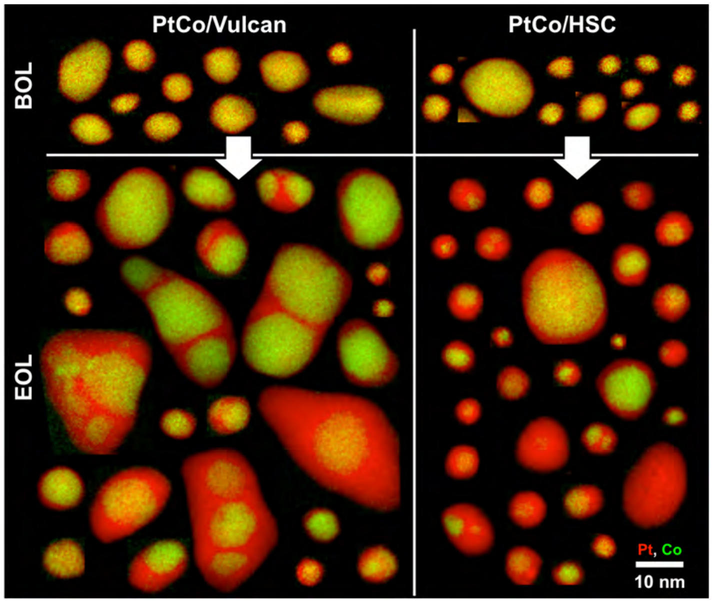
1. Structure of Catalytic Sites **2. Catalysts/Support Interactions** **3. Catalyst Aging Mechanisms**

Improved resolution means improved detection of local atomic structure of catalytic sites



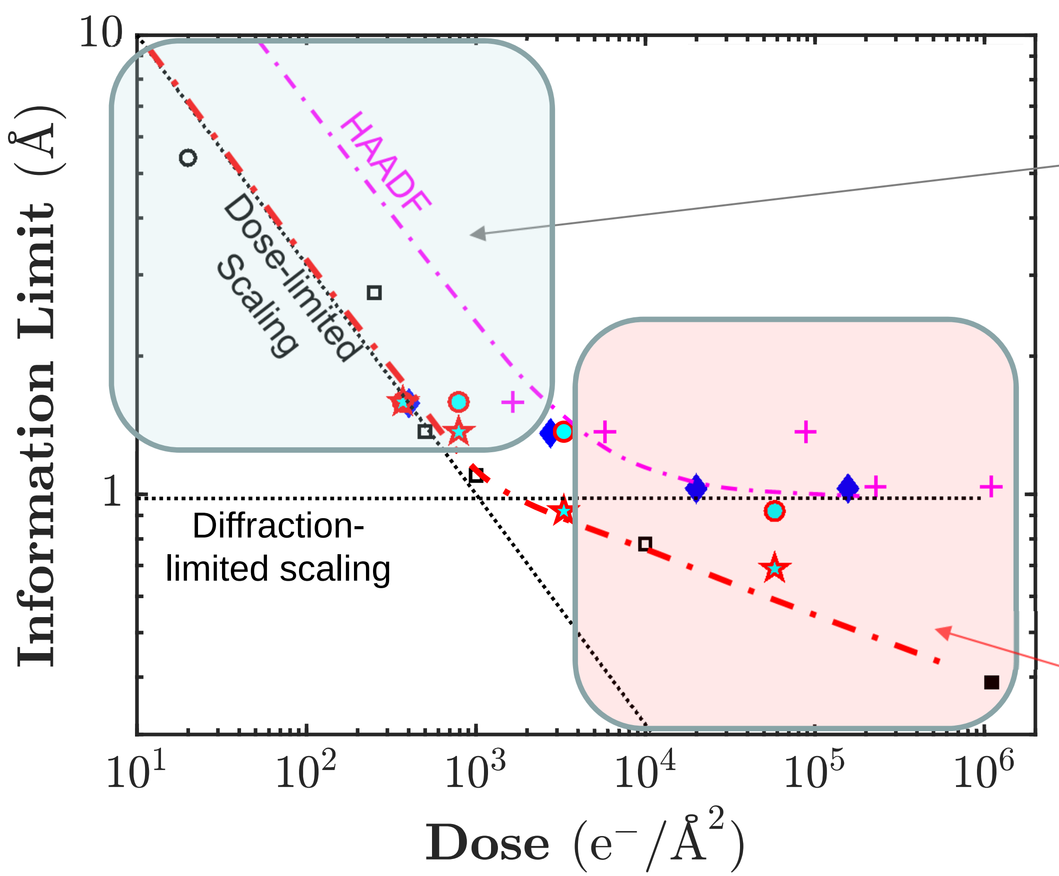
Sulfur monovacancy in MoS_2

Pt catalysts dispersed in High-surface-area C



Capabilities include in-situ and electrochemical liquid cell microscopy

Dose vs. Resolution: 2 Regimes



Low Dose:

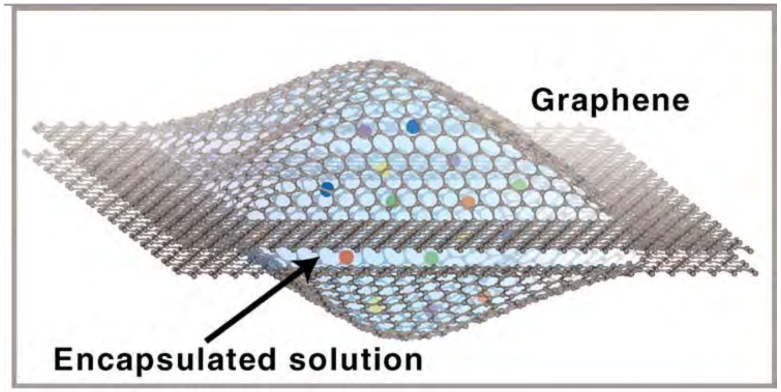
- Poisson Uncertainty>> Probe Size
- $d \propto 1/\sqrt{N}$
- Ptychography vs ADF: double info limit for the same dose

High Dose:

- Probe size set by diffraction limit
- ADF resolution saturates
- Ptychography resolution continues to improve with dose (2-3 x).

Imaging methods enabled by new detectors require ~ 10x less dose

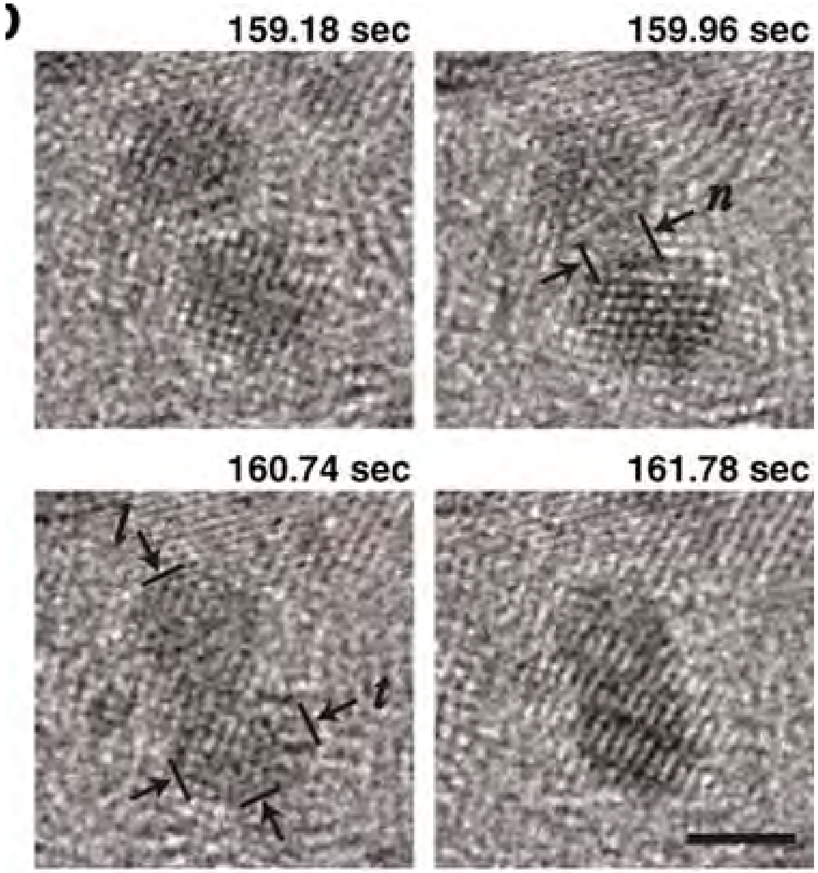
Best resolution = graphene liquid cell



Thin liquid + thin encapsulating sheets = atomic resolution Pt growth and coalescence

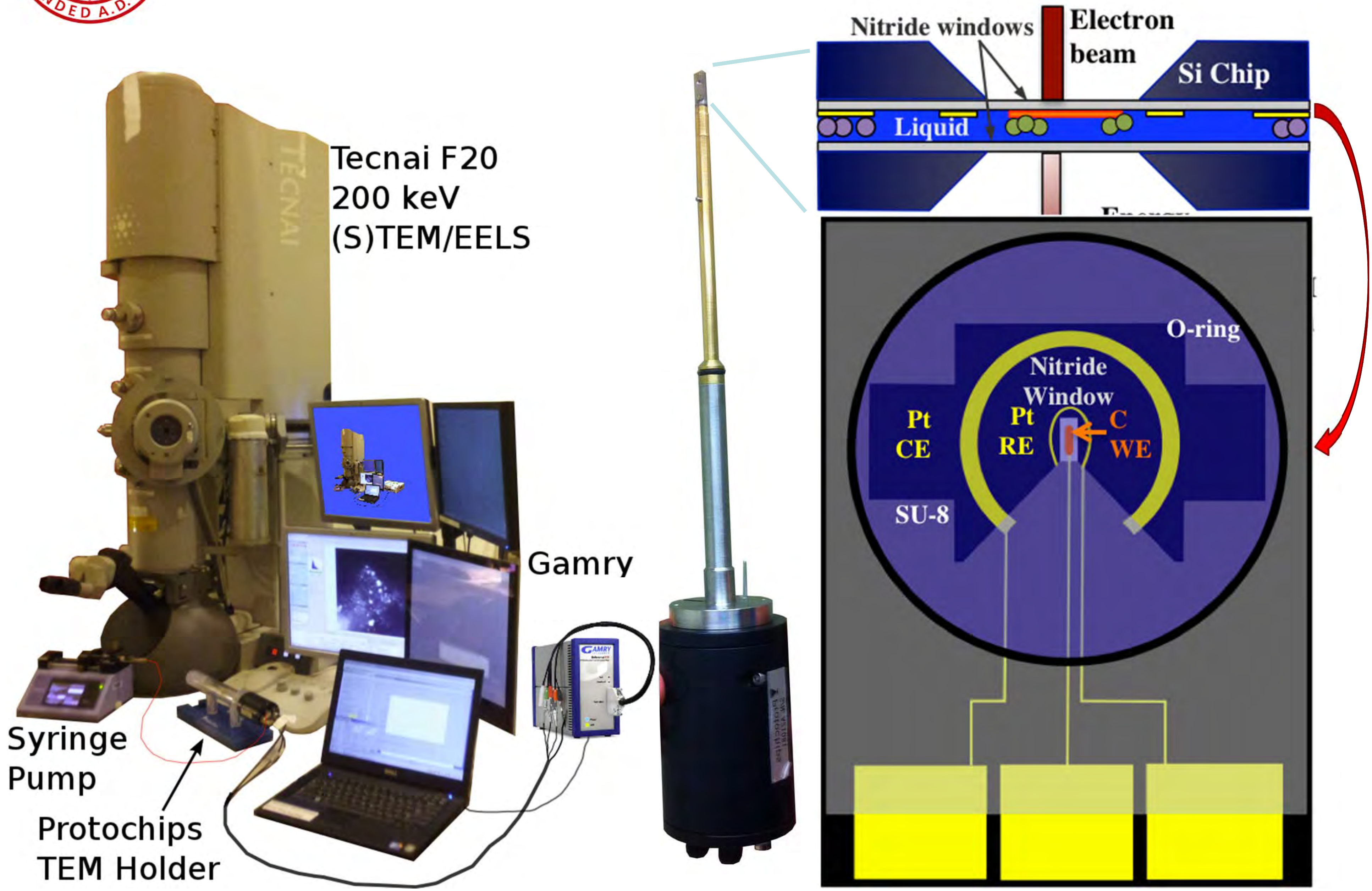
Beam induced phenomenon!
Electron beam can make a very reducing environment.

Pt containing solution exposed to beam



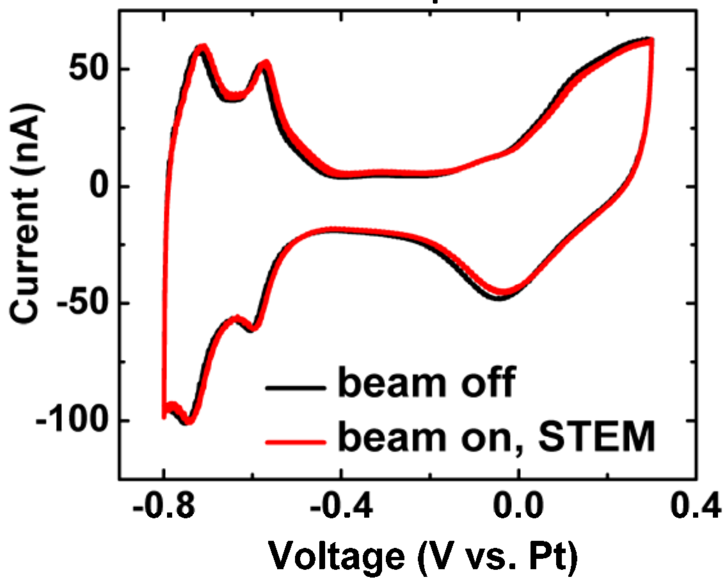
Yuk et al. Science **336** (2012)

TEM electrochemical cell

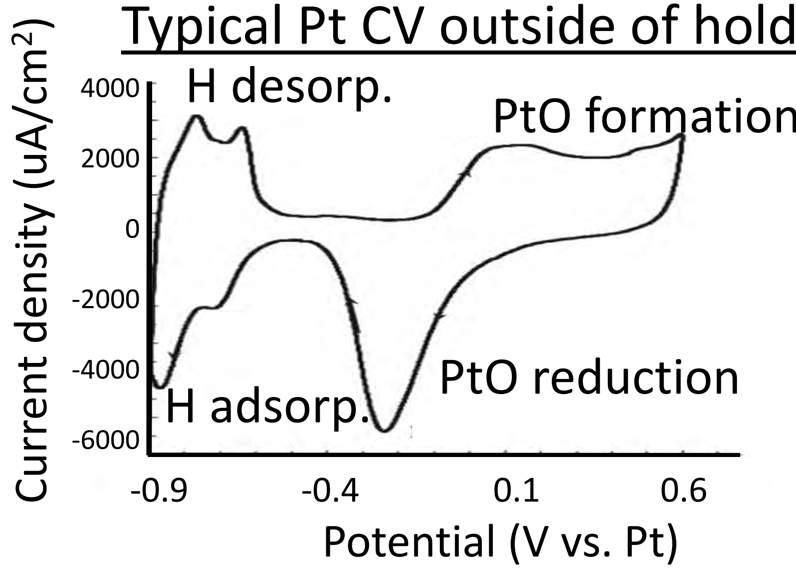


Electrochemistry in the TEM

CV of Pt film deposited on chip

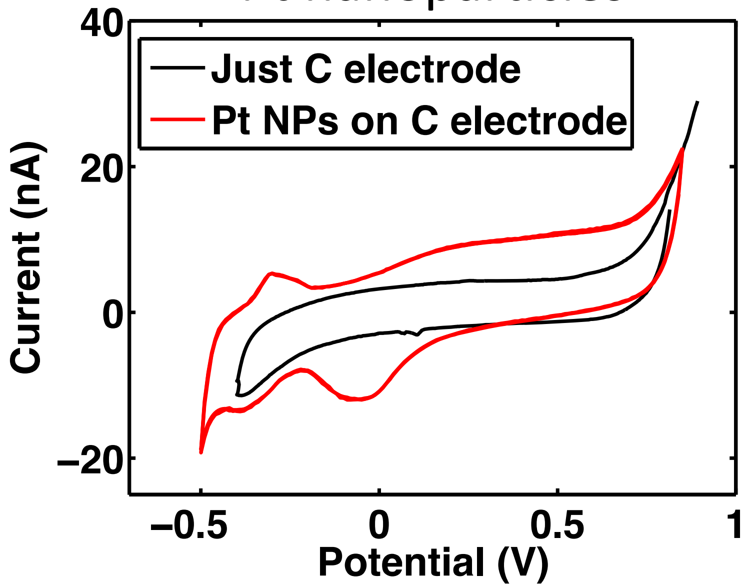


Typical Pt CV outside of holder



Adapted from M.G. Hosseini, et al. Electrochemica Acta, Volume 70, 30 (2012), 1–9

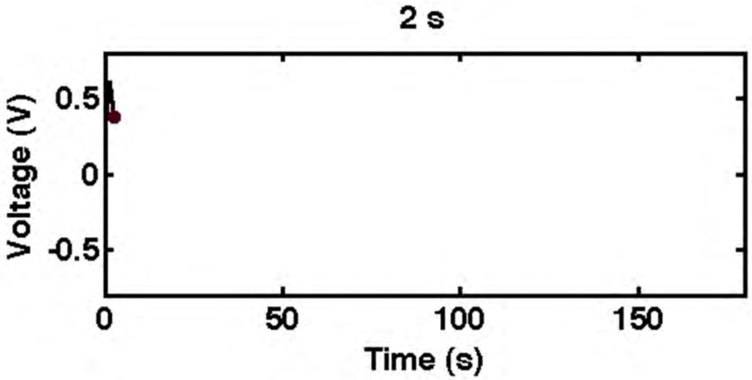
Pt nanoparticles

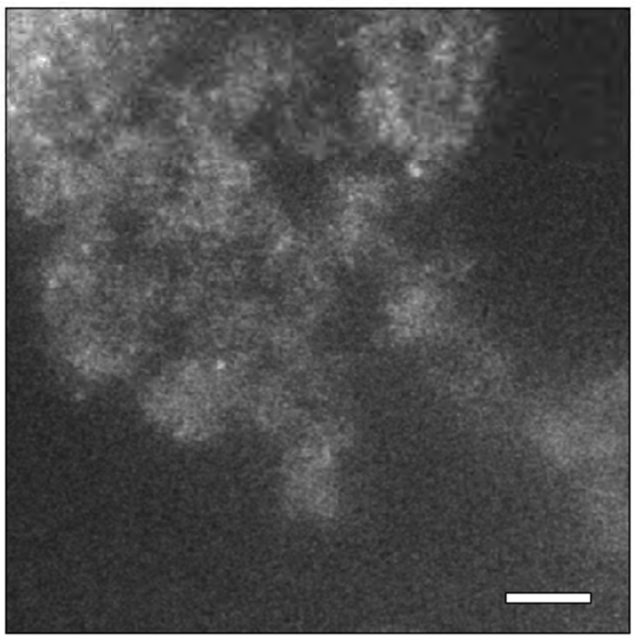


Similar behavior to a standard microelectrode!

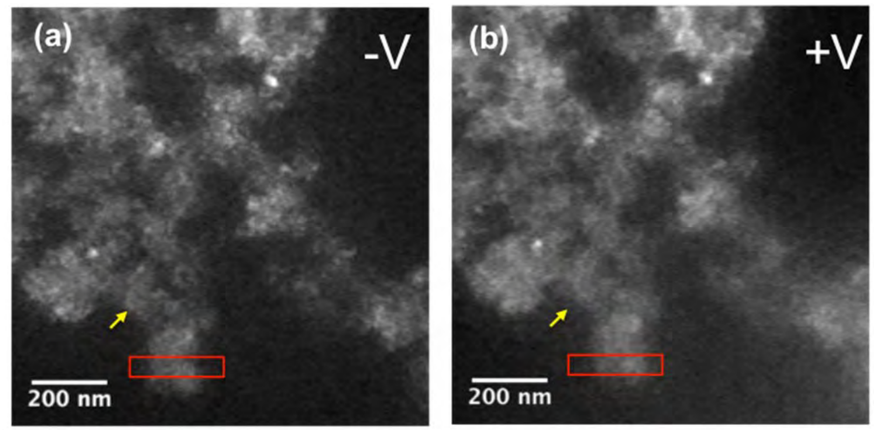
Holtz et. al. NanoLetters. 14(3) 1453 **2014**.

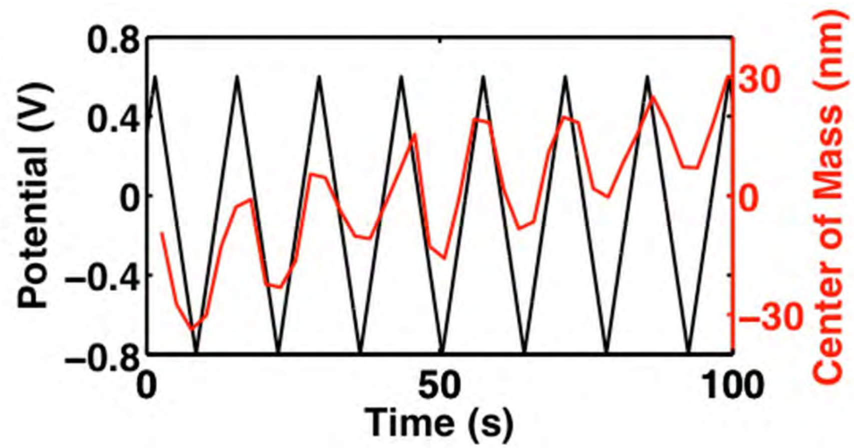
Carbon support bending during potential cycling





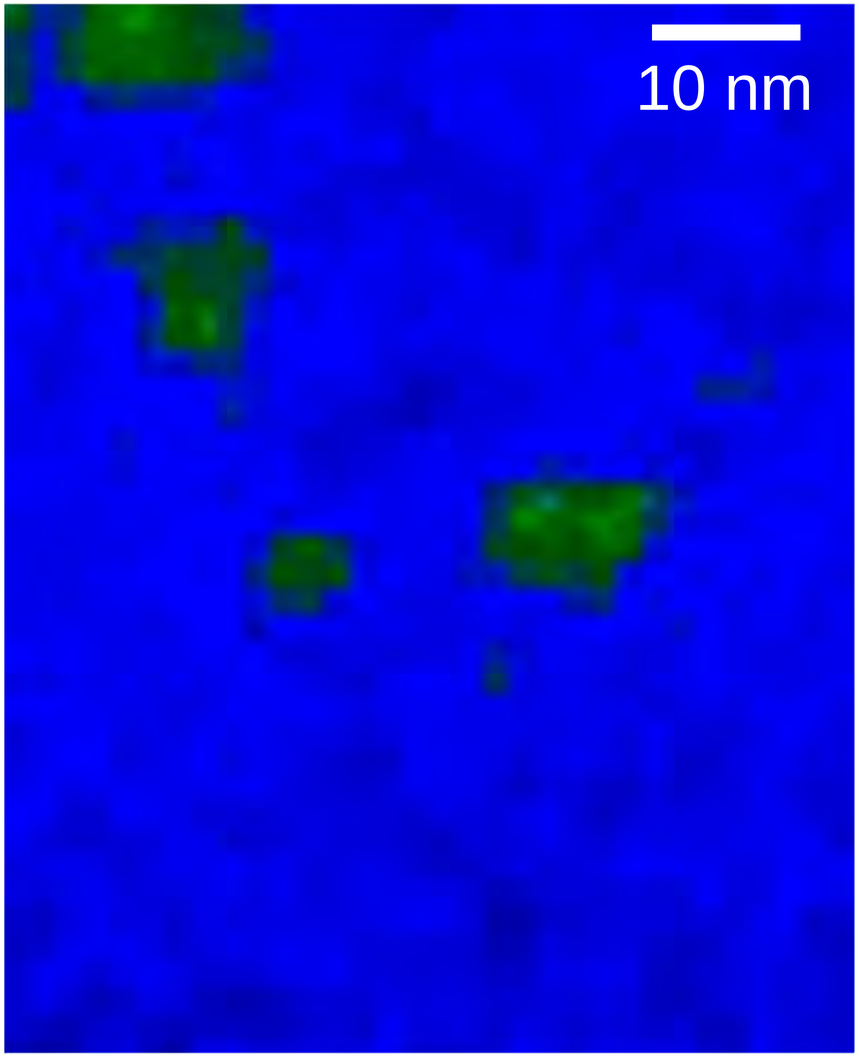
200 nm





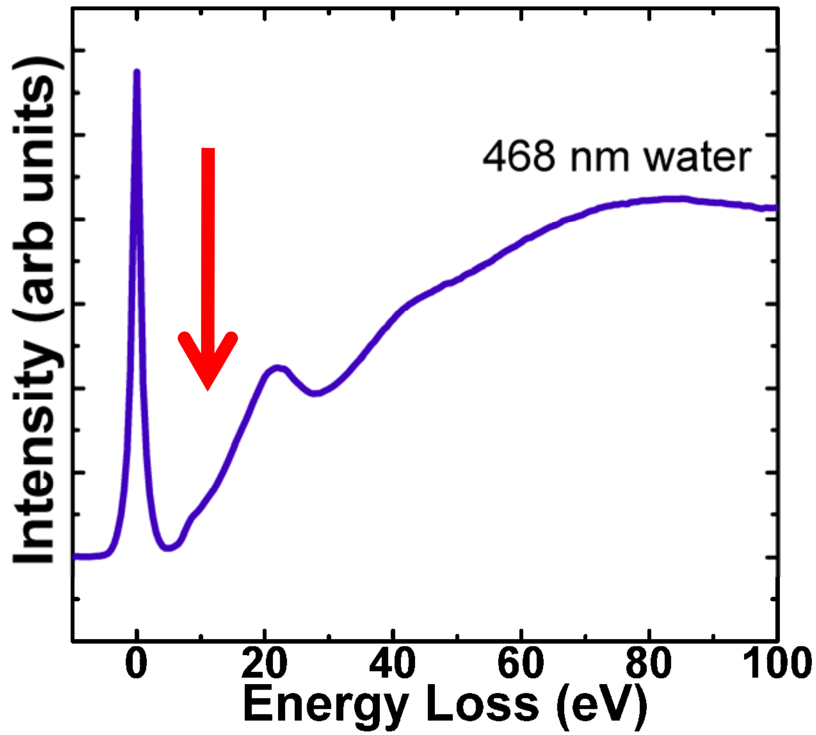
200 mV/s
0.1 M H2SO4

Watching Coalescence

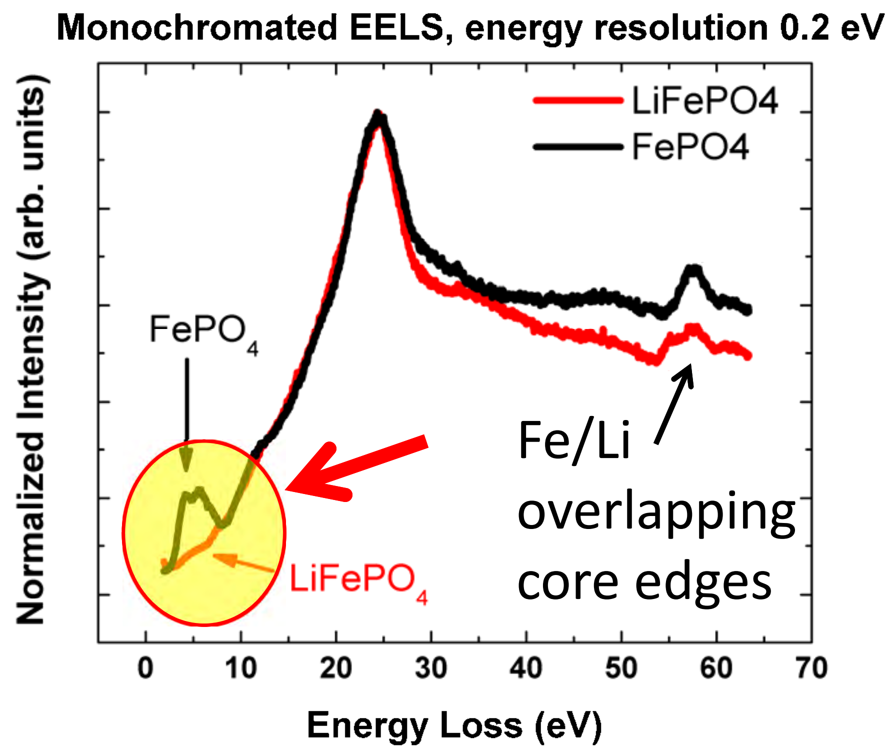


Cycling +0.5 V to +1.2 V at 500 mV/s for 220 cycles

Valence EELS for Batteries



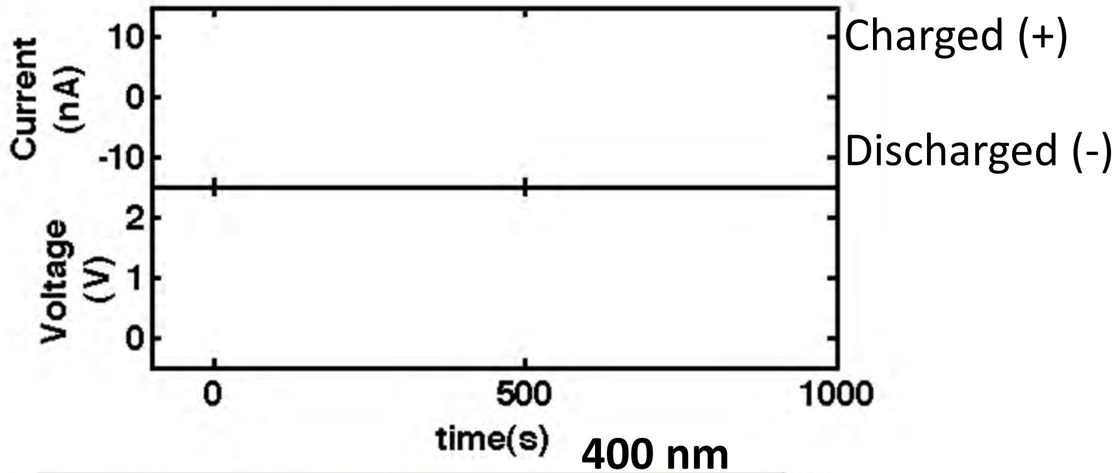
- Before Plasmon
  (in the optical gap!)
  monochromator helps

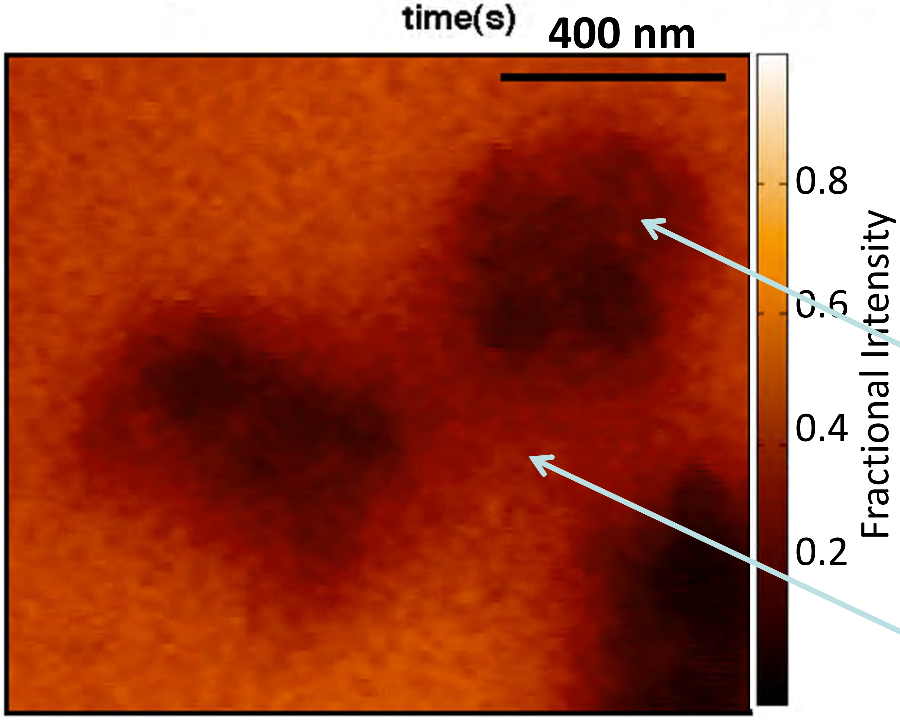


Holtz et. al. NanoLetters. 14(3) 1453 **2014**.

This is interesting for
Li-ion battery applications!
Want Rapid Spectroscopy

We can observe the lithiation *in situ!*

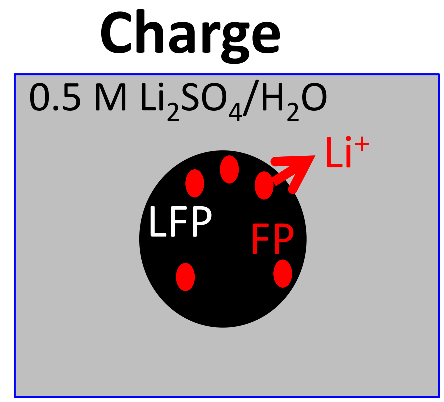


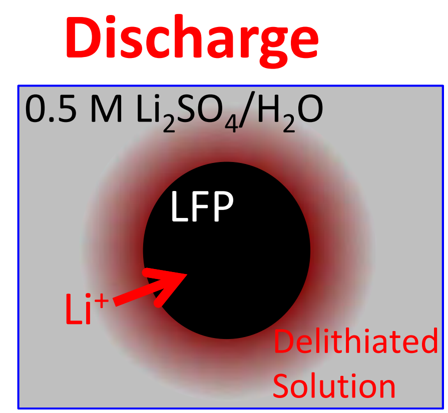


5 eV EFTEM image!

Particles delithiating on charge!

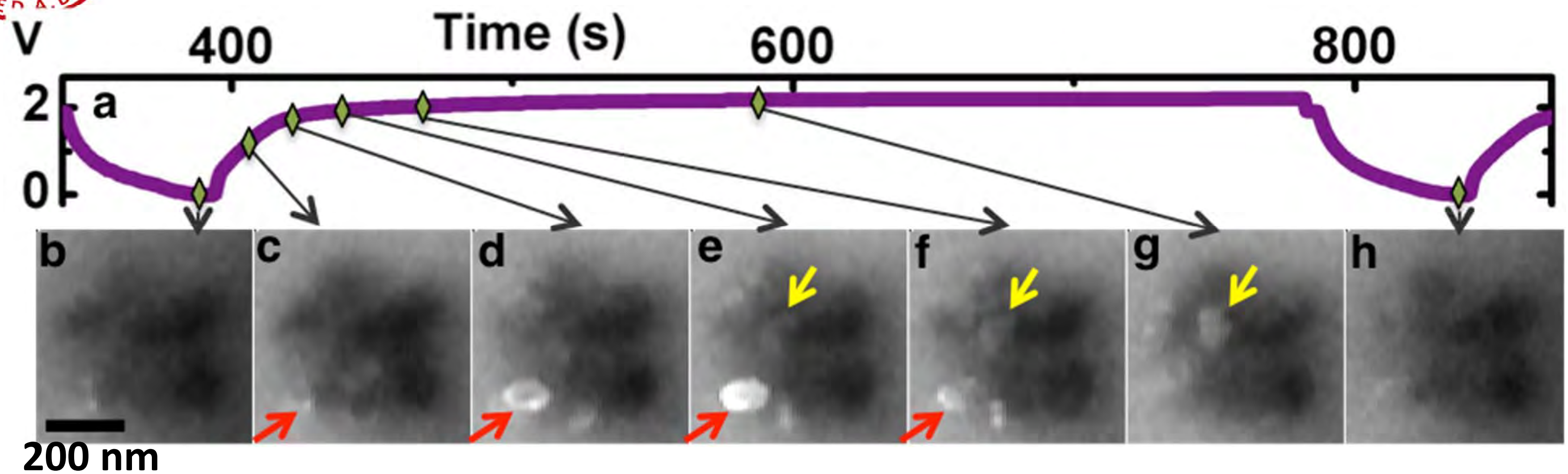
Solution becomes dark on discharge





Holtz et. al. NanoLetters. 14(3) 1453 **2014**.

Mechanism of Lithiation

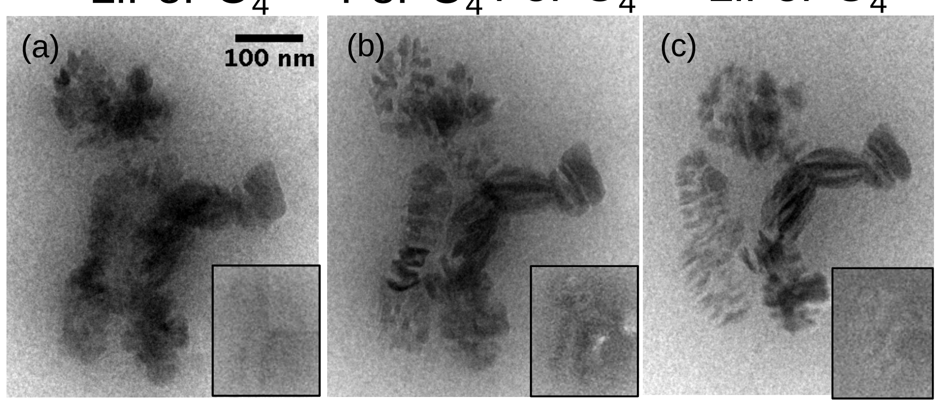


2 dominant modes of lithiation on same aggregate

Fracturing:

3 cycles + Charge1 cycle+ Discharge

$LiFePO_4$ -> $FePO_4$ $FePO_4$ -> $LiFePO_4$



Holtz et. al. NanoLetters. 14(3) 1453 **2014**.

Time and Length Scales for EChem

- *Transition States*: picoseconds & Angstroms
  - Today: need light activation

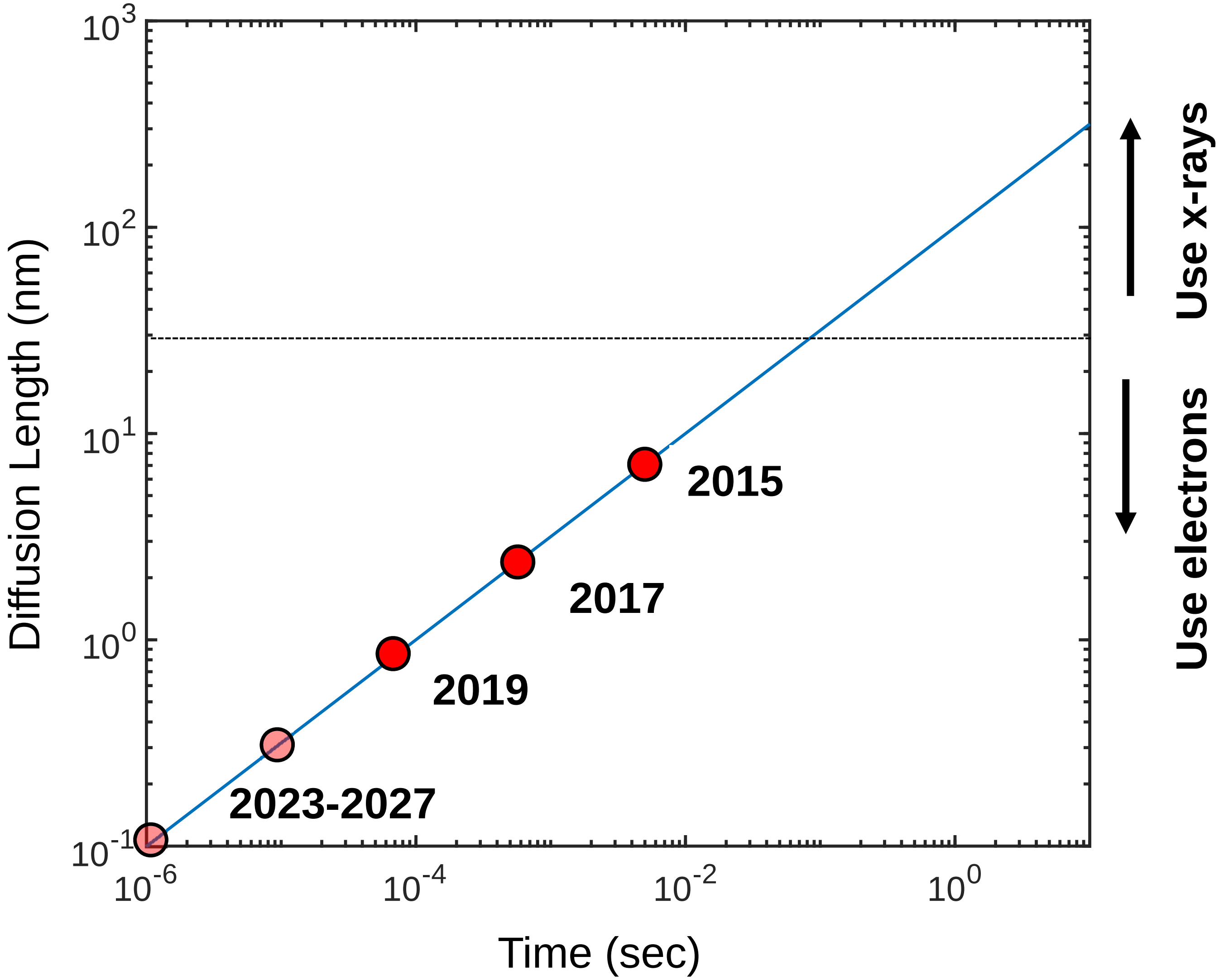
    Diffraction from crystals, but not imaging

    XFEL's are designed for fs, not ps!
  - Opportunities for ERL & next gen light sources
  - Ultrafast electron diffraction and imaging (2^{nd} harder)

- *Diffusion of ions*: $l = \sqrt{Dt}$
  - Spans ns (liquids) to seconds
  - But lengths scale as well
  - Opportunities for TEM & Synchrotrons

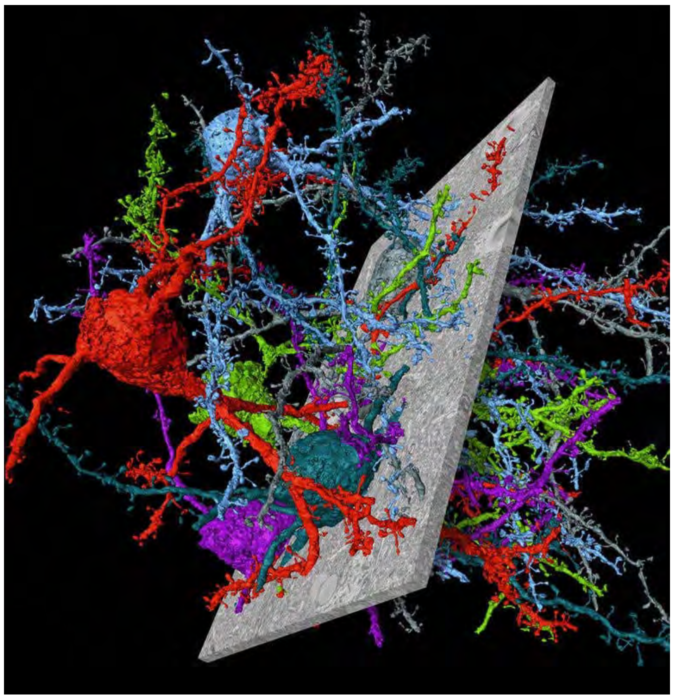
Detector Speed to Image Diffusion

For D~10^{-14} m^2/s - typical for Li in CoO_2



The Connectome: A multi-scale problem

Map the brain's interconnectivity of the
~10^{10} nerves and ~10^{14} synapses



MPI Frankfurt

2018: EM maps 0.4x0.4x1 mm^3 volume at ~30 nm resolution in 300-500 days (6 x 10^{12} voxels)

Today: EM maps 1x1x1 mm^3 volume at ~4x4x40 nm resolution in 90 days (1.5 x 10^{15} voxels)

Goal: Map 1 mm^3 (as 7 x 7 mm^2 x 20 microns) at 30 nm resolution in < 1 day. (36 x 10^{12} voxels)

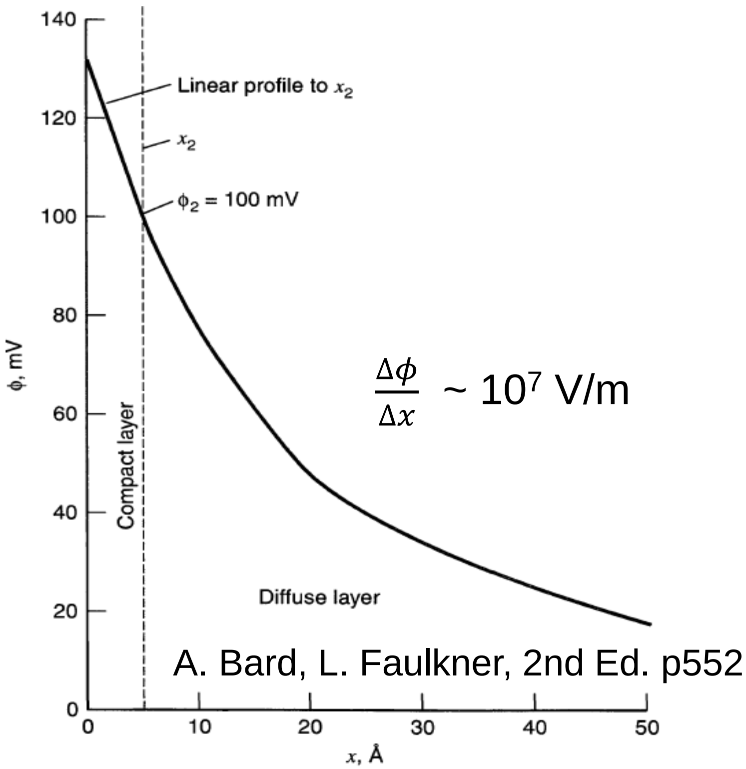
Do-able with a 1 MHz frame rate detector and out-of-focus ptychography at a beam line. (100 nm sampling, 50 projections = 7 hours & 4-16 x 10^{15} Bytes)

Next: Find and trace all connections!

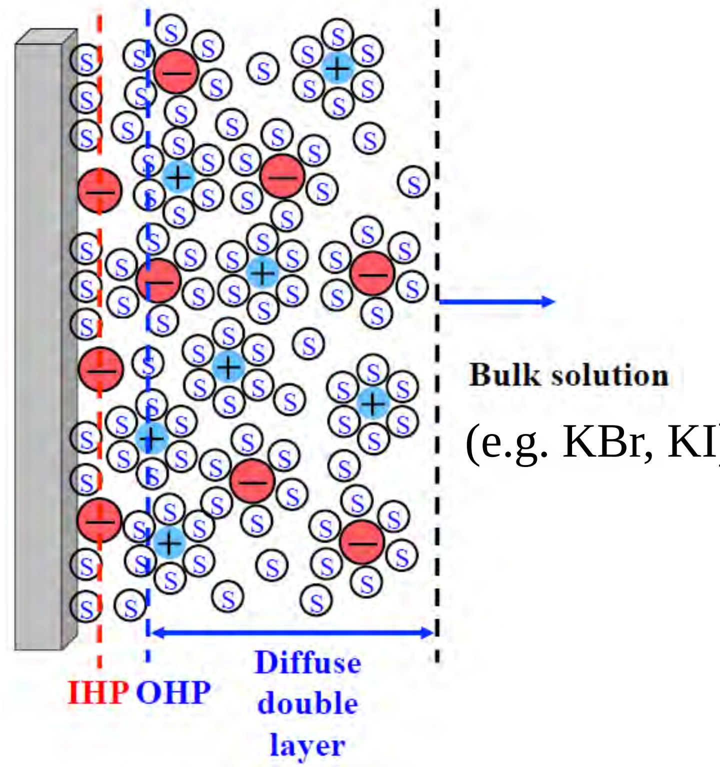
Can we resolve the Electrochemical Double Layer?

Gouy-Chapman-Stern (GCS) Model

Potential Profile of 0.01 M Solution(aq)



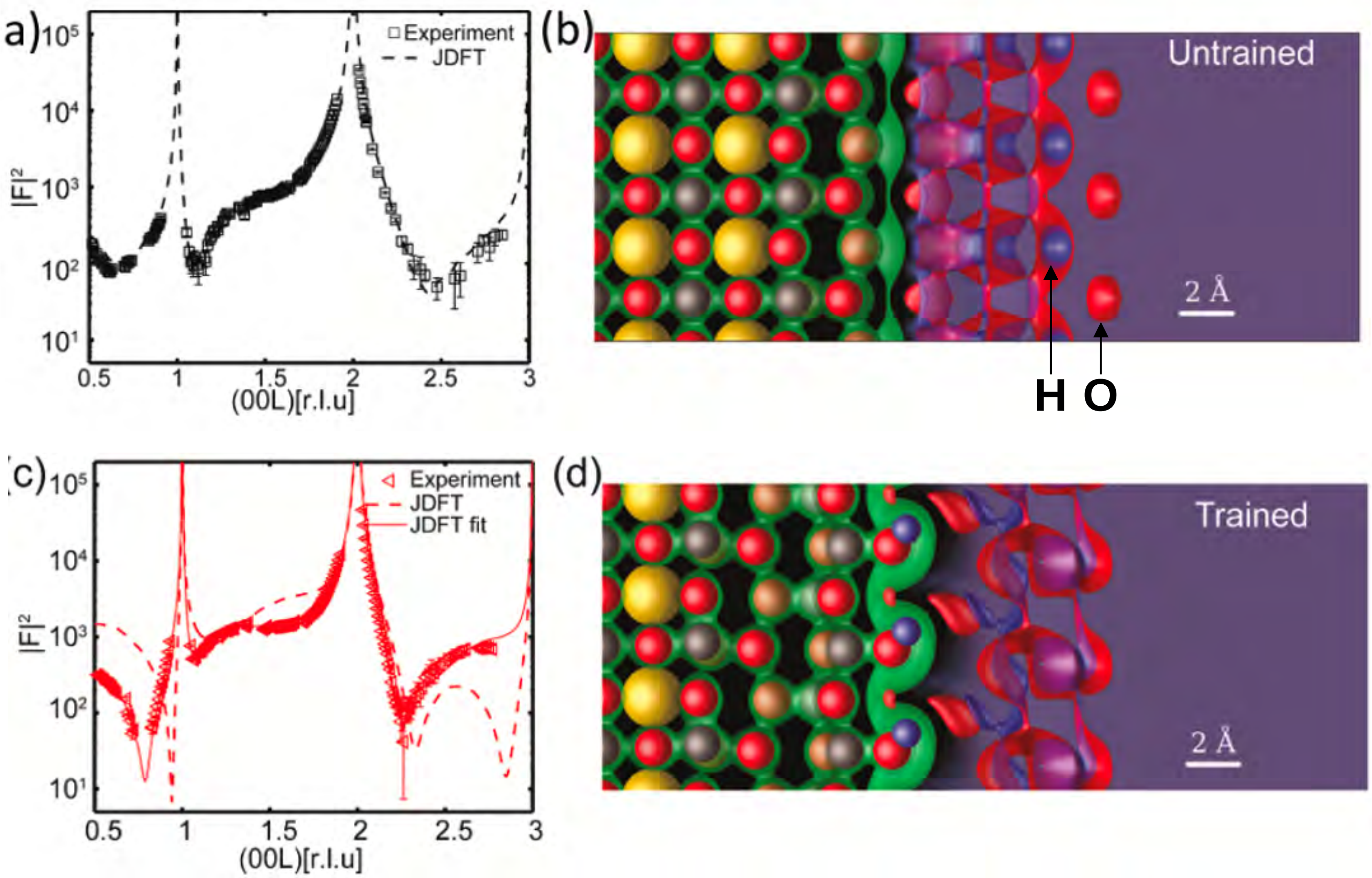
Anion Adsorption on Electrode Surface



- With heavy ions in solution, screening charge detectable by TEM
- Electric field measurable as deflection of the beam (DPC)
- At nanometer resolution, nanoparticles are as easy to study as crystals

Seeing the Double Layer in XRD?

X-Ray diffraction of Single-Crystal $SrTiO_3$ in water & JDFT prediction



flat

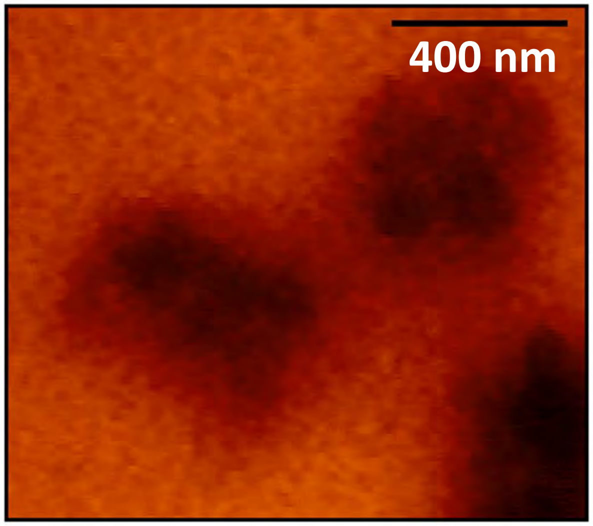
+defects

Plaza et al, JACS (2016) V138, 7816

With high-dynamic range detectors, density profile of the electrolyte should be accessible

Outlook

Electrochemistry in the TEM



- Radiation damage limits resolution (1-10 nm)
- CryoEM ~ 10-100x dose increase
- Single-Particle EM – atomic resolution by averaging
- EMPAD detector for dose-efficient imaging
- Multi-scale imaging enabled by fast detectors
- Embrace, do not fear big data.

U.S. DEPARTMENT OF ENERGY (BES+EERE)
NSF
CORNELL CENTER FOR MATERIALS RESEARCH
CABES Center for Alkaline based Energy Solutions
emc2 ENERGY MATERIALS CENTER at CORNELL
PARADIM PLATFORM FOR THE ACCELERATED REALIZATION, ANALYSIS & DISCOVERY OF INTERFACE MATERIALS

NSF

CORNELL CENTER FOR MATERIALS RESEARCH

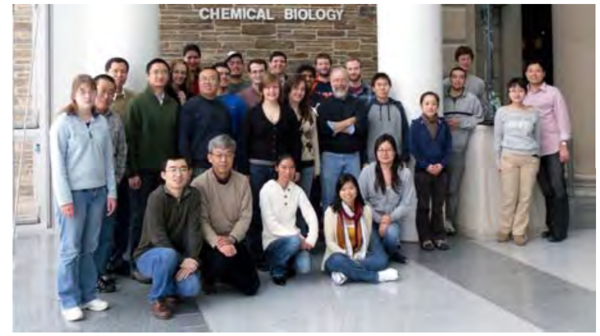
PARADIM

PLATFORM FOR THE ACCELERATED REALIZATION, ANALYSIS & DISCOVERY OF INTERFACE MATERIALS

CABES

Center for Alkaline based Energy Solutions

DEPARTMENT OF ENERGY · UNITED STATES OF AMERICA



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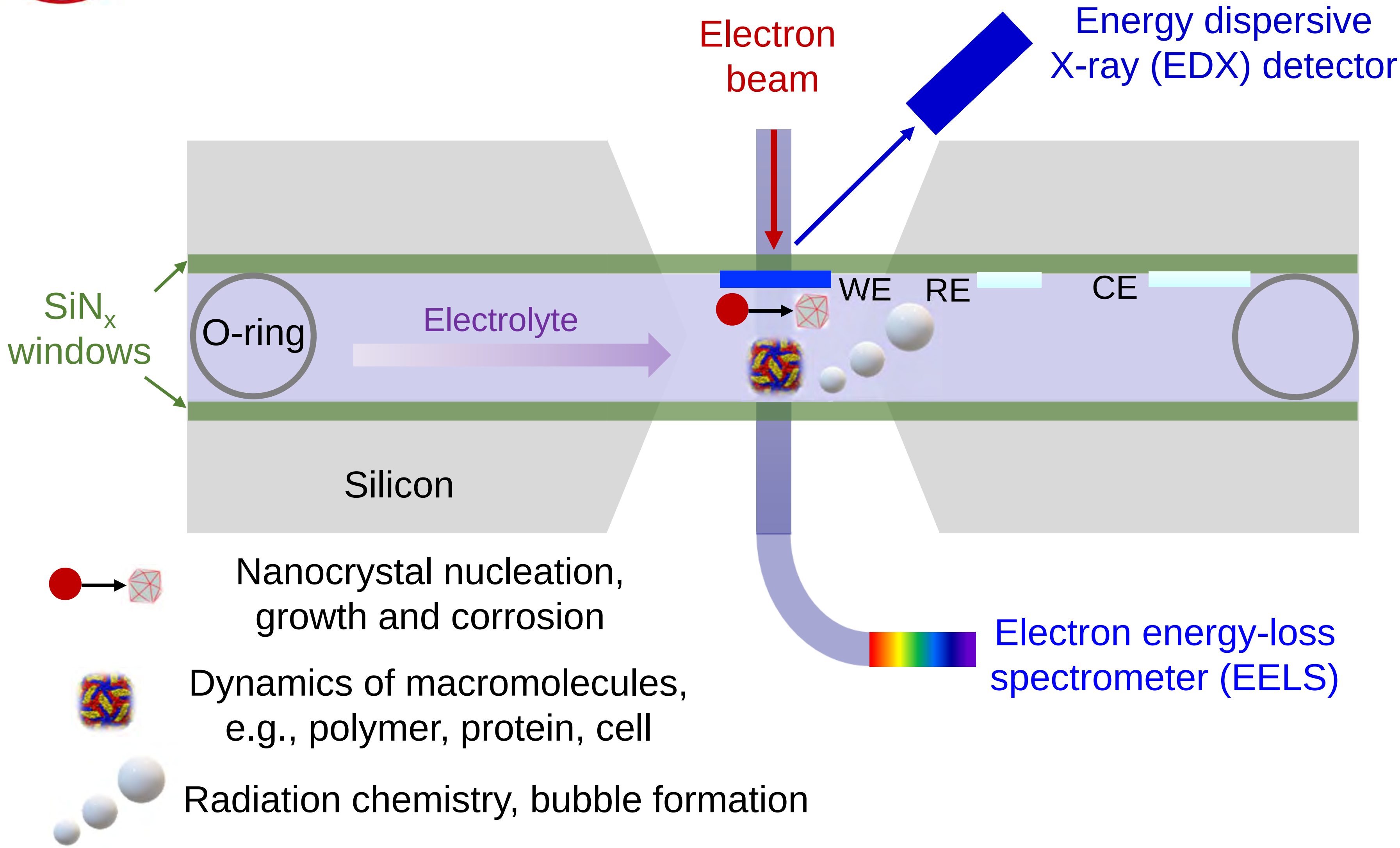
In Situ TEM to Tackle Dynamic (Electro)Chemical Reactions at the solid-liquid interface



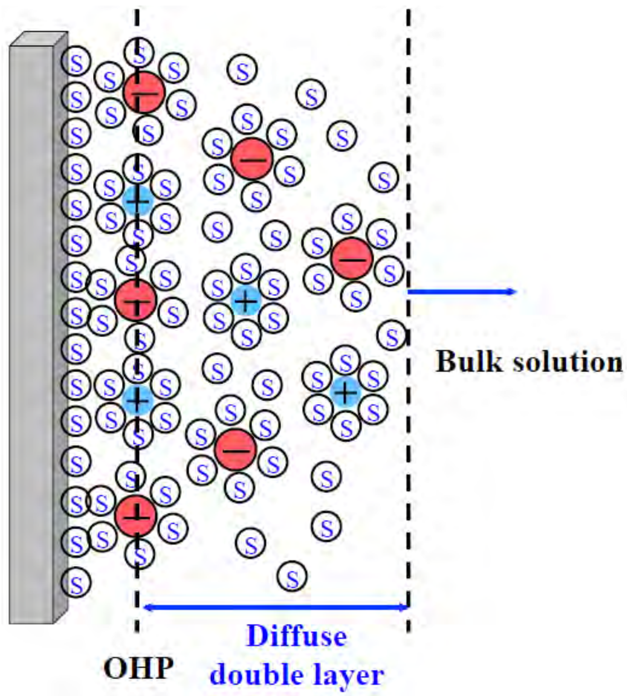
WE, CE, RE: three-electrode system
(working, counter and reference electrodes)

Electrochemical Double Layer at Various Conditions

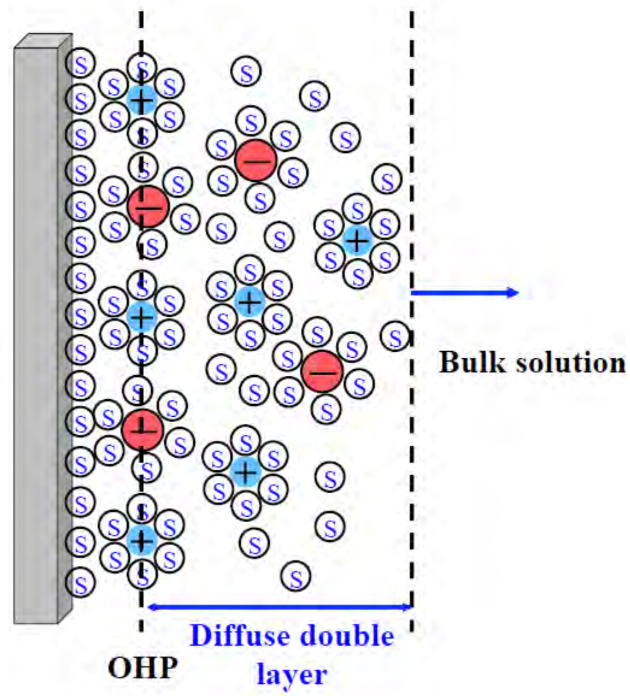
Potential of zero charge (E_{PZC})

the potential at which the electrode will be electrically neutral, relative to the solution

$E > E_{pzc}$



$E < E_{pzc}$



E_{pzc} of Hg in 1M solution

Electrolyte	E_{PZC} /V
NaF	-0.47
NaCl	-0.56
KBr	-0.65
KI	-0.82

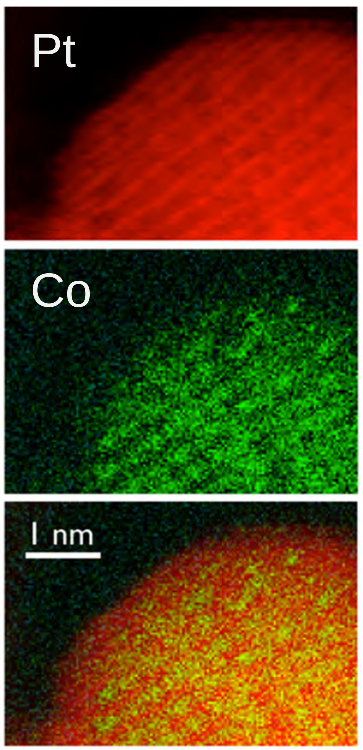
D. Grahame, *Chem. Rev.* 1947, 41, 441

The electrochemical double layer depends on applied potentials, types and concentration of electrolyte

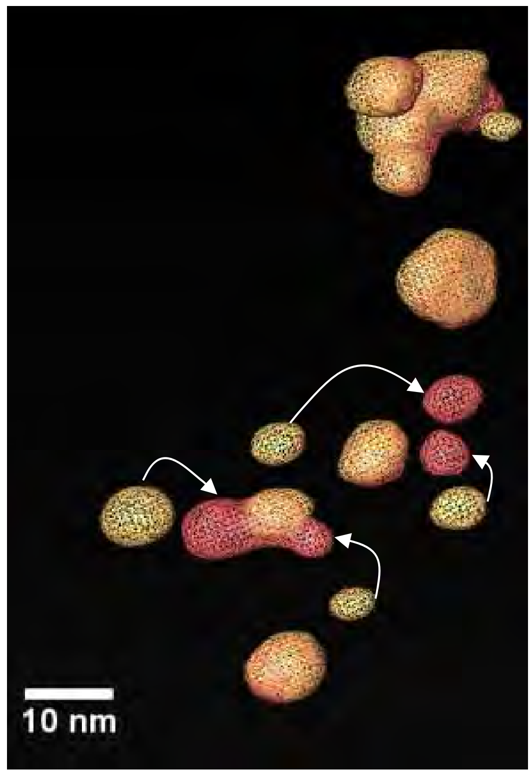
Seeing Electrochemistry Live at the Atomic Scale

David A. Muller, Cornell University

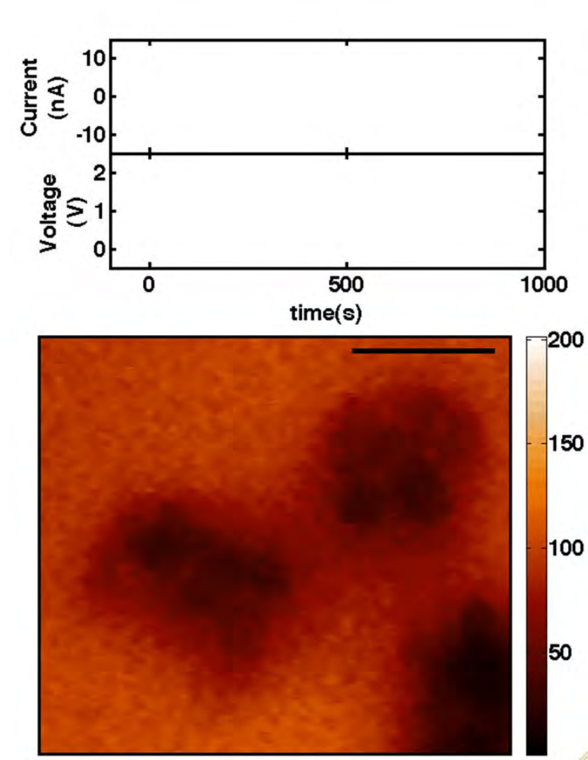
Ex Situ → ***In Situ/Operando***



Atomic Resolution

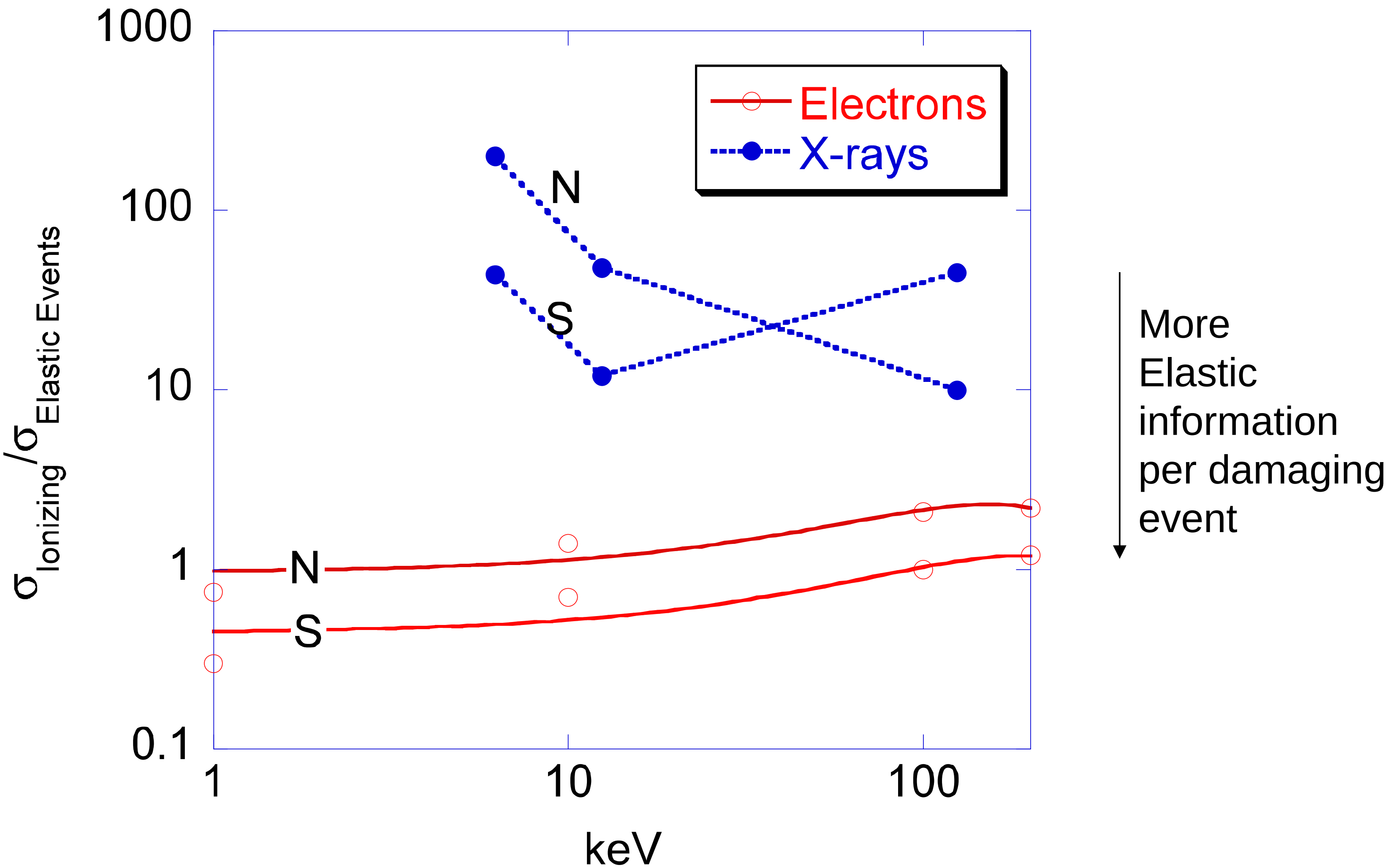


3D



Electrochemistry in liquids

Radiation Damage as a Fundamental limit

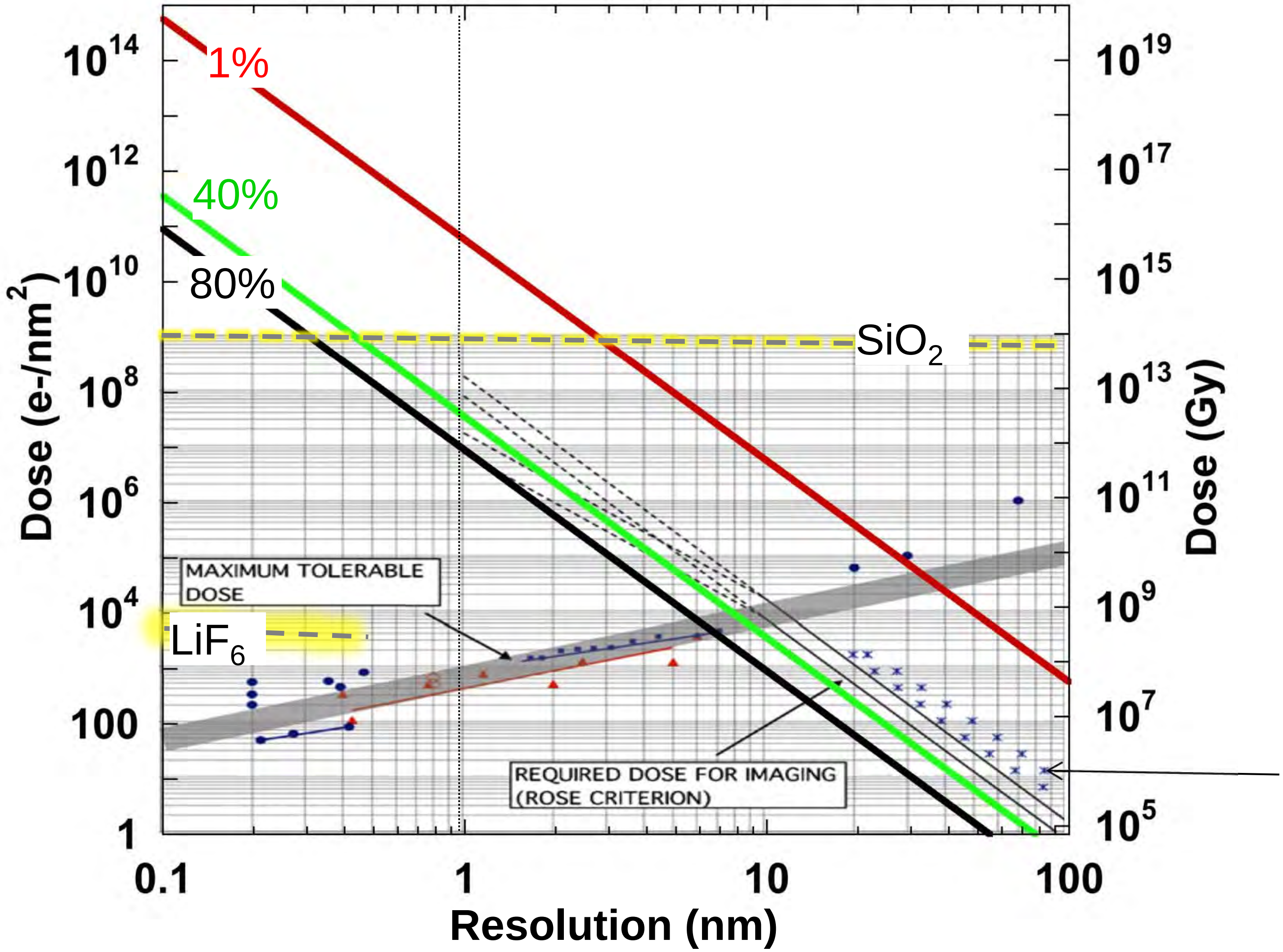


Data from Breedlove and Trammell, Science 170 (1970) 1310-1313

For electrons σ_i / σ_e ~ln (E)

Dose Required for 3-D Reconstructions is high

B. F. McEwen et al, Journal of Structural Biology **138** 47–57 (2002)
Saxberg & Saxton, Ultramicroscopy **6**, 85–90 (1981)
M.R. Howells et al, J. Electron Spec. Rel. Phenom. **170** 4 (2009)



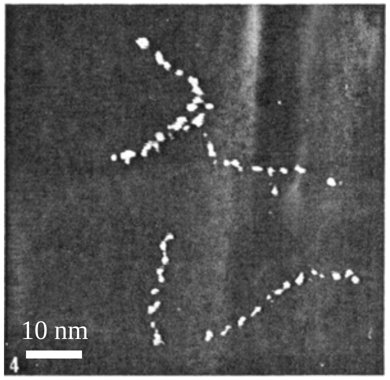
10 keV x-rays

$r \langle\ 1/(\mathrm{Dose})^{1/4}$

$r \langle\ 1/(\mathrm{Contrast})^{1/2}$

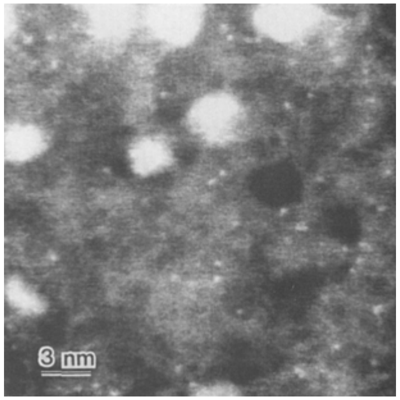
Dose-limited resolution for oxides is ~0.2-2 nm and ~3-10 nm for batteries

Single Atom Imaging: Catalysis and Dopants



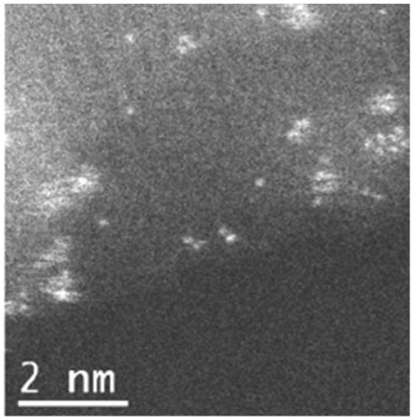
Th on a-C

Crewe *et al*., Science **168**, 1338 (1970)



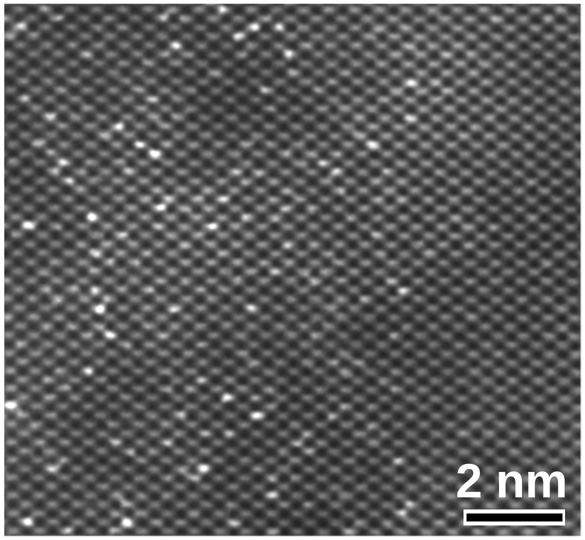
U on a-C

Treacy & Rice, J. Microscopy **156**, 211 (1989)



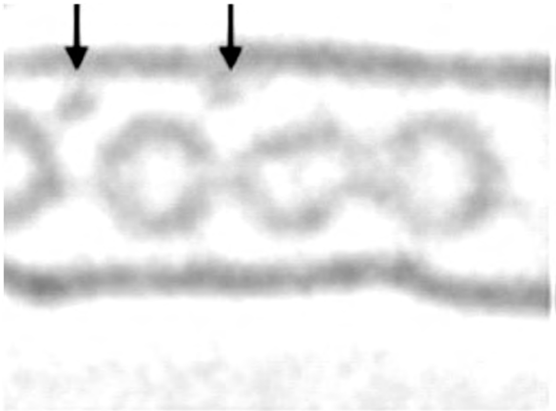
Pt on a-Al_2O_3

Blom et al, *Microsc. Microanal.* **12**, 483, 2006



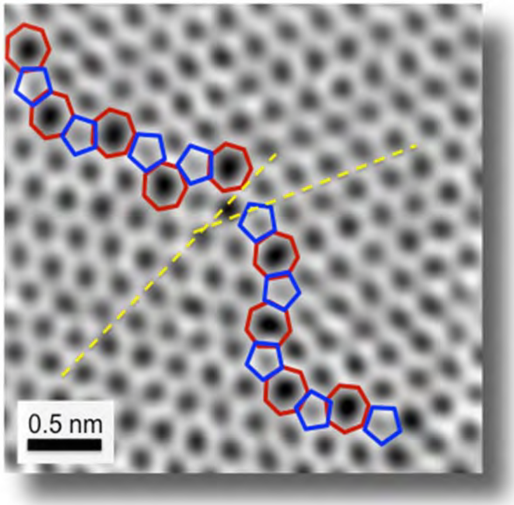
Sb in Si

Voyles *et al*., Nature **416** 826 (2002)



K-doped C_{60} peapods

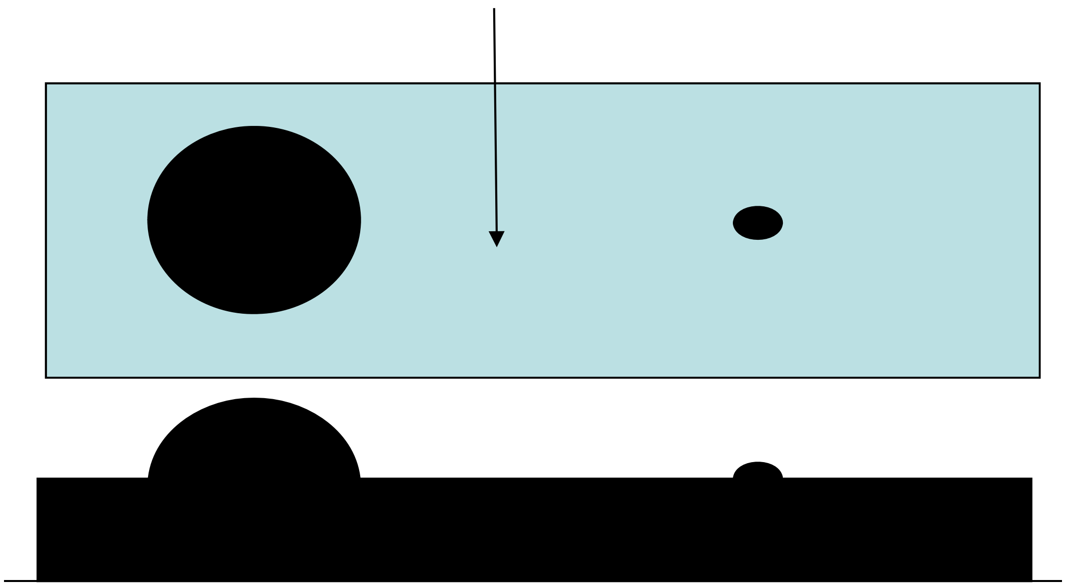
Guan *et al*., PRL **94**, 045502 (2005)



Graphene Grain Boundaries

Huang et al, *Nature* **469**, 389 (2011)

High Resolution= Thin Sections



Small features have low contrast (and for a fixed dose we trade 2D resolution for contrast)

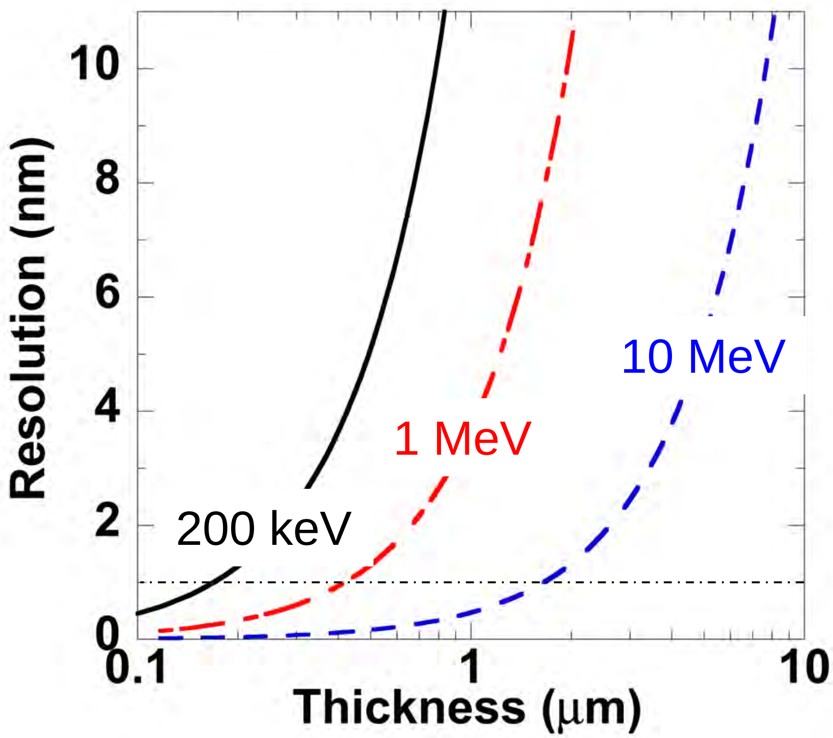
Resolution 〈 Sample Thickness

Need to make thin samples (true for x-rays as well as electrons)

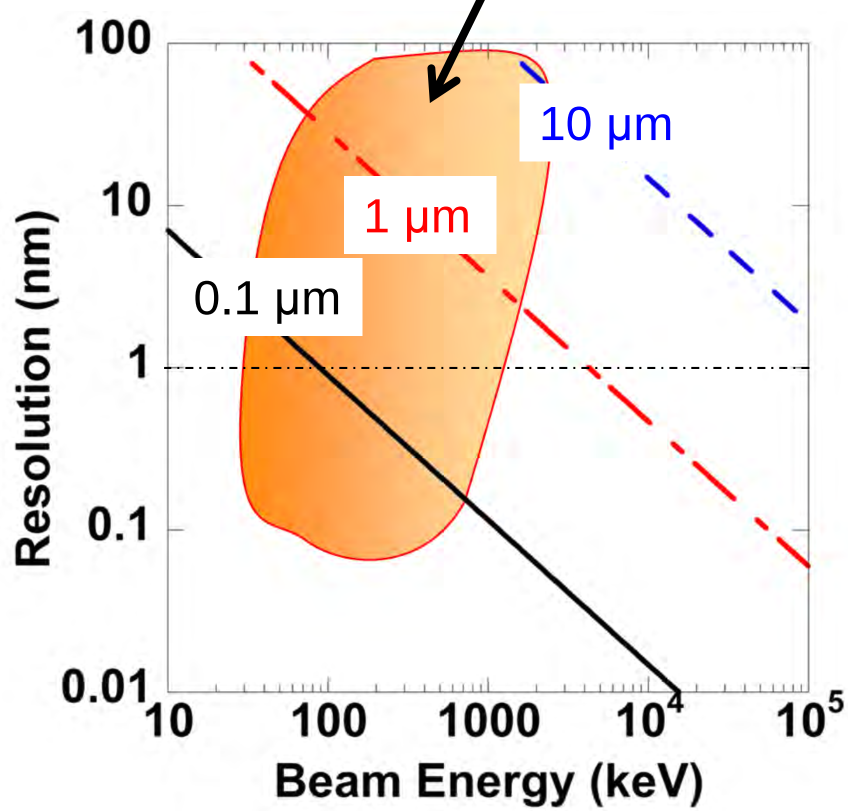
(unless we have a fluorescence detection method & there is only 1 object)

Beam Spreading (in Water)

Beam Spreading $b \propto \sqrt{\rho}\,\frac{Z}{E}\,t^{3/2}$



Electron's
Home court advantage



By changing the collection angle, can trade off
a linear improvement in resolution (~ x 2)
for an exponential drop in signal

Appl. Phys. Lett. **88** 243116 (2006)

Beam Spreading (in Water)

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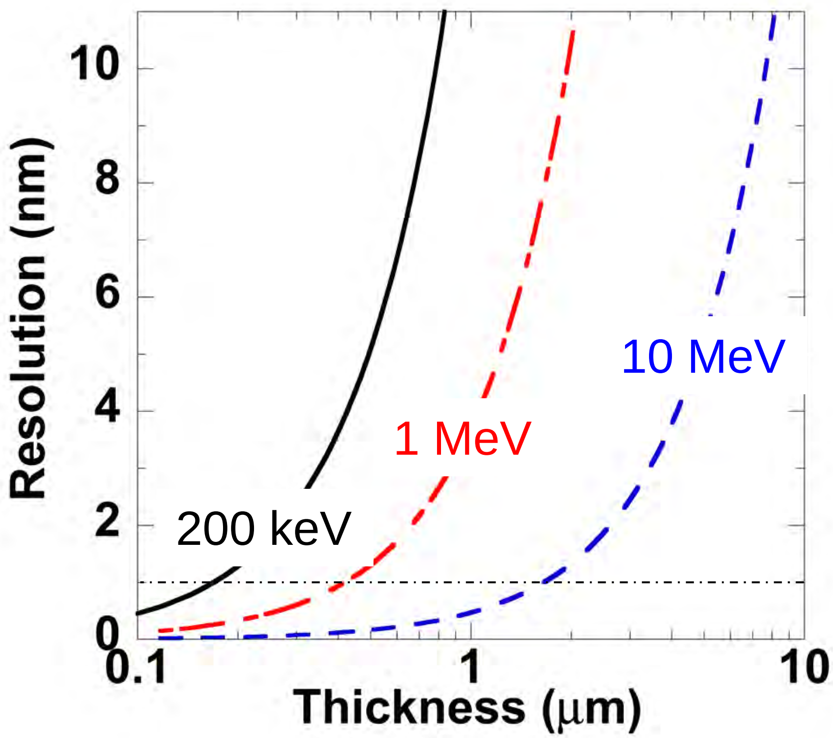
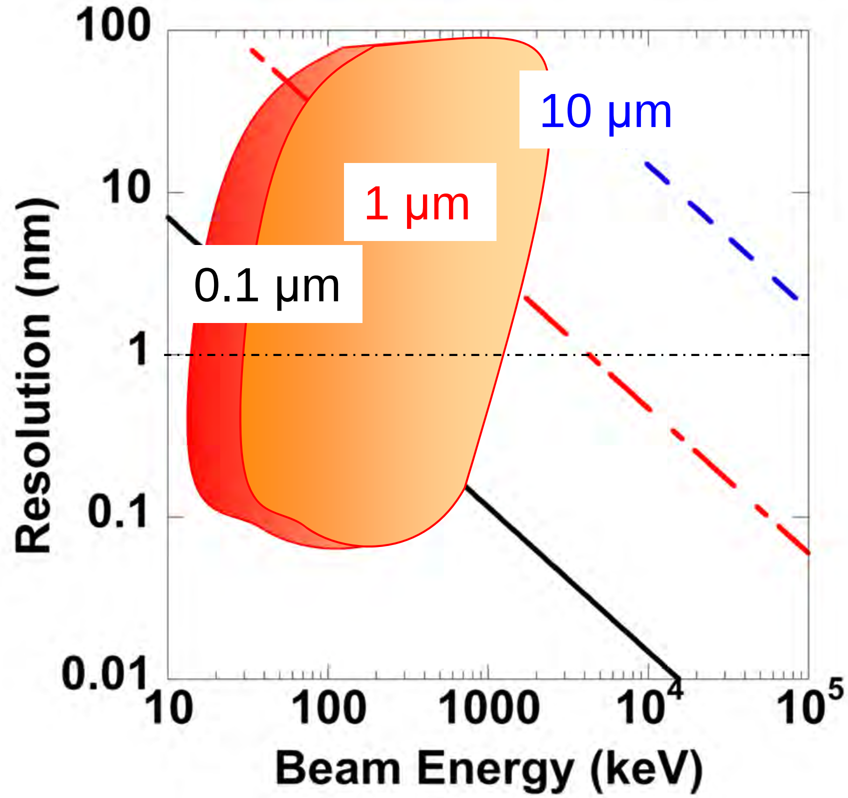


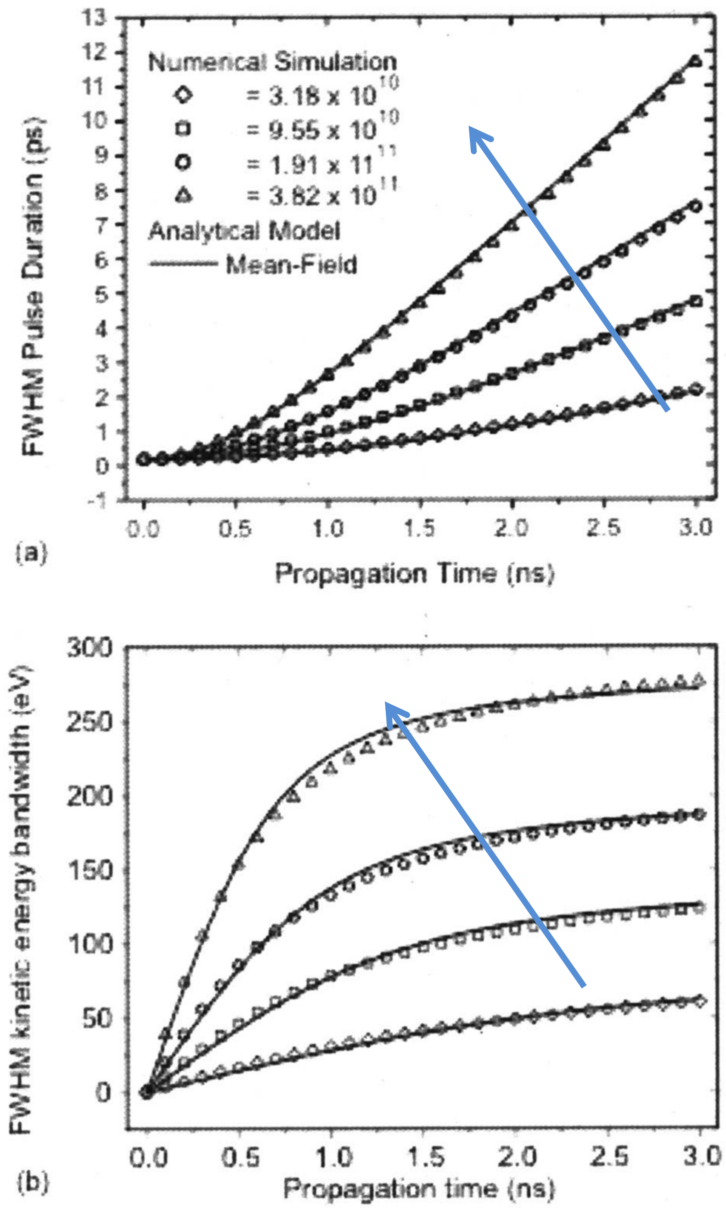


By changing the collection angle, can trade off
a linear improvement in resolution (~ x 2)
for an exponential drop in signal

Appl. Phys. Lett. **88** 243116 (2006)

Coulomb Blur Limits Resolution

King et al, Journal Of Applied Physics **97**, 111101 (2005)



Typical e^- transit times are 5-20 ns

Increasing current density degrades pulse duration

(10^{21} e/m^2 for atomic resolution)

Increasing current density degrades energy spread

Chromatic blur limits spatial resolution

Soln: Either - Reversible single e^- pump probe (atomic resolution, fs times)
- Single shot

(0.3 nm in 100 ns, 10 nm in 10 ns)

What Electrons do well

Resolution Limits

- 0.05 nm, 10 meV (0.1 nm & 50 meV together)
- Higher brightness Sources
- Radiation Damage limits the imaging of UV-sensitive materials (~10x better for electrons for elastic imaging)

Tomography

-0.2 - 3 nm resolution at 0.1-1 μm thick

- 10 nm for 10-20 microns @ MeV

-Atomic resolution looks possible in inorganics

EELS & EDX Imaging (not time-resolved)

- 2D Chemical information at the atomic scale
- 3D at the 1-nm scale

Magnetic & Electric Field Imaging ($\mathbf{F}=q\mathbf{E}+q\mathbf{v}\times\mathbf{B}$)

- 0.3 – 3nm (holography, Lorentz)

What Electrons do Badly

Spectroscopy in thick samples (> 1 µm)

- XRF and IXS (especially for Li and other light elements)

Imaging degrades rapidly beyond a few microns

- XRT at 1-10 nm in a few microns or thicker

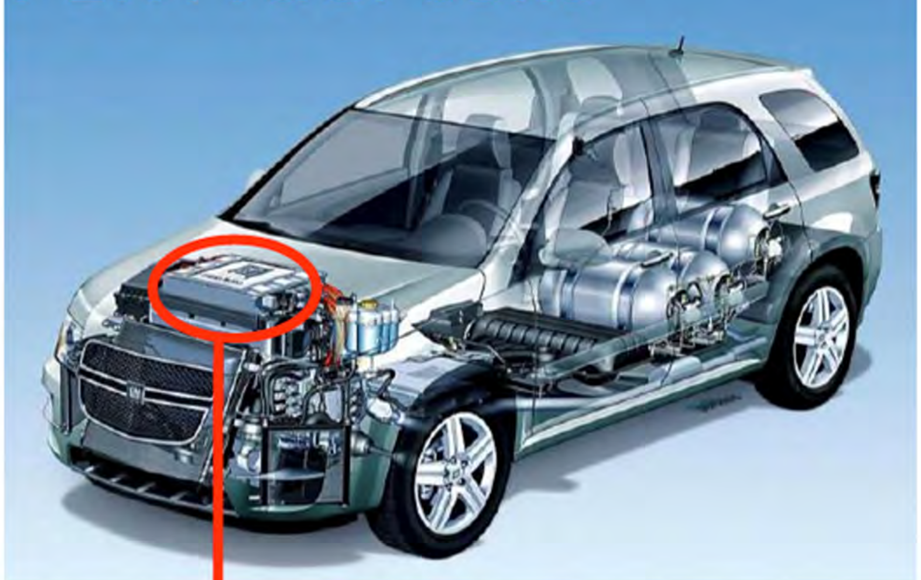
Time-resolved studies

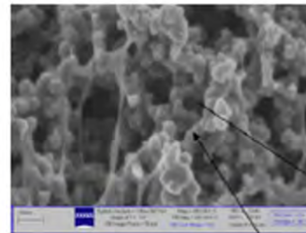
- Electrons are not bosons, and are not neutral (Coulomb Blur)
- Pump-Probe – 1 electron at a time
  - slow, but atomic resolution at fs-ps
- Single-Shot - 0.3 nm at 1 µs
  - 10 nm at 1 ns
  - Faster than this and x-rays will win.

Spin Detection

- Electrons are not neutral (charge dominates)
- EMCD is not as efficient as XMCD – vortex beams may get to 0.1 nm

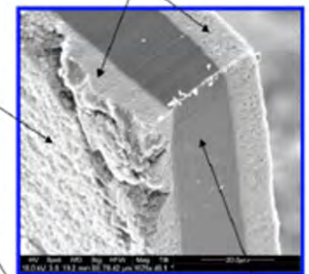
PEM fuel cells





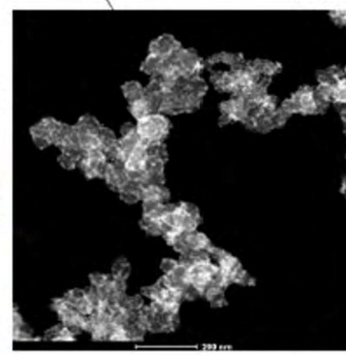
Top down electrode image (FESEM). Porous structure comprised of high structure carbon blacks bound together with a perfluorosulfonic acid polymer (ionomer). The carbon blacks are decorated with 2 nm Pt particles.

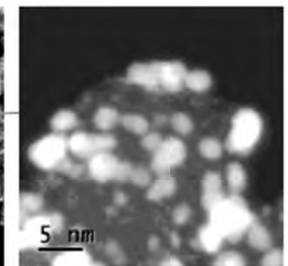
Electrodes

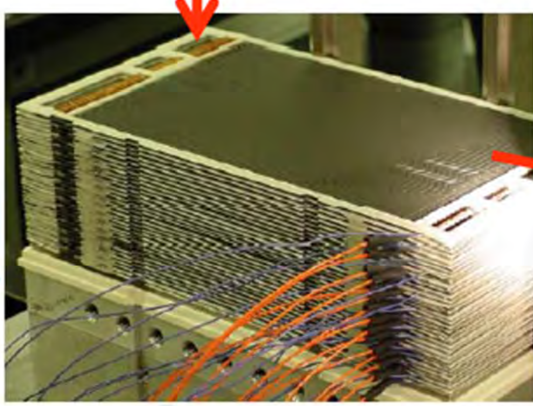


Membrane electrode assembly (MEA) cross section (SEM)

Membrane







Anode (HOR): (CATALYST REQUIRED)

$H_2 = 2\,H^+ + 2\,e^-$

Cathode (ORR): (CATALYST REQUIRED)

$0.5\,O_2 + 2\,H^+ + 2\,e^- = H_2O$

PEM Fuel Cell Overall reaction:

$H_2 + 0.5\,O_2 = H_2O$

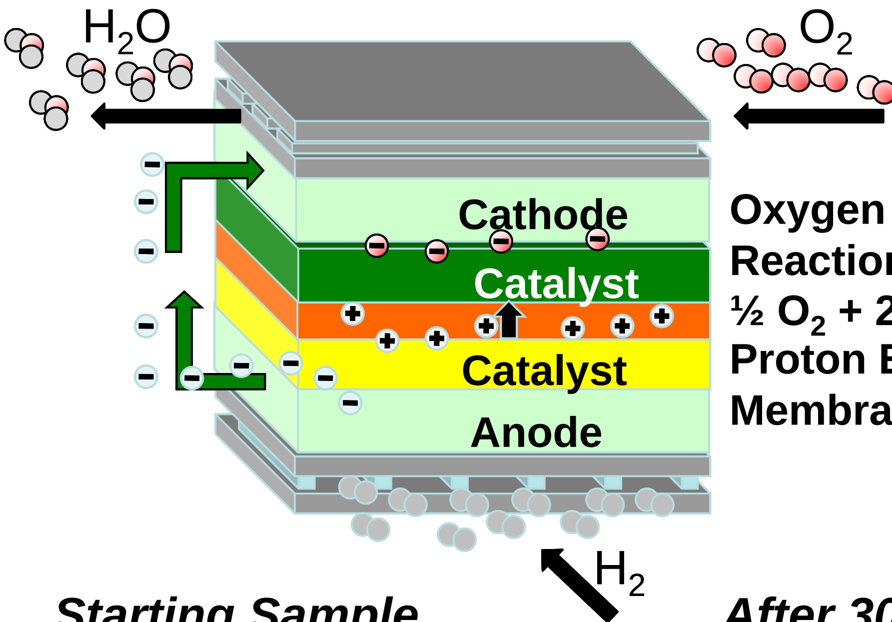
DESIGN BUILD SELL

THE WORLD'S BEST VEHICLES

General Motors Company

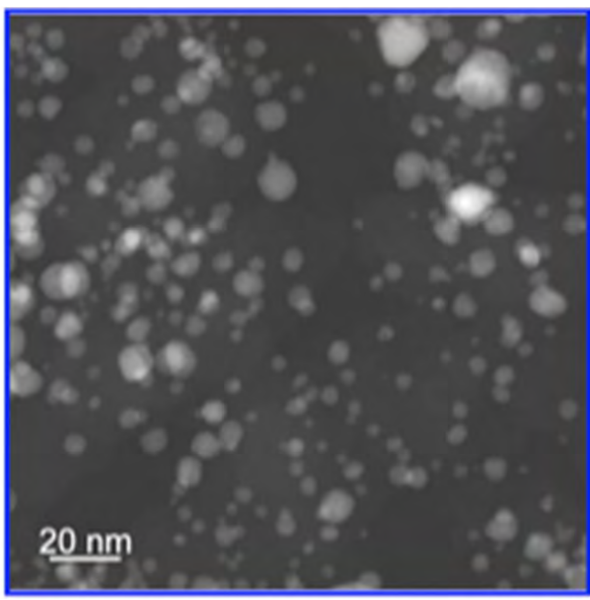
7

Pt-Co nanoparticles for electrocatalysis

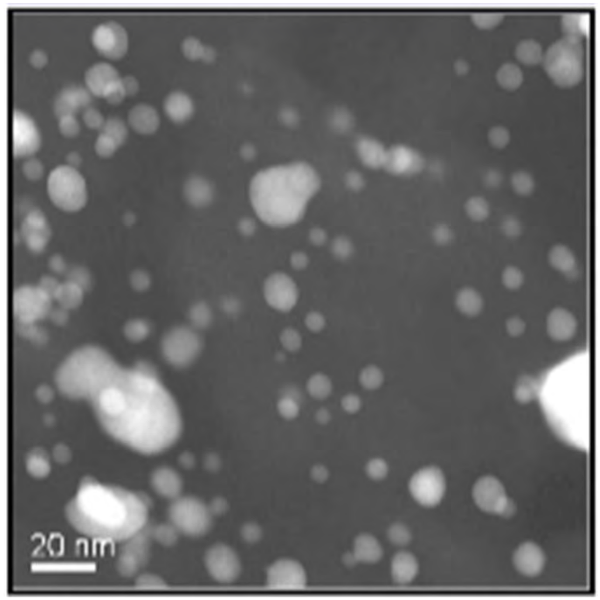


Oxygen Reduction Reaction:
½ O_2 + 2e- → O^{2-}
Proton Exchange Membrane

Starting Sample



After 30k Voltage Cycles

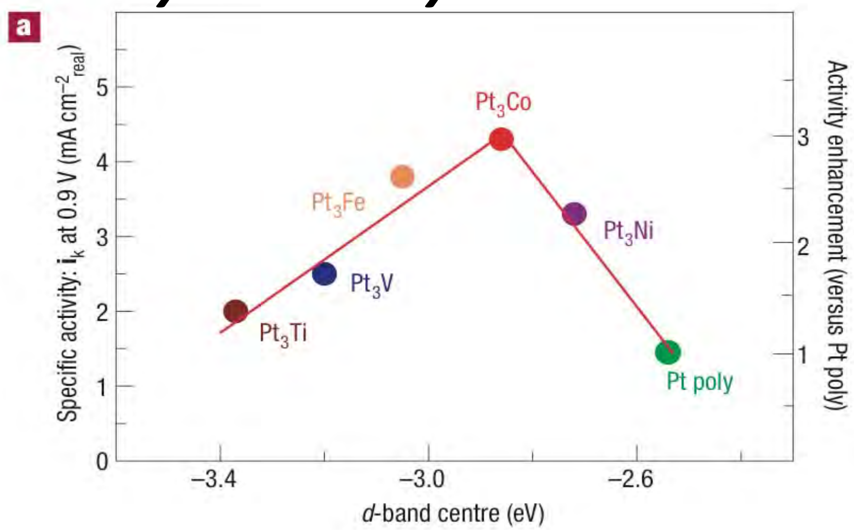


- Loss of catalytic surface area
- 37% drop in specific activity

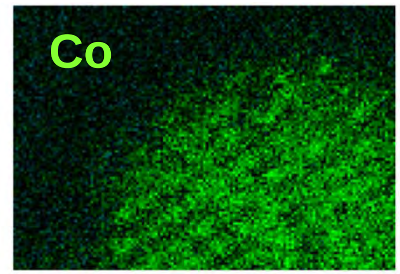
What microscopic mechanism is responsible?

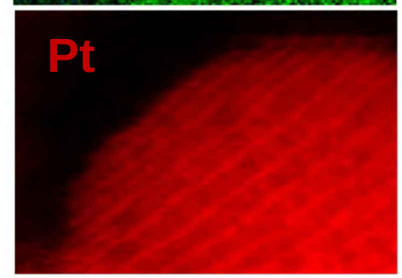
Band Engineering of Catalysts?

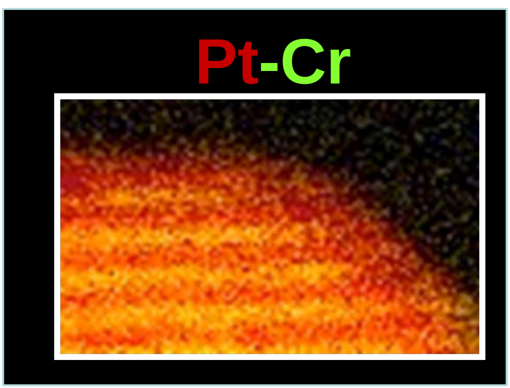
Catalytic Activity vs d-band Center

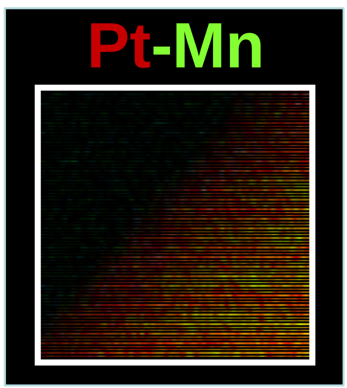


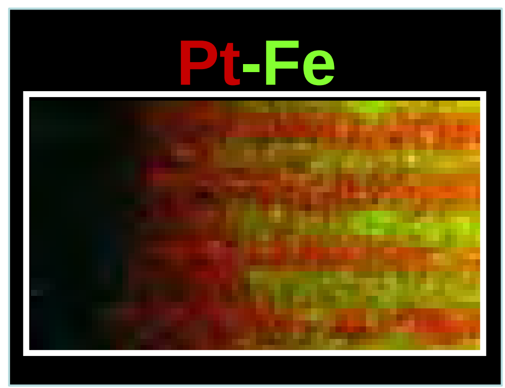
V. R. Stamenkovic et al. *Nature Mater.* **6**, 241 (2007).

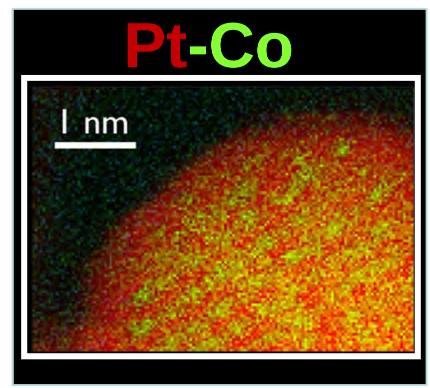






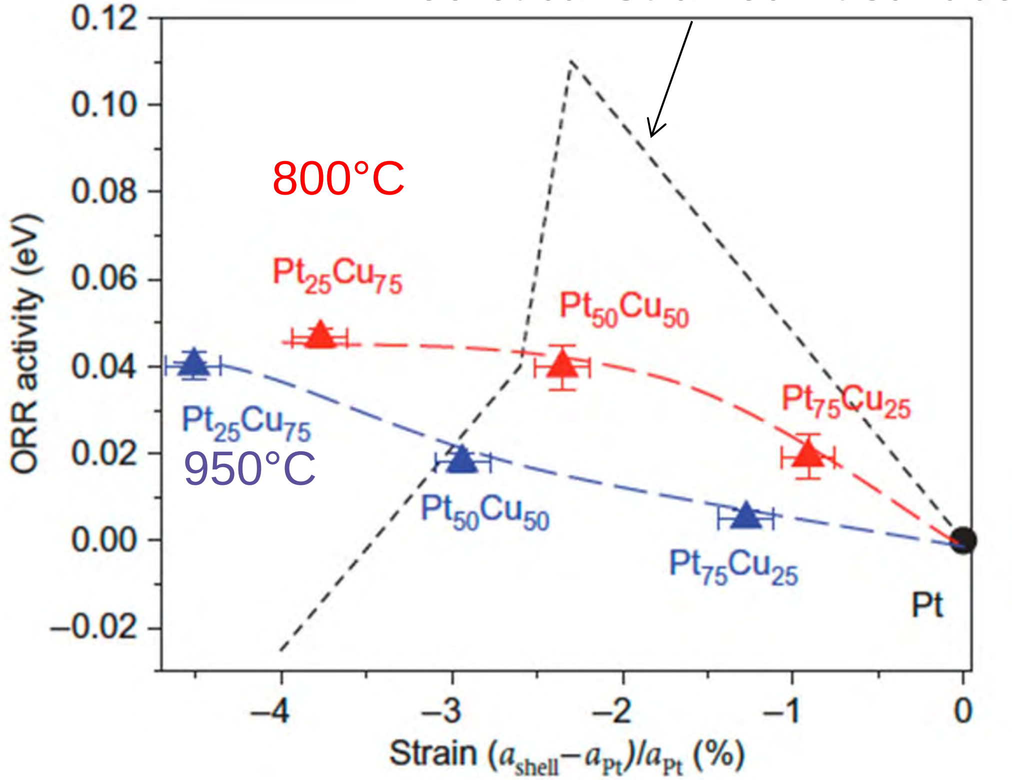




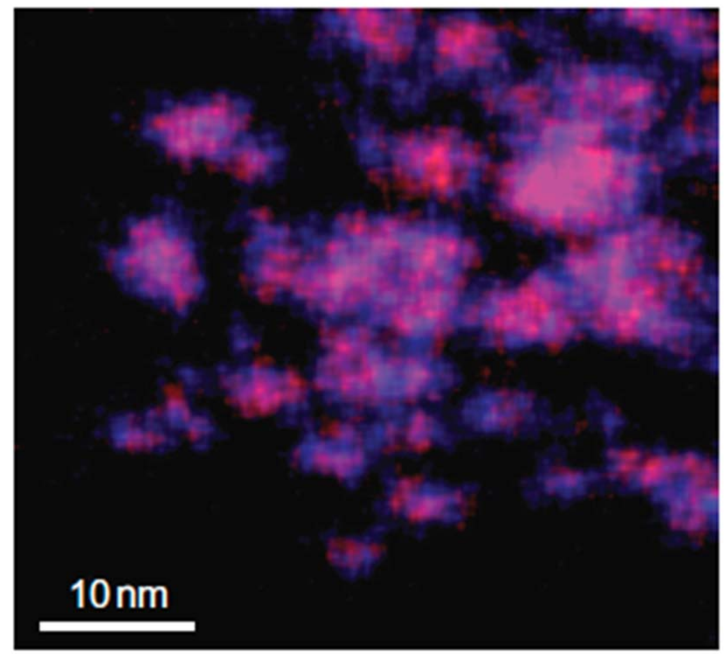


~ 3 monoloayers of Pt segregation after a few cycles

ORR Activity should track applied strain
(*d*-band shifts with strain)



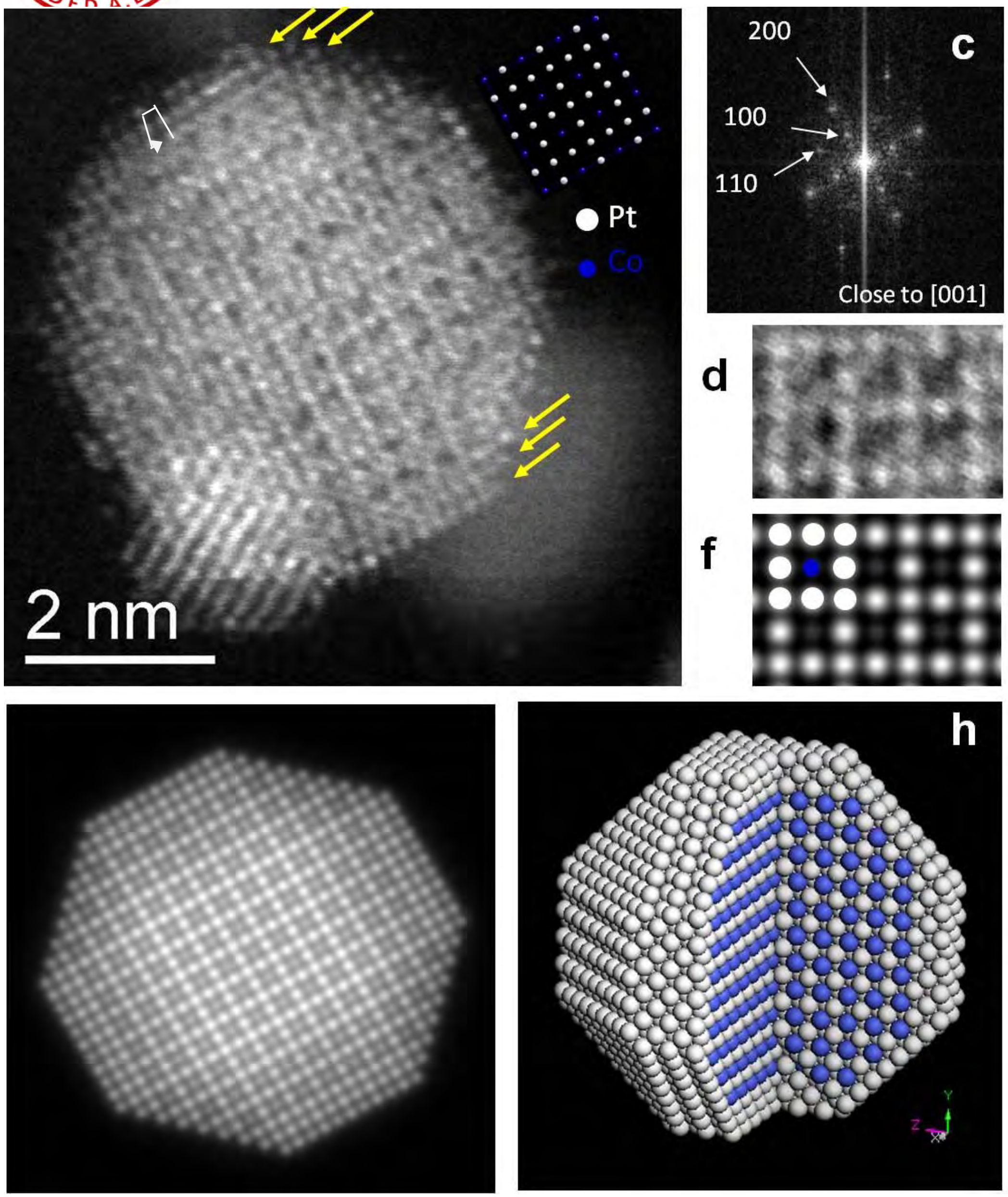
EDX map of Pt/$PtCu_3$

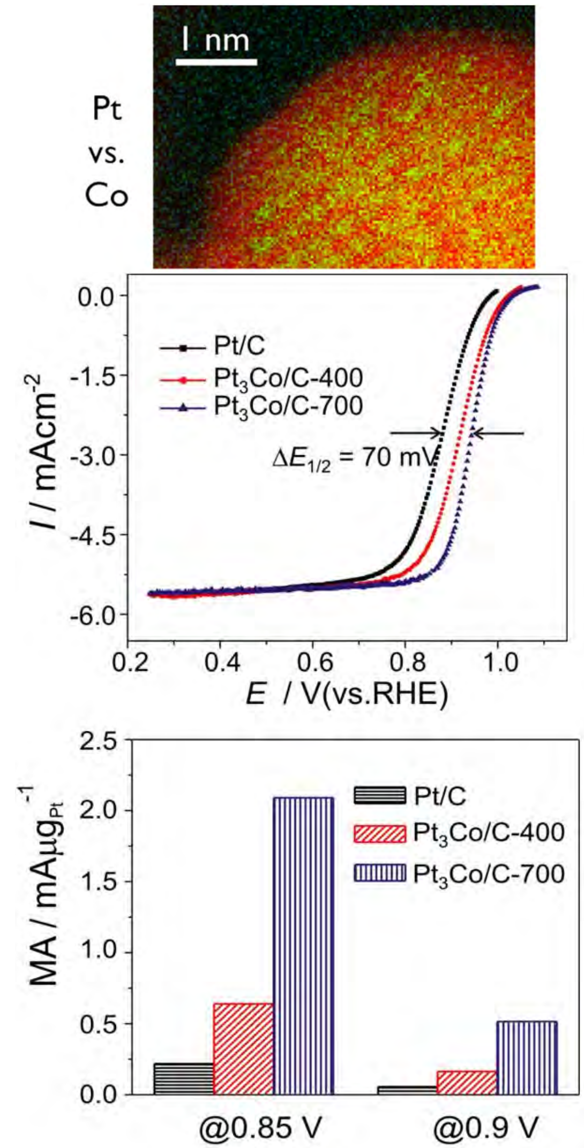


P. Strasser et al. *Nat. Chem.* **2**, 454 (2010).

Why?

Pt_3Co ORR Catalyst
Ordered Intermetallic vs. Disordered Alloy

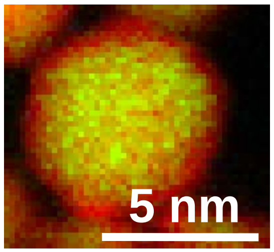




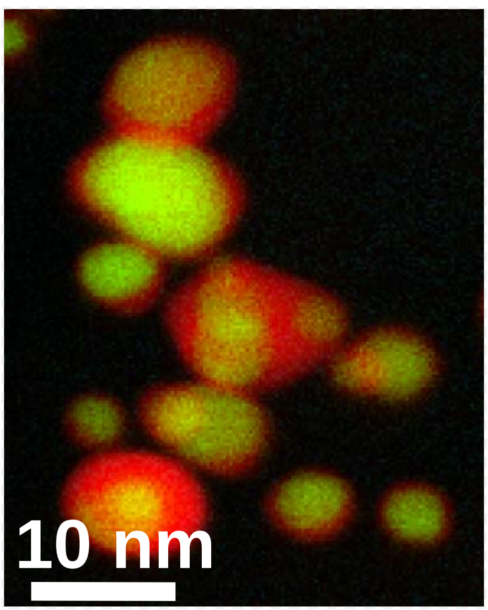
Wang et al, Nature Materials, **12**, 81 (2013)
Also *Pt_3Fe_2 Prabhudev, ACS Nano (2013)*

Determining the Coarsening Mechanism

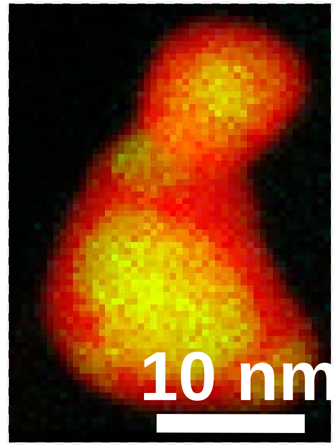
Starting Sample

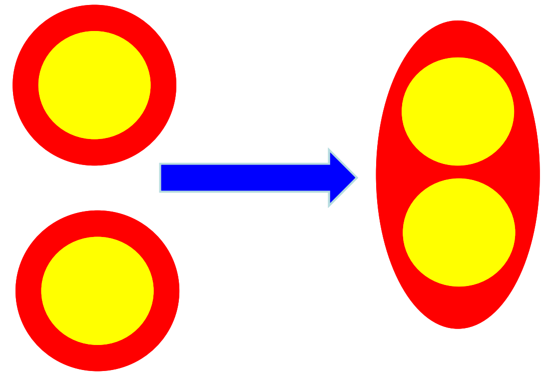


End of Lifetime



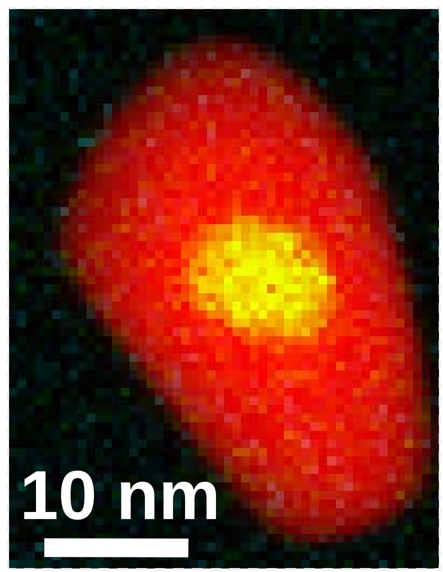
Coalescence

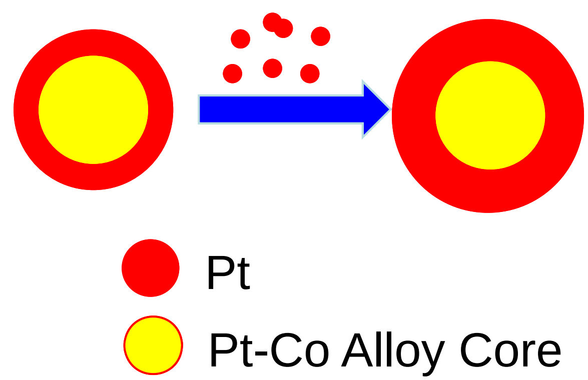




Ostwald Ripening

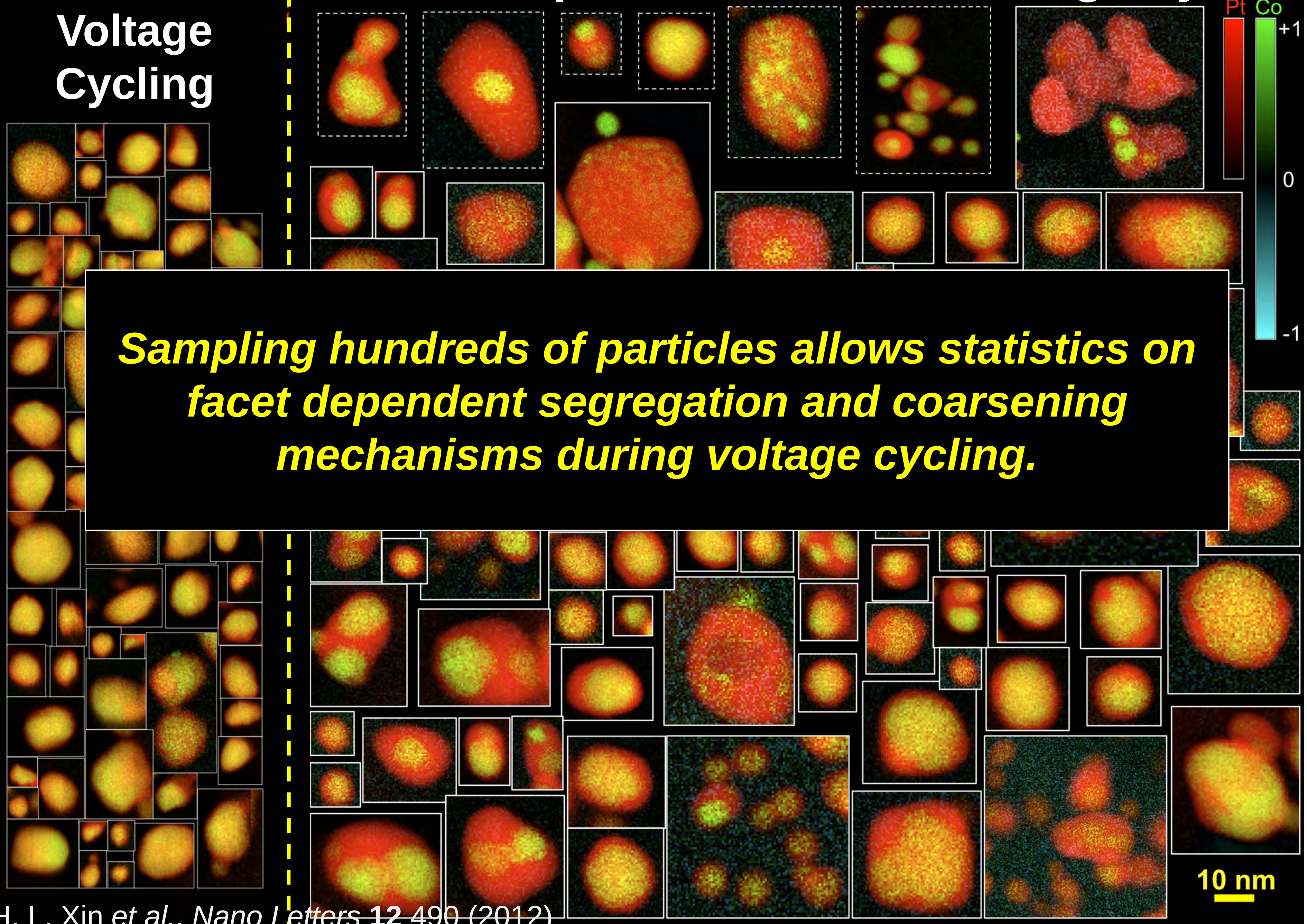
thru dissolution (Pt,Co) and redeposition (Pt)





Pt-Co Before Voltage Cycling

Pt-Co particles 30 000 voltage cycles

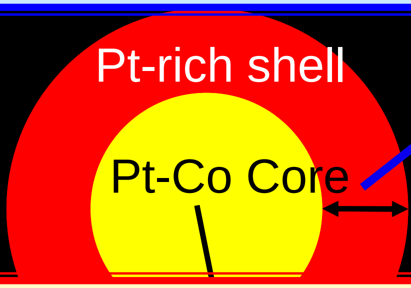


Sampling hundreds of particles allows statistics on facet dependent segregation and coarsening mechanisms during voltage cycling.

H. L. Xin *et al.*, *Nano Letters* **12** 490 (2012)

Statistical Comparison: Pre- and Post-Cycling

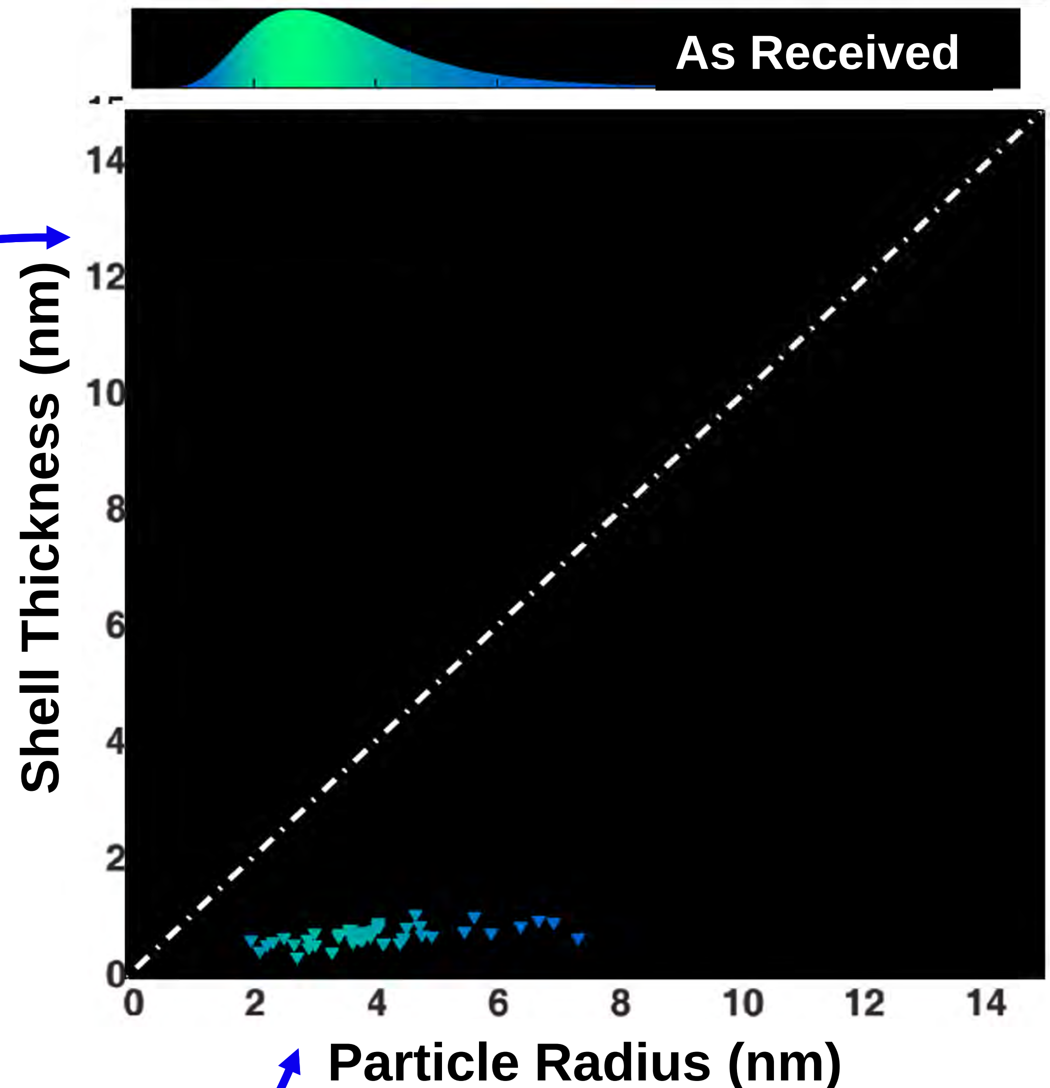
As Received:
~ 2.5 monolayer
(5.7 ± 0.3 Å) Pt shell



Voltage Cycled:

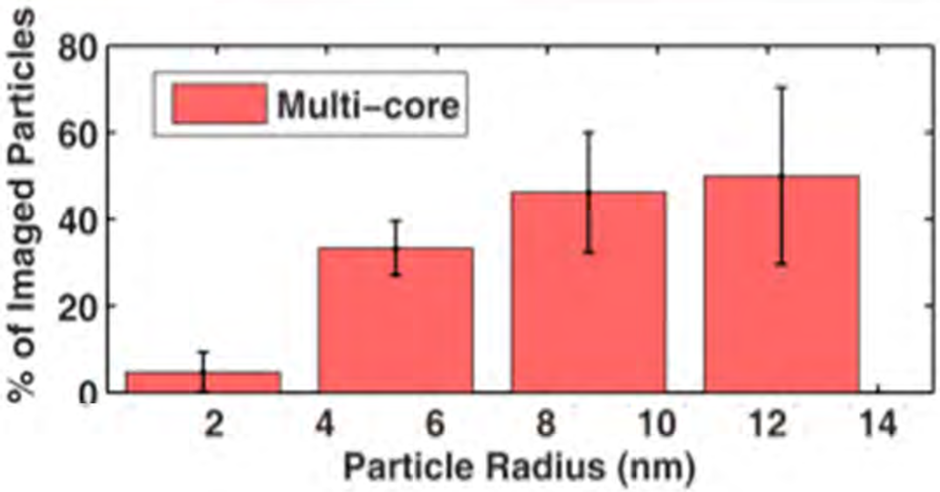
- Strong dependence of shell thickness on particle size.

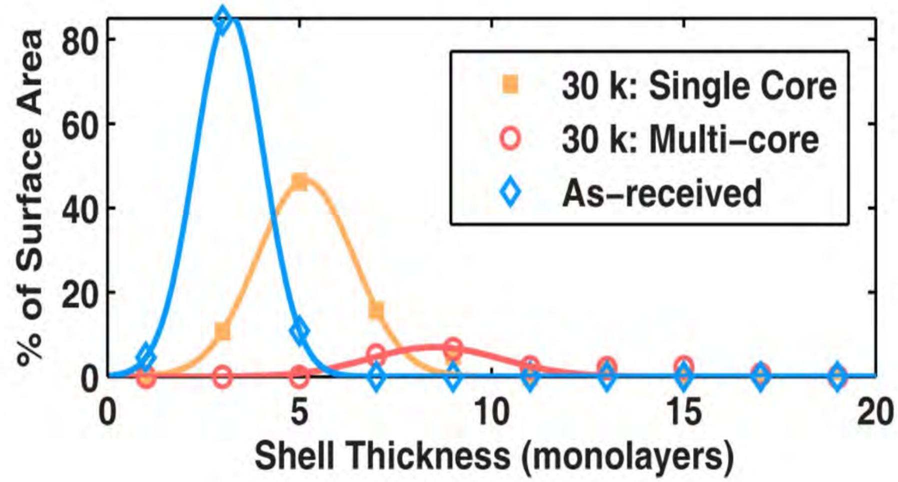
- Large Particles approaching total depletion of Co.



H. L. Xin *et al.*, *Nano Letters* **12** 490 (2012)

Statistics on Particle Coarsening Mechanisms





About half the large particles are multi-core

More Pt re-deposition onto multi-core particles

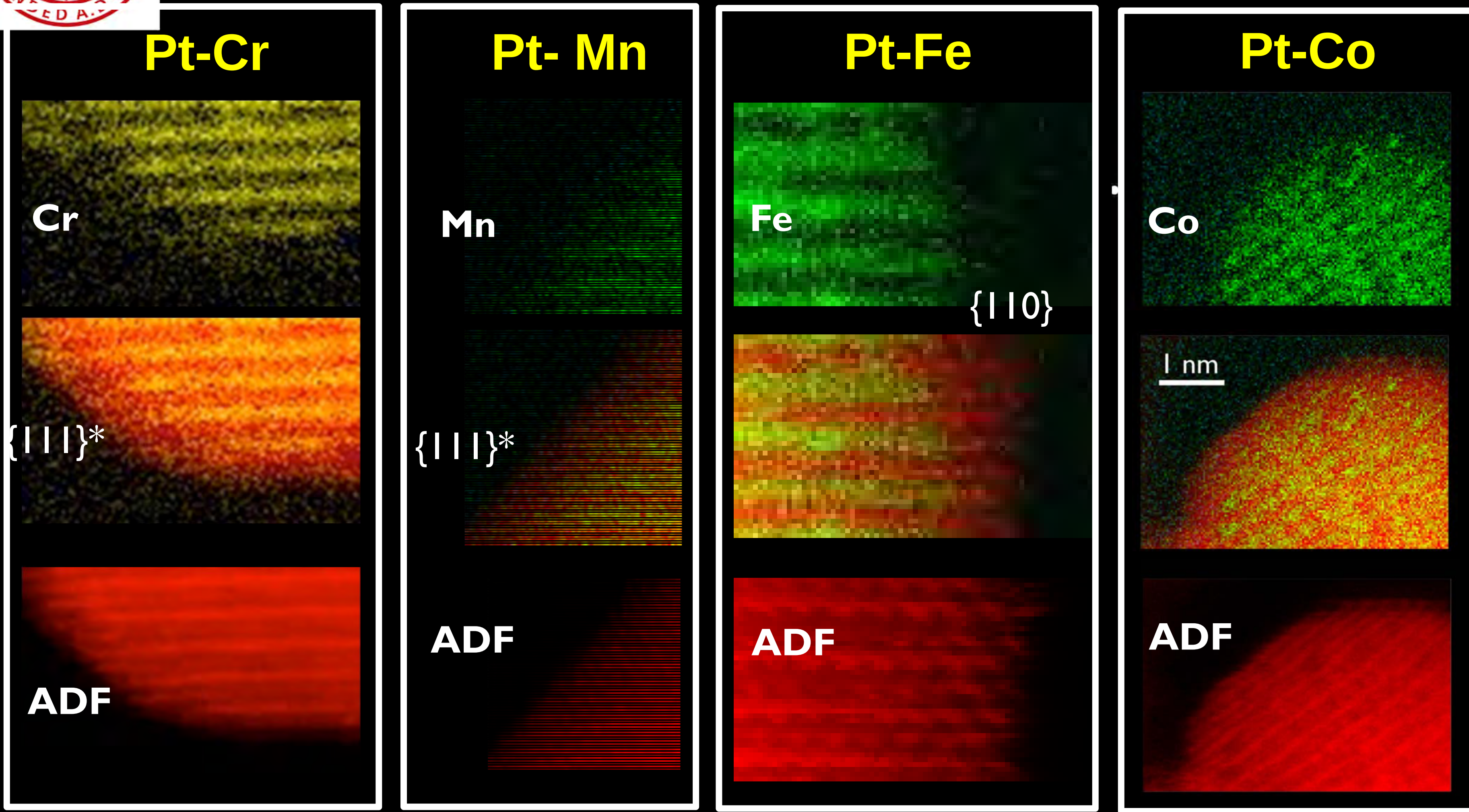
Ostwald ripening only:
Adds 2 monolayers of Pt to shell

Coalesced:
• Adds 5 monolayers of Pt to shell

Ostwald Ripening is faster on highly-curved coalesced particles

Xin *et al.*, *Nano Letters* **12** 490 (2012)

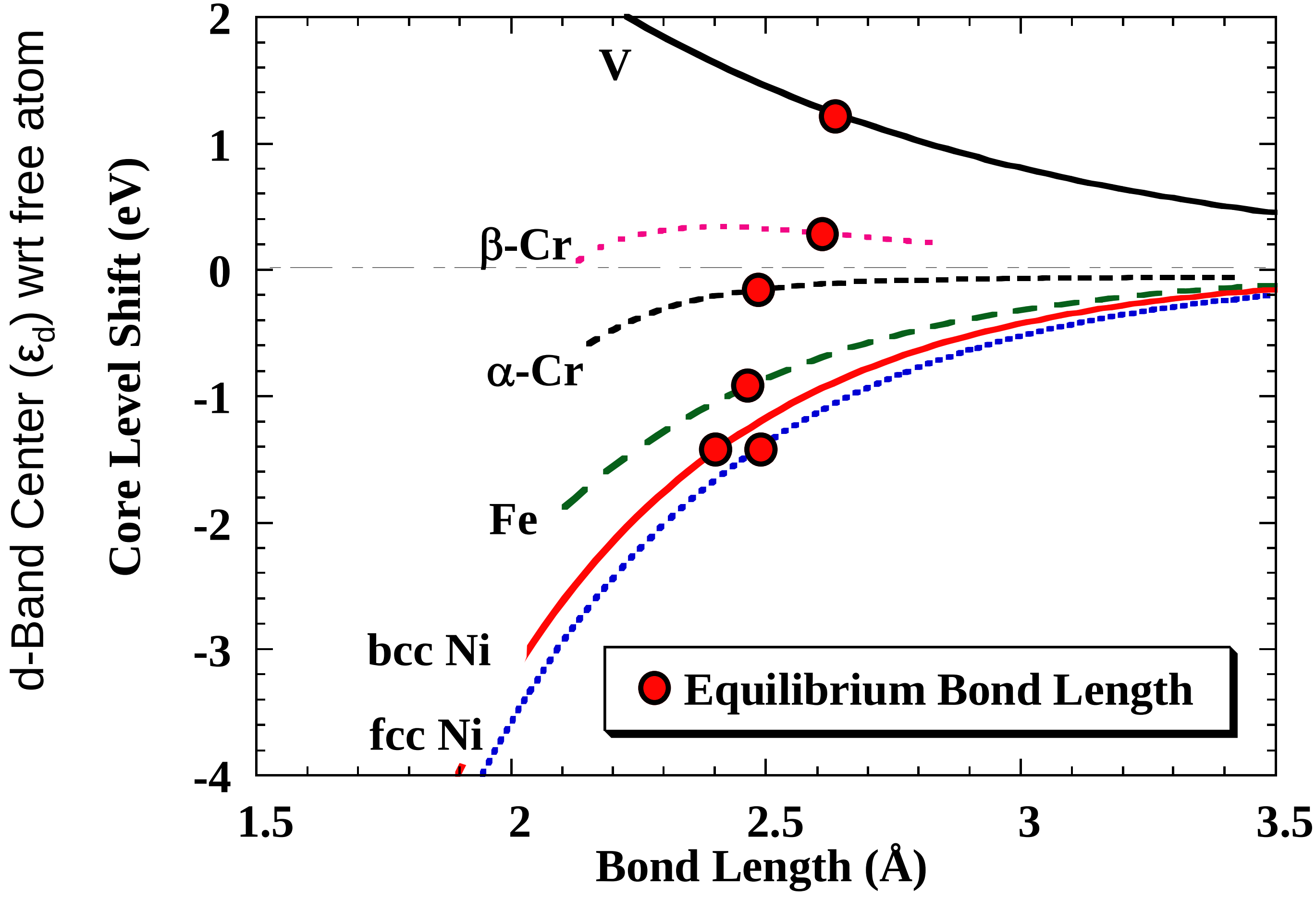
Atomic Resolution imaging of segregation



~ 3 monoloayers of Pt segregation after a few cycles

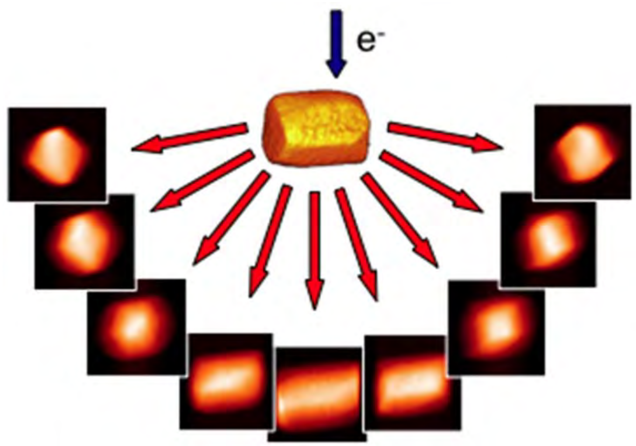
Core Level Shifts in Metals
(CLS tracks d-Band center)

We expect $\delta\varepsilon_d \propto \frac{(N_d - 5)}{10}\sqrt{z}\exp(-\beta r)$

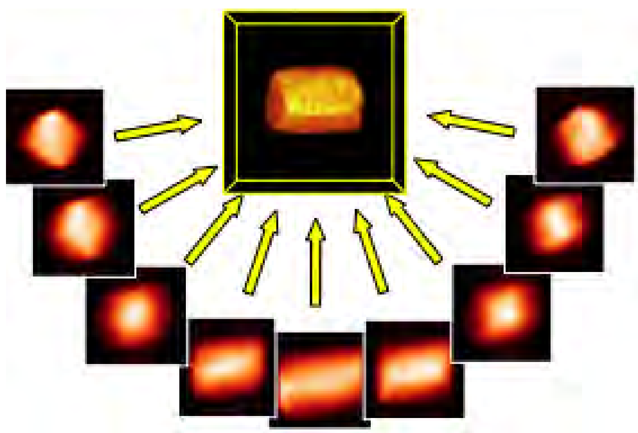


D. A. Muller, *Ultramicroscopy*, **78**, 163 (1999)

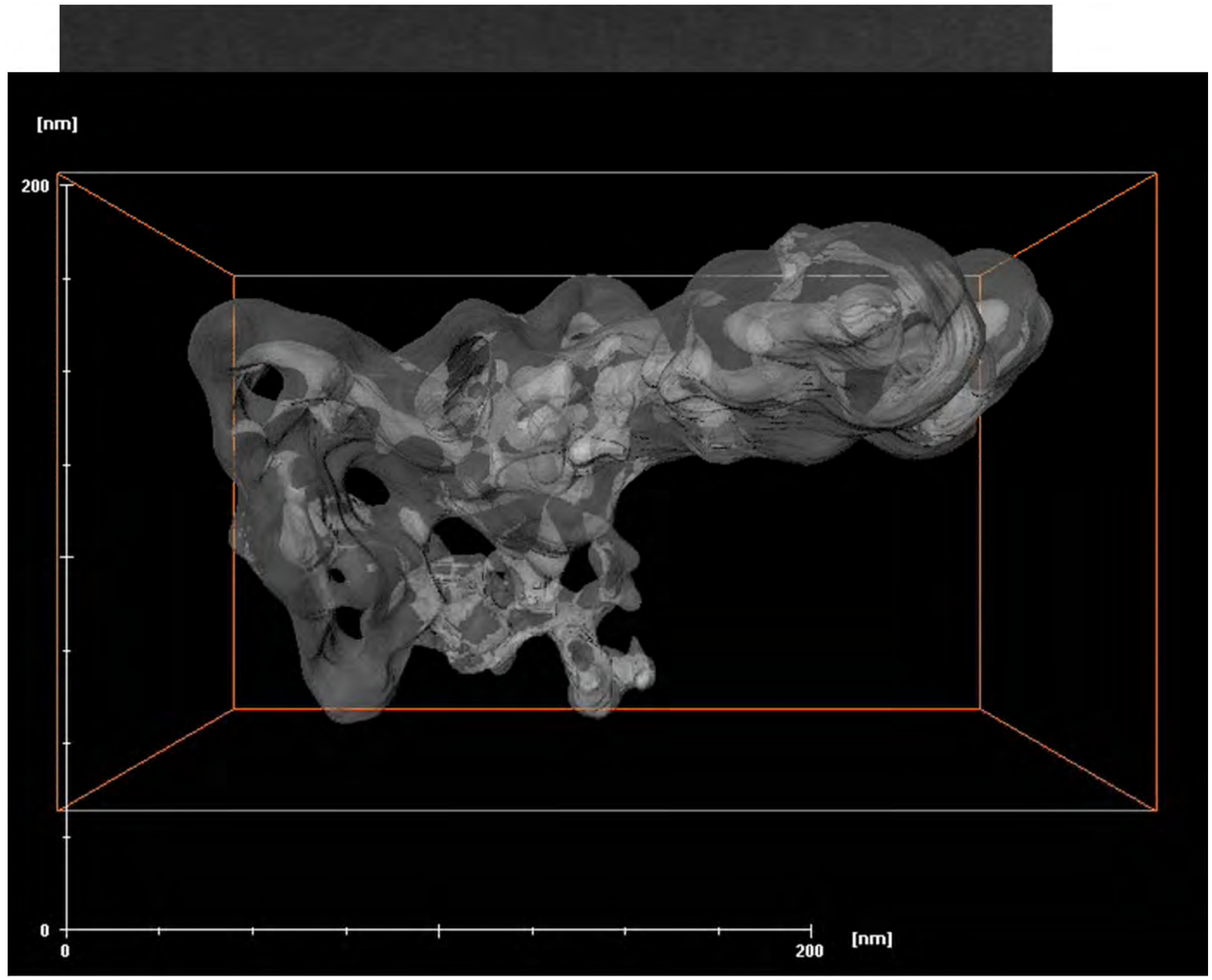
3D Reconstruction by Electron Tomography



Tilt from -70 to +70 degree



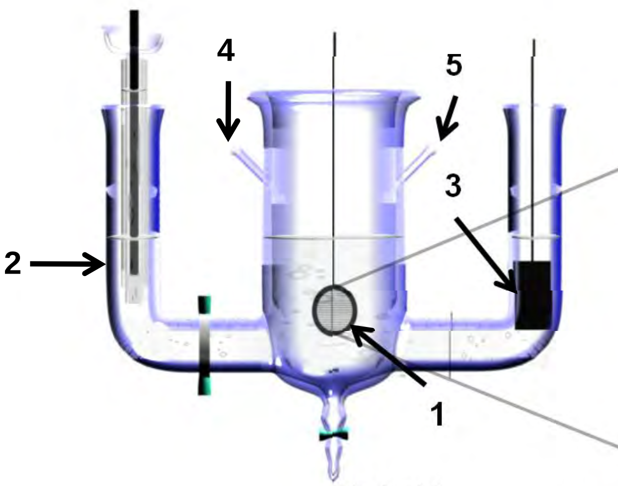
Reconstruction by back projection



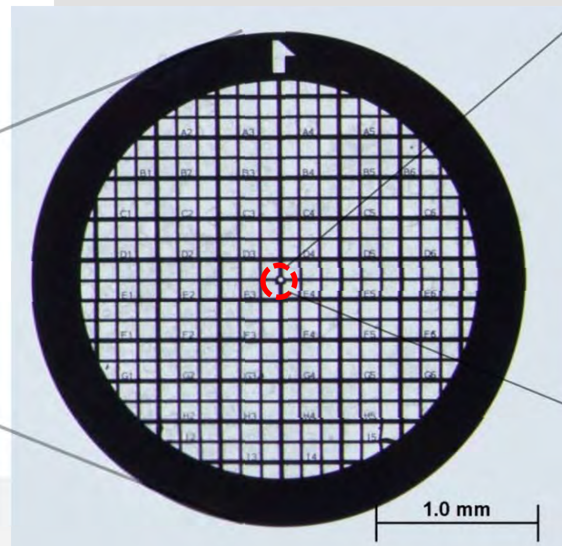
http://youtu.be/DVsJqhd0oJU

Z. Y. Liu et al, *Journal of The Electrochemical Society,* **155** B979 (2008).

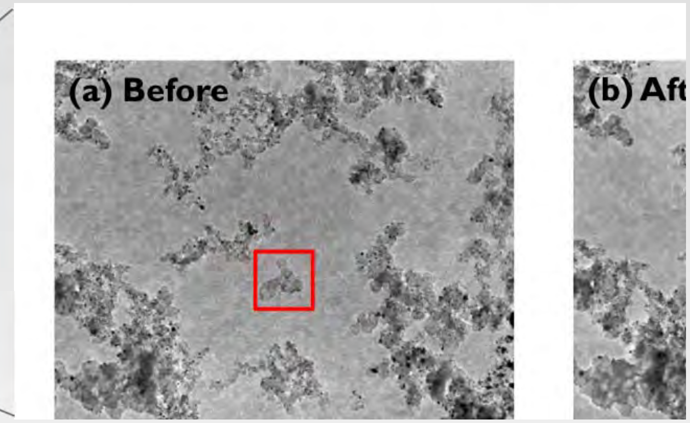
E-Chem on a Grid: Observe Coarsening during Voltage Cycling of Pt_3Co

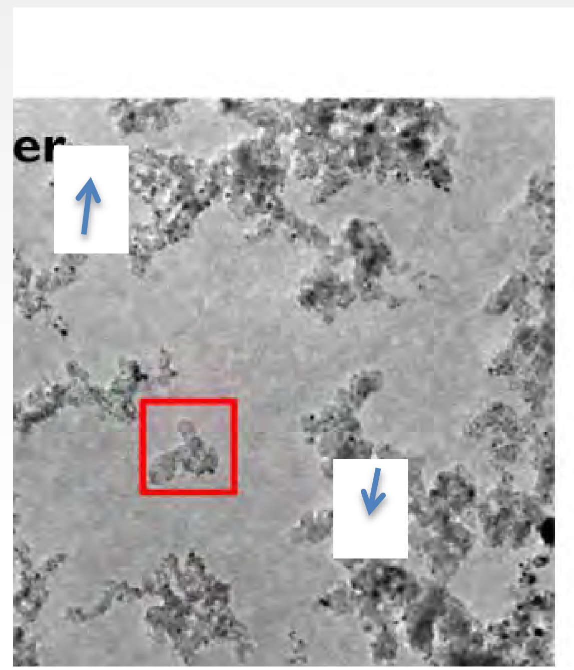


1. Gold index grid (working electrode)
2. Reversible Hydrogen Electrode (reference electrode)
3. Platinum foil (counter electrode)
4. Argon gas inlet
5. Argon gas outlet



Pt_3Co on Vulcan

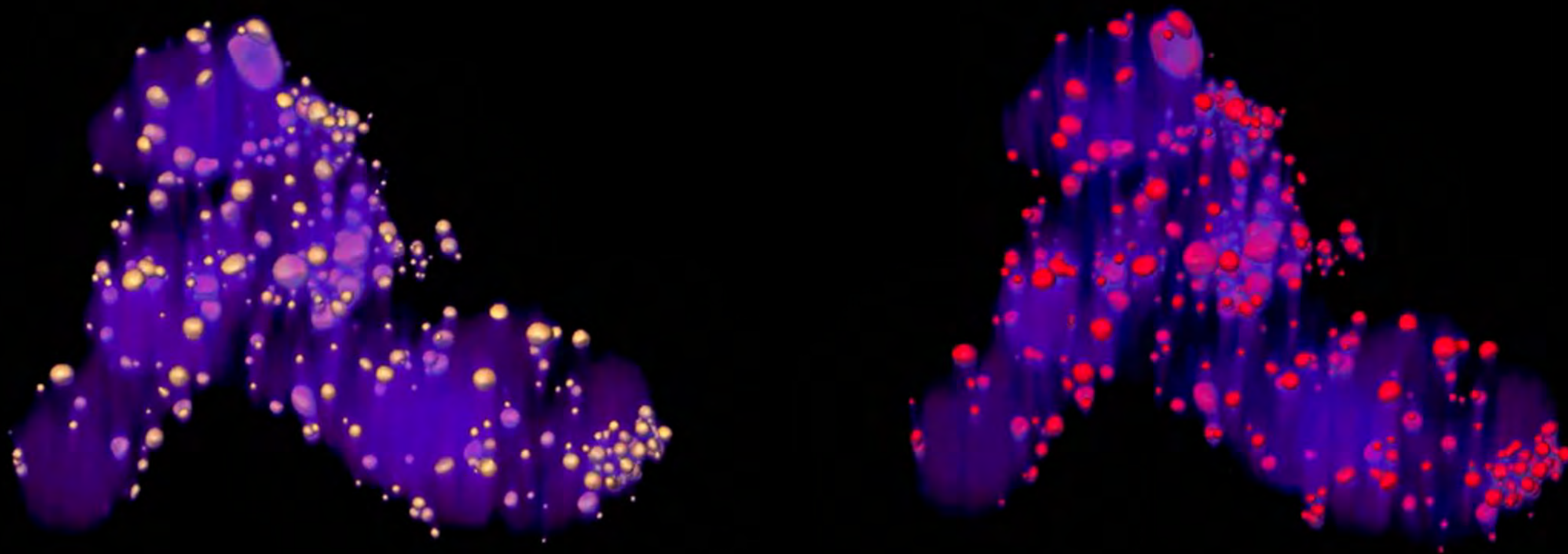




Enables 3-D imaging for the first time of the same region before and after

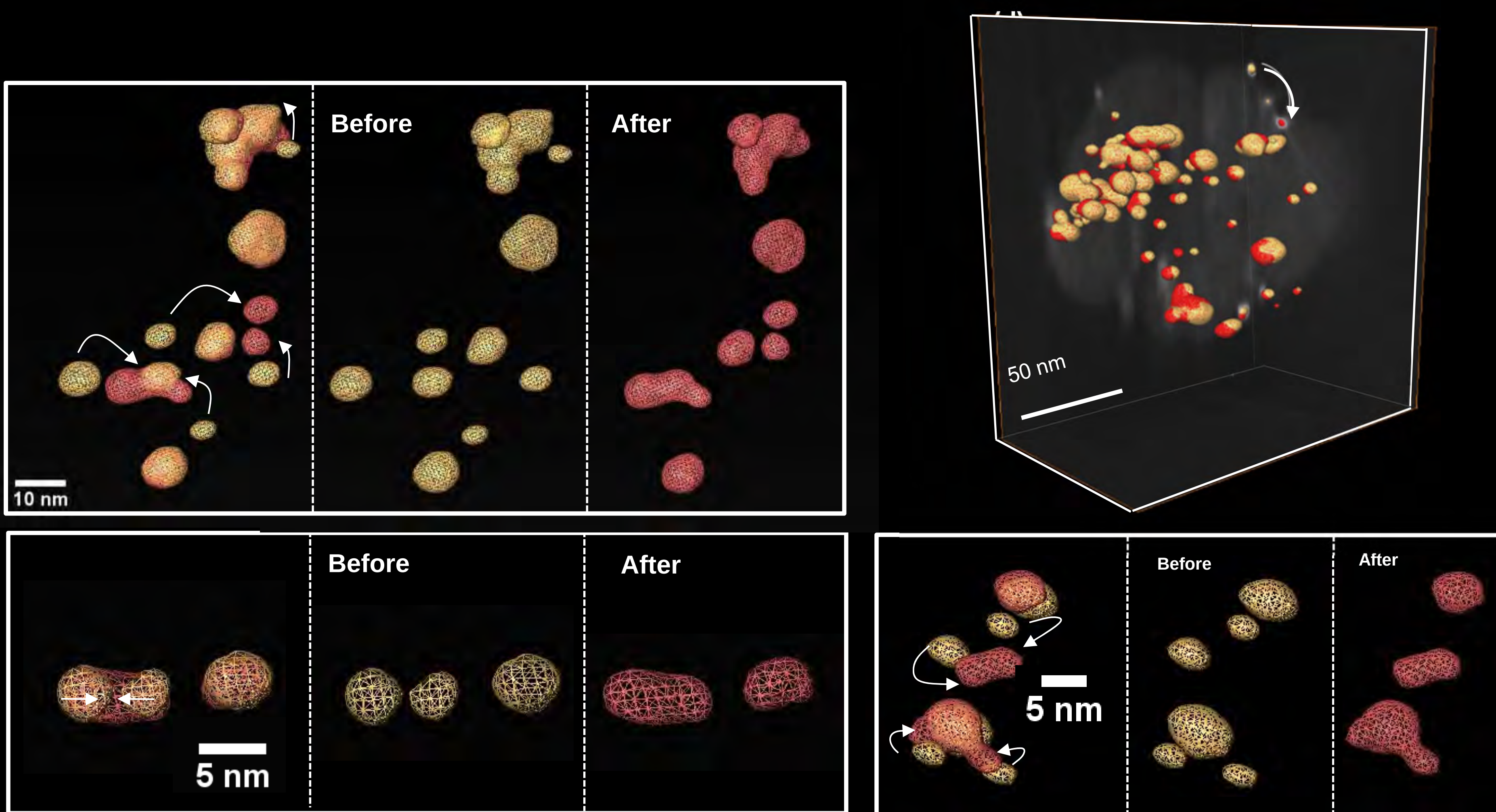
Yu, et al, Nano Letters, **12**, (9), 2012.

Before vs. After



Yu, et al, Nano Letters, **12**, (9), 2012.

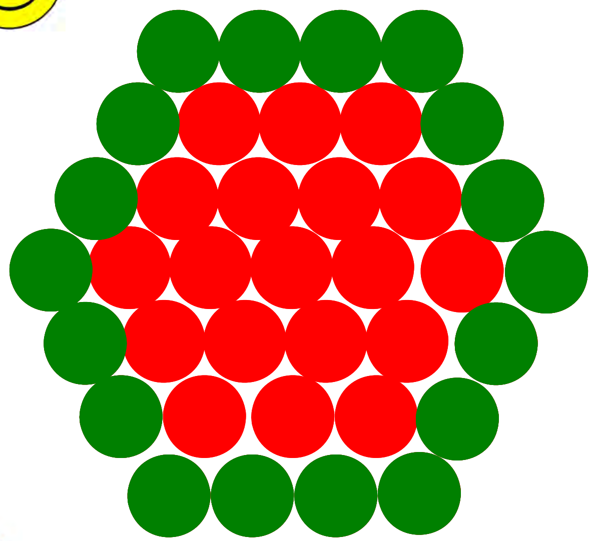
Tracking Particle Coalescence in 3D



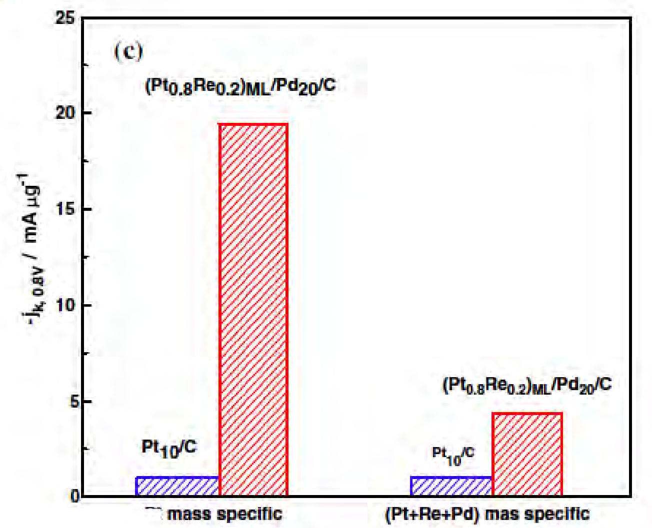
Yu, et al, Nano Letters, **12**, (9), 2012.

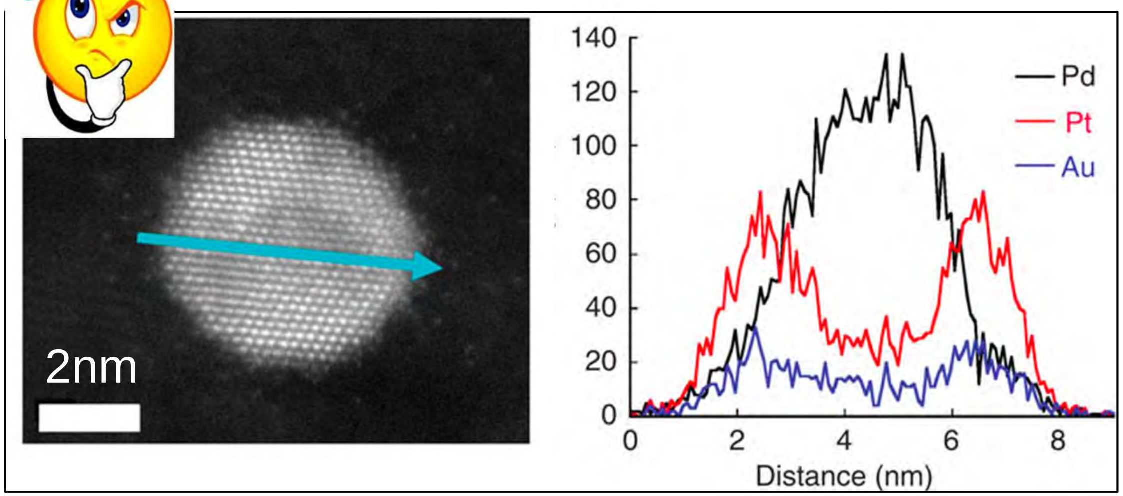
Pt Monolayer Reduces Cost of Fuel Cell

Pd@Pt



Pt Mass Activity Increases ×10



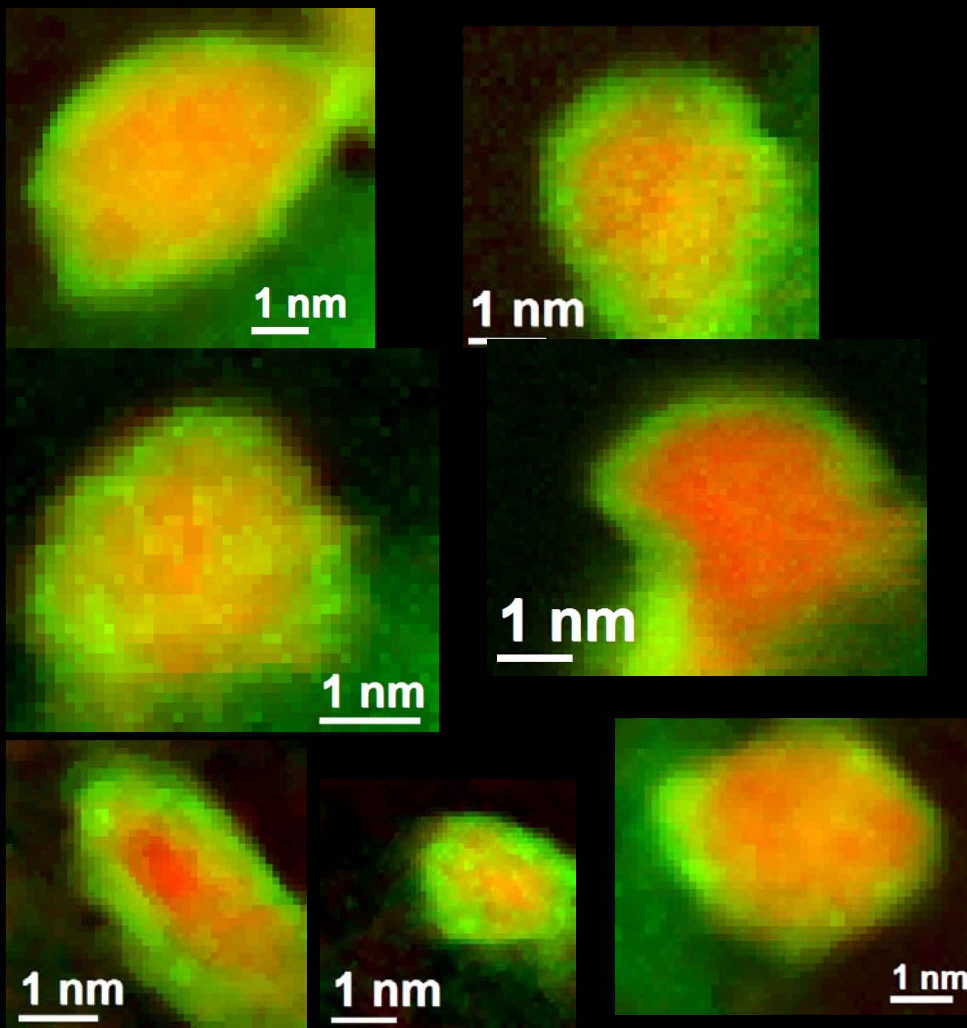


- Statistics -> Uniformity
- Durability -> Practical

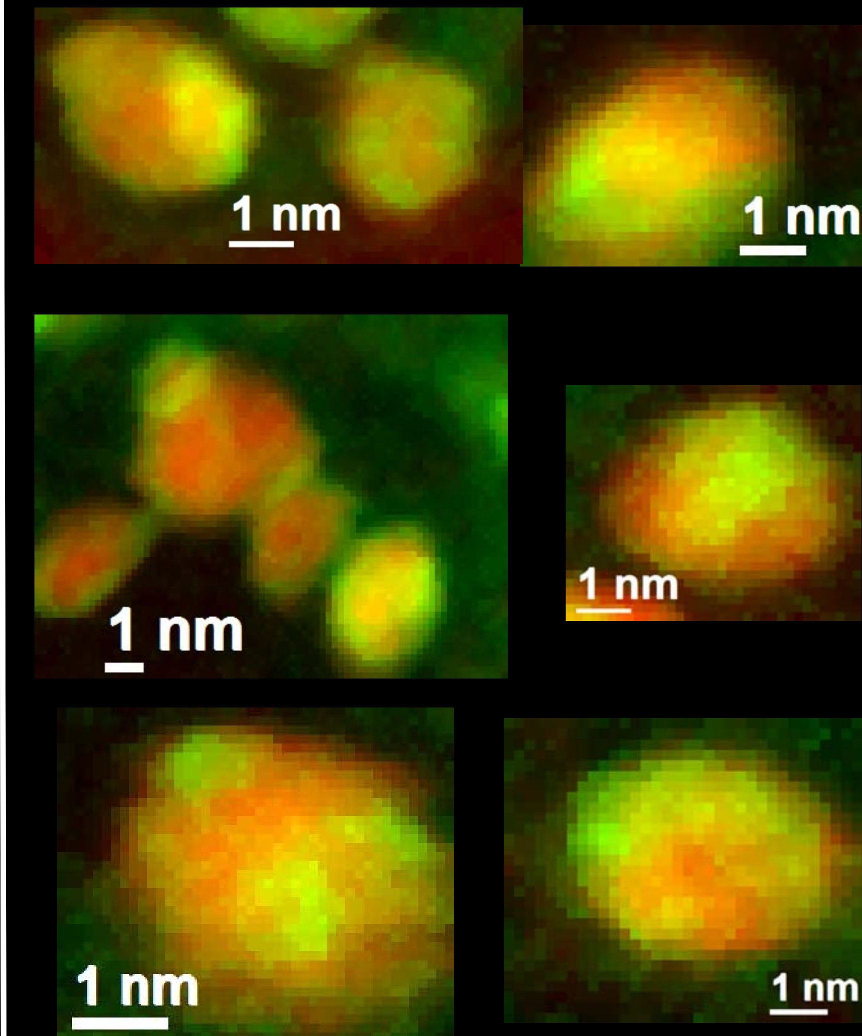
RR. Adzic, et al @ BNL
Top Catal., 2007, 46:249–262
JPCB, 2005, 109, 22701-22704
Nature Comm., 2012, 3,1115

As Prepared Pd@Pt: Not Uniform

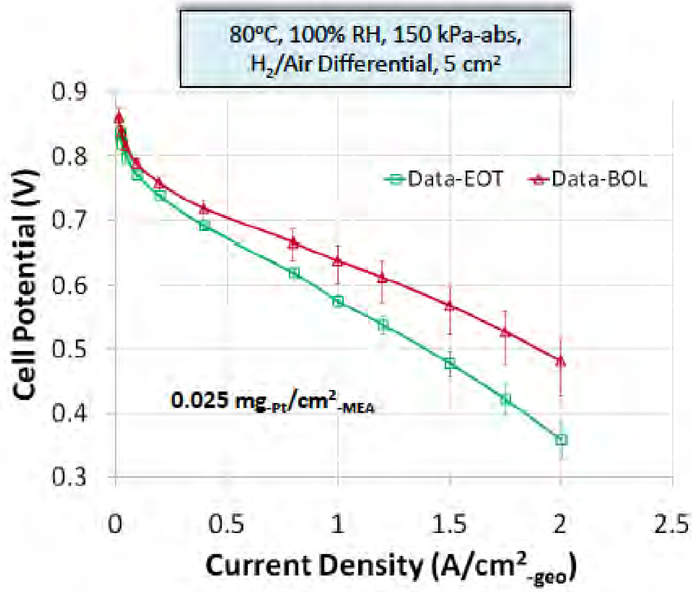
Core-Shell



Not Core-Shell



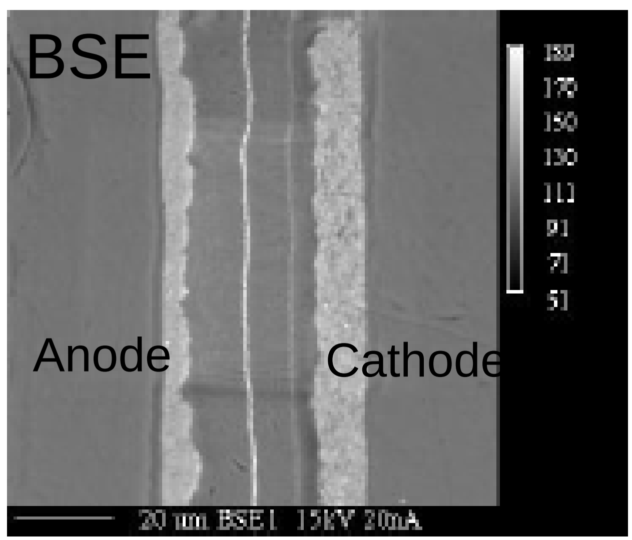
Fuel Cell Testing

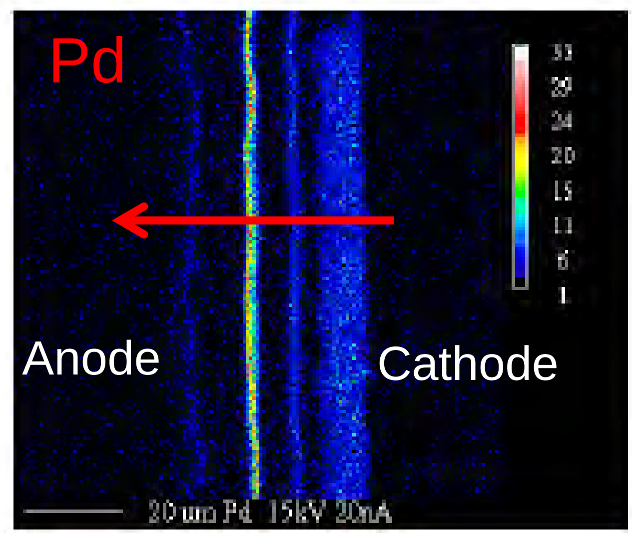


Samples	BOL	EOT
Pt Surface Area ($m^2{}_{\text{-Pt}}/g_{\text{-Pt}}$)	88	45
Mass Activity ($A/mg_{\text{-Pt-eq}}$)	0.298	0.217

Pd migration to anode!!!

EPMA mapping of fuel cell slice (EOT)

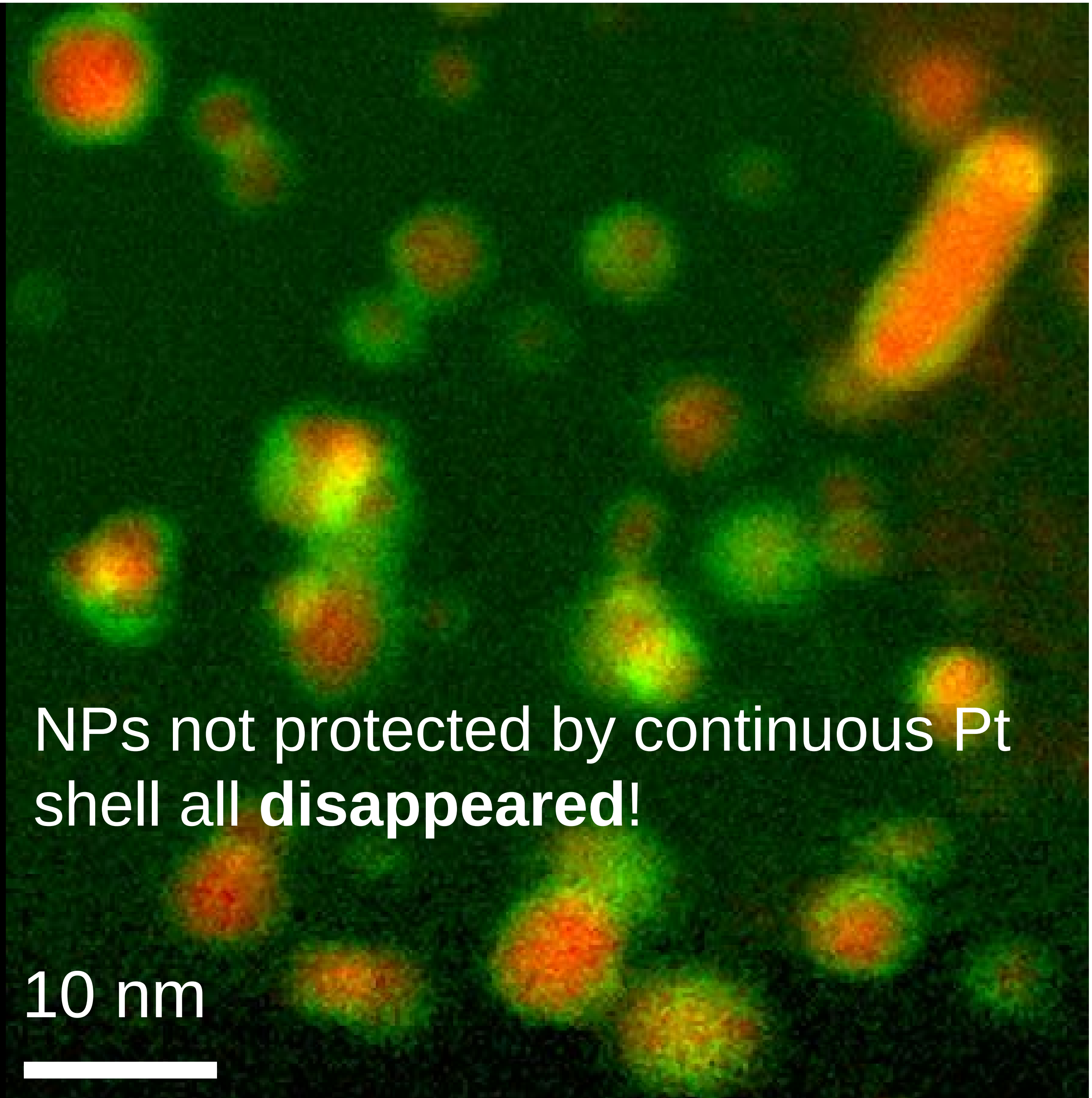




Cathode Pd@Pt After Aging

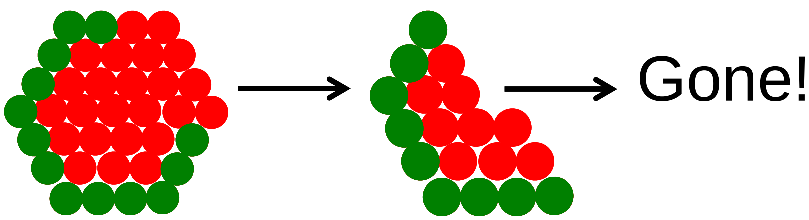
- ✓ New Spectrometer (Enfinium)
- ✓ Dual EELS
- ✓ Larger energy range
- ✓ Faster readout speed

Improved
~ 300 by 300



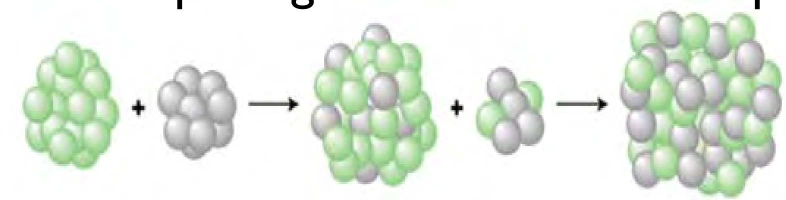
Catalyst Degradation Mechanism

1. Dissolution

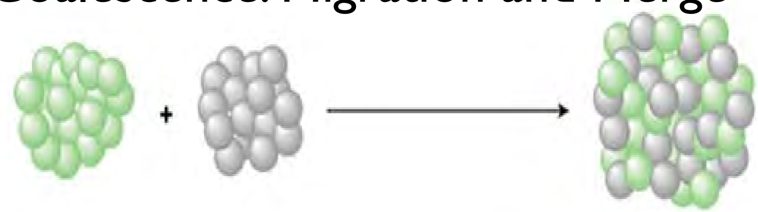


2. Coarsening

2a.Ostwald ripening: Dissolution + Redeposition



2b. Coalescence: Migration and Merge



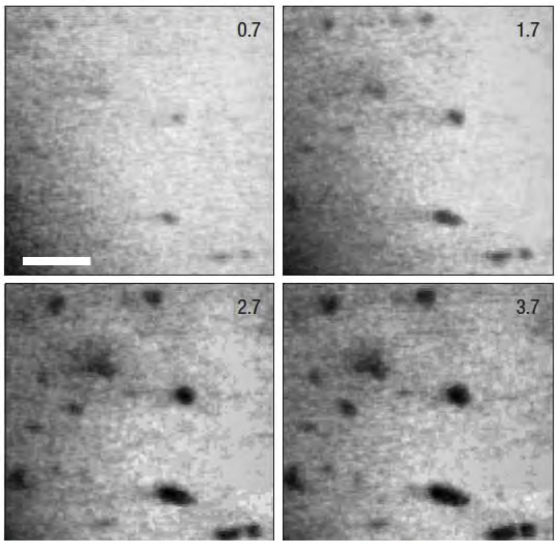
Pt-Pd

Pt-Co?

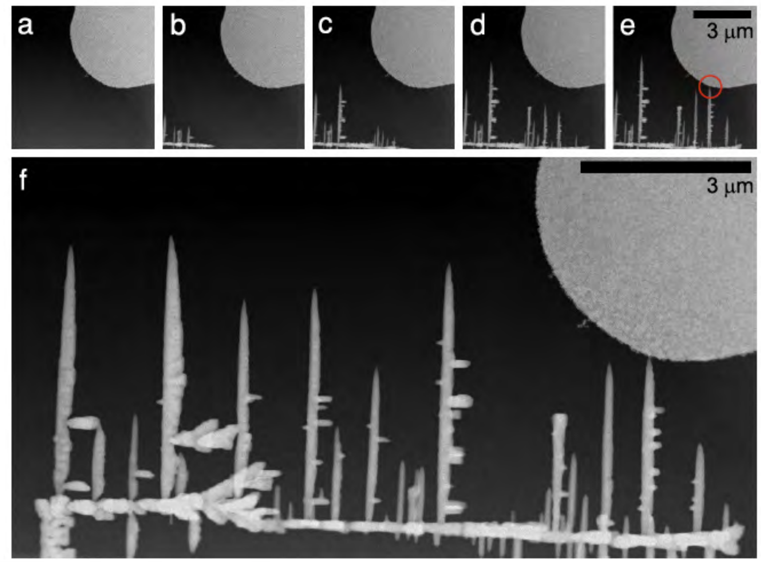
Is there any *in-situ* method to track the same locations of nanoparticles?

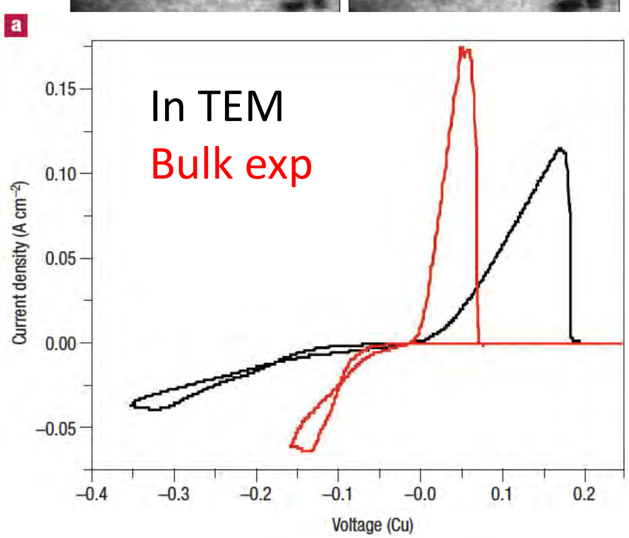
Can we do electrochemistry in the TEM?

Electrodeposition of Copper

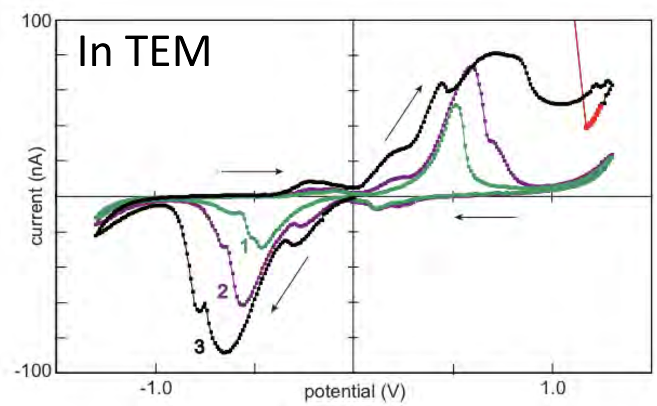


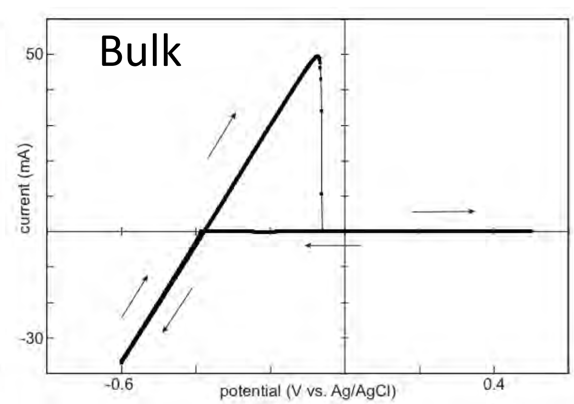
Growth of Pb dendrites





M.J. Willamson, Nat Mat. **2** (8), 532 (2003)



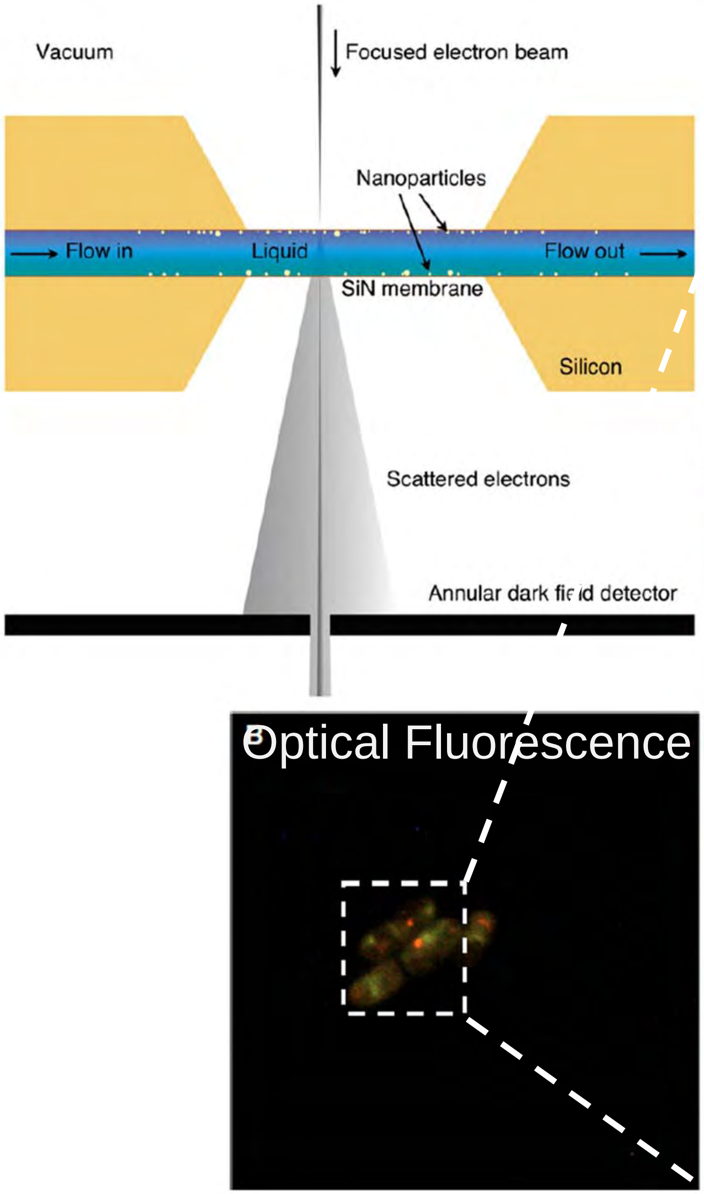


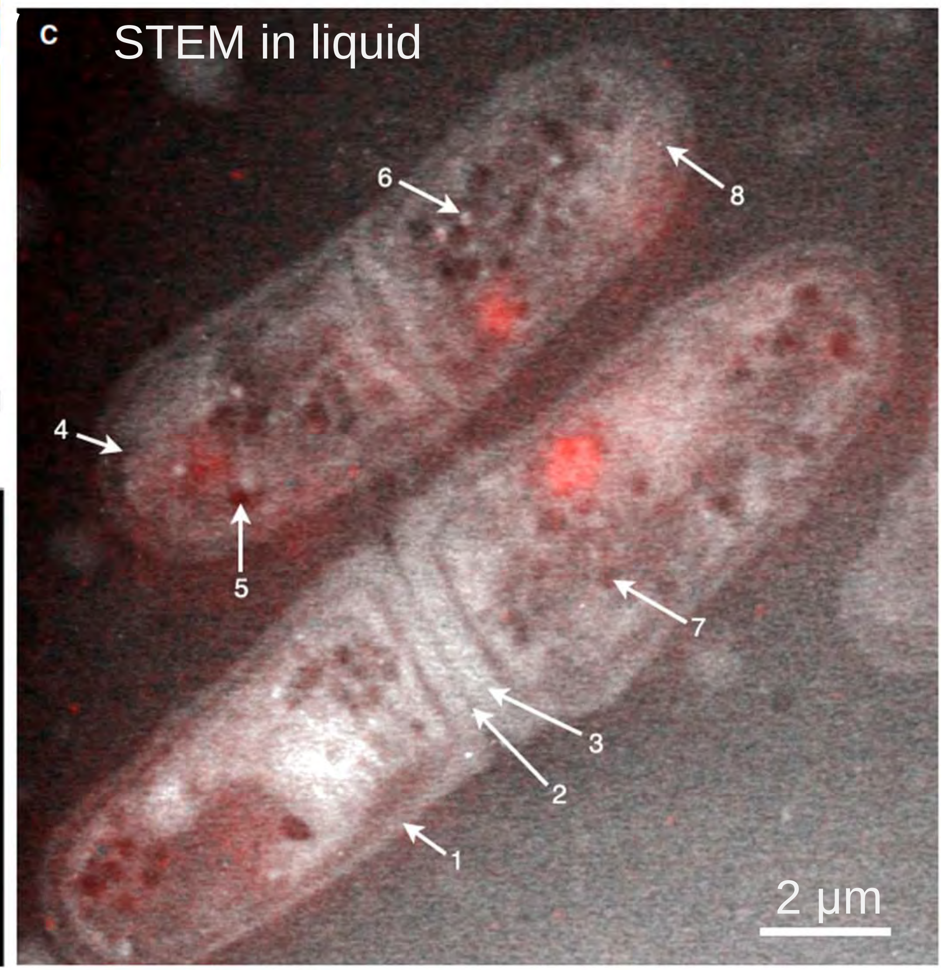
E.R. White, ACS Nano. **6** (7), 6308 (2012)

Electrochemistry in a TEM is not trivial!

TEM in Liquids

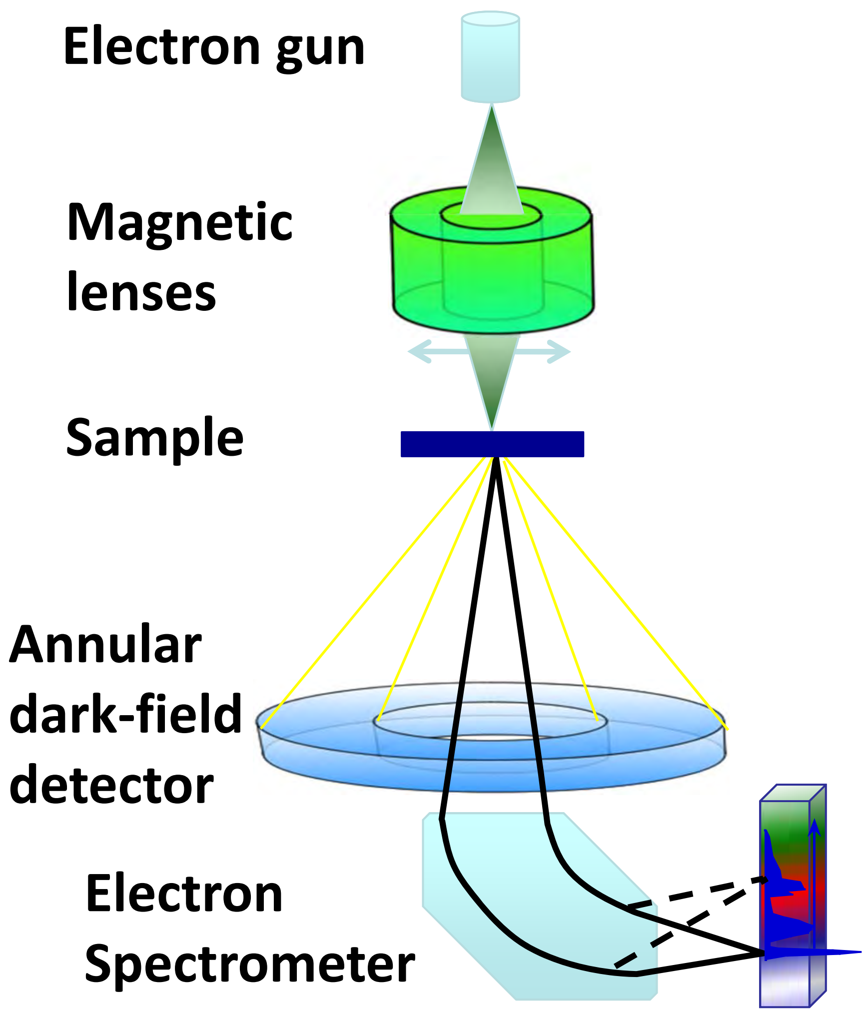
Peckys et al, "Fully Hydrated Yeast Cells Imaged with Electron Microscopy". *Biophysical Journal* **100**, 2522 (2011).





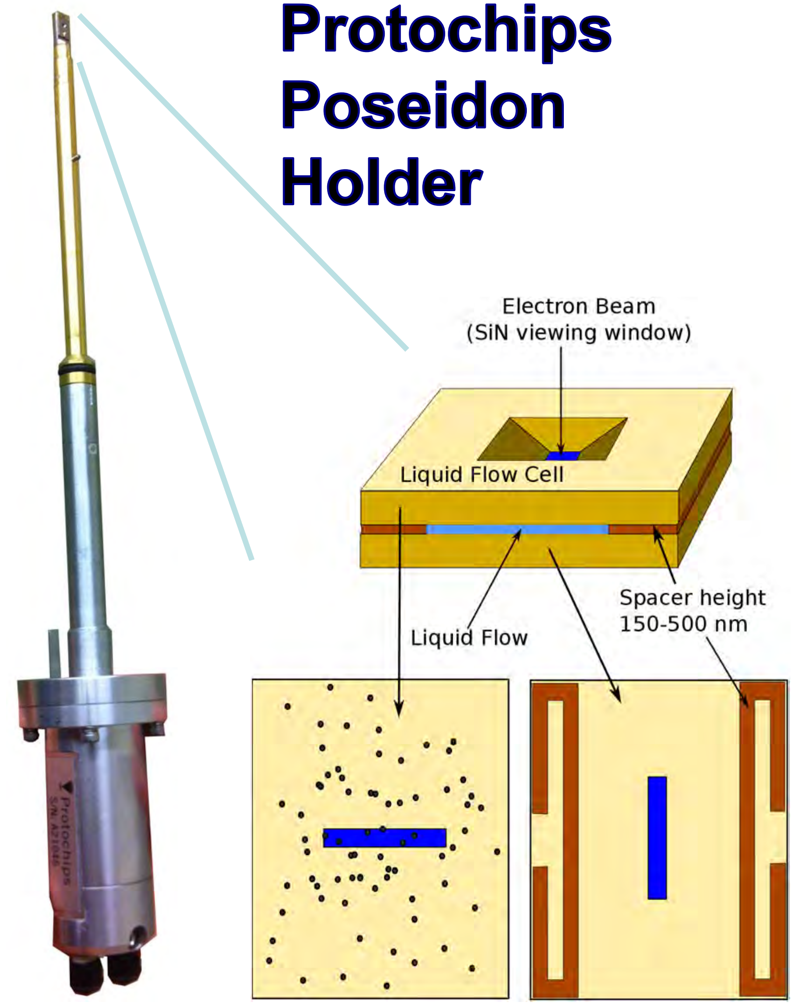
Liquid cell *in situ* TEM

Scanning Transmission Electron Microscope (STEM)

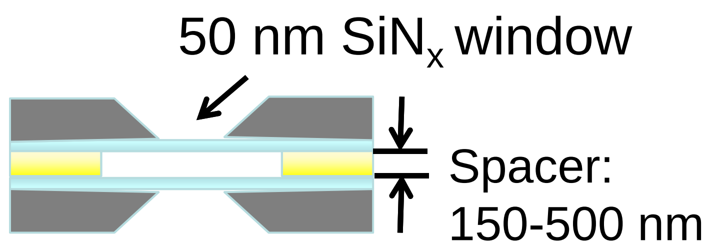


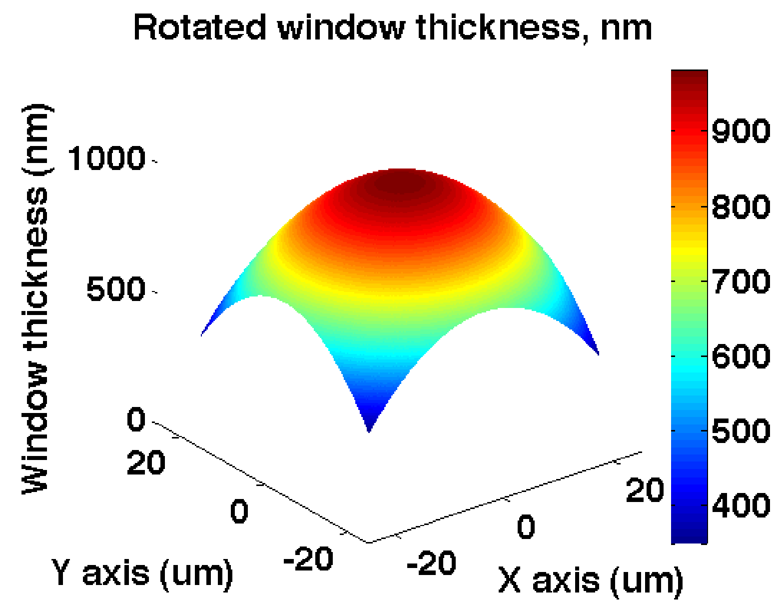
STEM-Electron energy-loss spectroscopy

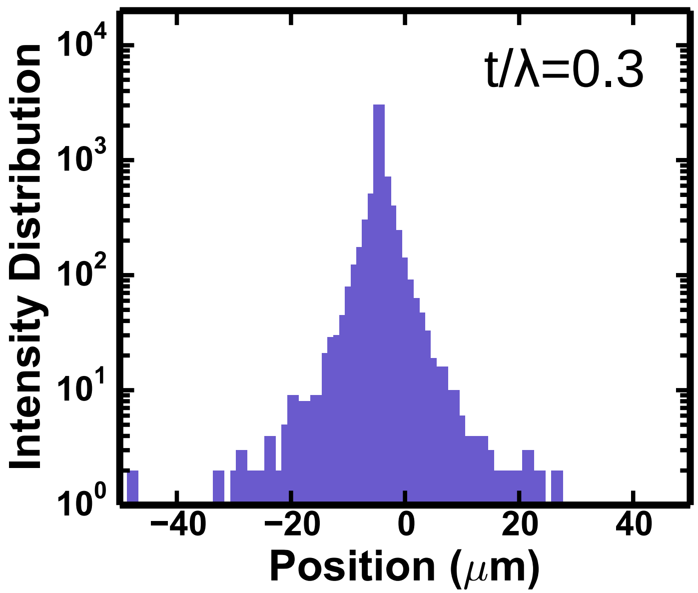
Protochips Poseidon Holder

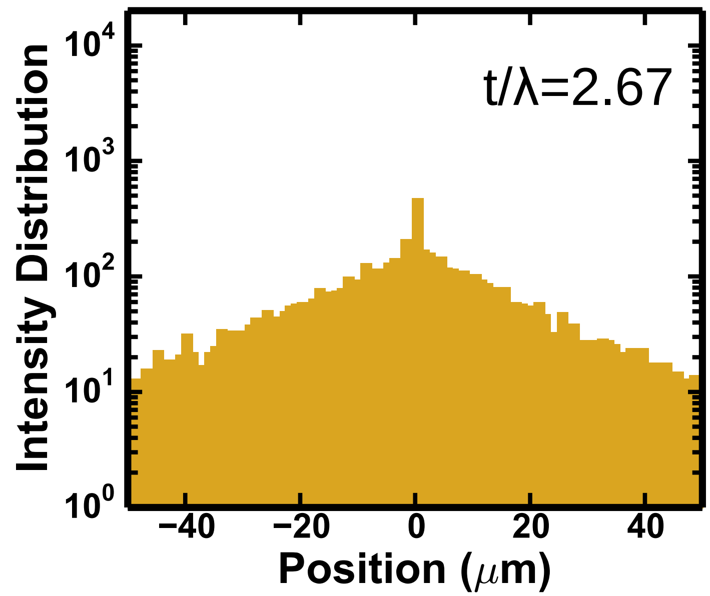


Challenge #1: Thickness of the liquid layer



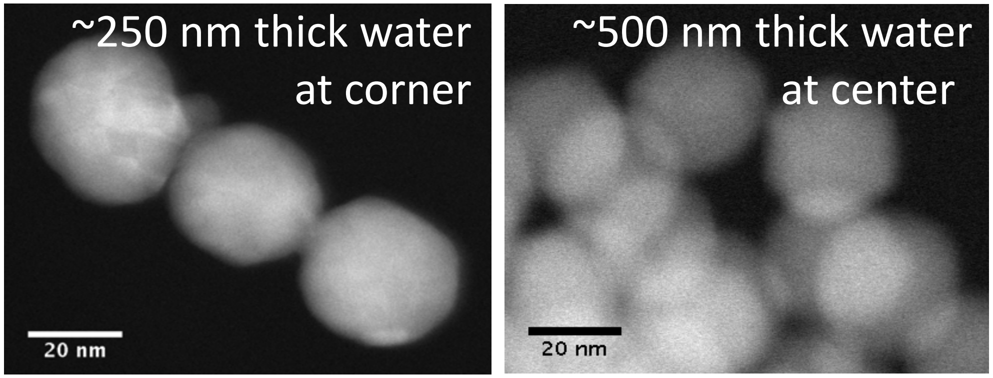




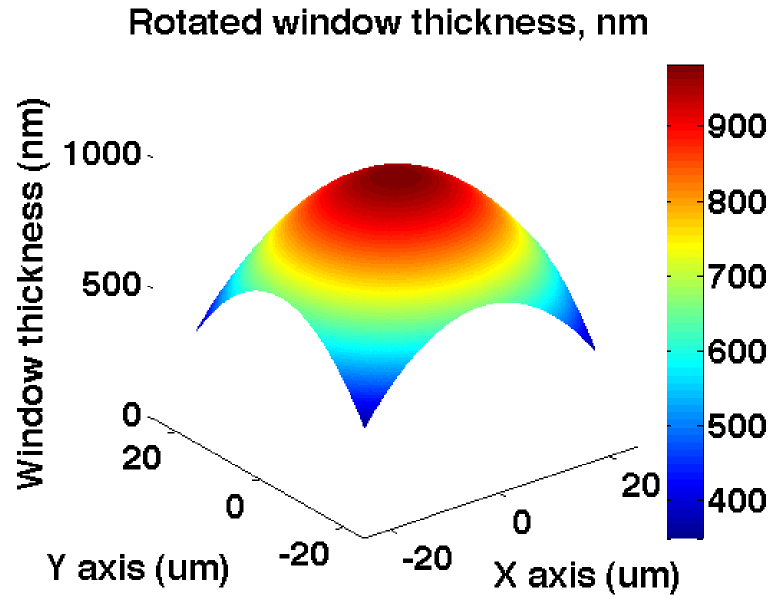


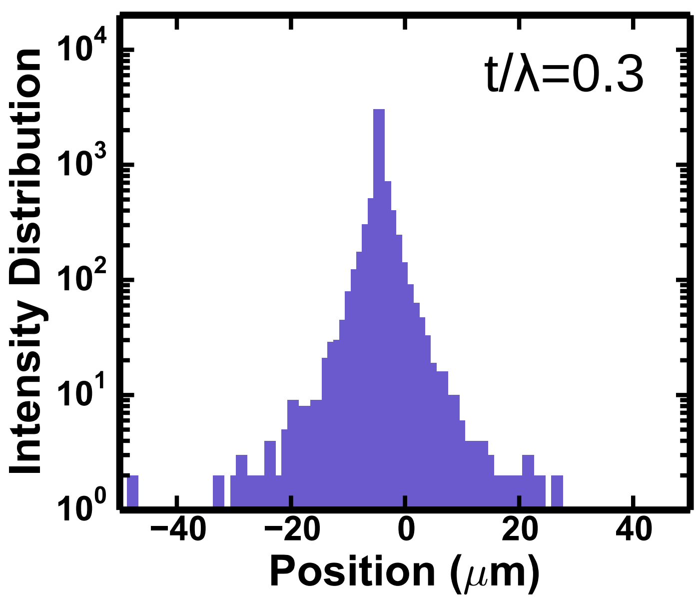
Challenge #1: Thickness of the liquid layer

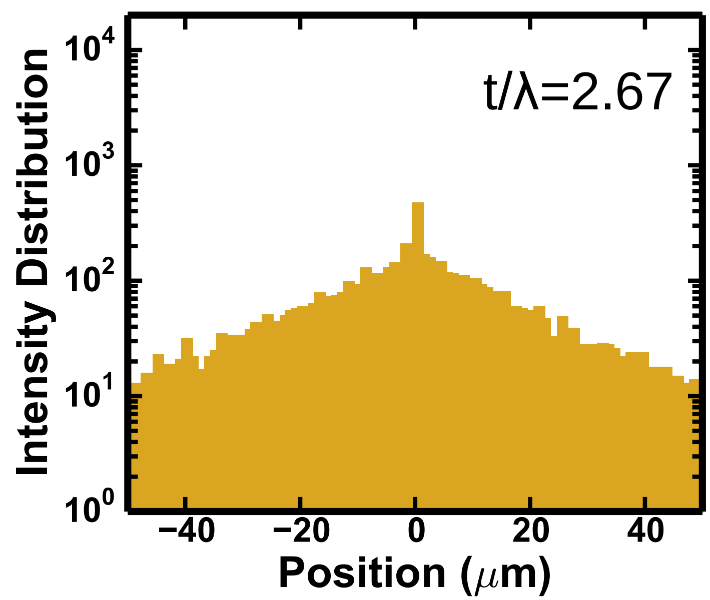
Gold nanoparticles in water



Reasonable to expect ~nm resolution in STEM

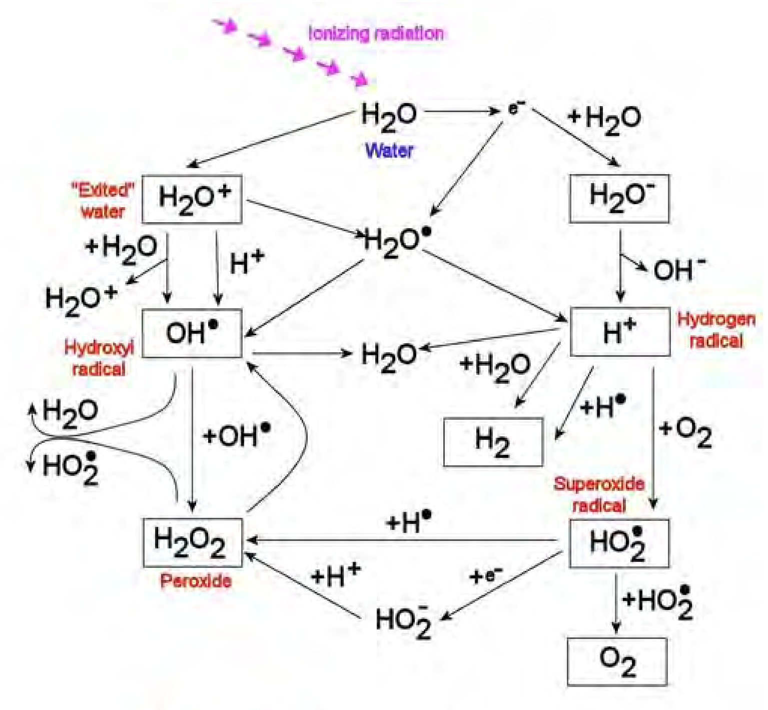






Challenge # 2: Electron Beam Effects

High energy electron beam interacts with the solution.
For water, this causes the production of radicals:

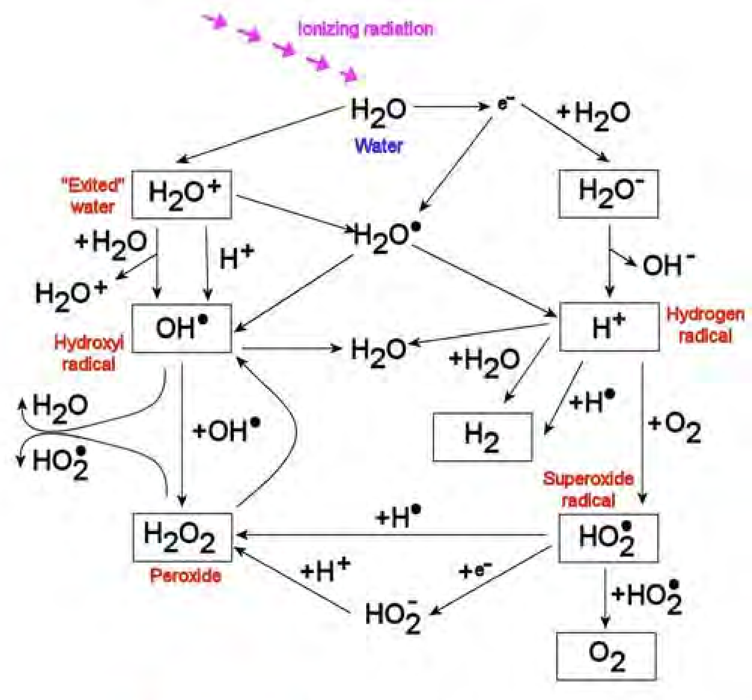


Radiolysis of intracellular water (H20)

S.M. Carr, “Ionizing Radiation and Life.”2012

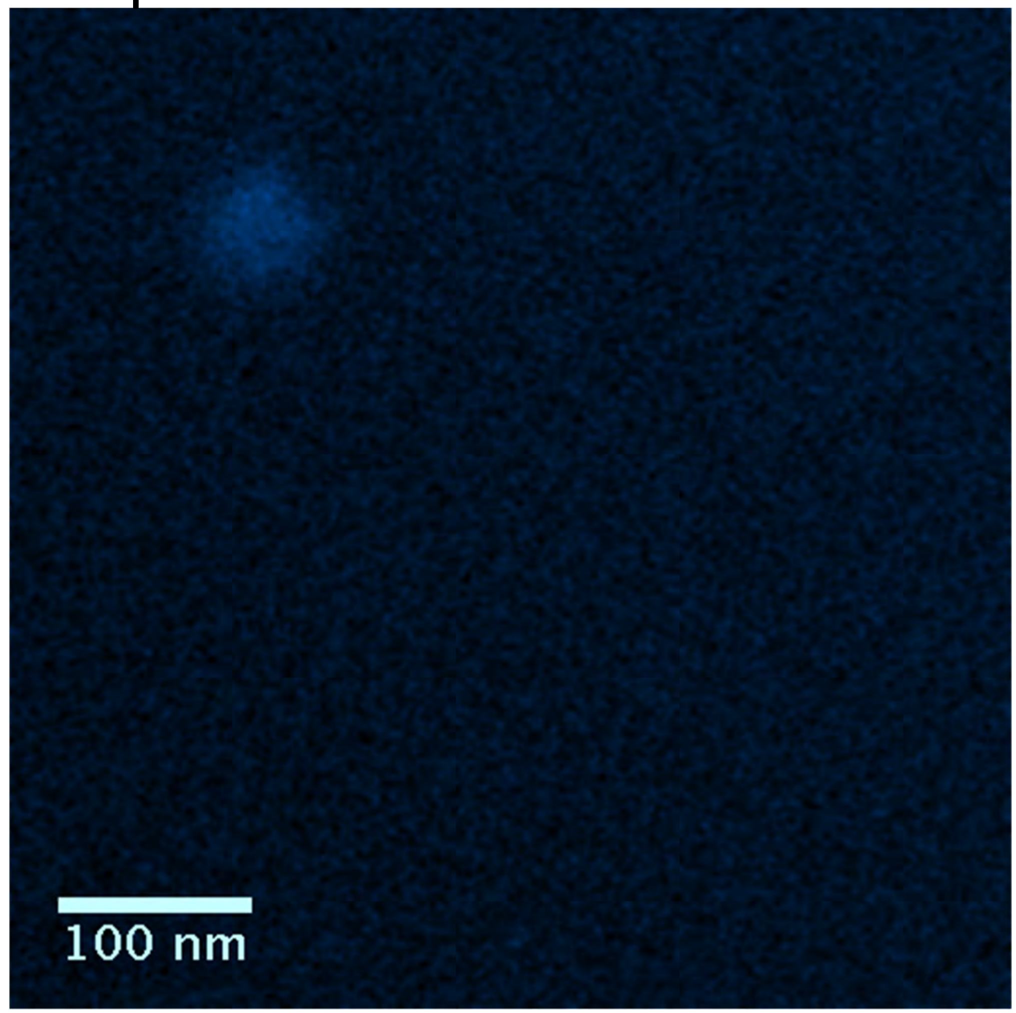
Challenge # 2: Electron Beam Effects

High energy electron beam interacts with the solution.
For water, this causes the production of radicals:



Radiolysis of intracellular water (H_20)

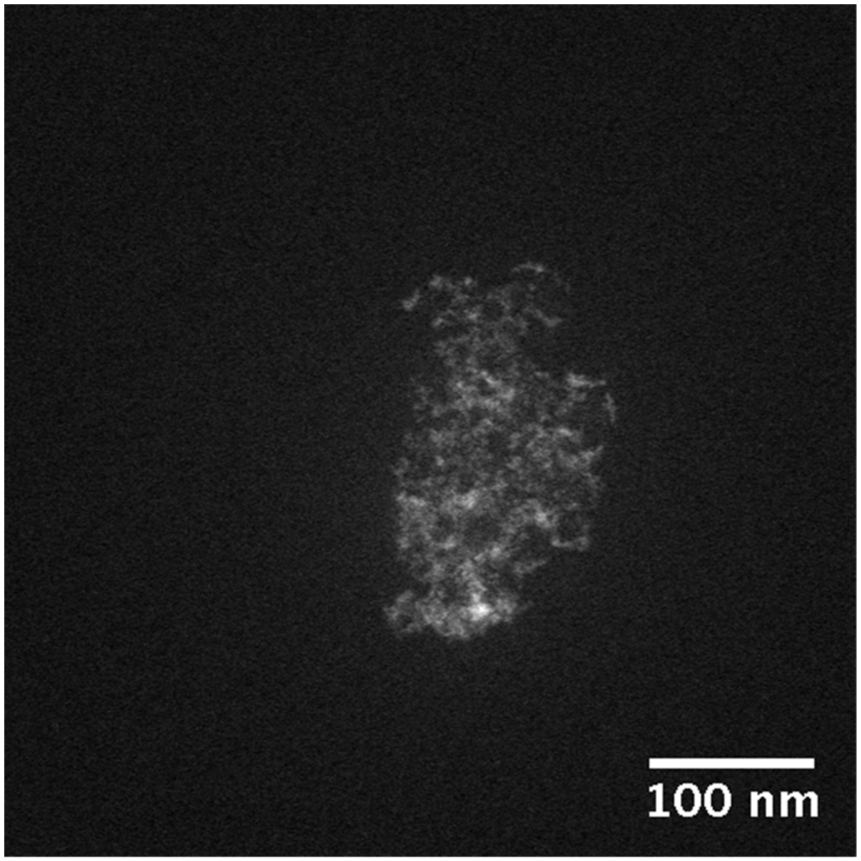
S.M. Carr, “Ionizing Radiation and Life.”2012



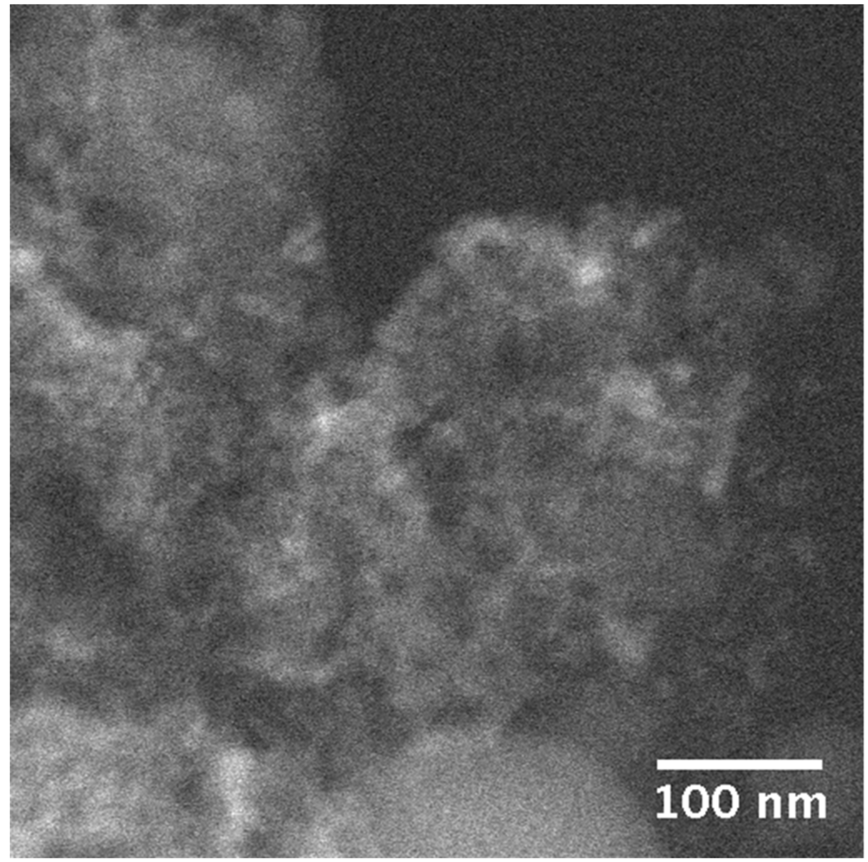
$AgNO_3$ precursor with excess sodium citrate surfactant

Beam damage and pH

0.1 M H_2SO_4



0.1 M NaOH (Pt in **AAEM**)



In base, and especially with an ionomer/membrane, we need low resolution studies!

Overcoming beam interactions

- Lower dose (at cost of signal)
- Short acquisition times or intermittent imaging

- "Low" resolution studies:
  dose ~ resolution^{-2}
  If 100,000 e-/nm^2 for 1 Å,
  1000 e-/nm^2 for 1 nm
  10 e-/nm^2 for 10 nm

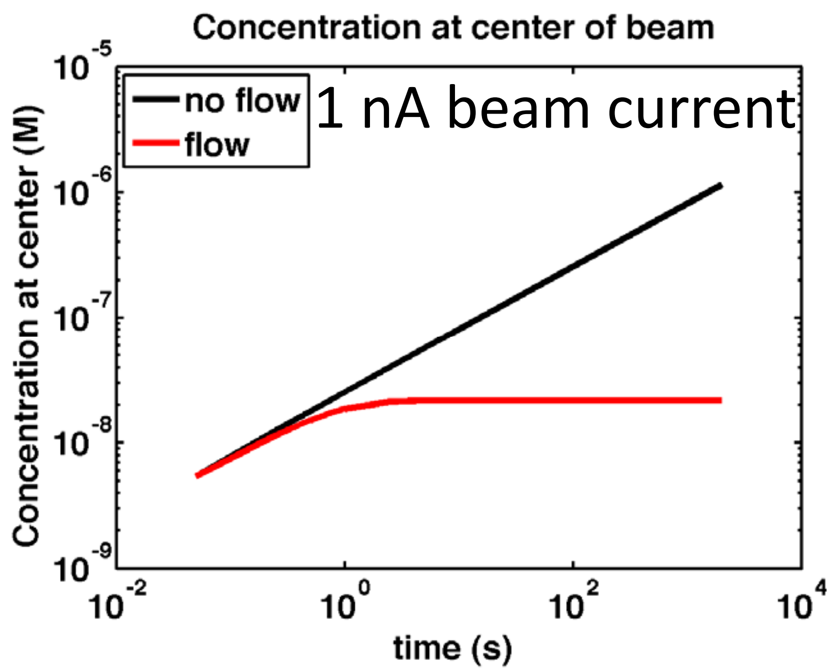
- ***High*** operating voltages:
  2 kinds of damage:
  - Knock on
  - Ionization/radiolysis
    dominating effect!

•Flow solution to prevent accumulation of free radicals

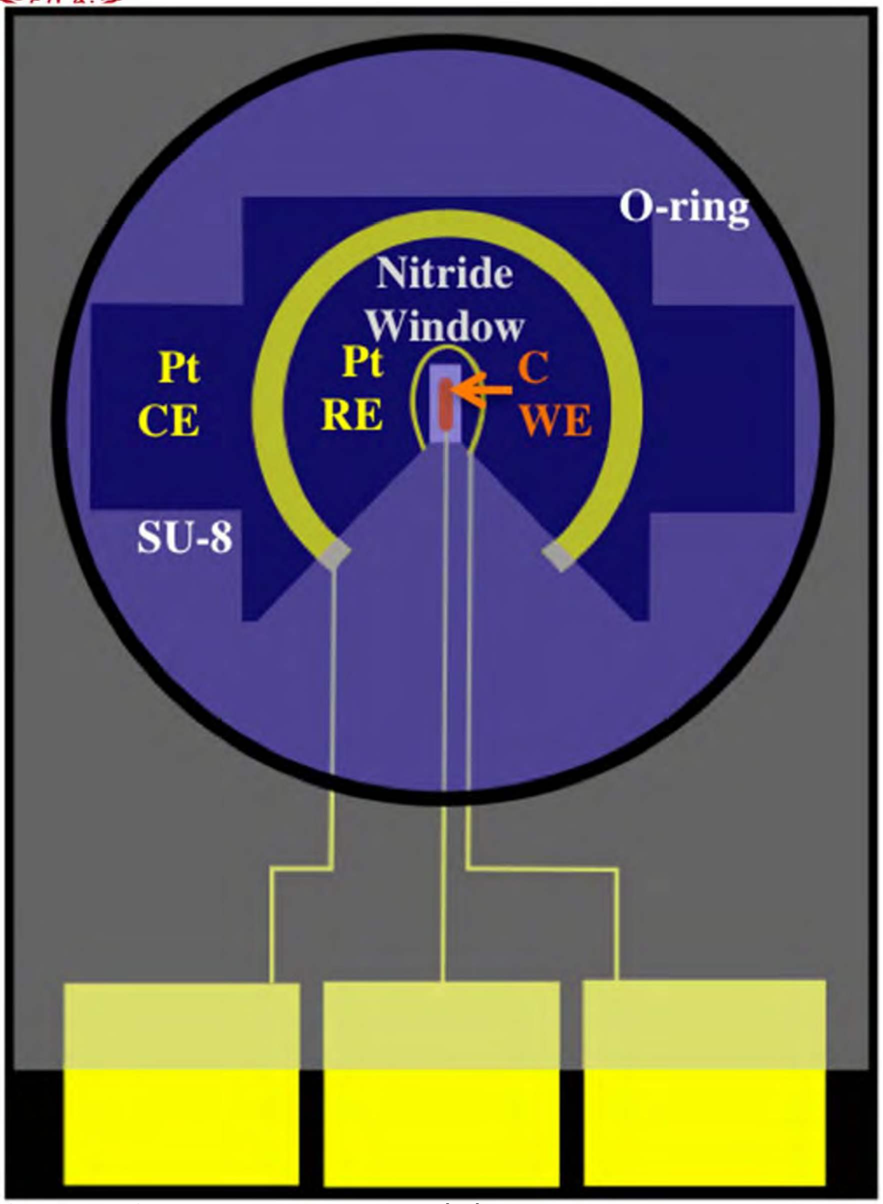
$$\frac{\partial C}{\partial t} = D\nabla^2 C$$

Change in concentration

Diffusion



Electrochemical Cell Chip Design

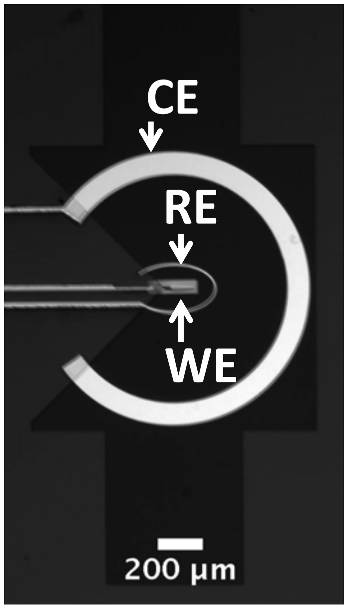


Holtz et. al. NanoLetters. 14(3) 1453 **2014**.

- electrochemistry from the material of interest, not the chip
  - Electrode only on viewing window
  - SU-8 covering contact leads
  - Electrode with minimal features (Carbon, not Au)
- low scattering from working electrode
- Quantitative electrochemistry with 3-electrode configuration
  - Floating potentiostat sensitive to pA current (Gamry)

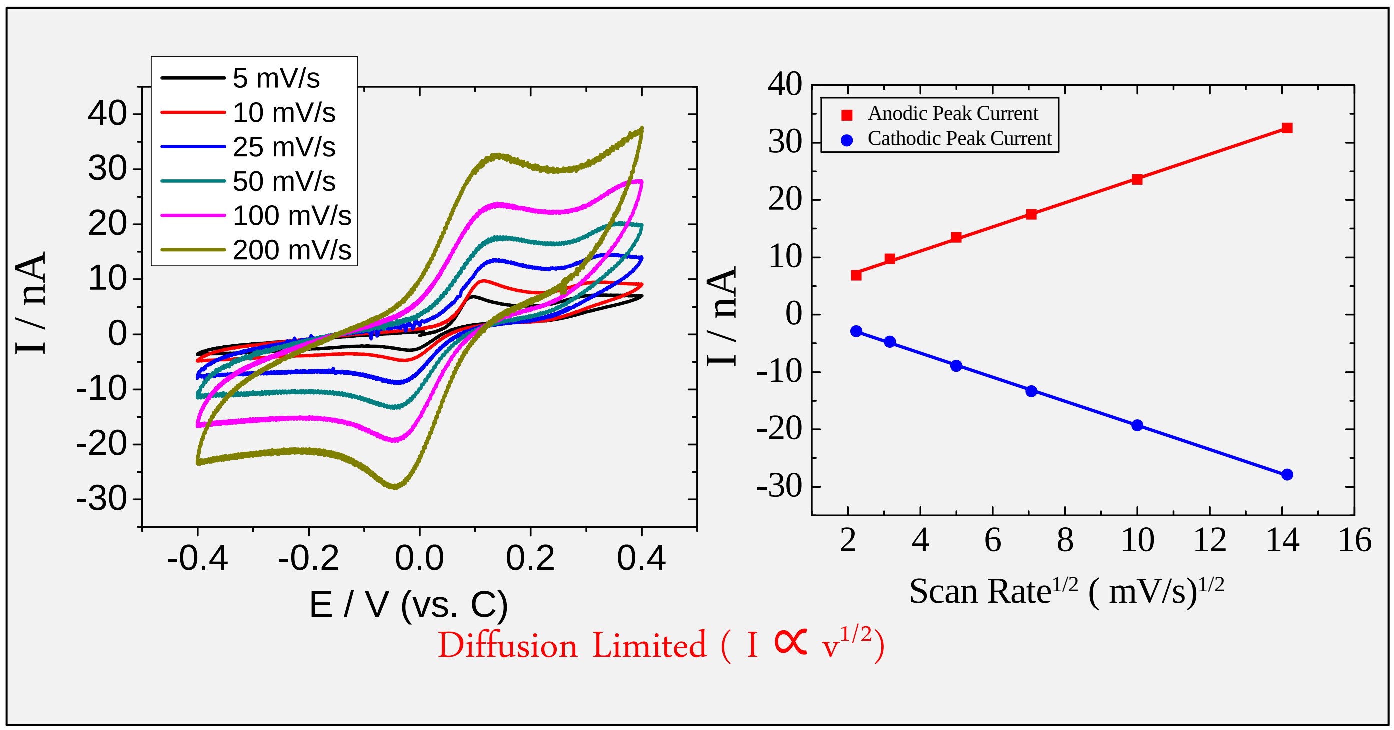
CVs inside TEM with Electron Beam on

2 mM ferrocenemethanol in 0.2M Phosphate Buffer



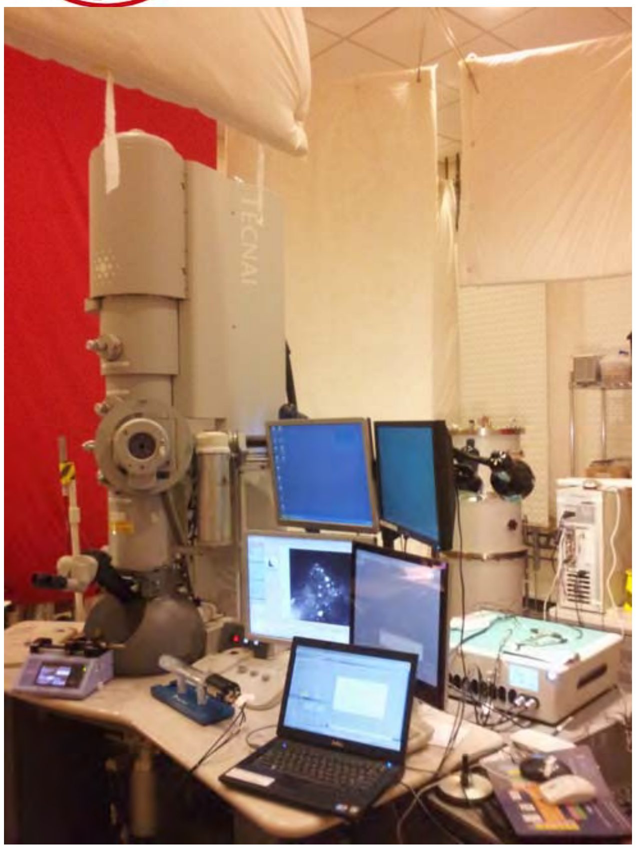
Use Pt Wire as WE

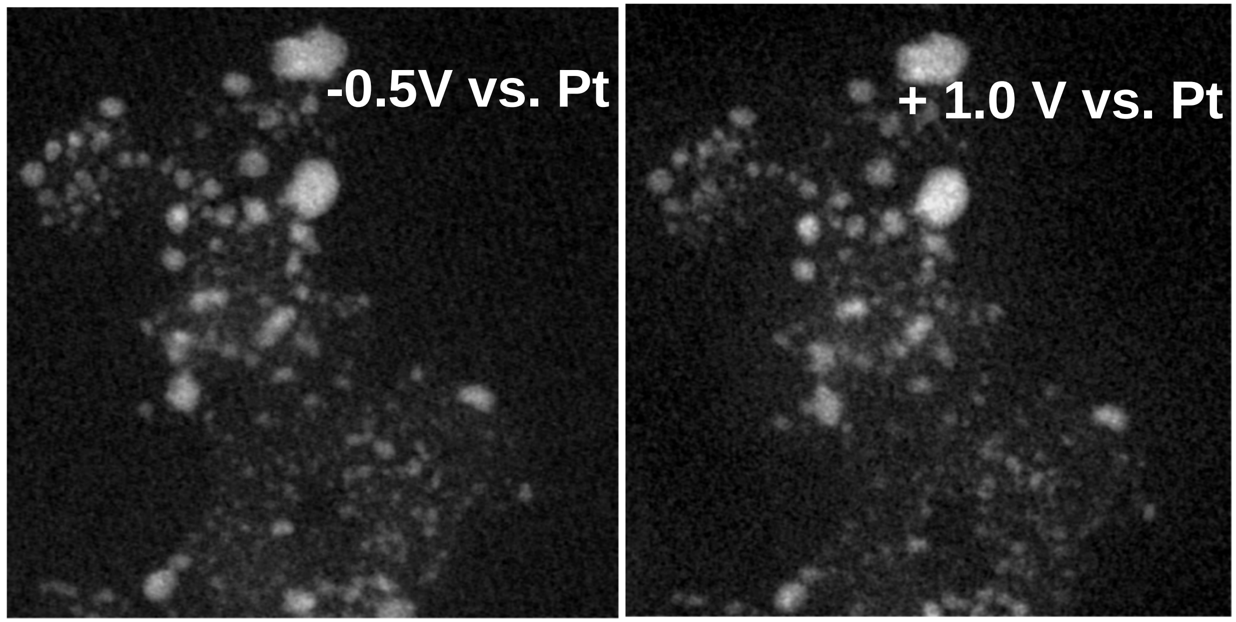
2 mM FcMeOH
0.2 M PSB



Similar electrochemical behavior to a standard microelectrode!

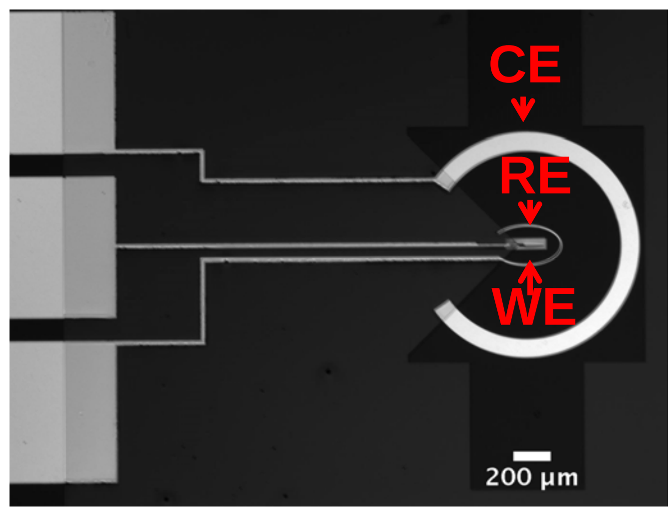
In-situ Electrochemical Cycling of Fuel Cell Catalysts



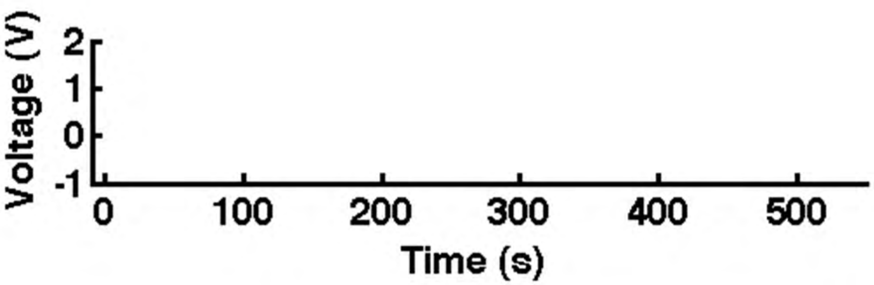


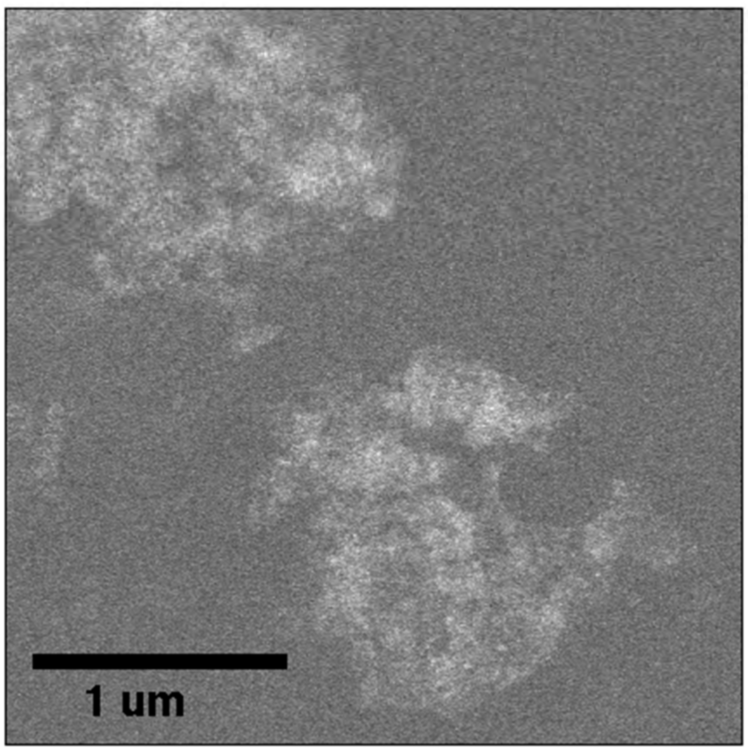
Pt_3Co/C in 0.1 M Perchlorate Acid

In-situ Electrochemical Holder

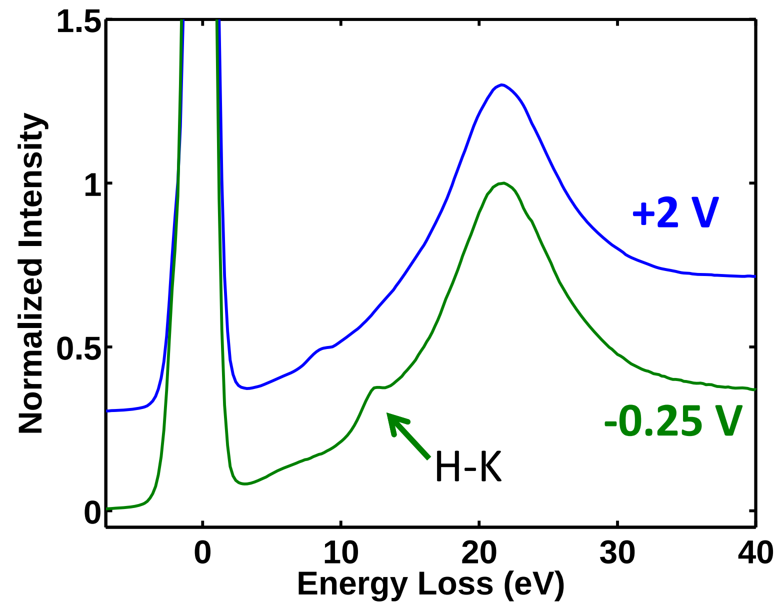


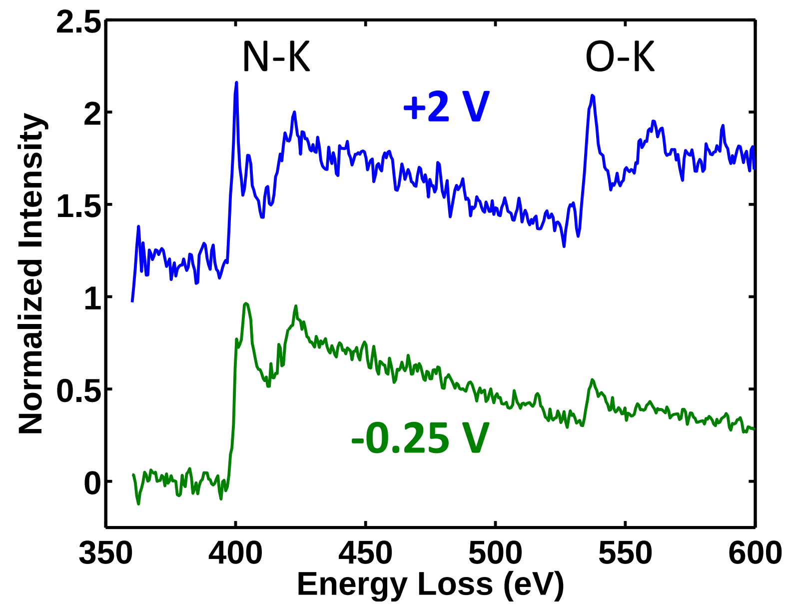
Generating H_2 and O_2 bubbles in the TEM



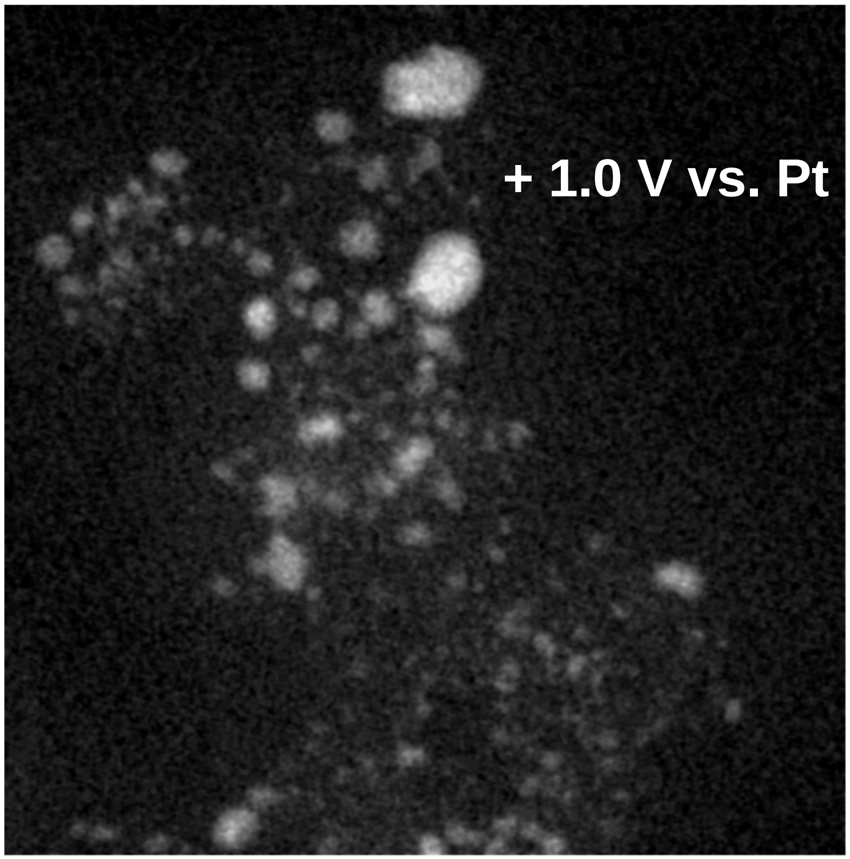


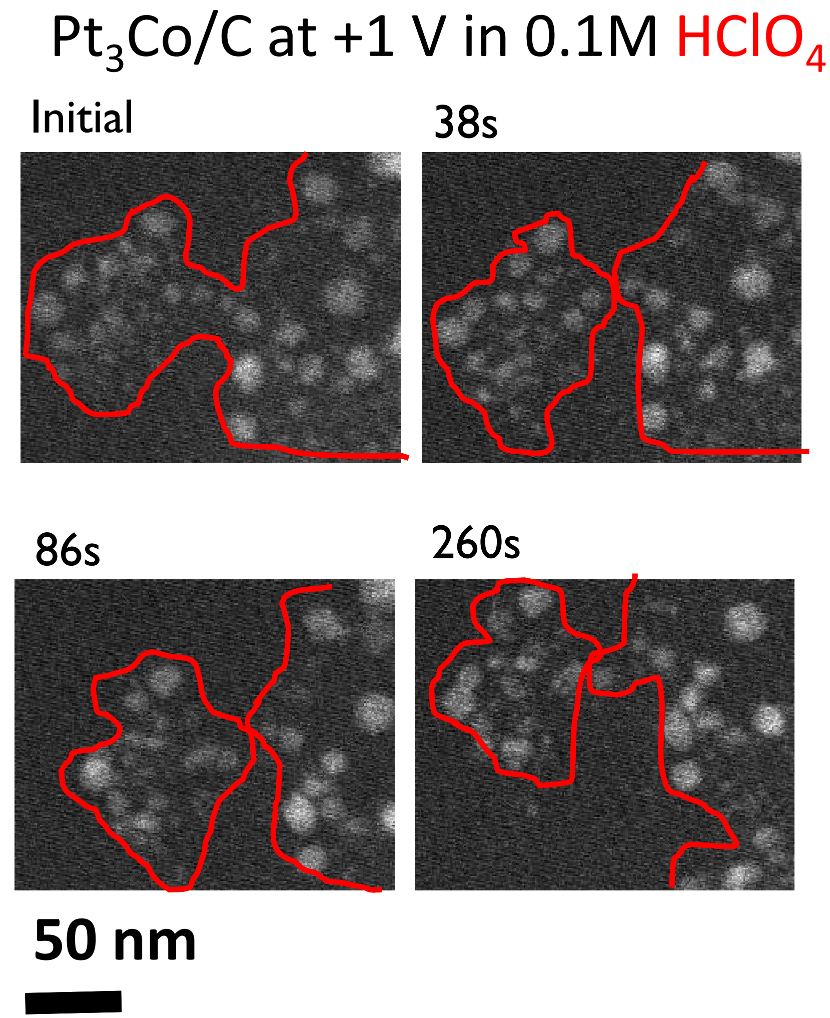
Not driven by radiation damage!
Driven by electrochemistry!





Fuel Cell Electrochemistry in the TEM

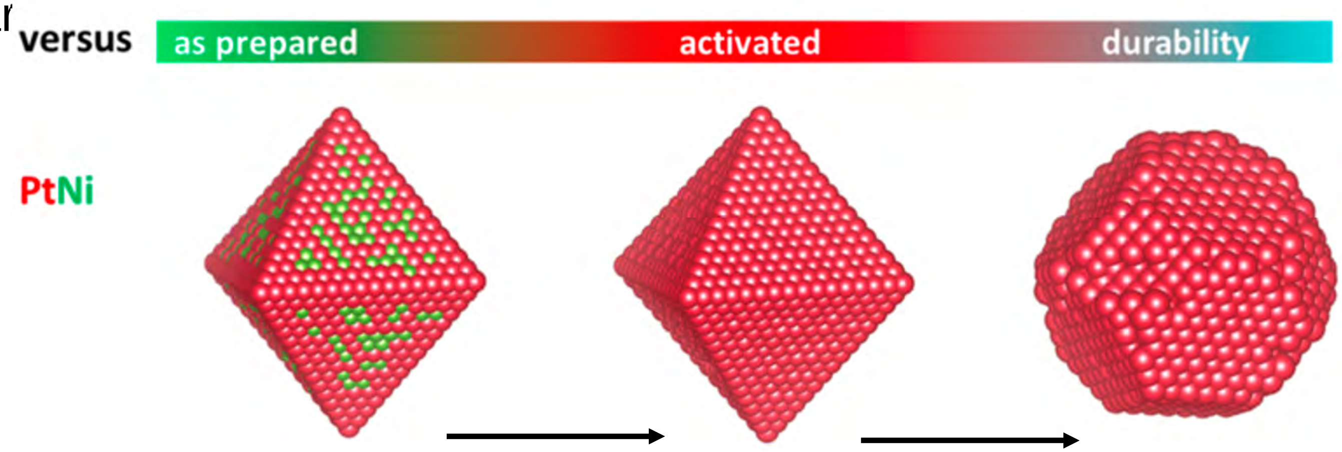




Cycling +0.5 V to +1.2 V at 500 mV/s for 220 cycles

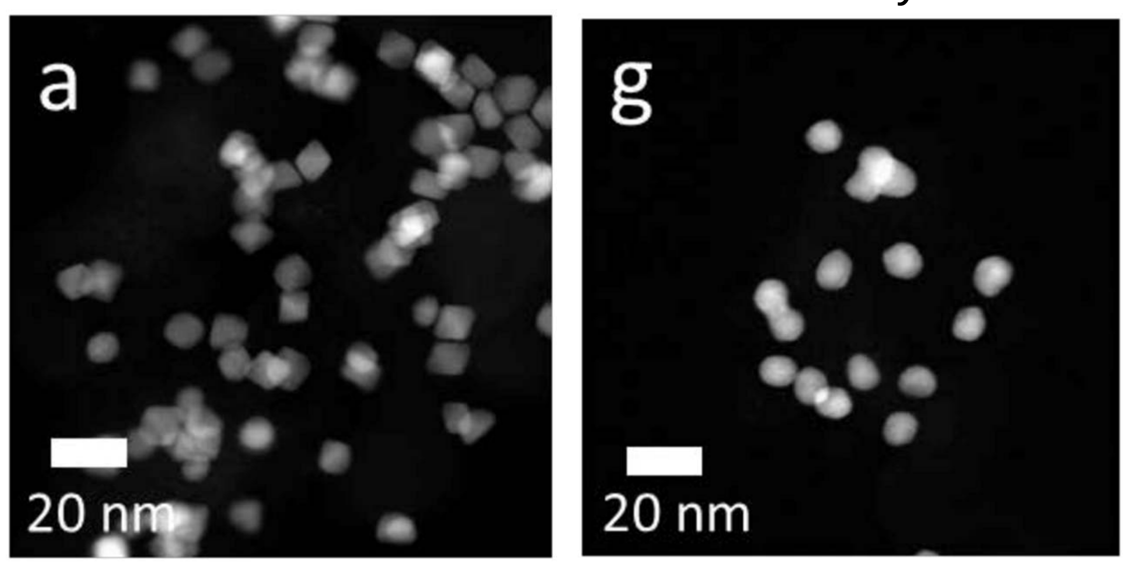
Highly active fuel cell catalyst: PtNi

Activity of Pt-Ni surfaces: (111) >> (110) > (100) : want octahedral par



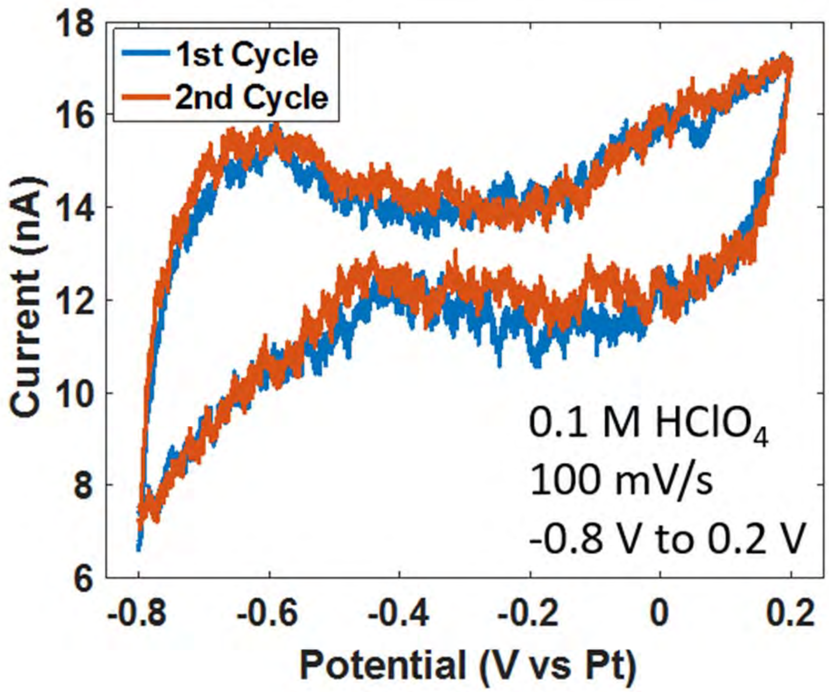
lose Ni on surface lose octahedral shape

initial after 8k cycles

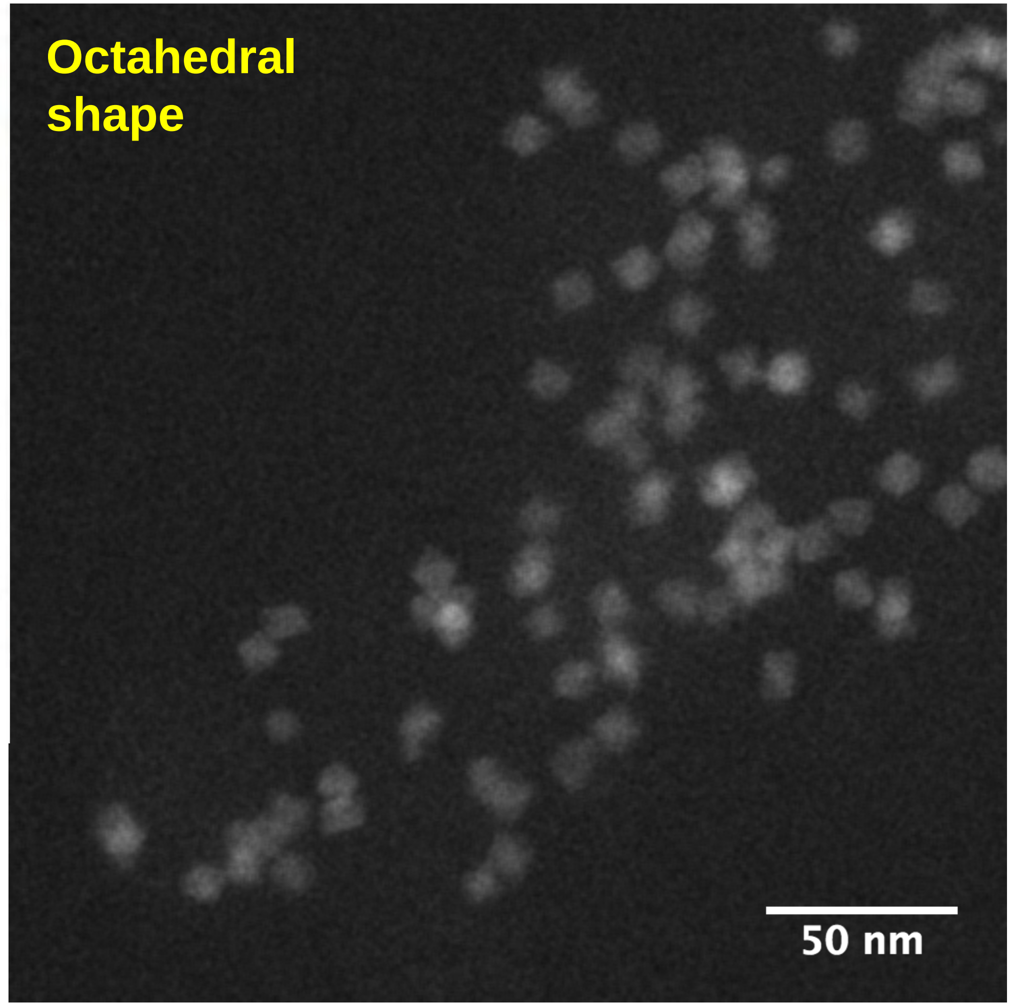


Vera Beermann, et al. NanoLetters, 2016,

PtNi catalyst in electrochemical cell



PtNi octahedra in 250-320 nm 0.1M $HClO_4$

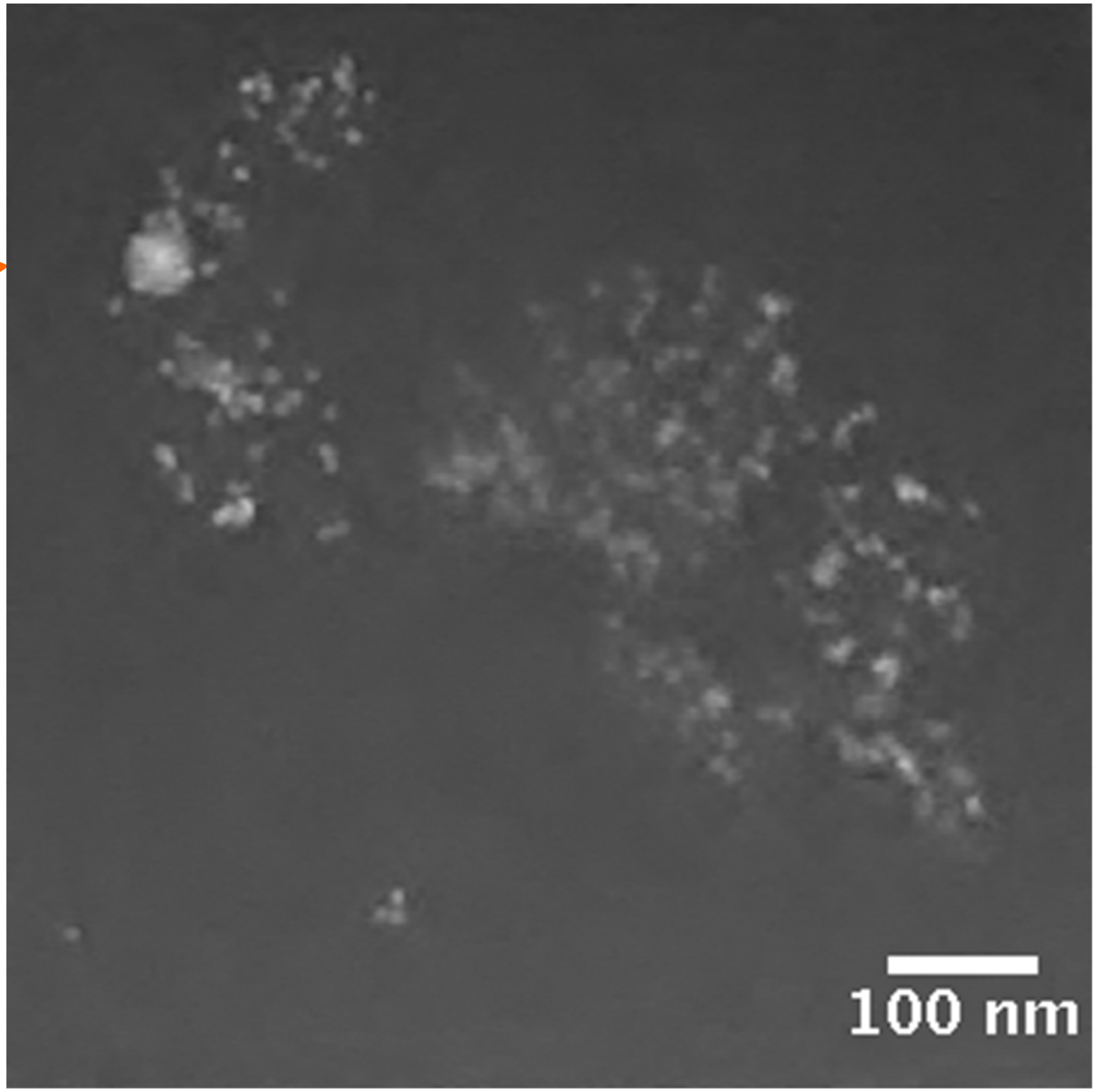


First 20 CV up to 0.2 V vs Pt: Nickel particles disappear while octahedral shape remains

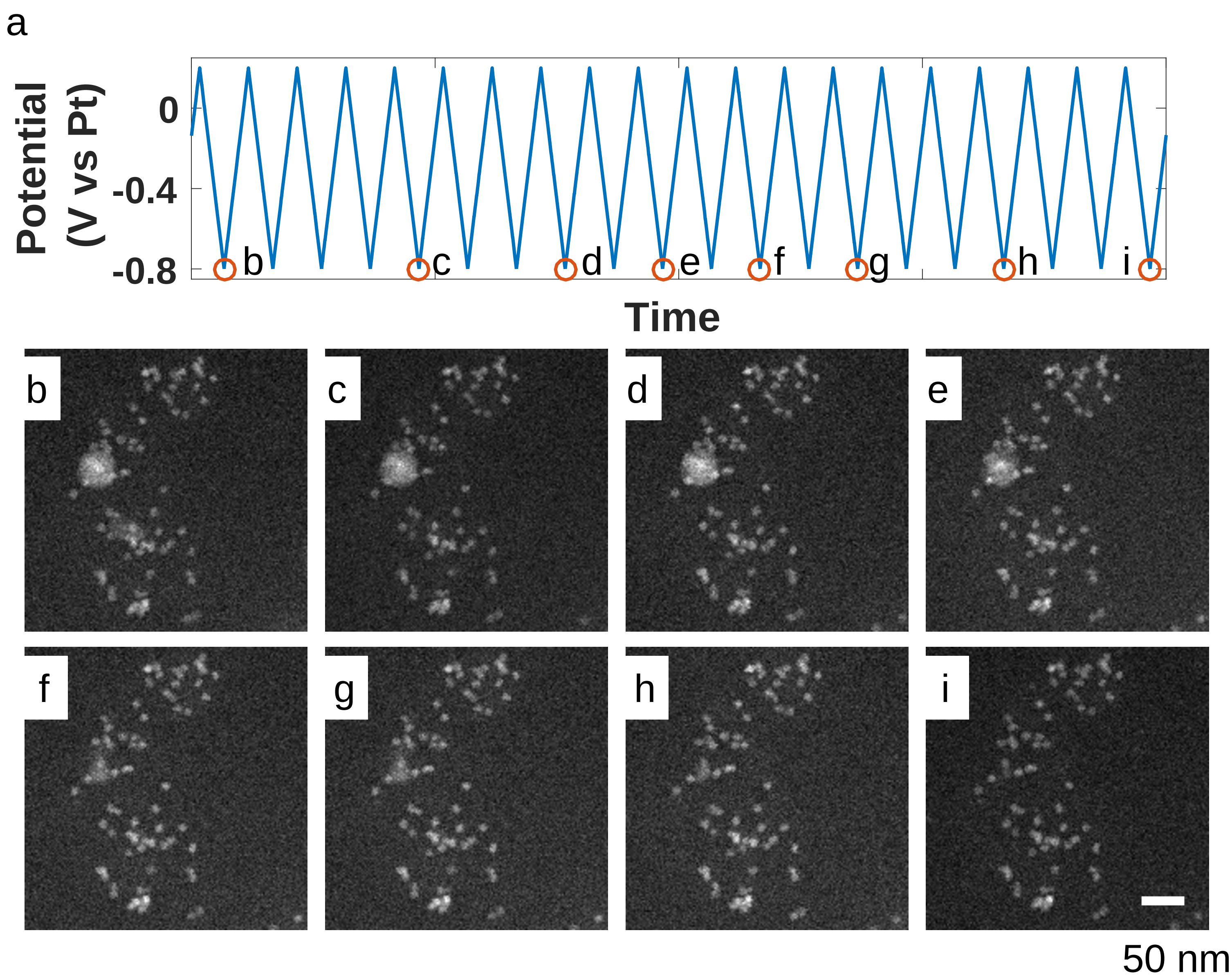
Ni-rich particles disappear during cycling, leaving behind a Pt-rich core.

Ni becomes spongy before disappearing.

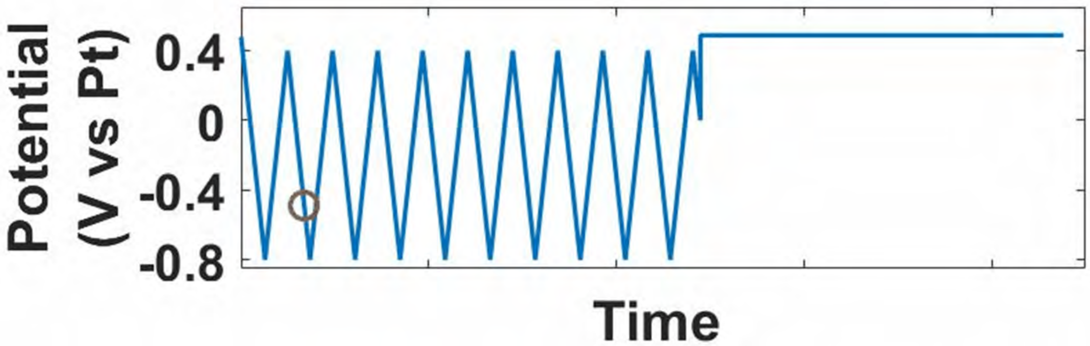
PtNi octahedra are stable during potential cycling from -0.8 V to 0.2 V vs Pt
(0 to 1 V vs RHE)



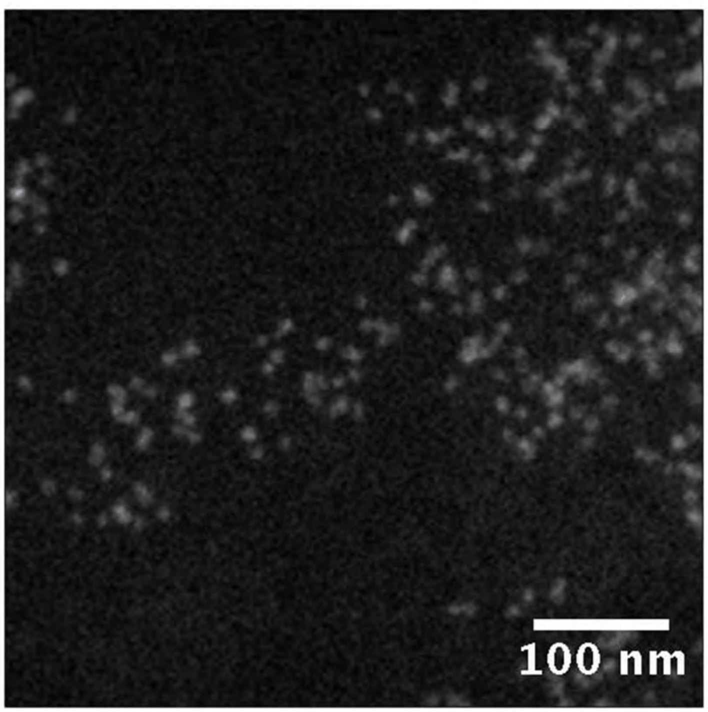
First 20 CV up to 0.2 V vs Pt: Nickel particles disappear while octahedral shape remains

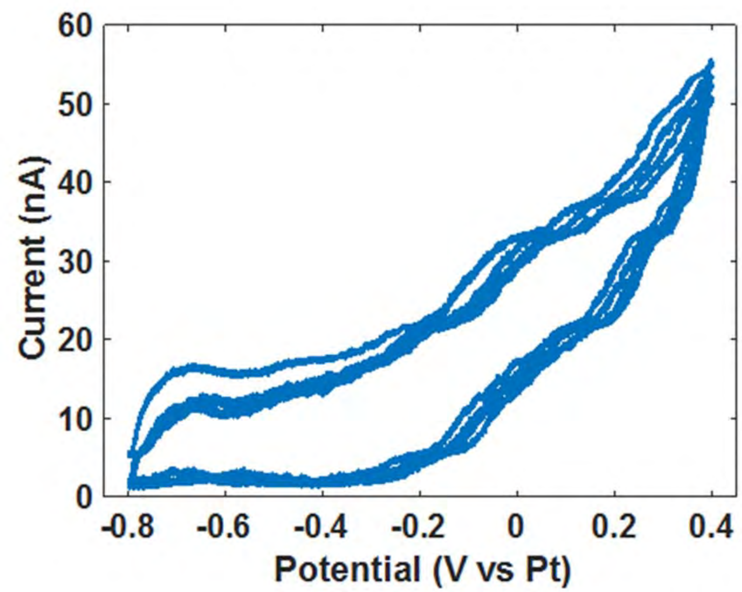


10 CV's from -0.8V to 0.4V vs Pt
Then: high OCV potential (>~0.5V) coalesces PtNi

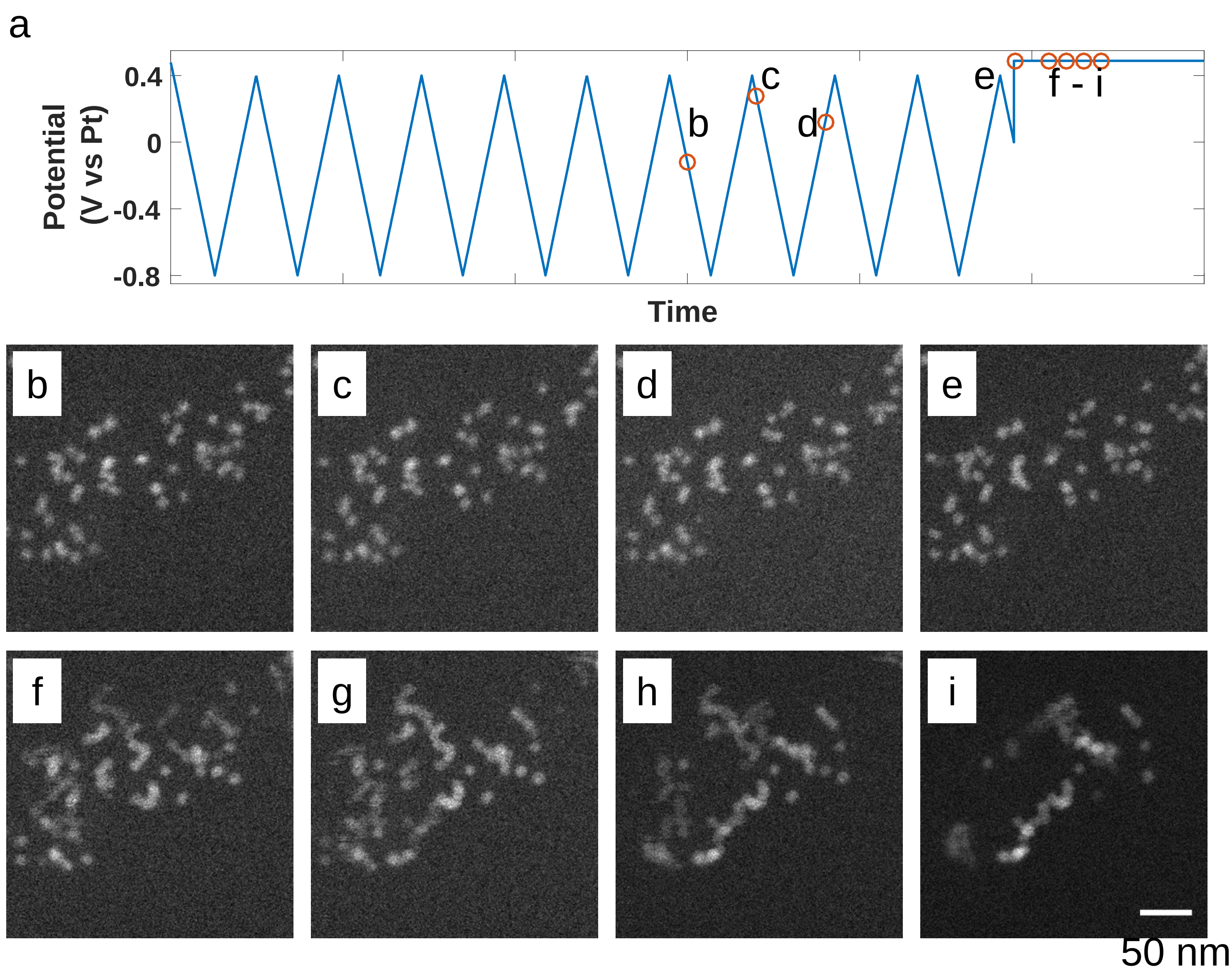


- Control your starting and shut down potentials!
- Cycling to 0.4 starts to soften the facets
- Holding at high potential coalesces particles



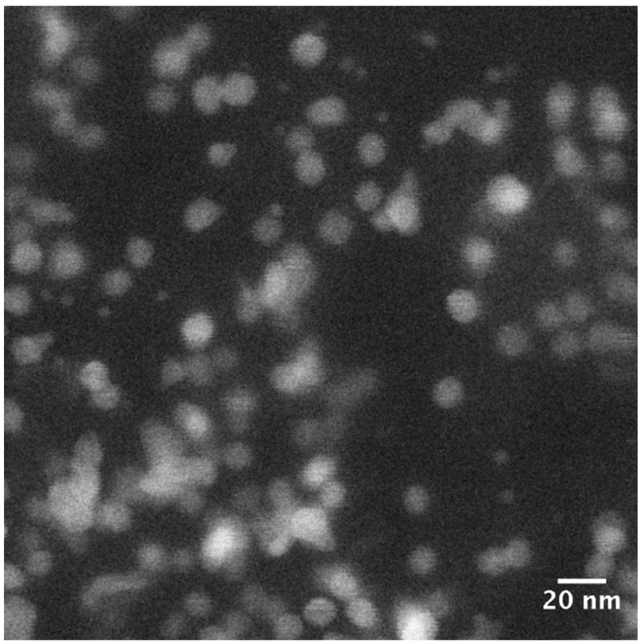


10 CV's from -0.8V to 0.4V vs Pt then: high OCV potential (>~0.5V) coalesces PtNi



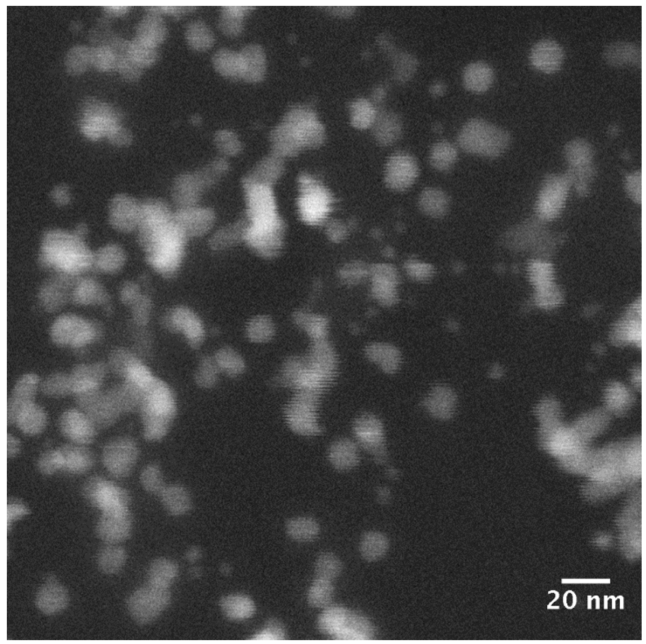
After holding at high potential, particles on the electrode have lost their shape

elsewhere
on the electrode



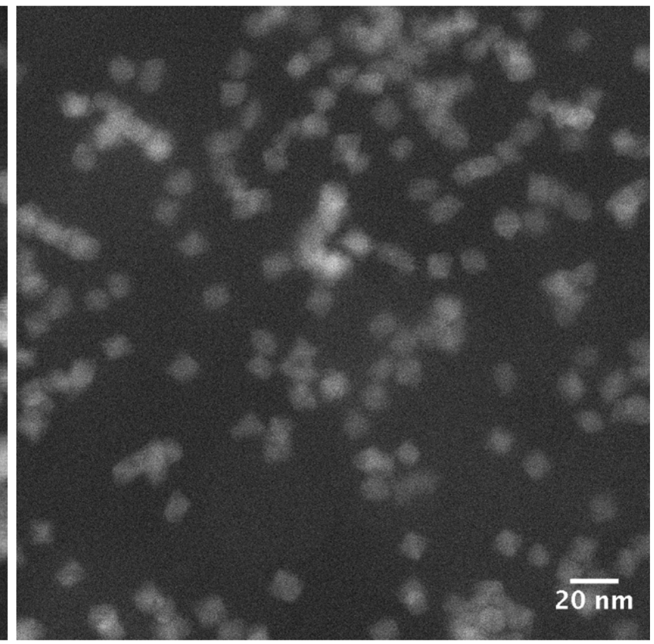
octahedral shape is no longer clear after cycling to higher potential

elsewhere
on the electrode



particles appear larger

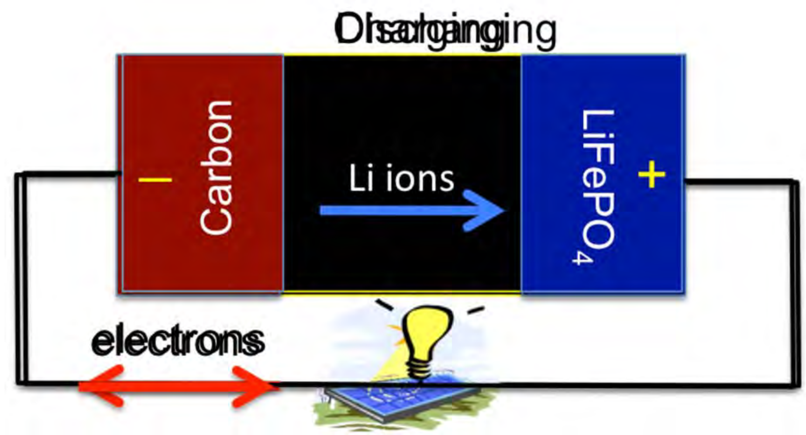
off the electrode

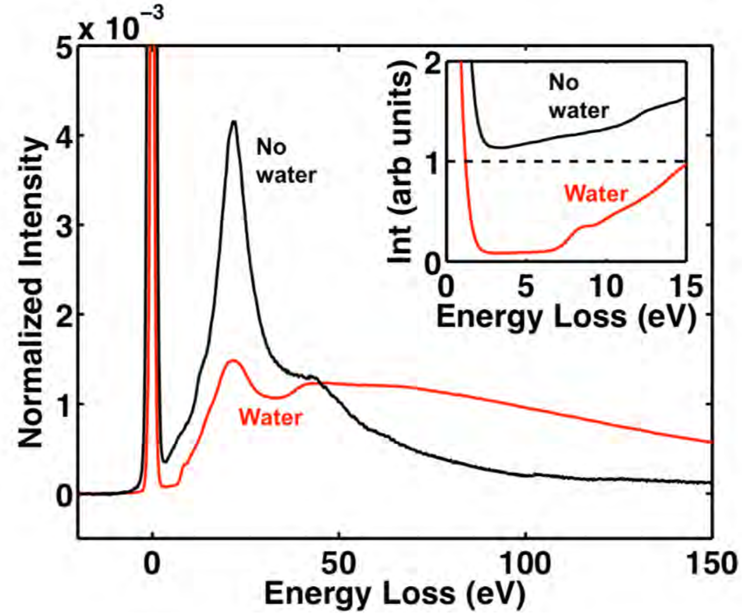


where there was no electrochemistry, the particles retain their octahedral shape

Liquid cell TEM for Li-ion batteries

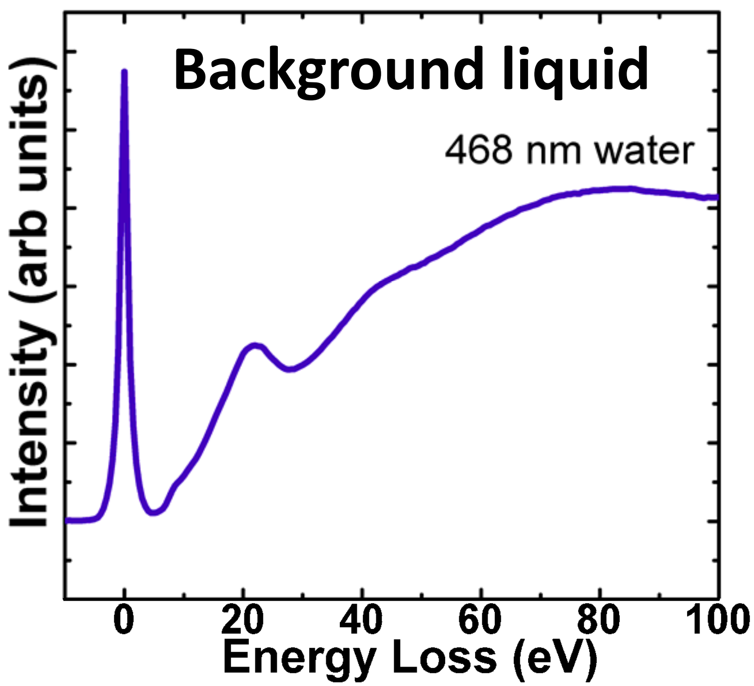
- Li-ion batteries
  - Complex electrochemical system where interfaces are critical
  - Lithiation mechanism often the limiting factor – Li^+ transport in nanoscale materials
  - Inhomogeneous degradation
- Lithium is a challenging element to observe in the TEM:
  - Li K edge (54 eV) is overwhelmed by liquid plasmons

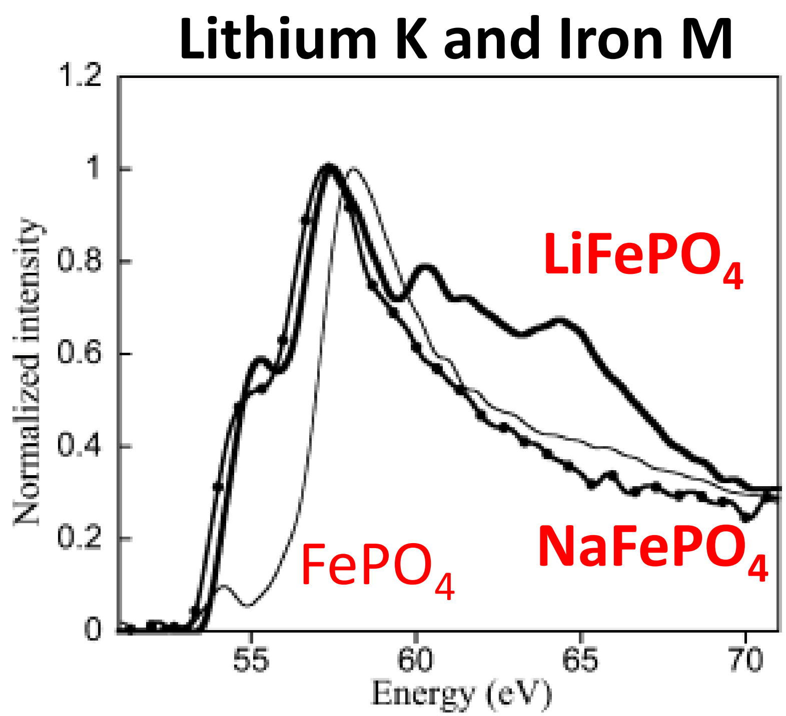




How to track *Lithium*?

- Lithium is a challenging element to observe in the TEM
  - Small elastic cross section (~Z^2)
  - Li invisible by x-ray
  - Li K edge (54 eV) is overwhelmed by liquid plasmon and overlaps with transition metal M edges

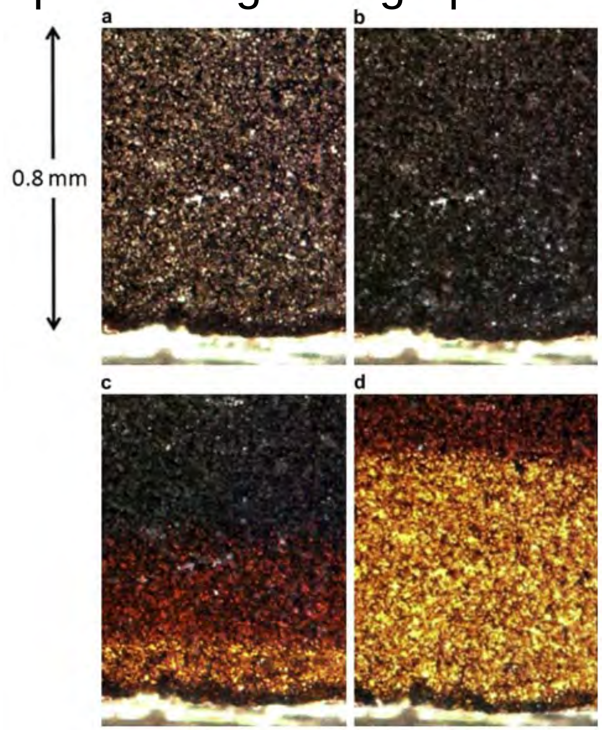




P. Moreau, Micron 43 (2012) 16–21

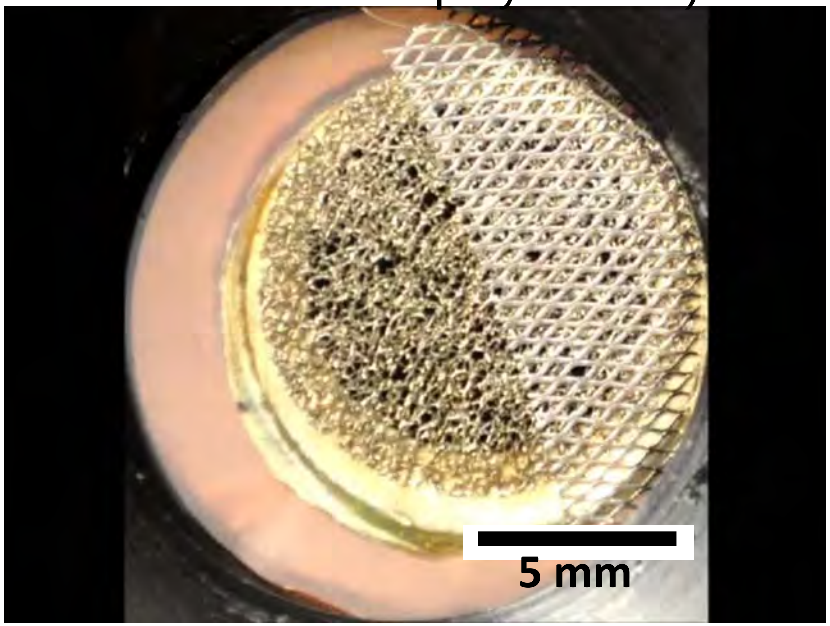
Observing the Lithiation State in *In Operando* Batteries

Optical images of graphite lithiation



Harris, et al. Chem. Phys. Lett. (2010)

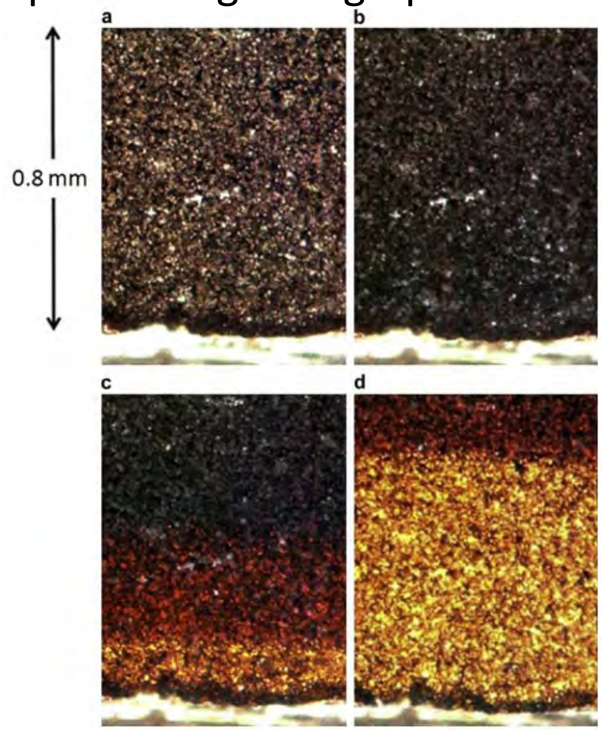
Color changes in Li-Sulfur
(Red = Long-chain polysulfides
Green = Shorter polysulfides)



- Chemists rely on color changes: (dis)charging changes the electronic structure (few eV) = optical transition
- Valence EELS probes the unoccupied DOS = we can observe these electronic structure changes

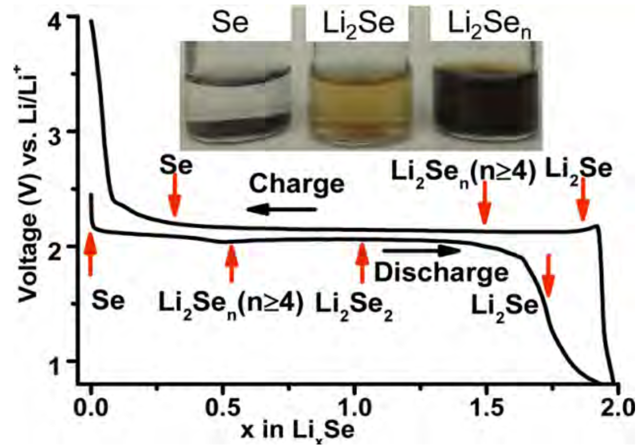
Observing the Lithiation State in *In Operando* Batteries

Optical images of graphite lithiation



Steve J. Harris, et al. Chem. Phys. Lett. (2010)

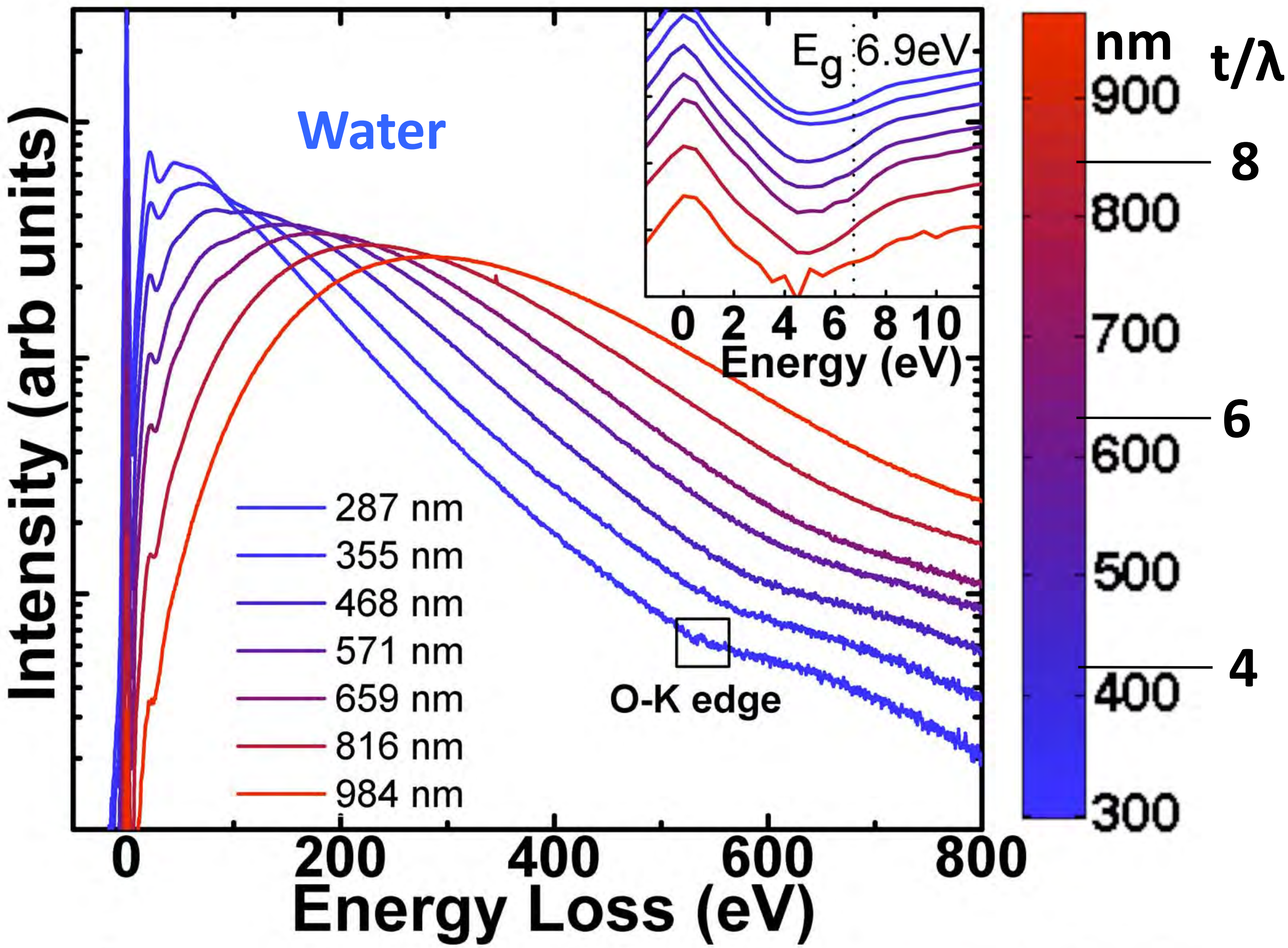
Optical images of Li/Se lithiation



Janjie Cui, et al. J. Am. Chem. Soc. 2013.
DOI: 10.1021/ja402597g

- Electrodes change color: (dis)charging changes the electronic structure (few eV) = optical transition
- Valence EELS probes the unoccupied DOS = we can observe these electronic structure changes

Thickness limitations of core-loss EELS

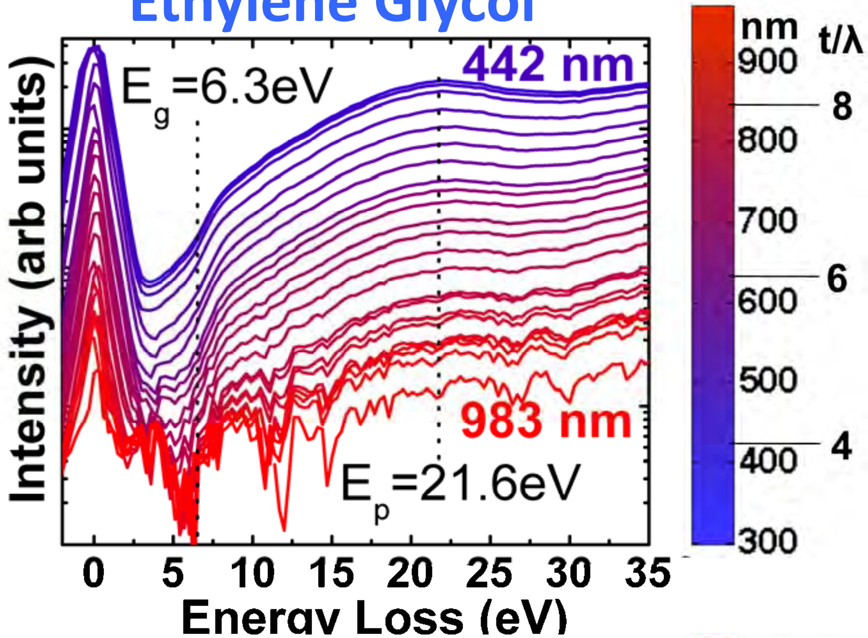


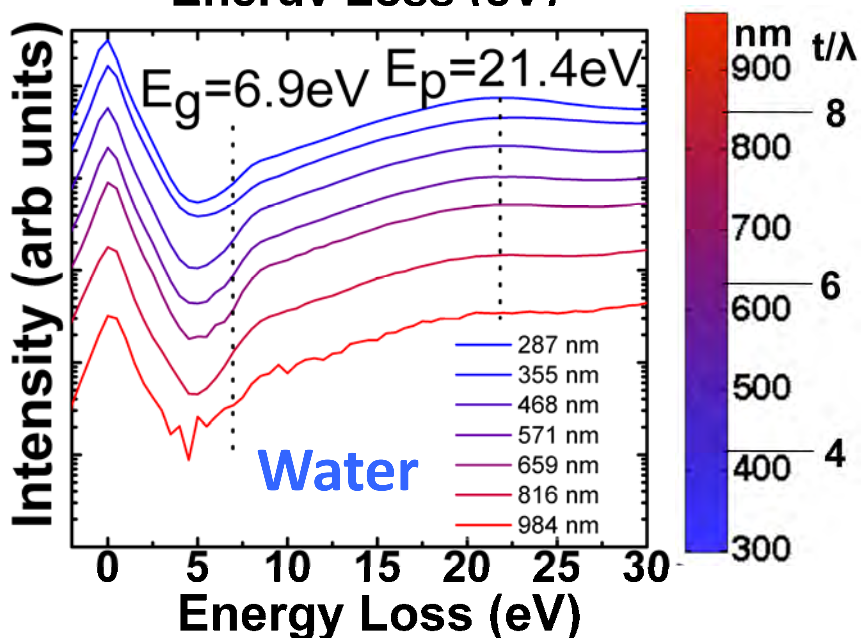
O-K core loss EELS – detectable < 3 λ (~300 nm)

At higher thicknesses the bulk Plasmon overwhelms the signal.

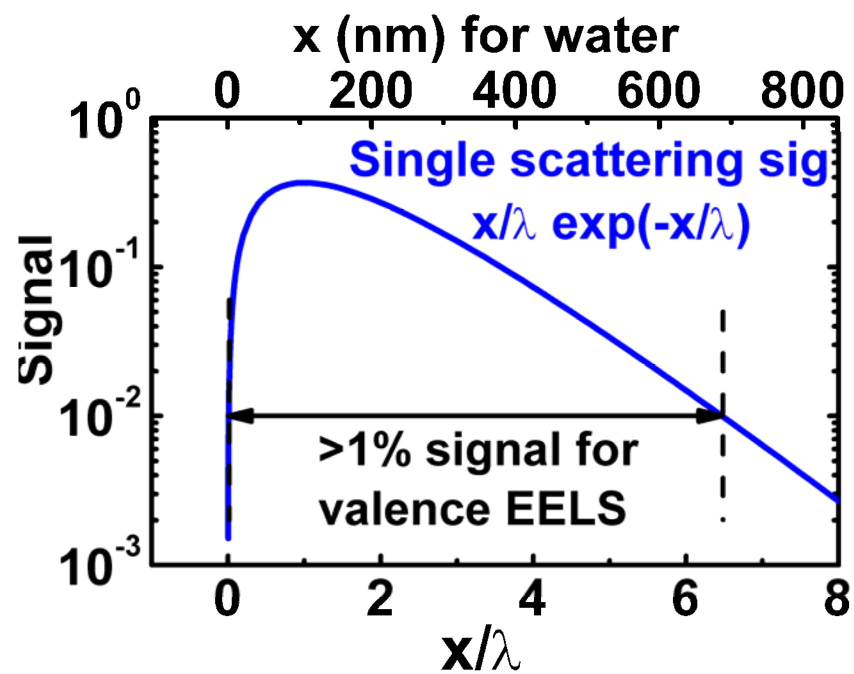
Thickness limitations of valence EELS

Ethylene Glycol





Poisson distribution - single scattering

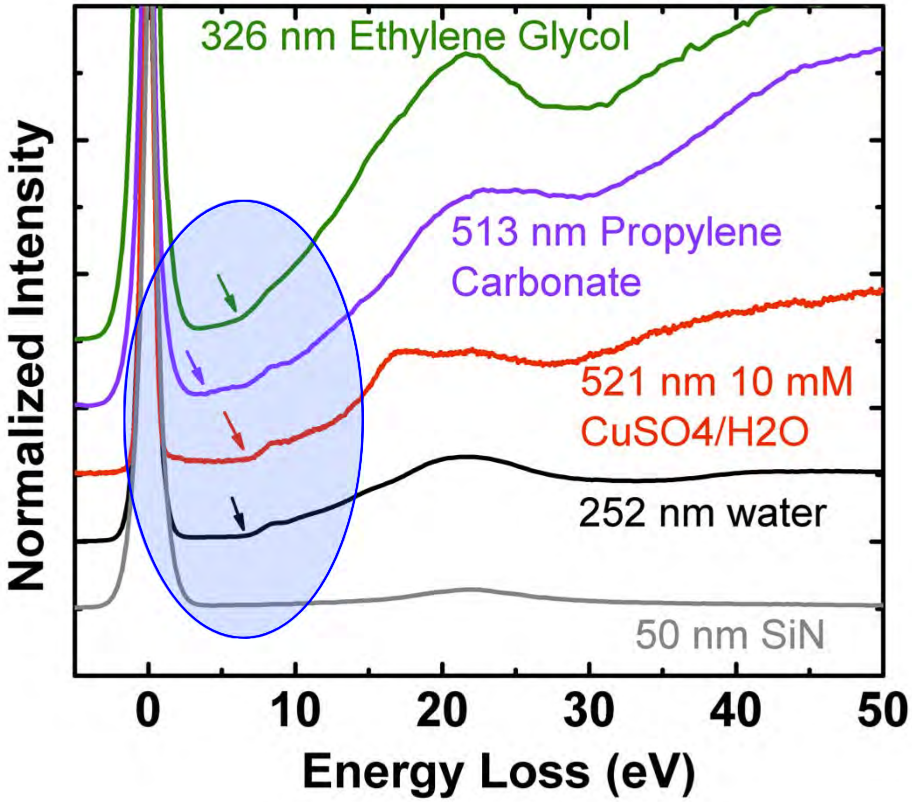


Valence EELS – resolvable < 6.5 λ

There is little lower-energy plural scattering to obscure the signal.

Holtz et. al. Microsc. Microanal. 19, 1-9, 2013.

Valence EELS



Gives information about:

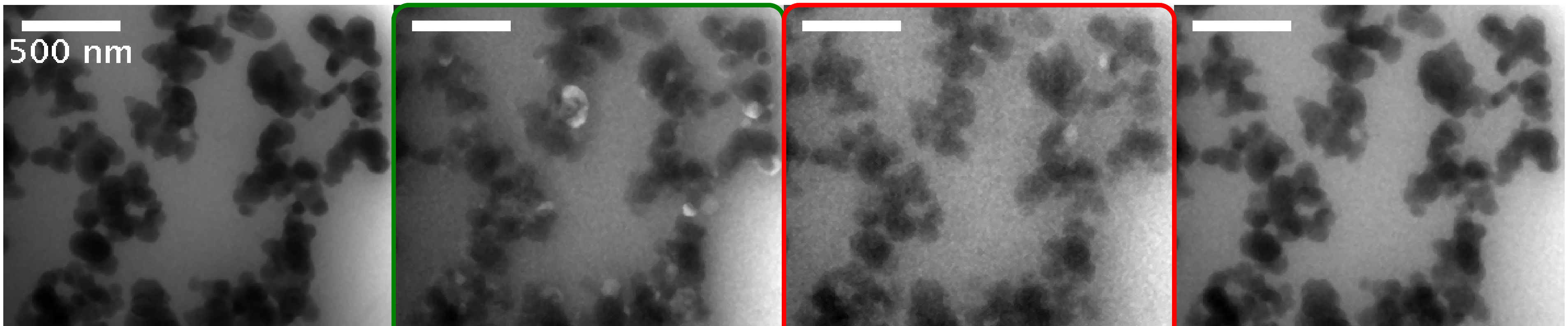
- Optical gap
- Local electron density
- Thickness
- Can see "optical transitions"

Resides at lower energies
➔ less affected by multiple scattering

Liquid	Optical Gap by EELS (eV)	Optical Gap by UV-VIS (eV)	
Water	6.9	6.5*	*from CRC
10mM CuSO4 / Water	5.8	4.1	
Propylene Carbonate	4.2	5.5	
Ethylene Glycol	6.3	6.3	

$LiFePO_4$ in Liquid by Energy Filtered TEM ‘Optical’ Spectroscopy at nm resolution

Chemical (not diffraction) contrast!



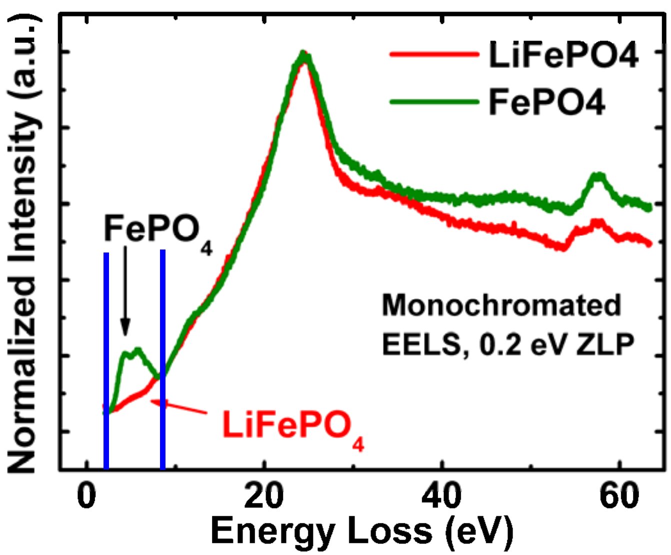
0 eV

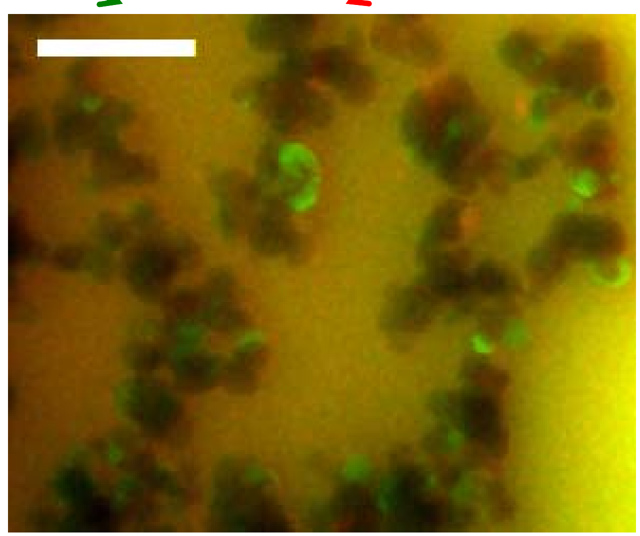
5 eV
$FePO_4$

10 eV

25 eV
Plasmon of liquid

Monochromated EELS, 0.2 eV resolution (DRY)





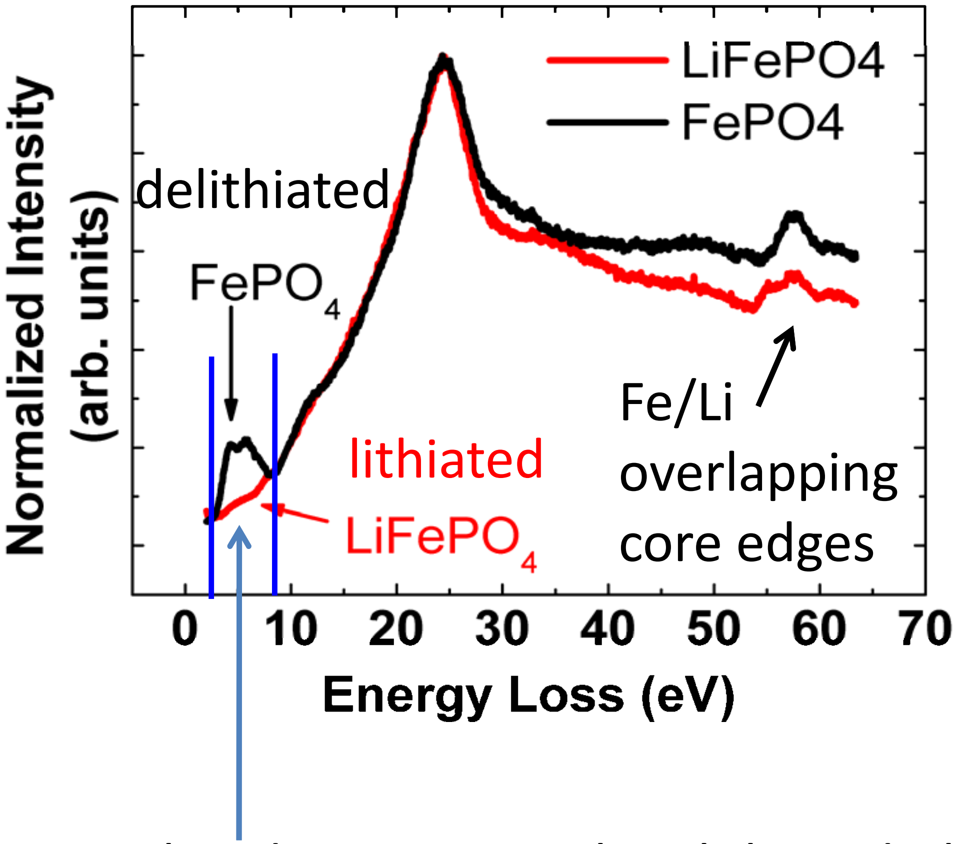
$FePO_4$ region at 5 eV

Interband transition at 10 eV

Holtz et. al. Microsc. Microanal. 19, 1-9, 2013.

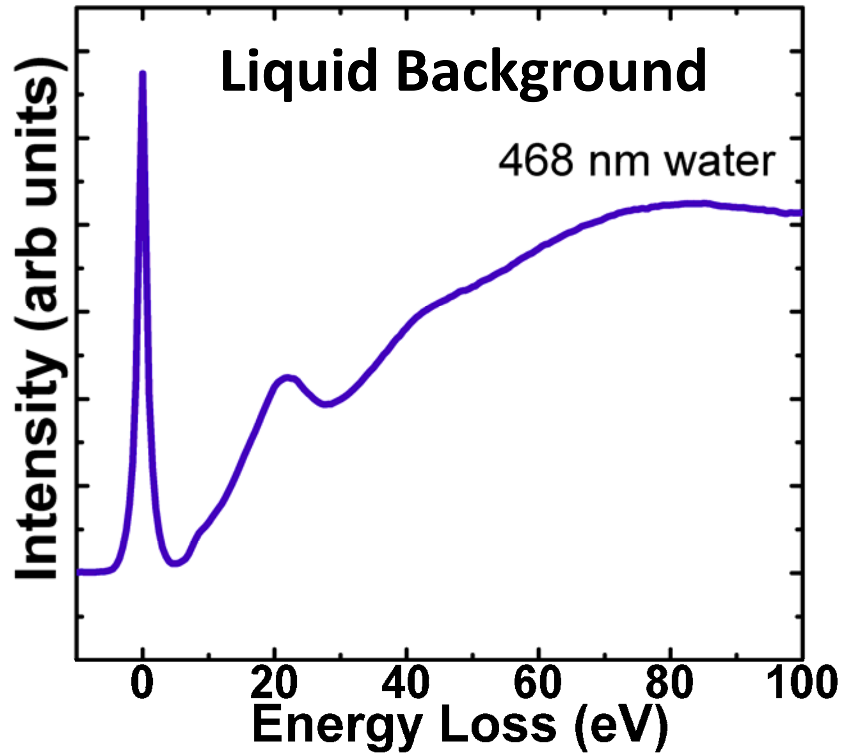
Valence EELS of $LiFePO_4$: a battery cathode

Monochromated EELS, 0.2 eV resolution



Interband transition, when lithiated, the Fe bands are filled & peak disappears

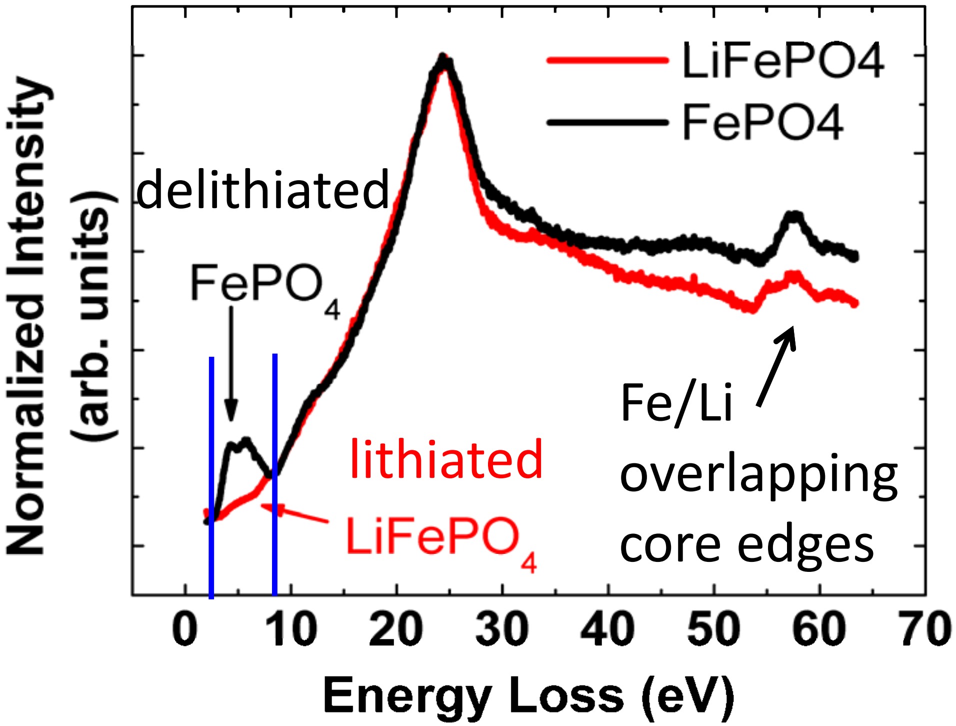
EELS of water



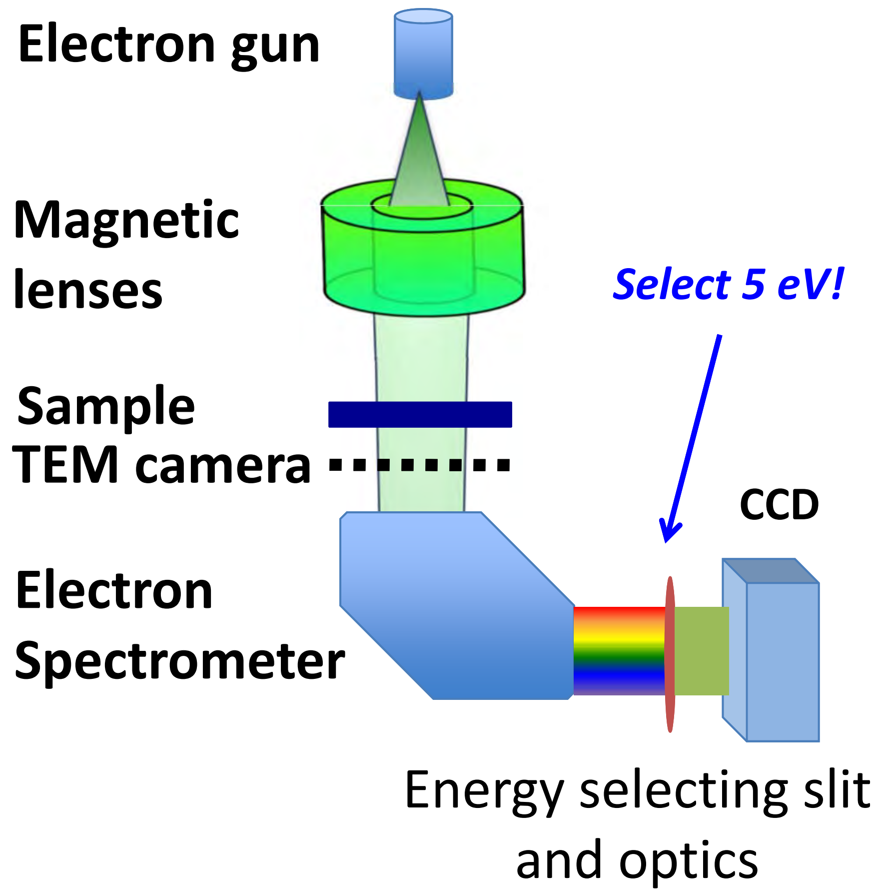
- Best possible signal to background in liquid
- Large cross section for scattering = strong signal

Valence EELS for Batteries

Monochromated EELS, 0.2 eV resolution



Transmission Electron Microscope (TEM)

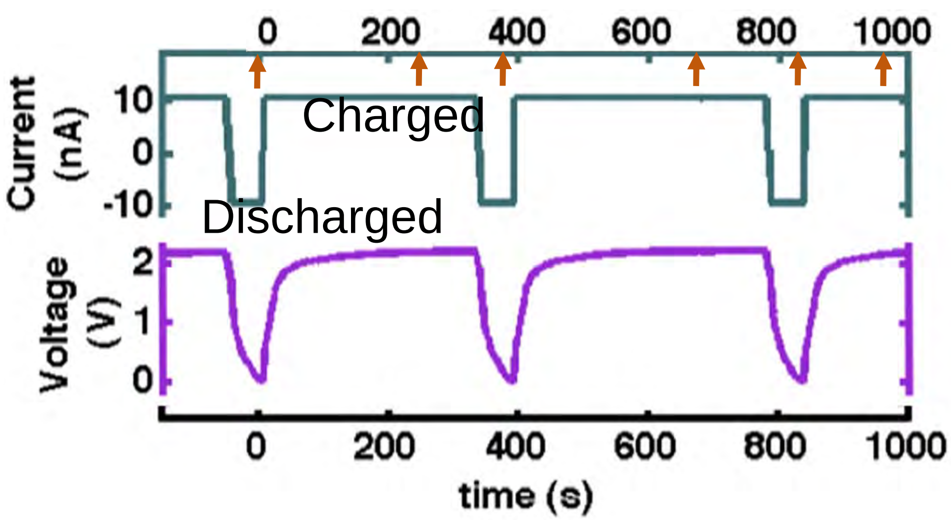


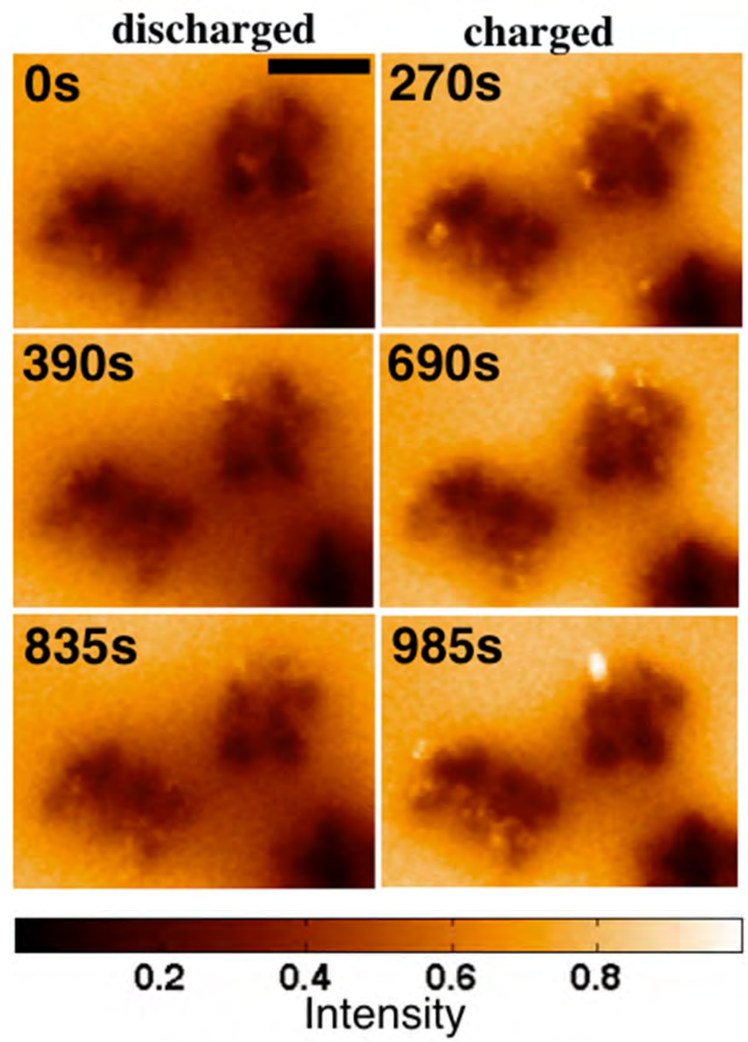
Energy-Filtered TEM (EFTEM)

Want *rapid* spectroscopic images of the 5 eV signal!

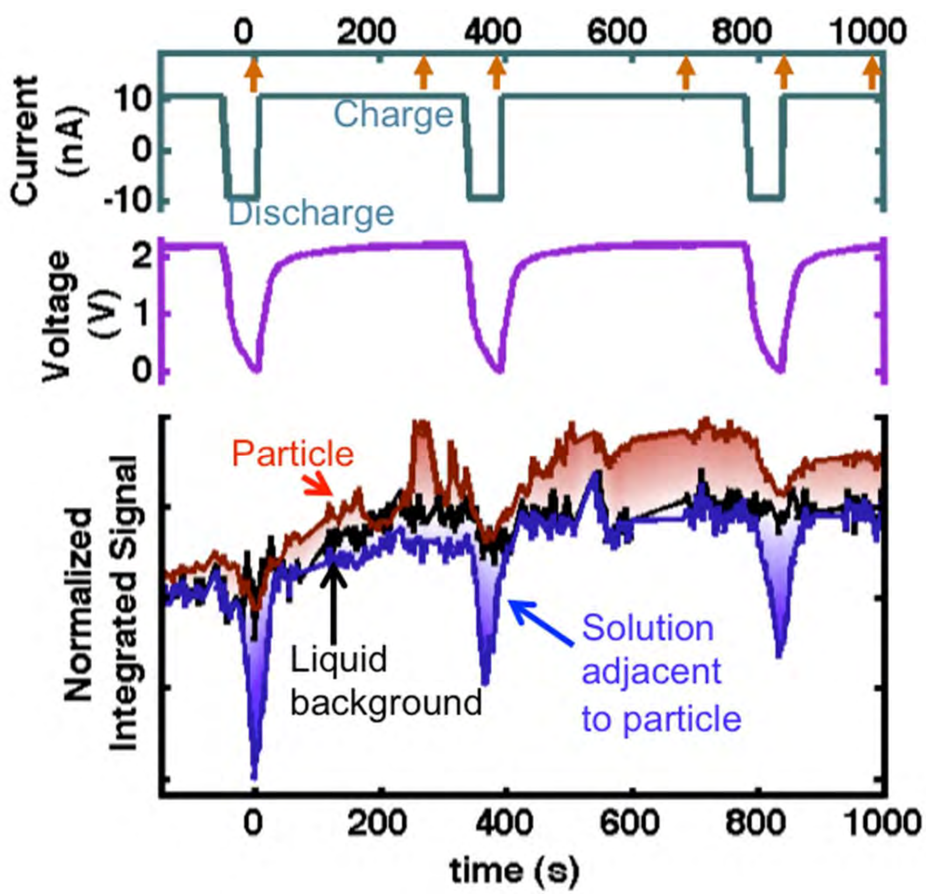
EFTEM imaging!

5 eV Images: Bright = $FePO_4$
Li Concentration Change during Cycling

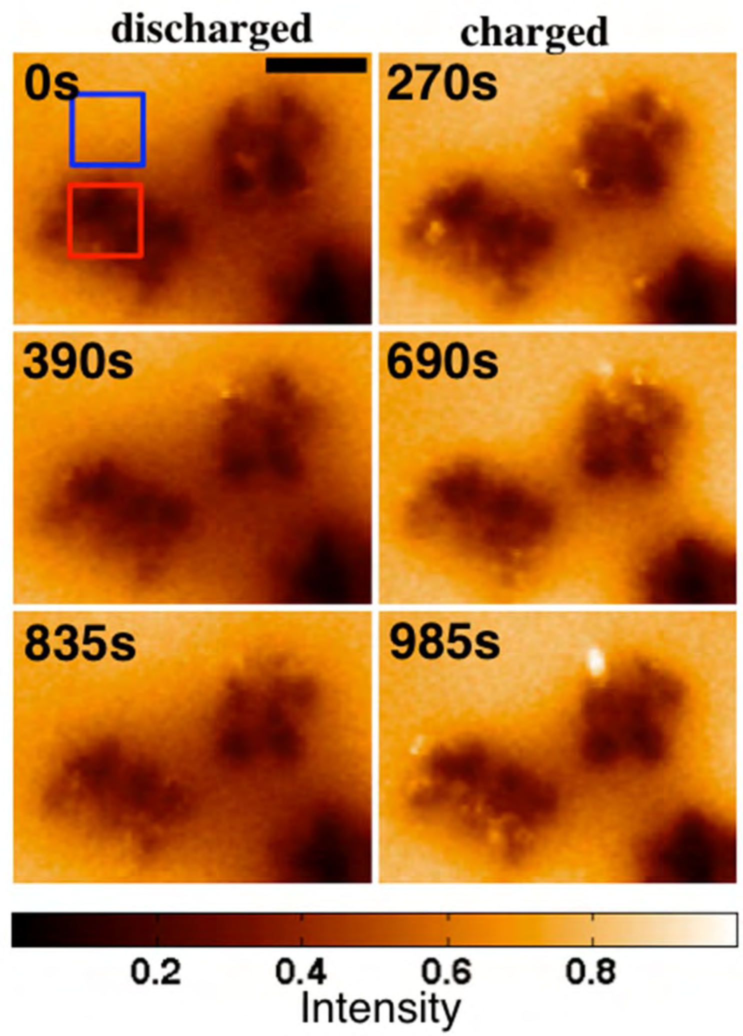




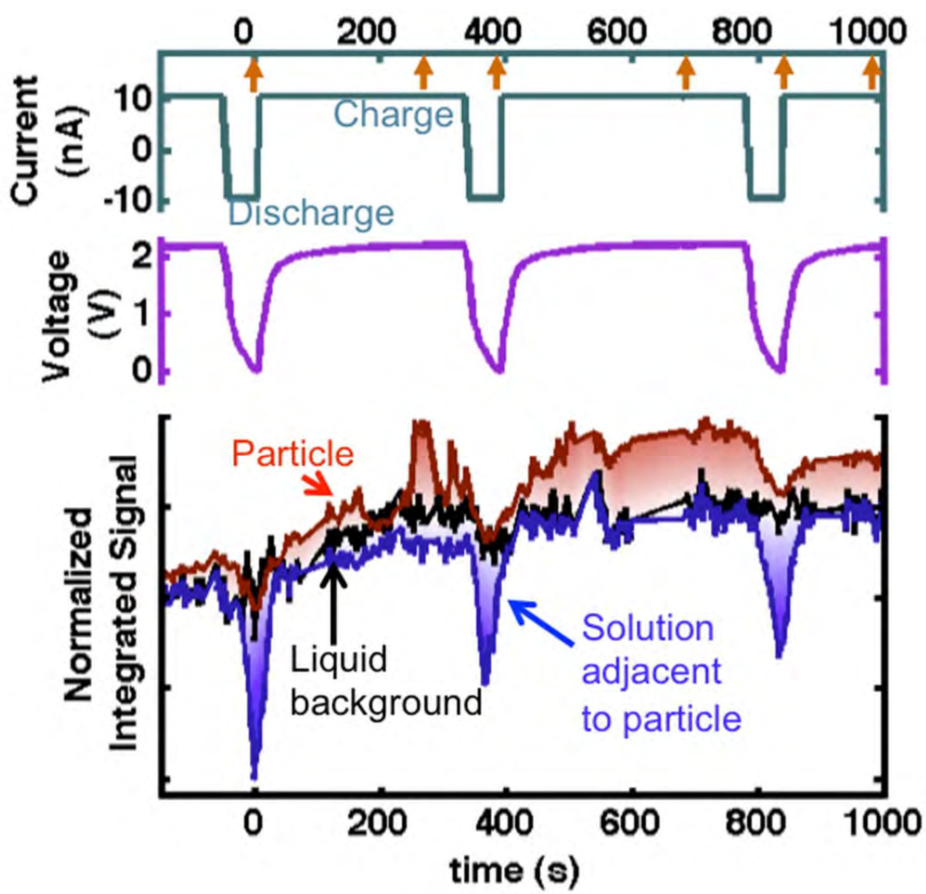
5 eV Images: Bright = $FePO_4$
Li Concentration Change during Cycling



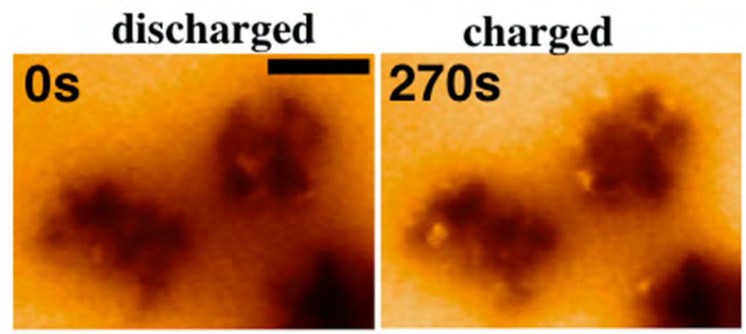
Intensity from $FePO_4$ tracks charging!

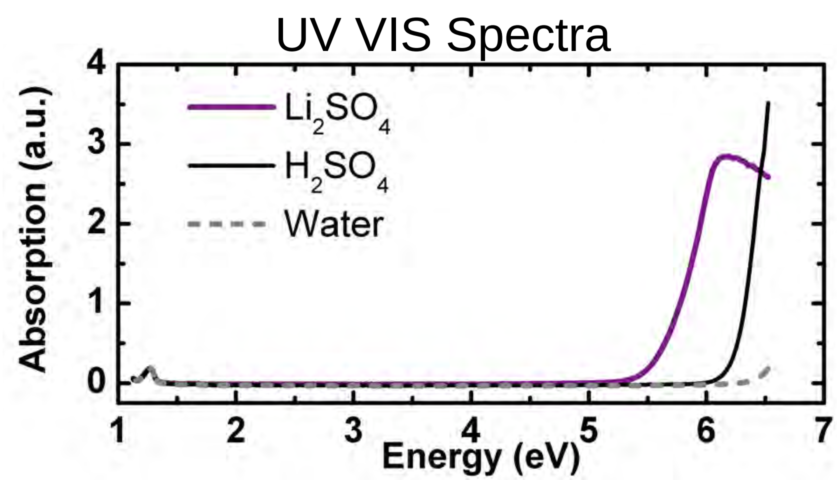


5 eV Images: Bright = $FePO_4$
Li Concentration Change during Cycling



Intensity from $FePO_4$ tracks charging!
Intensity in solution tracks $LiSO_4^-$ follows discharging!

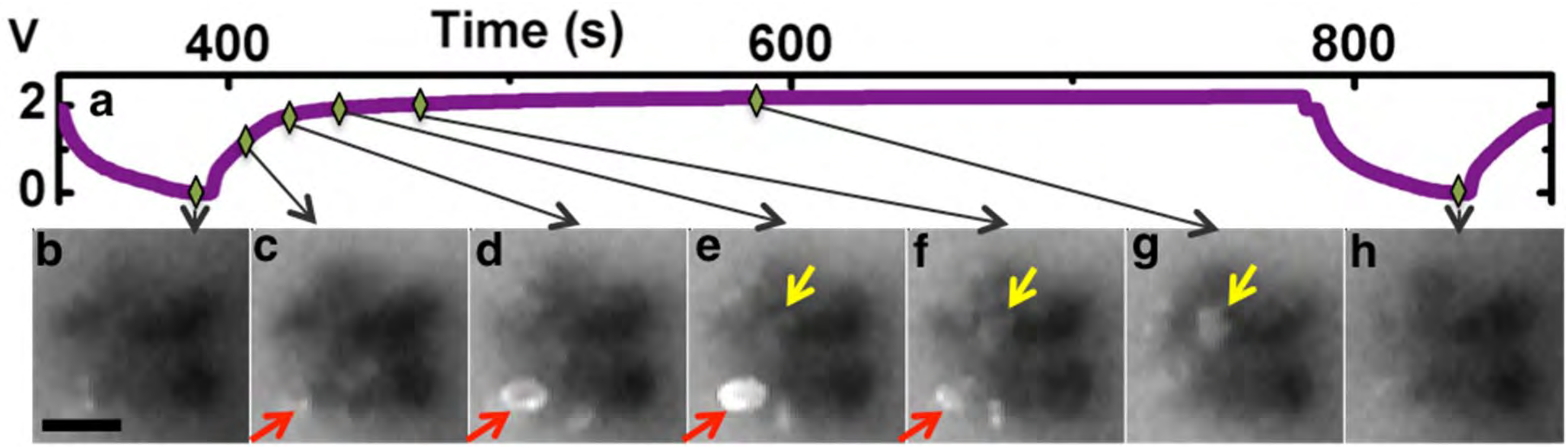




$Li_2SO_4 \rightarrow Li^+ + LiSO_4^- \leftrightarrow 2Li^+ + SO_4^{2-}$

JDFT shows $LiSO_4^-$ is the cause of bright 6 eV signal!

Mechanism of Lithiation



2 dominant modes of lithiation for this experiment:

We see

(red) core-shell type structures during growth of the $FePO_4$

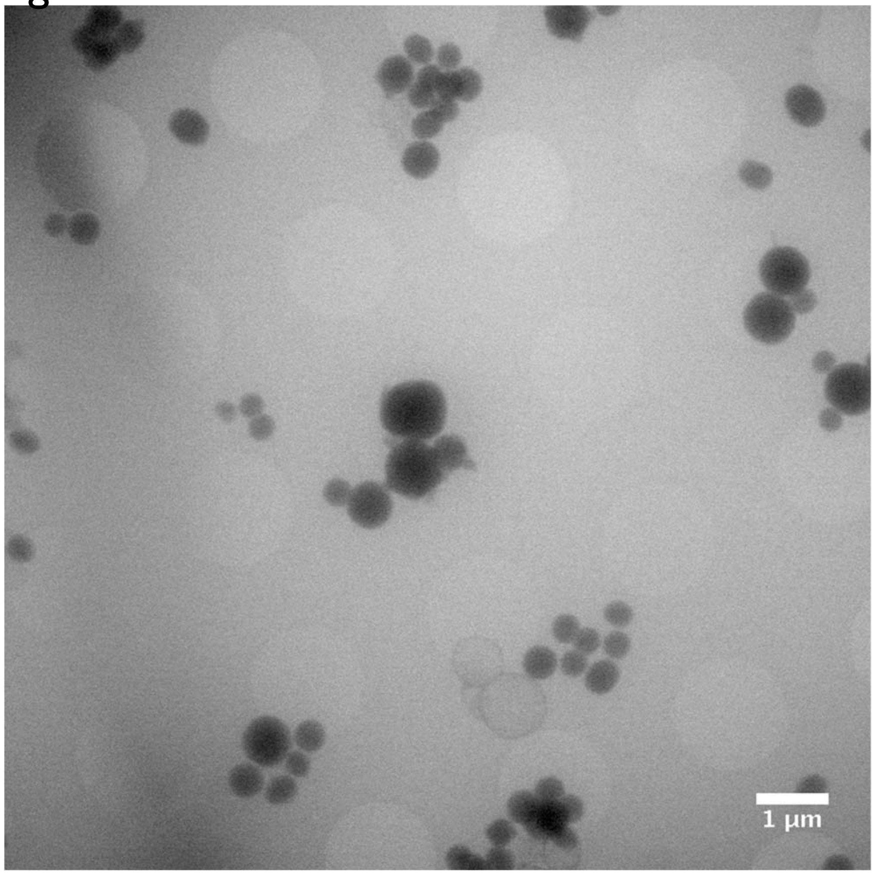
(yellow) Propagating from Left to Right

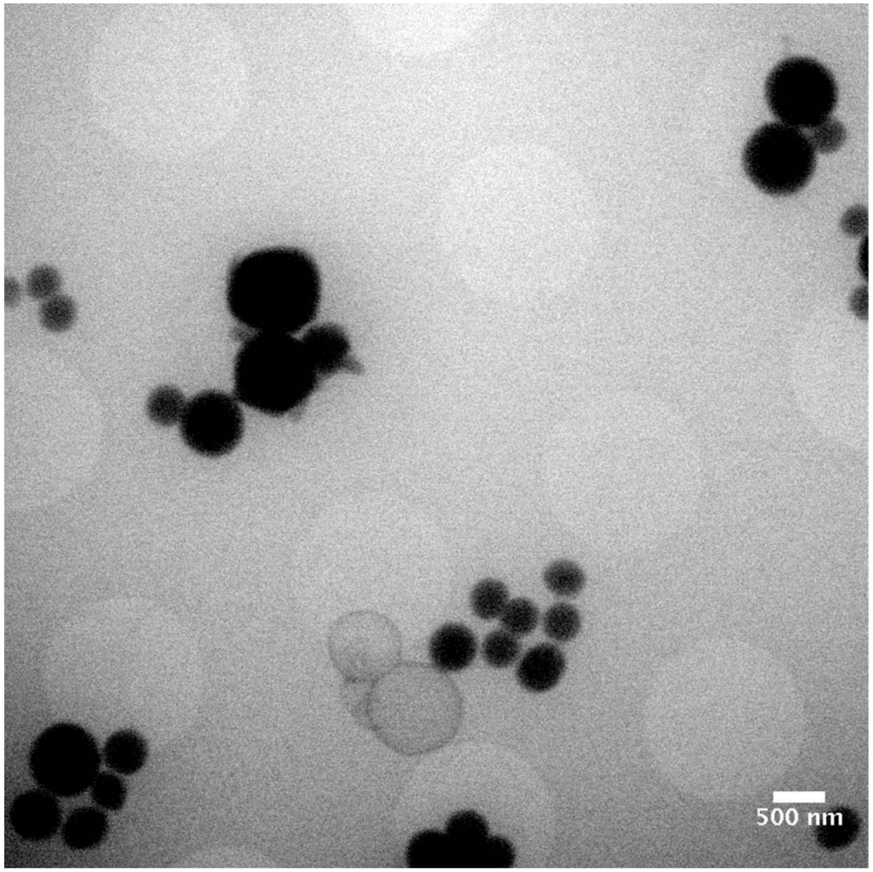
Highly dependent on particle size and experimental conditions

AirSTEM Images of Sulfur in PAN

Another way to image the encapsulated sulfur effectively is to make sure that there is no sublimation hence we image our samples in air instead of vacuum.

Therefore, sample was then taken out of the F20 (Vacuum STEM) and imaged in the AirSEM using our homebuilt Air-STEM detector



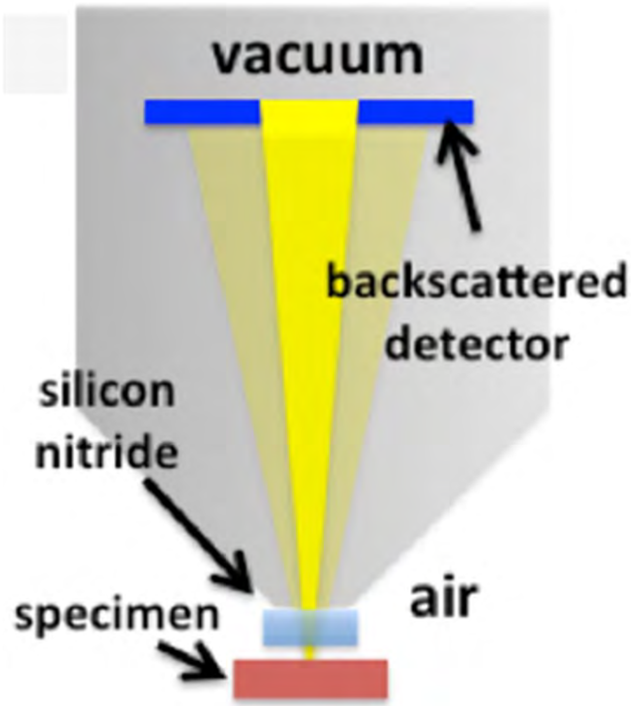


As you can the resolution of the F20 and Air-STEM are comparable!

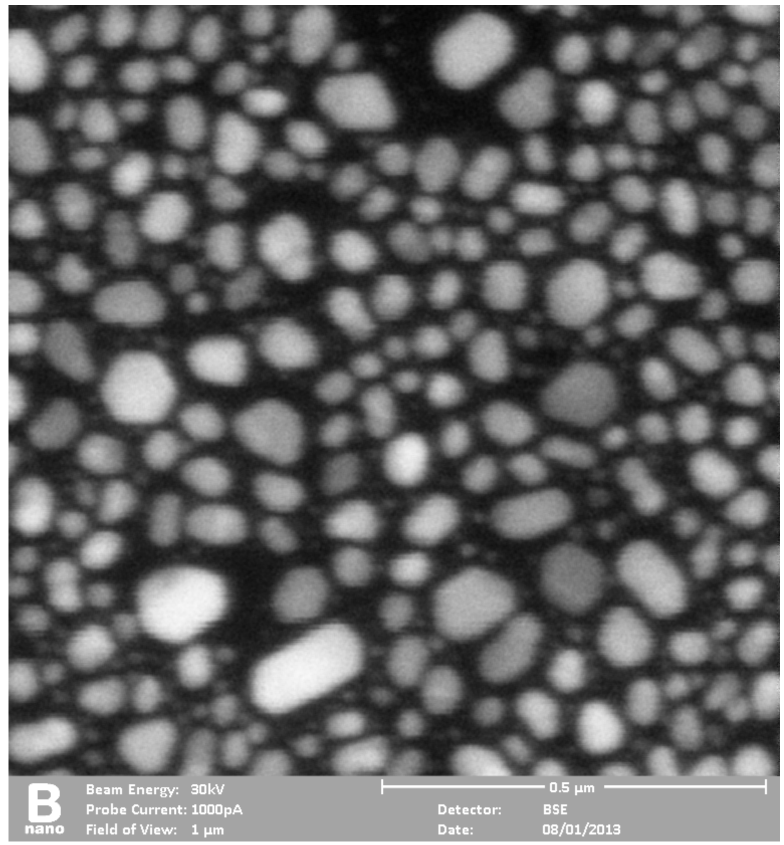
Images taken by K. Nguyen

airSEM: Scanning Electron Microscopy without a Vacuum Chamber

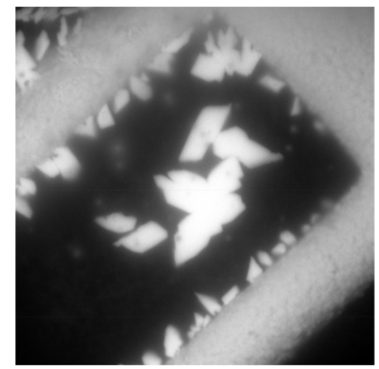
- Sample is in air, can be wet or insulating



A thin, electron transparent membrane separates the column from air



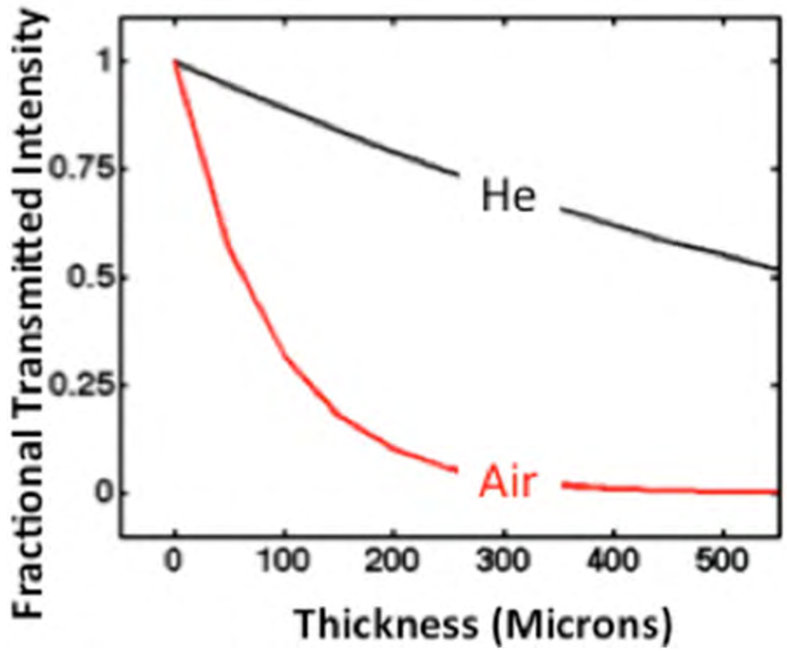
~ 8nm resolution on Au nanoparticles



Watching Pb dendrites Grow in solution

Can image through 50-100 microns of air

How Much Unscattered Beam is left?



As long as some unscattered beam is left, we can form a high-resolution image

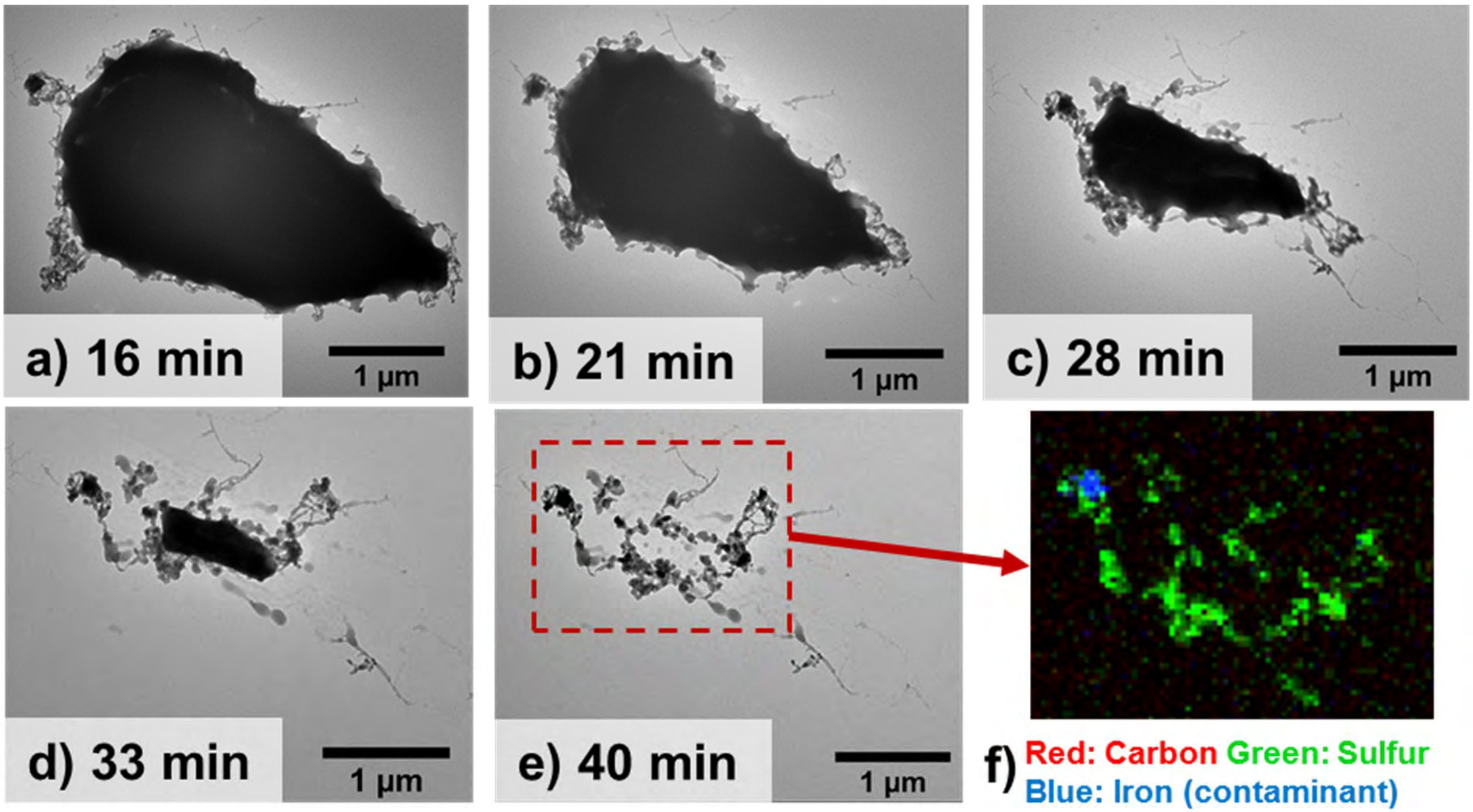
Mean free path in air is 150 μm at 30 keV → 30% loss at 50 μm

But mean free path in silicon nitride is 30 nm! (our membrane is 20 nm) → 50% loss

Solution: Graphene window - even 6 ML would give only a 5% loss

Sulfur Sublimates at Room Temperature in the TEM

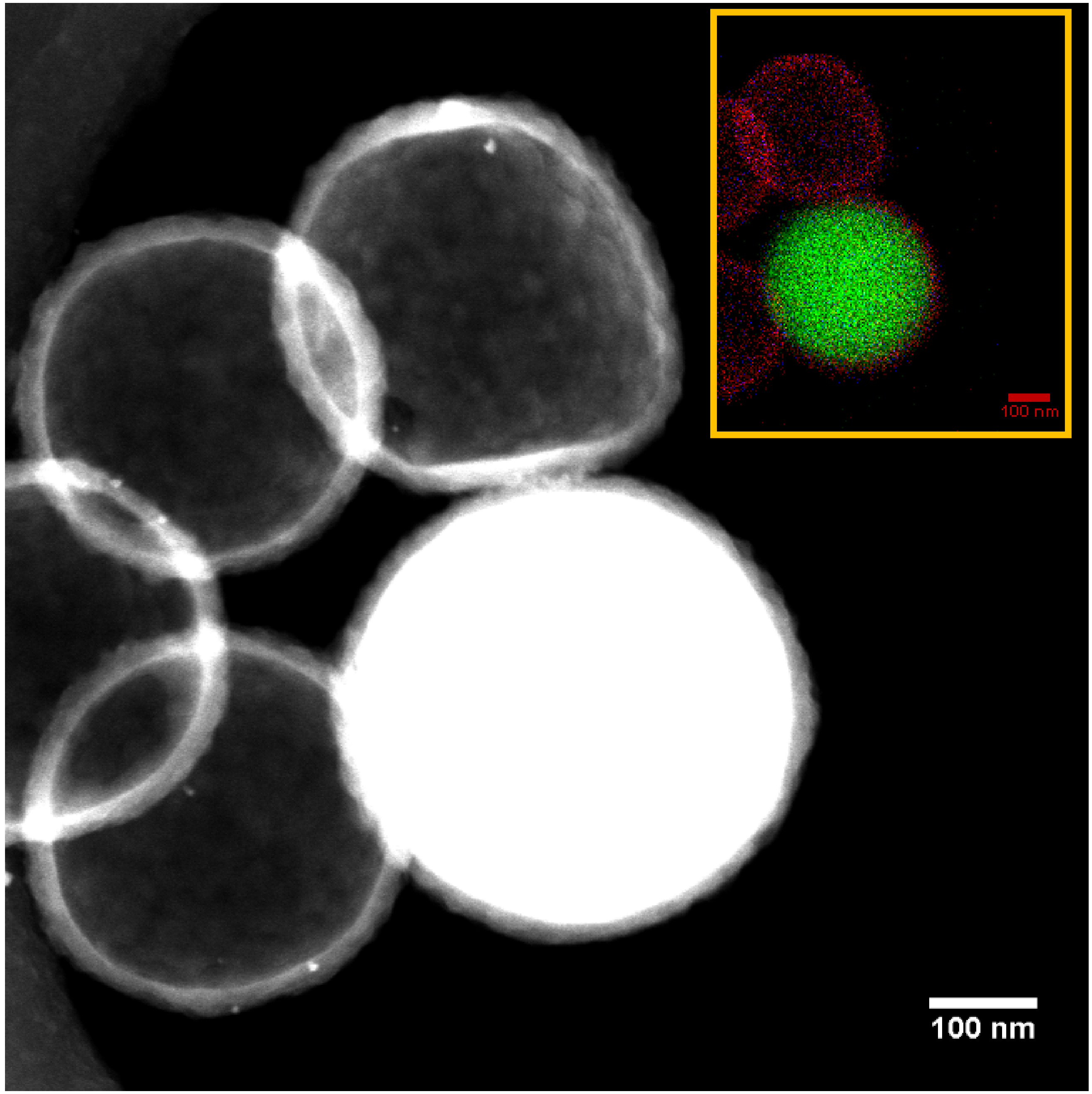
Sublimation rates is ~ 1 ML/second (same as bulk)



Remnant is "white sulfur" - amorphous & polymeric

T=18^{o}C, P= 8.8×10^{-8} Torr, Beam off between images

Sulfur in PAN

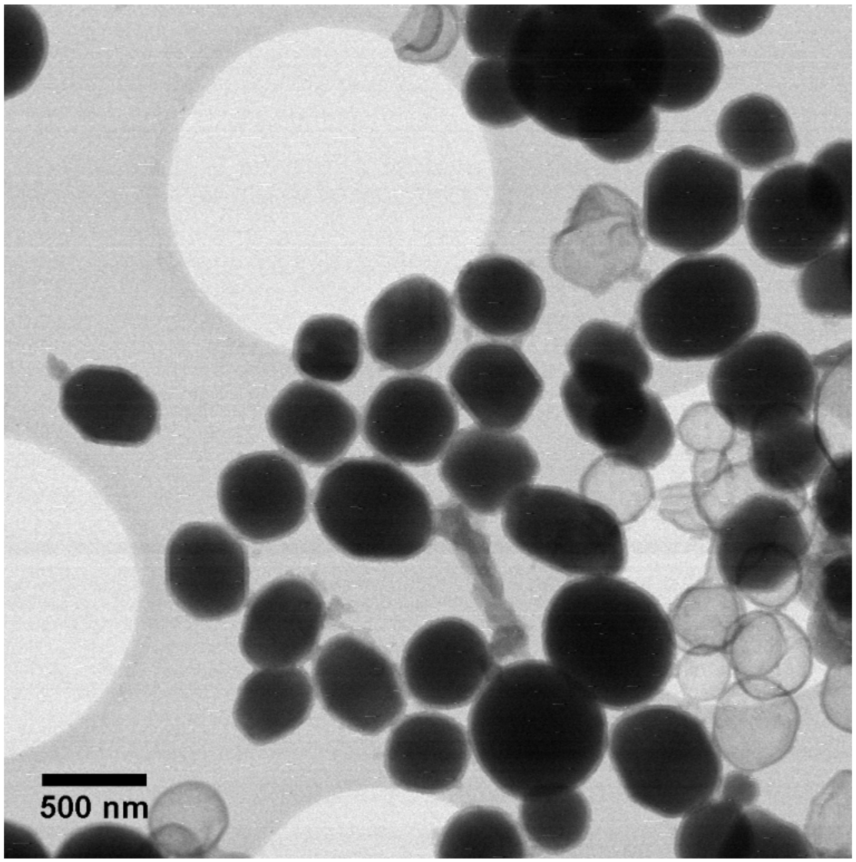


Red = Carbon
Green = Sulfur

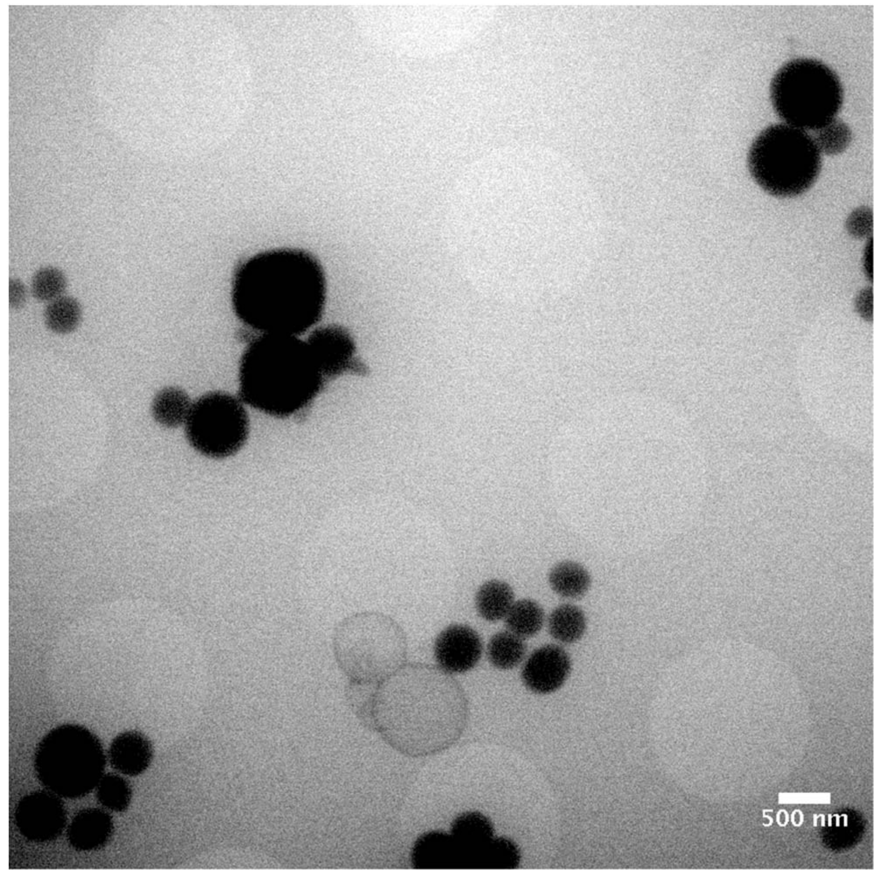
Images taken by B. Levin

Bright-Field STEM Images of Sulfur-filled PAN Shells

200 keV Tecnai F20

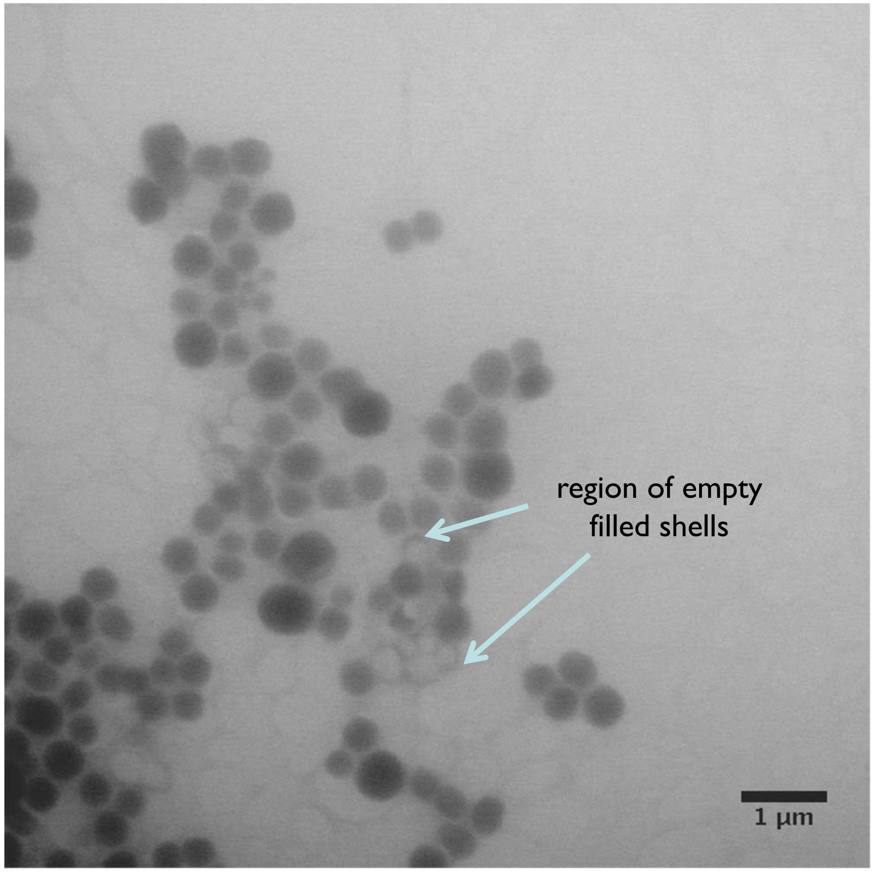


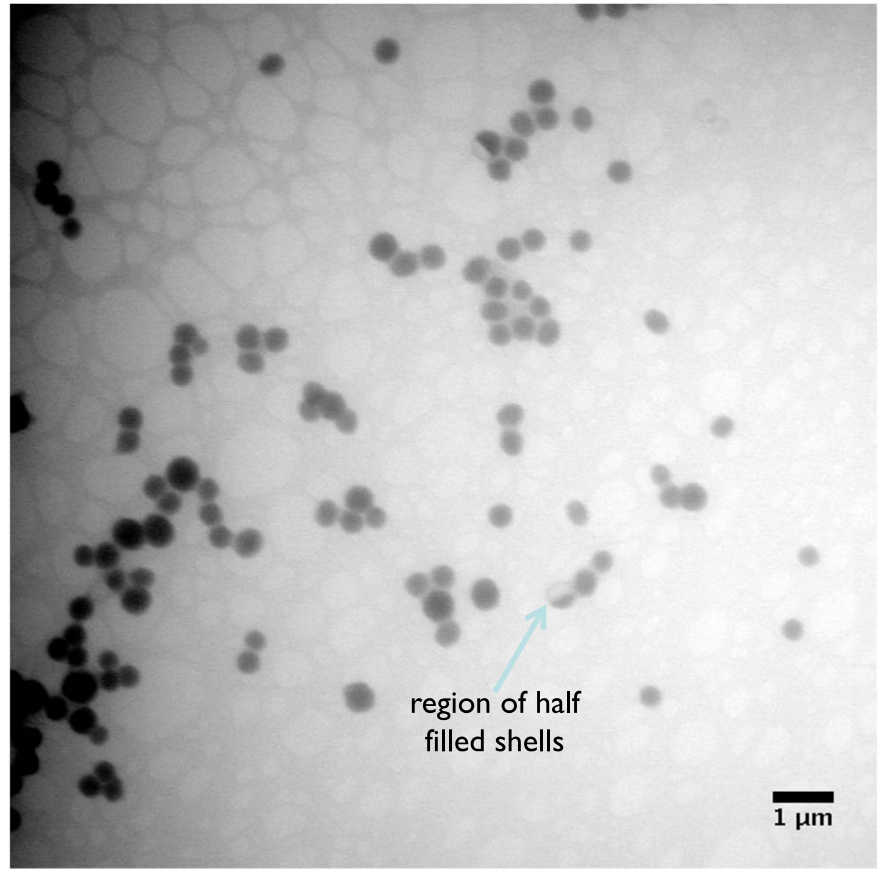
30 keV bNano AirSTEM



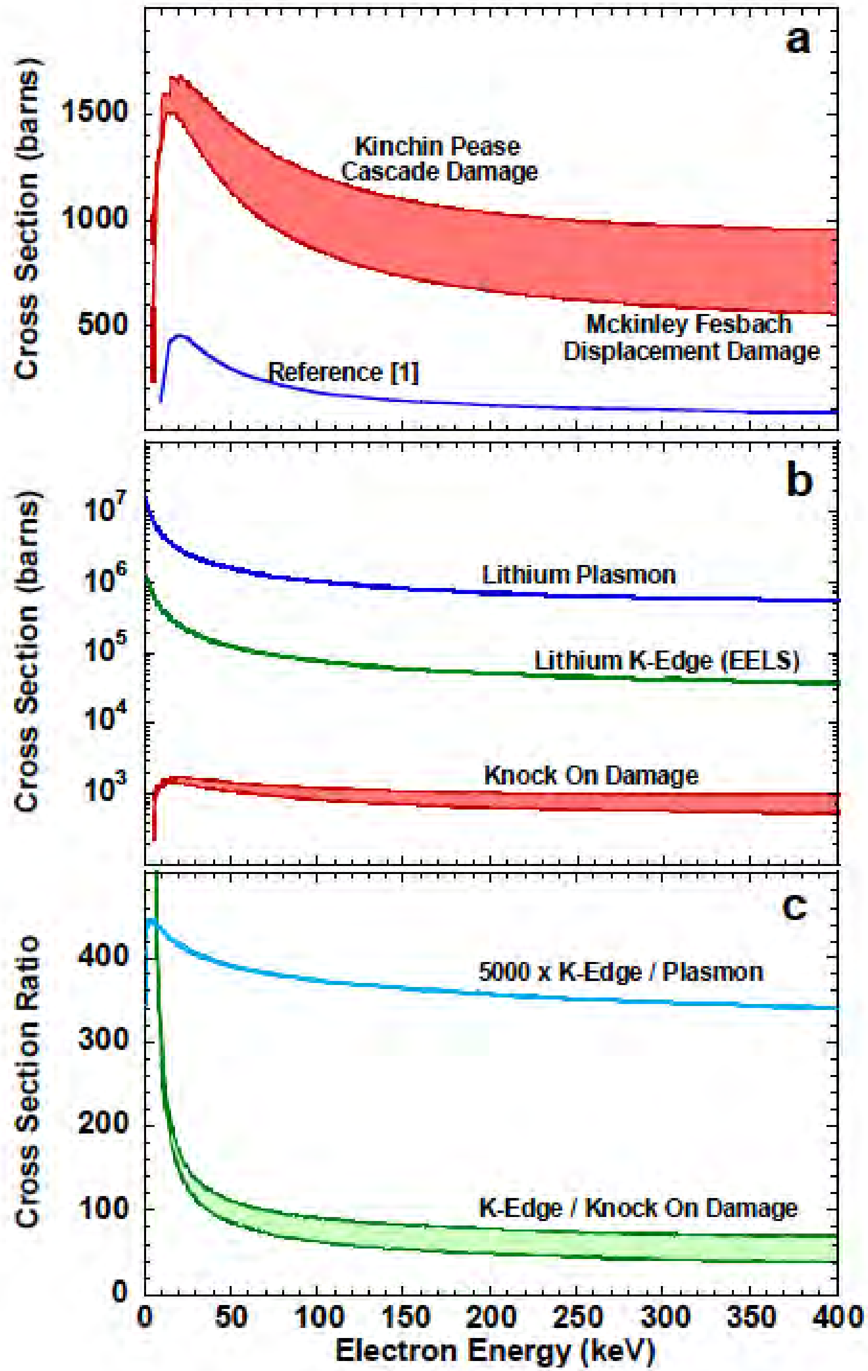
Sulfur sublimates in vacuum – leaving empty shells if there were large pores

Fresh sample: AirSTEM: Most shells filled, But a few empty shells and (new!) half-filled shells

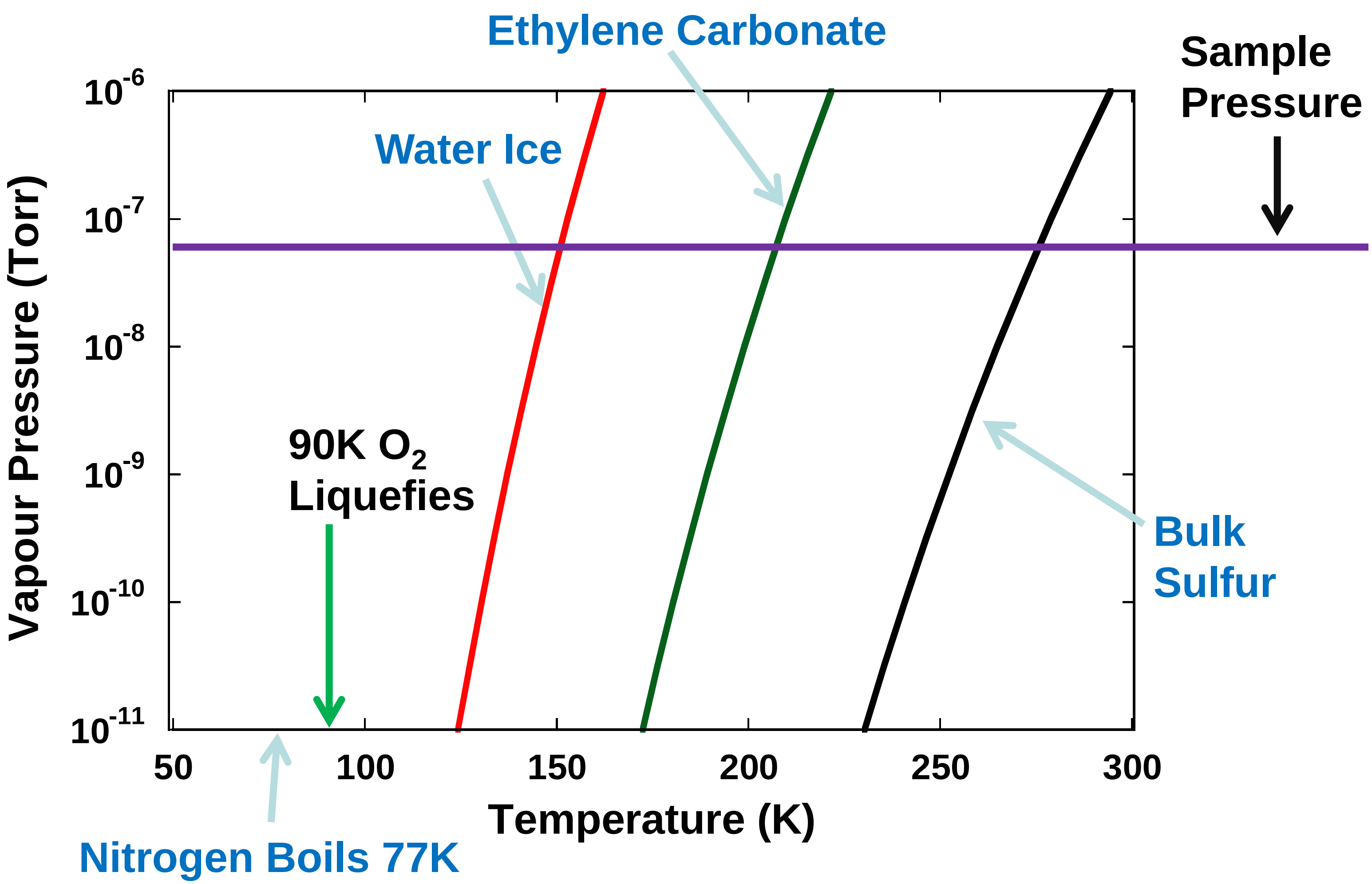




Images taken by K. Nguyen


a
Cross Section (barns)
1500
1000
500
Kinchin Pease
Cascade Damage
Mckinley Fesbach
Displacement Damage
Reference [1]
b
Cross Section (barns)
10^7
10^6
10^5
10^4
10^3
Lithium Plasmon
Lithium K-Edge (EELS)
Knock On Damage
c
Cross Section Ratio
400
300
200
100
0
5000 x K-Edge / Plasmon
K-Edge / Knock On Damage
0
50
100
150
200
250
300
350
400
Electron Energy (keV)

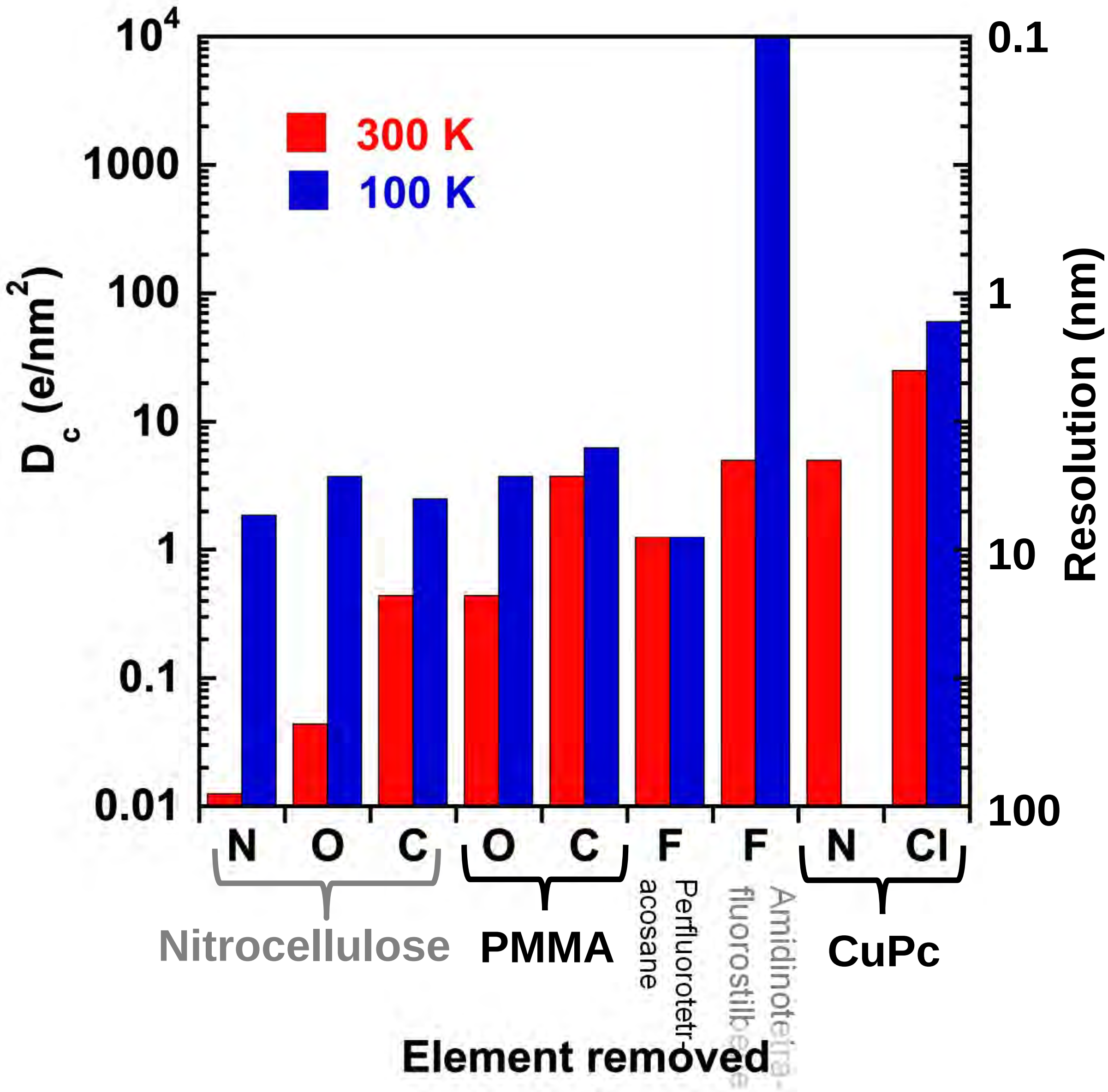
Why do we want a cryo-holder?



Verevkin et al. Fluid Phase Equilibria 268 1 (2008)

Critical Dose for Mass Loss

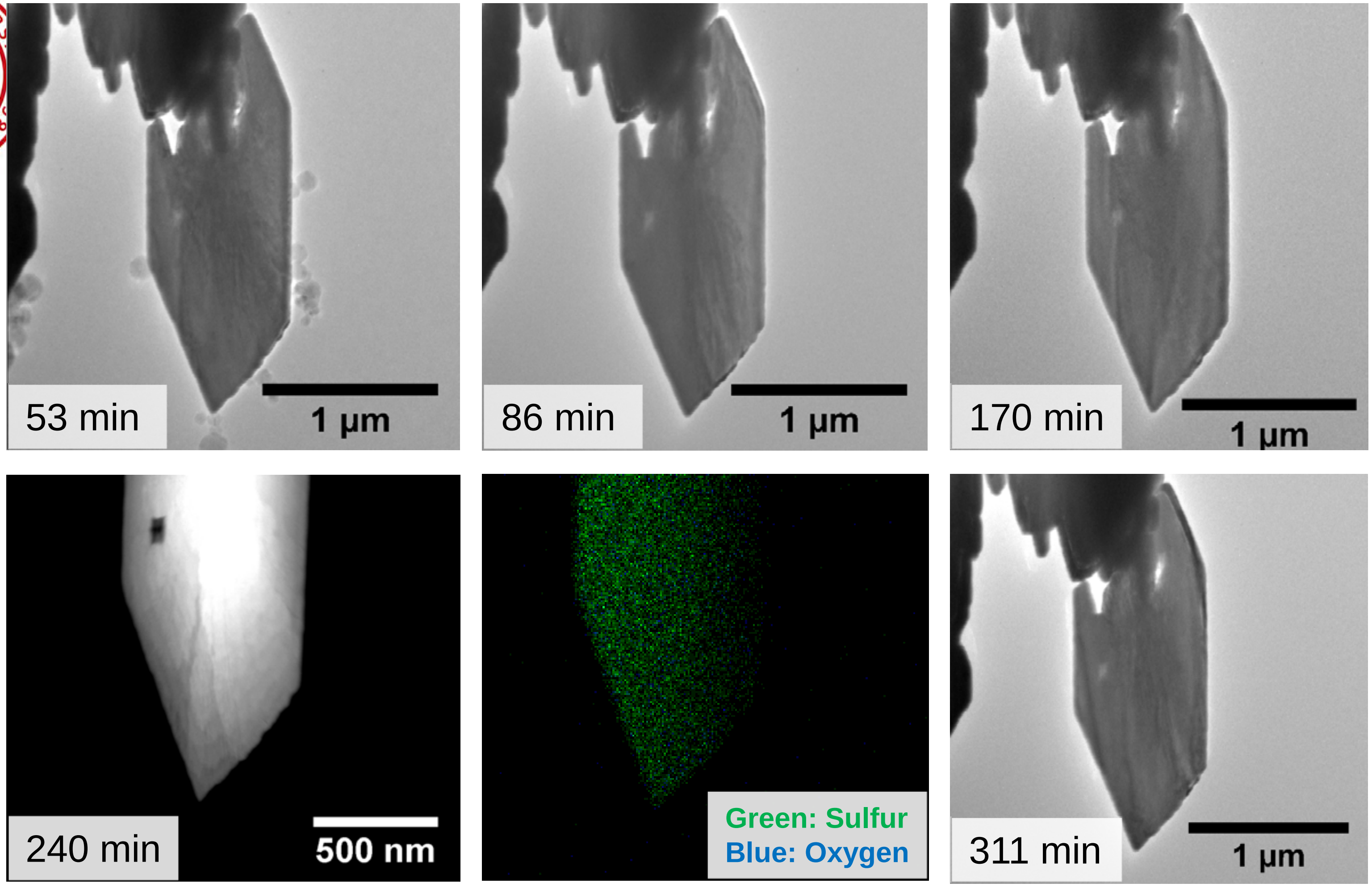
Typical 10-50 x decrease in mass loss on cooling -> 3-7x resolution improvement



Sensitivity to Radiation Damage

G = # of Reactions/100 eV of *deposited* energy

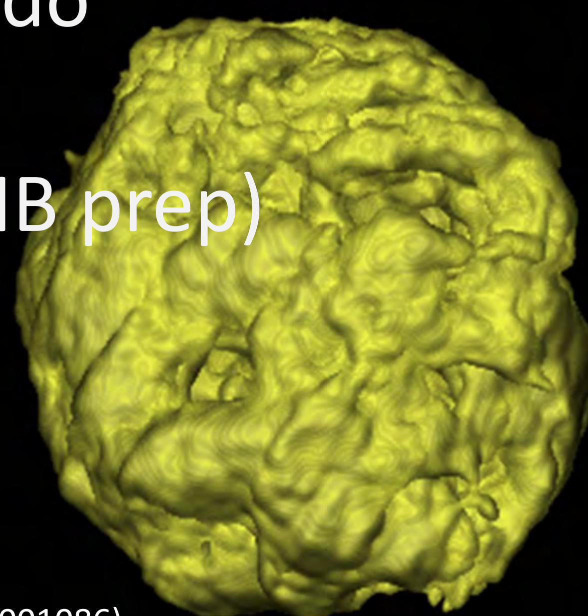
Compounds and sites of attack	G_{-M} (loss)	G_{H_2}	G_{CO_2}	G_{CO}	G_{H_2O}	G_{CH_4}
Hydrocarbons,						
saturated						
C–H, C–C	6–9	3.8–5.6				0.2–0.7
unsaturated						
C–H, C–C	11–10	0.8–1.2				0.13
aromatic						
C–H, side chain C–C	0.2–1	0.01–0.18				
Alcohols						
HC–OH, C–COH	3–6	3.5–4.5		0.04–0.23	0.3–0.9	
Ethers						
C–H, C–OR	7	2.0–3.6		0.06–0.13		
Aldehydes and ketones						
C–H, C–C=O	7	0.8–1.2		0.6–1.6		0.1–2.6
Esters						
C–H, O=C–OR	4	0.5–0.9	0.3–1.6	0.15–1.6		0.4–2.0
Carboxylic acids						
C–H, C–COOH	5	0.5–2.3	0.5–4.0	0.1–0.5	0.1–2.2	0.5–1.4
Amino acids	G_{-M}	G_{H_2}	G_{CO_2}	G_{NH_3}		
Leucine						
C–H, C–NH_2, C–COOH	14	0.5	2.8	5.1		
Valine						
C–H, C–NH_2, C–COOH	8	0.2	0.6	4.1		



Time series of images on Sulfur particle including HAADF and EDX to identify Sulfur. Temperature -175°C, pressure $8.83x10^{-8}$ Torr. Particle is clearly unchanged by time in vacuum, in contrast to Sulfur at room temperature. Ice contamination in the first image burned away under the beam within ~2 min. Very little ice seen in EDX.

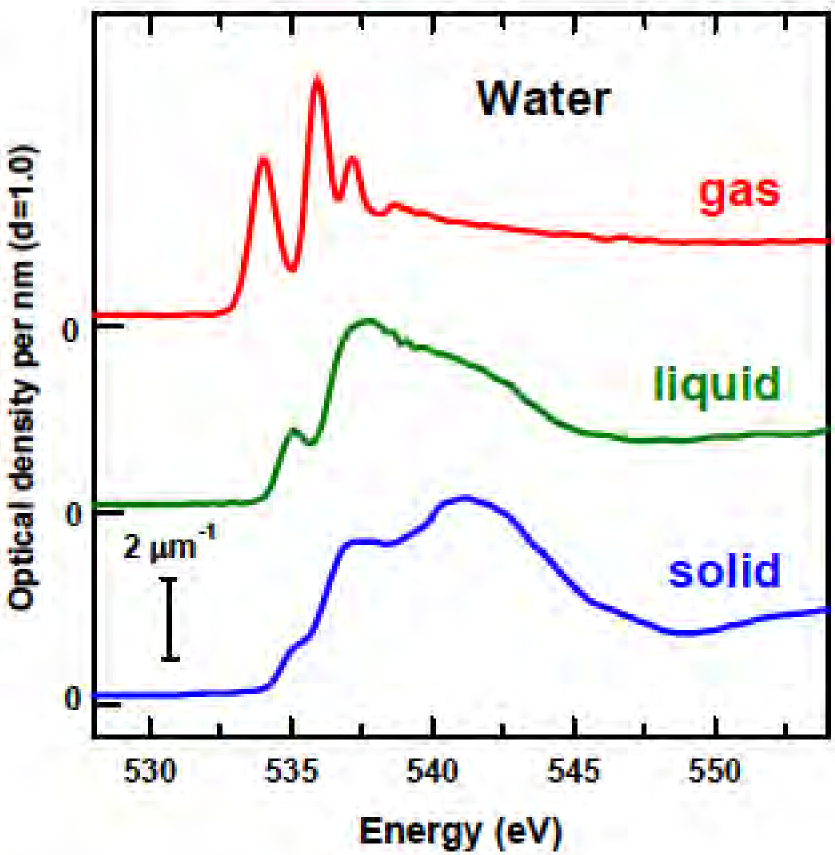
Capabilities

- Atomic-scale composition and bonding
- 3D Imaging at the nanoscale
- *In-situ* liquid flow, electrochemical cycling to observe reactions at TV rate
- Air-SEM for larger-scale in-operando experiments
- Cryo-electron microscopy (+cryoFIB prep)
  - Organic/inorganic interfaces
  - Liquid/Solid interfaces



Work supported by the Energy Materials Center at Cornell, DOE EFRC BES (DE-SC0001086).
EM Facility support from the NSF MRSEC program (DMR 1120296).

Oxygen K-Edge of H_2O



XAS Data from Adam Hitchcock

New Detectors in Cryo-EM:

THE REVOLUTION WILL NOT BE CRYSTALLIZED

MOVE OVER X-RAY CRYSTALLOGRAPHY. CRYO-ELECTRON MICROSCOPY IS KICKING UP A STORM IN STRUCTURAL

In a basement room, deep in the bowels of a steel-clad building in Cambridge, a major insurgency is under way.

A hulking metal box, some three metres tall, is quietly beaming terabytes' worth of data through thick orange cables that disappear off through the ceiling. It is one of the world's most advanced cryo-electron microscopes: a device that uses electron beams to photograph frozen biological molecules and lay bare their molecular shapes. The

NATURE **525** (2015) 172

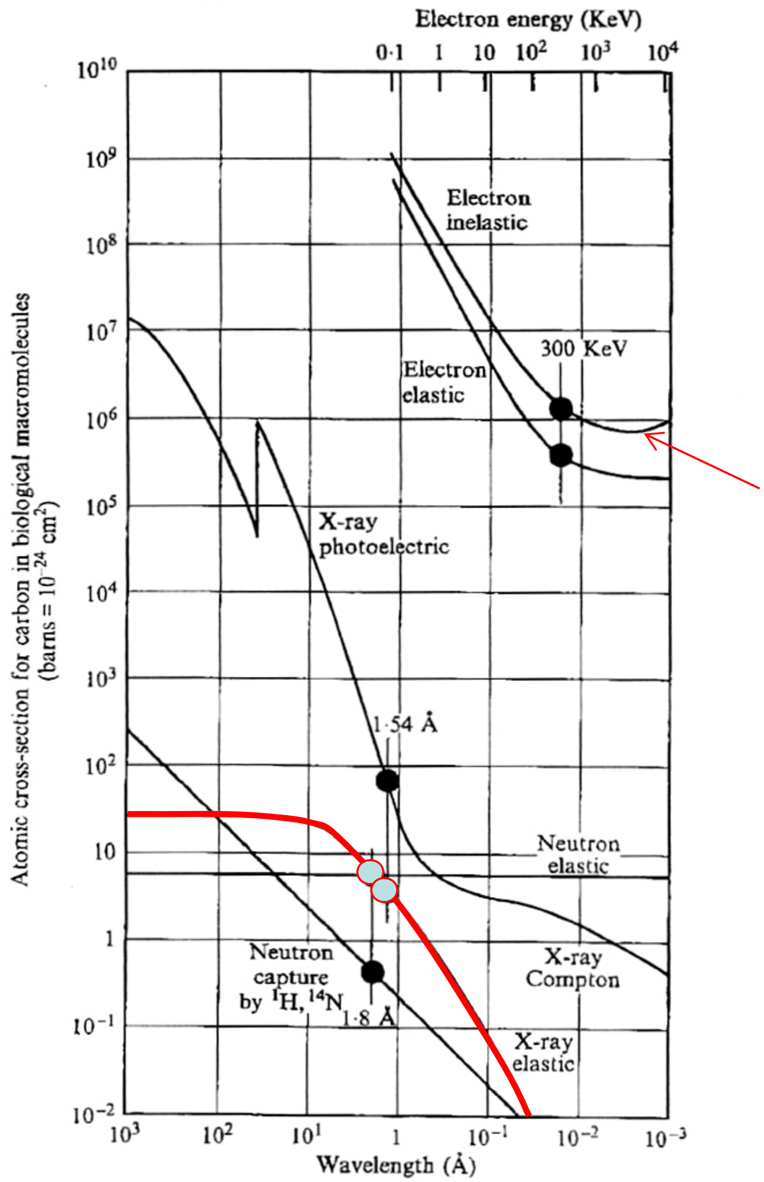
‘ribosomania’

“X-ray crystallography has largely fallen by the wayside in the laboratory of Venki Ramakrishnan, who shared the 2009 Nobel. For large molecules, “it’s safe to predict that cryo-EM will largely supersede crystallography”, he says.”

The Nobel Prize in Chemistry 2017 was awarded jointly to Jacques Dubochet, Joachim Frank and Richard Henderson
"for developing cryo-electron microscopy for the high-resolution structure determination of biomolecules in solution."

How Bad is Radiation Damage?

R. Henderson, Quarterly Reviews of Biophysics 28 (1995) 171-193.



It's not the cross-section, but

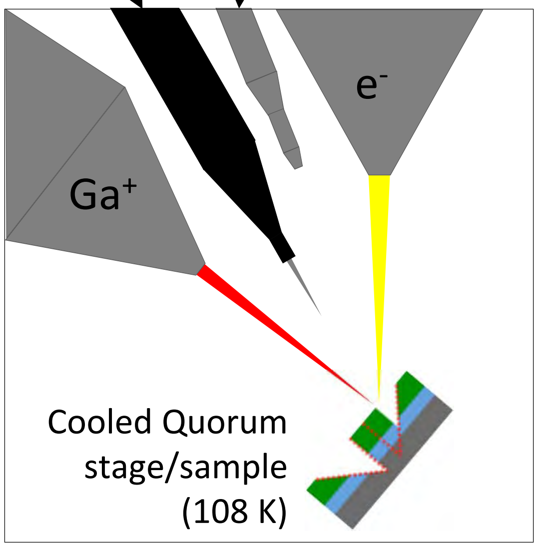
How many damaging events per useful imaging event?

Least Damage:
Elastic imaging - Electrons wins
Inelastic imaging - Soft X-rays win

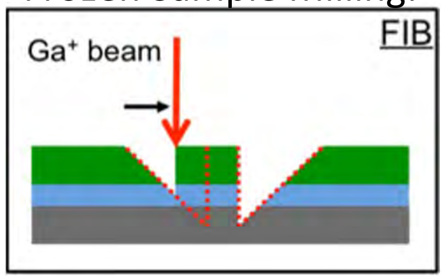
Cryo-FIB lift-out

Cooled OmniProbe Nanomanipulator

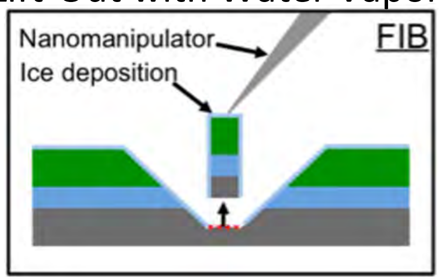
FEI Gas Injection System (GIS)



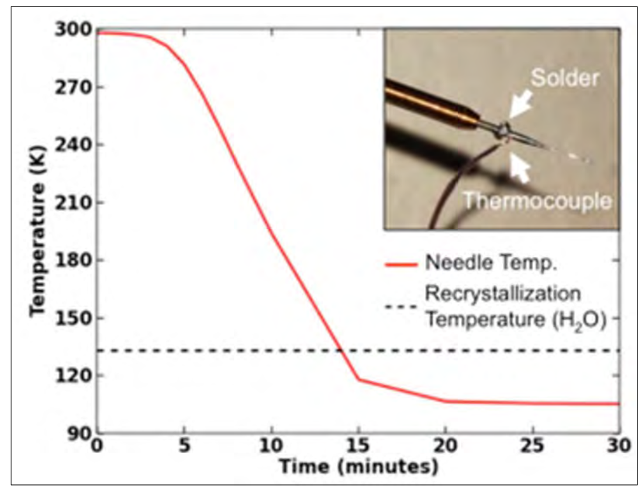
Frozen Sample Milling:



Lift-Out with Water Vapor:



Needle Cooling:

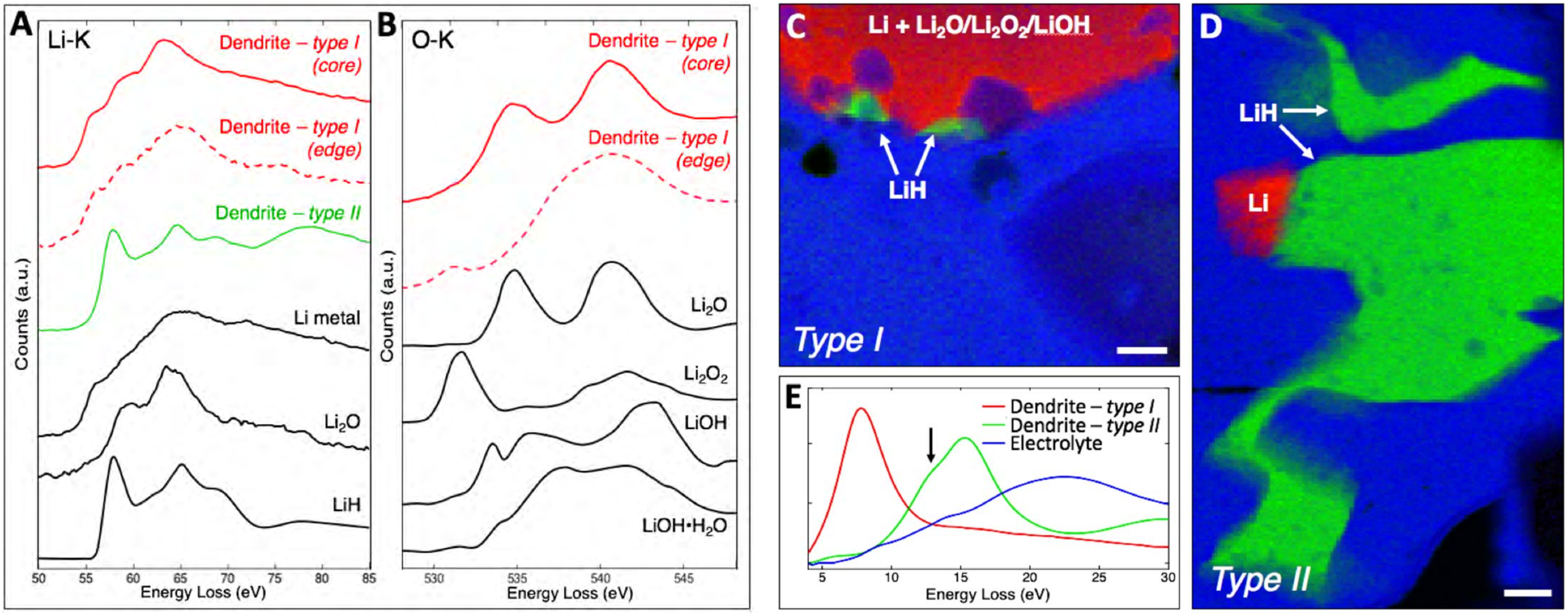


Use water vapor instead of Pt for attachment.

Cooled nanomanipulator maintains the sample temperature during lift-out.

MJ Zachman, E Asenath-Smith, LA Estroff, LF Kourkoutis, Microsc. Microanal. 22, 1338–1349 (2016)

Two structurally and chemically distinct dentrite structures



Type I dendrite:

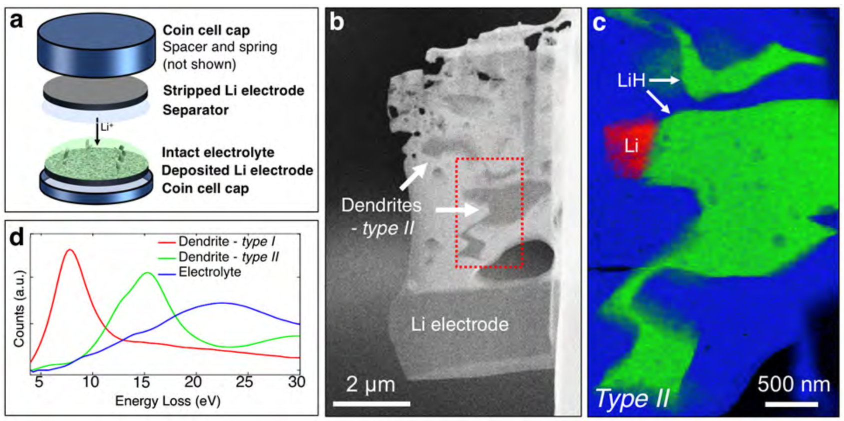
- lithium metal, partially oxidized at its core
- transitioning to peroxide and hydroxides near the surface

Type II dendrite:

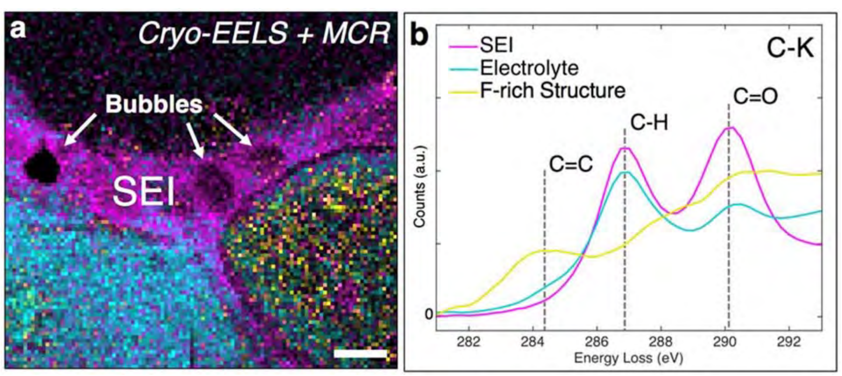
- uniform lithium hydride

Cryo-STEM for characterization of liquid/solid interfaces

Nanoscale mapping of dendrites in Li metal coin cell battery



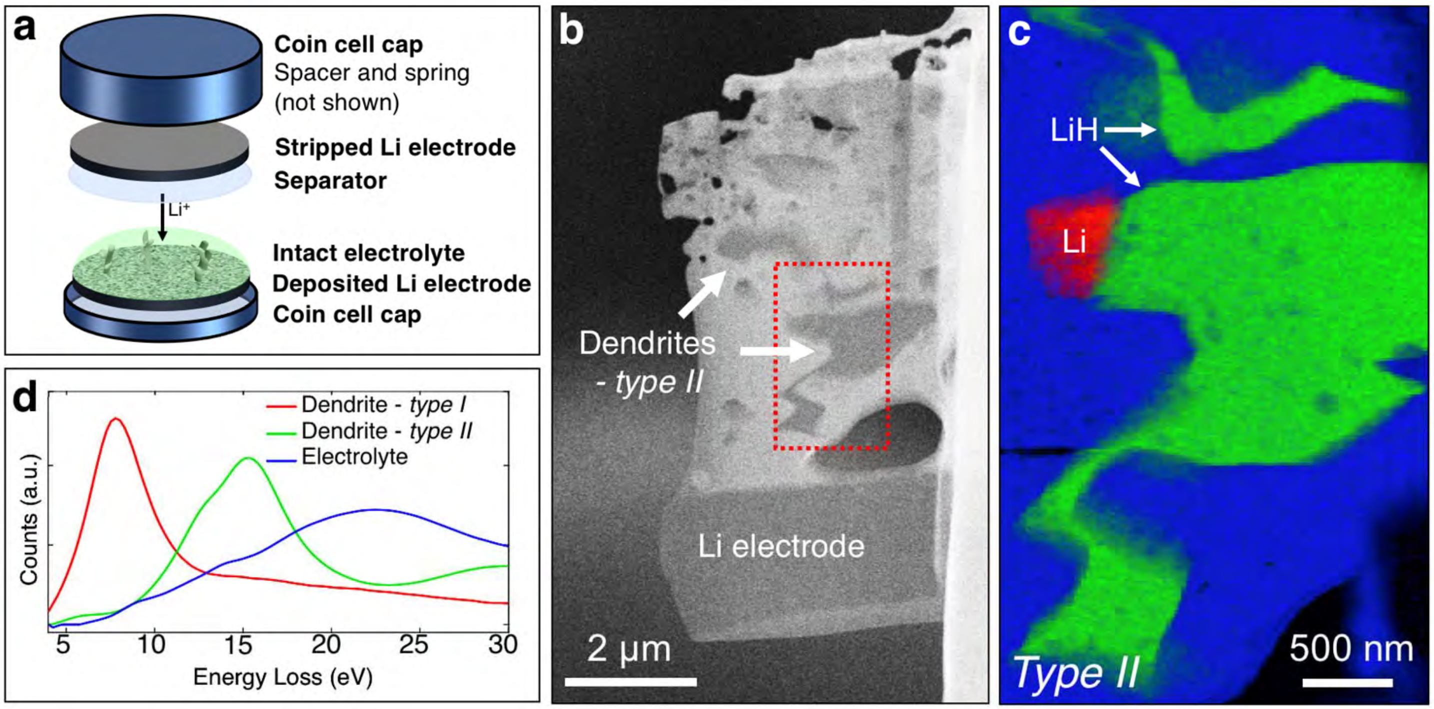
Spatial variations of carbon bonding



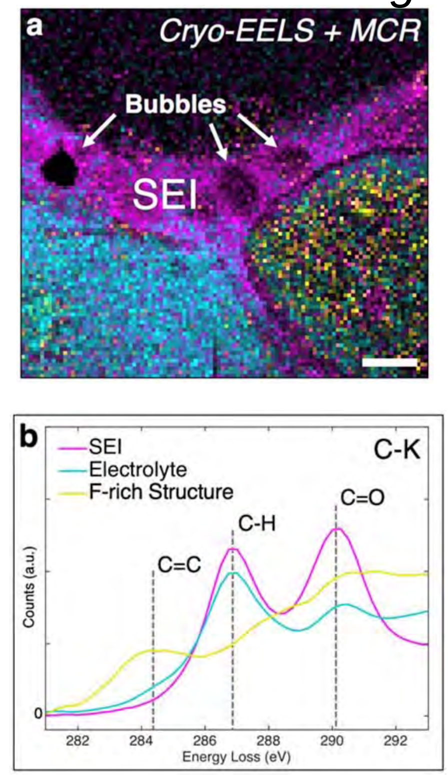
- High-resolution characterization of structure, chemistry and bonding of materials and devices by electron microscopy and spectroscopy at both room and cryogenic temperatures
- Demonstrated an approach to access buried liquid-solid interfaces by cryo-FIB and cryo-STEM/EELS
- Application of these techniques to image the structure and chemistry of reactive or beam sensitive materials and of processes at liquid/solid interfaces such as those in Li-metal coin cell batteries

Cryo-STEM for characterization of liquid/solid interfaces

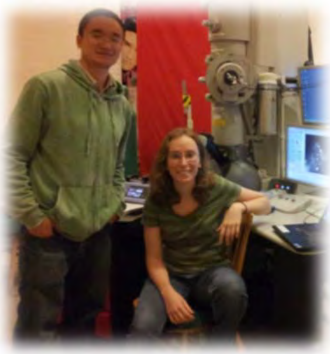
dendrites in Li metal coin cell battery



Spatial variation of carbon bonding



Acknowledgements



Abruña Group
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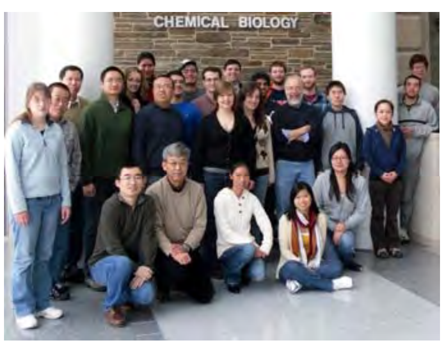

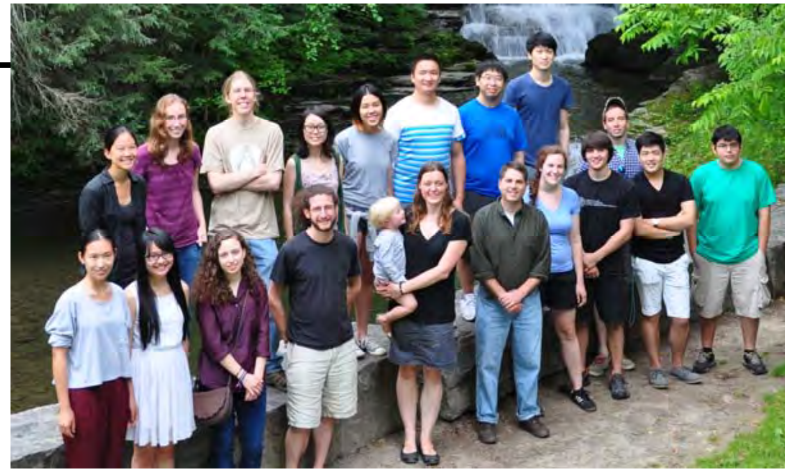

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J. Zhang
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Rohit Makharia
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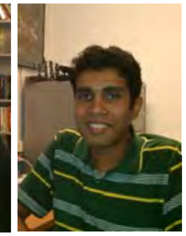
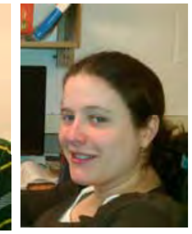

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Shankar Sundararaman
Katie Schwartz
Kendra Letchworth-Weave

Corning
Weirong Jiang

Microscopes
John Grazul
Mick Thomas
Earl Kirkland
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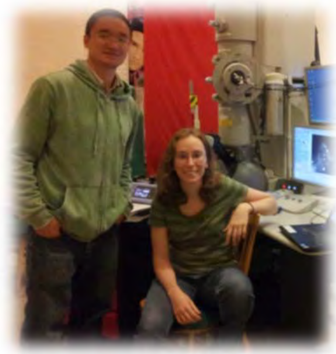

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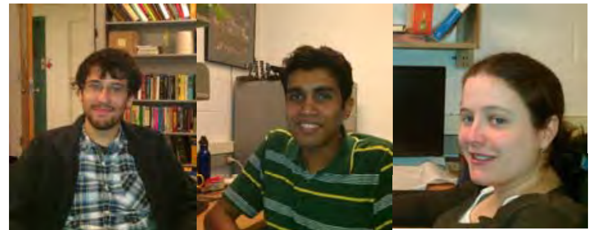

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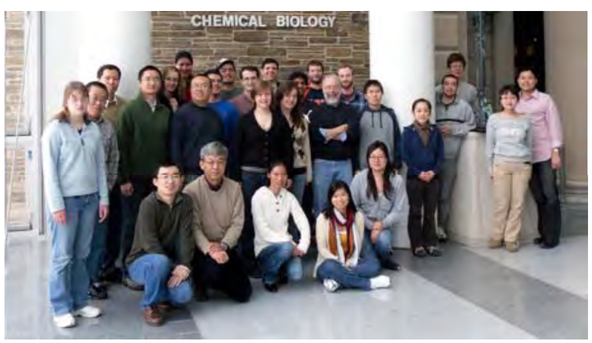
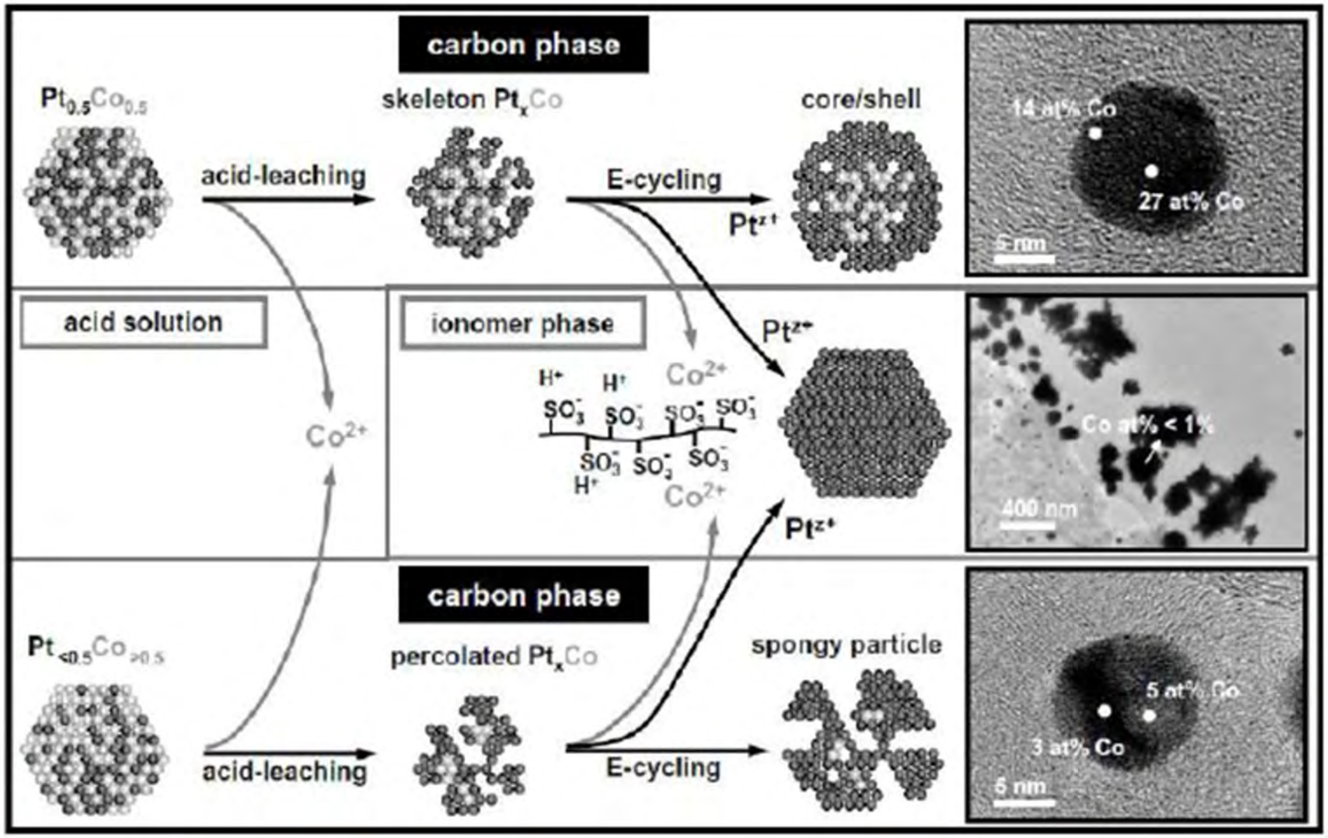


Protochips (John Damiano)
Gamry (Burak Ulgut)

Work supported by the Energy Materials Center at Cornell, DOE EFRC BES (DE-SC0001086). EM Facility support from the NSF MRSEC program (DMR 1120296).



Core-shell structure

arose from acid leaching of relatively Pt-rich particles (skeleton Pt surface) followed by electrochemical cycling to smooth out the surface Pt layer.

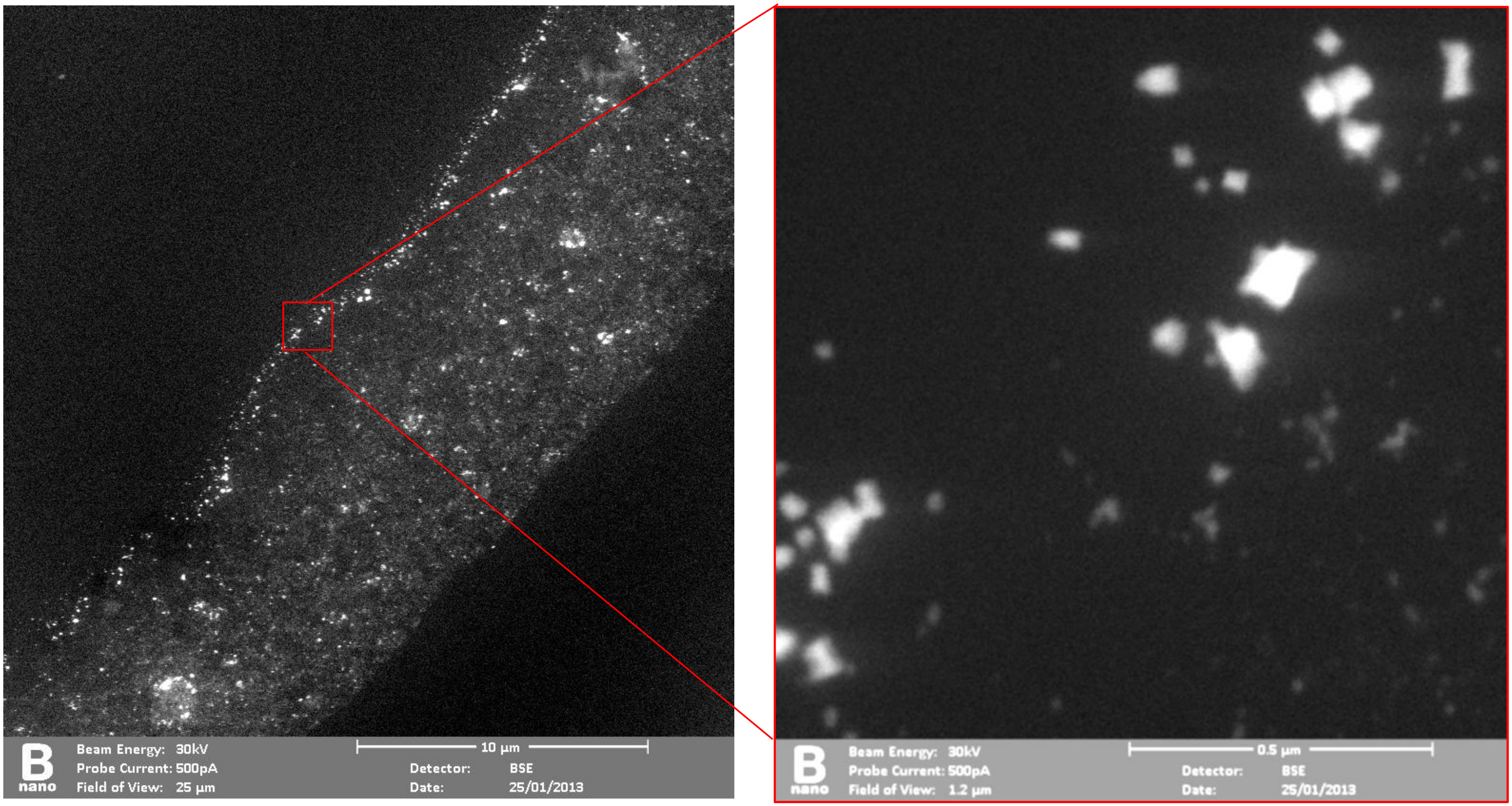
(small to intermediate particles

Spongy ("percolated") structure

arose from acid leaching of Co-rich particles.
(large particles)

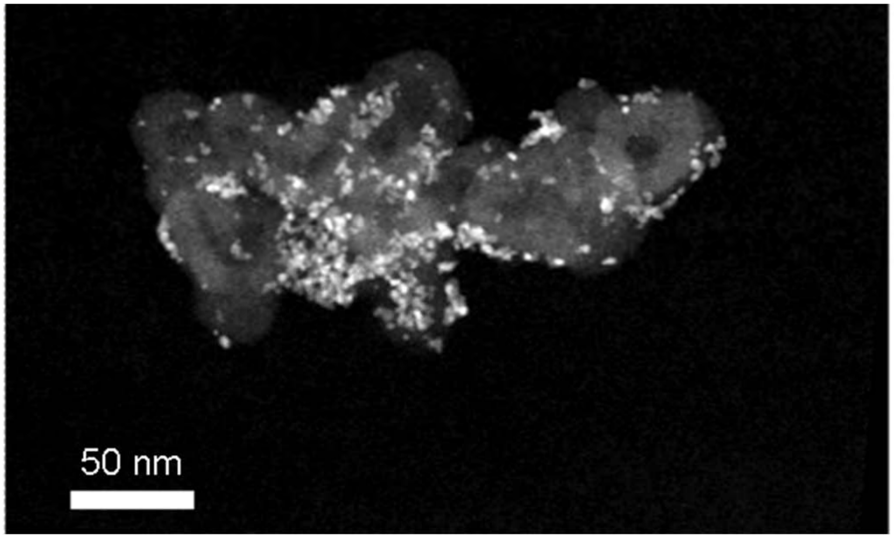
S. Chen, H. A. Gasteiger *et al.*, JECS, 157, A82 (2010)

Air-SEM Backscatter images of Pt_3Co Nanoparticles in a Fuel Cell Cathode after 30k Cycles

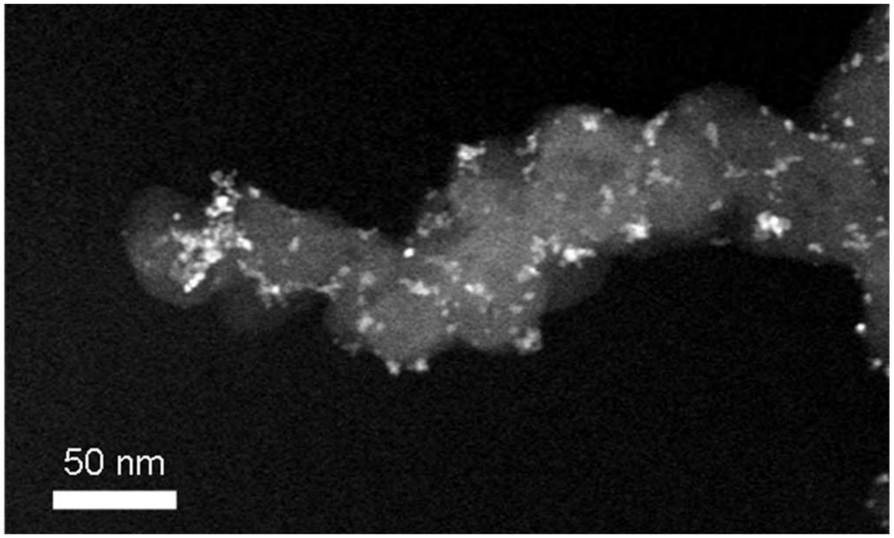


Effects of Corrosion in 2D

Corroded Carbon Support



Non-corroded Carbon Support



- Corroded carbon shows holes - pore? Voids? Connectivity?
- Does the Pt catalyst get inside the holes?

Collaborators

Microscopy
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Protochips
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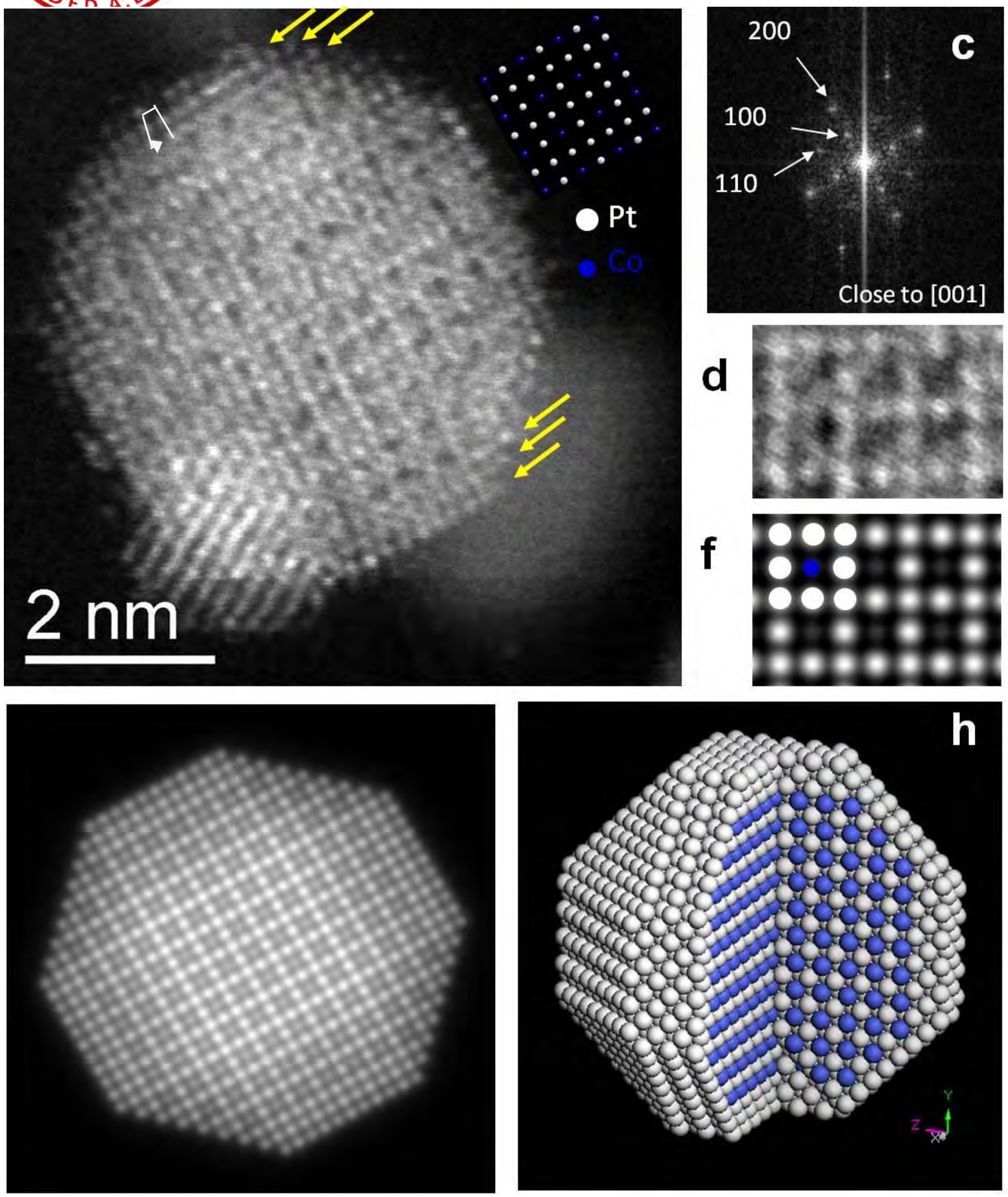
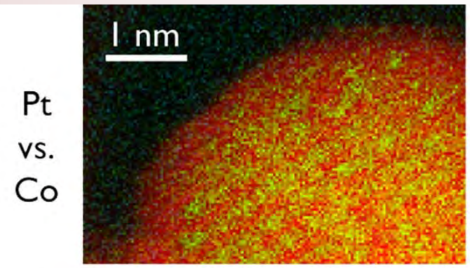
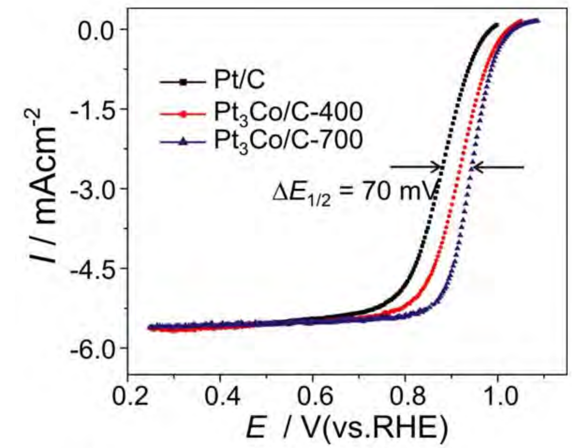
John Damiano

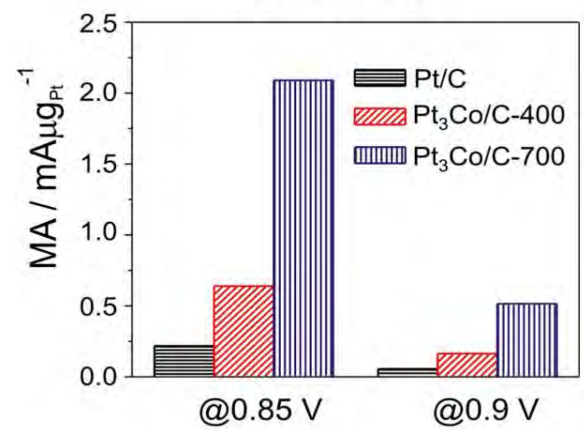
EMC[2] is an Energy Frontier Research Center funded by the DOE, BES Award # DE-SC0001086.

Ordered Intermetallic vs. Disordered Alloy





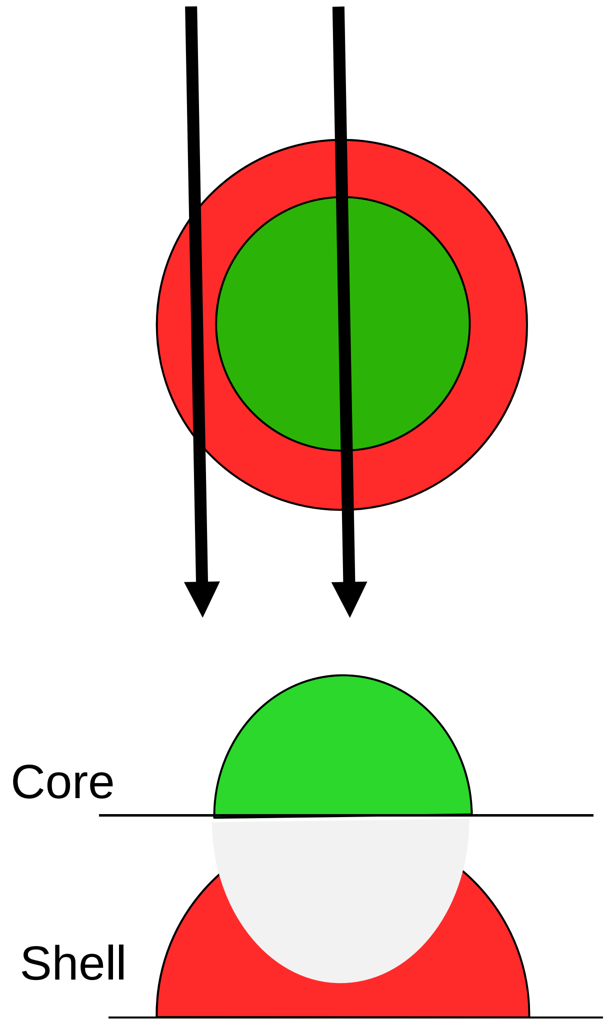




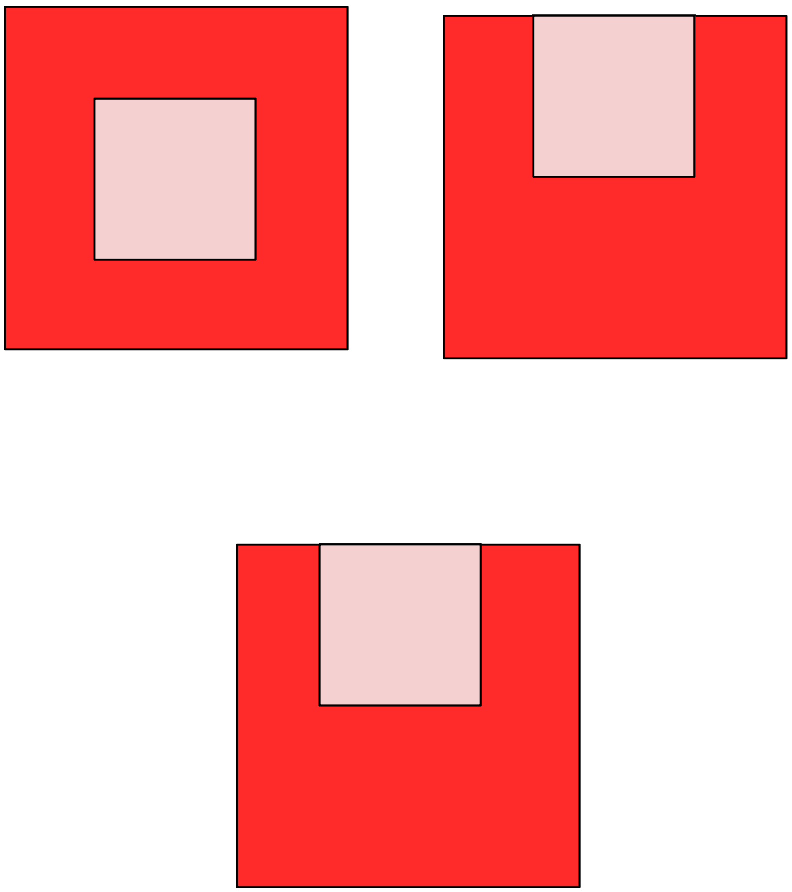
Wang, et al, Nature Materials, 2012, *in press*

Imaging in Projection

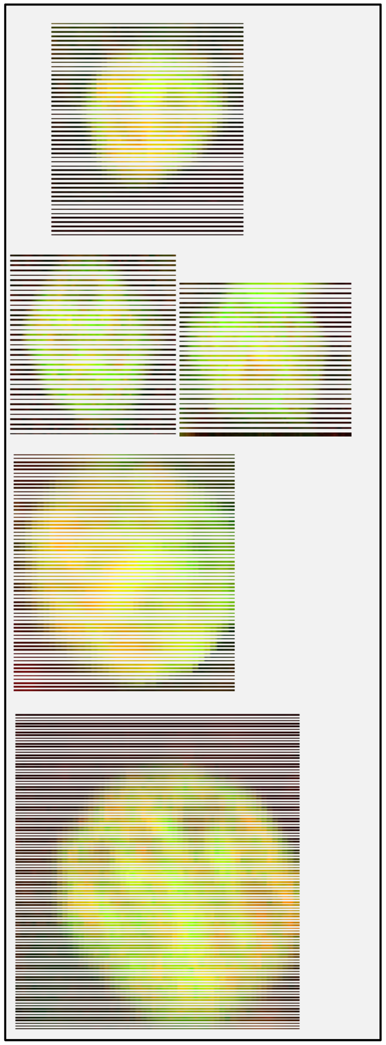
Core-Shell

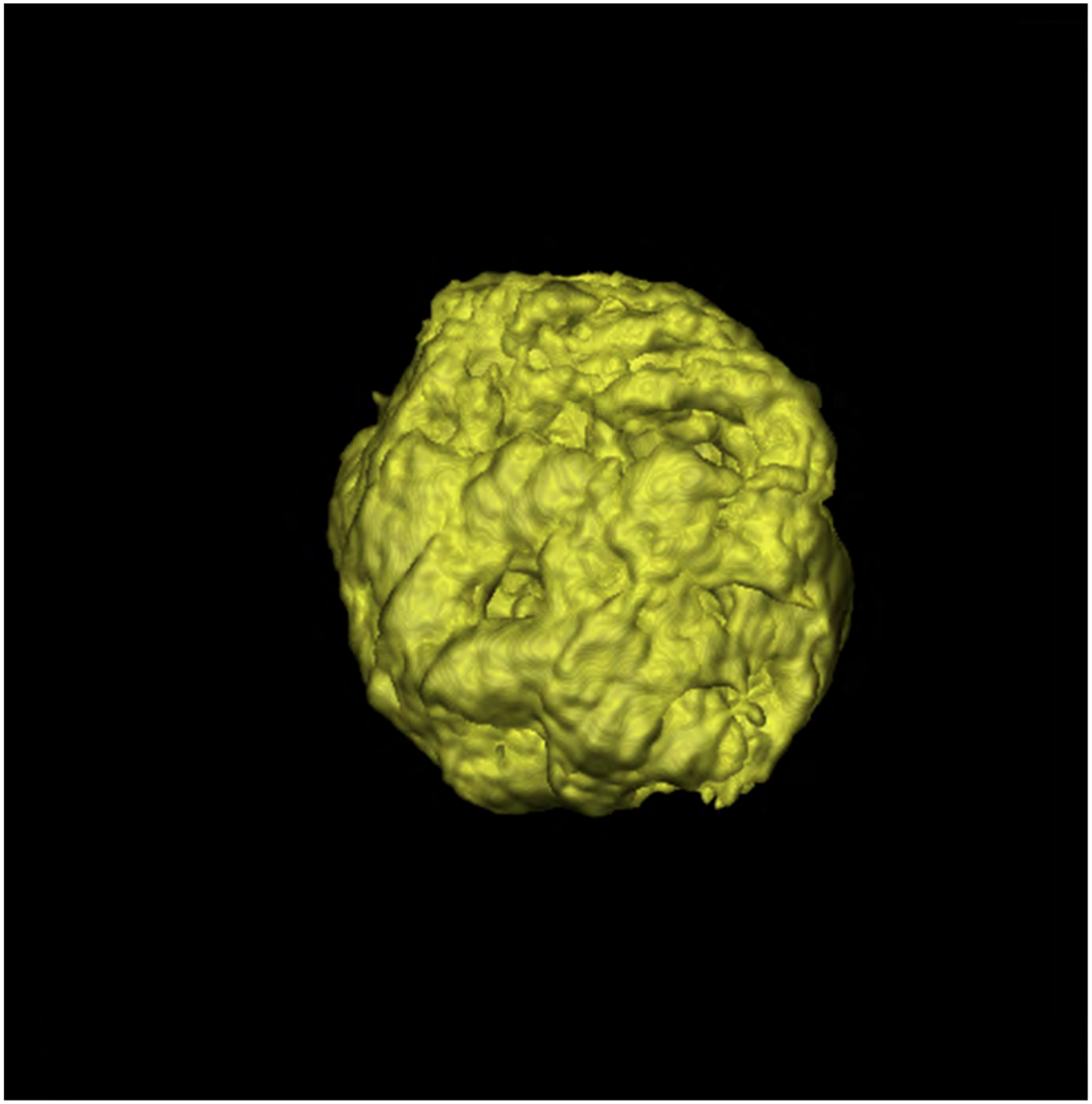


Inside or Outside?

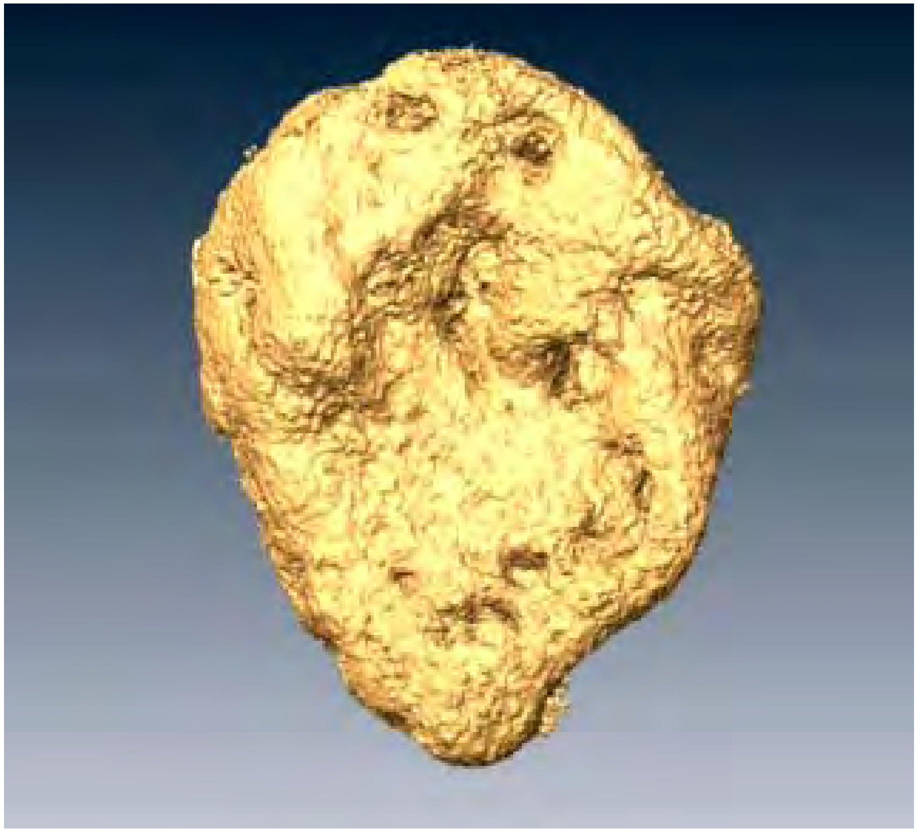


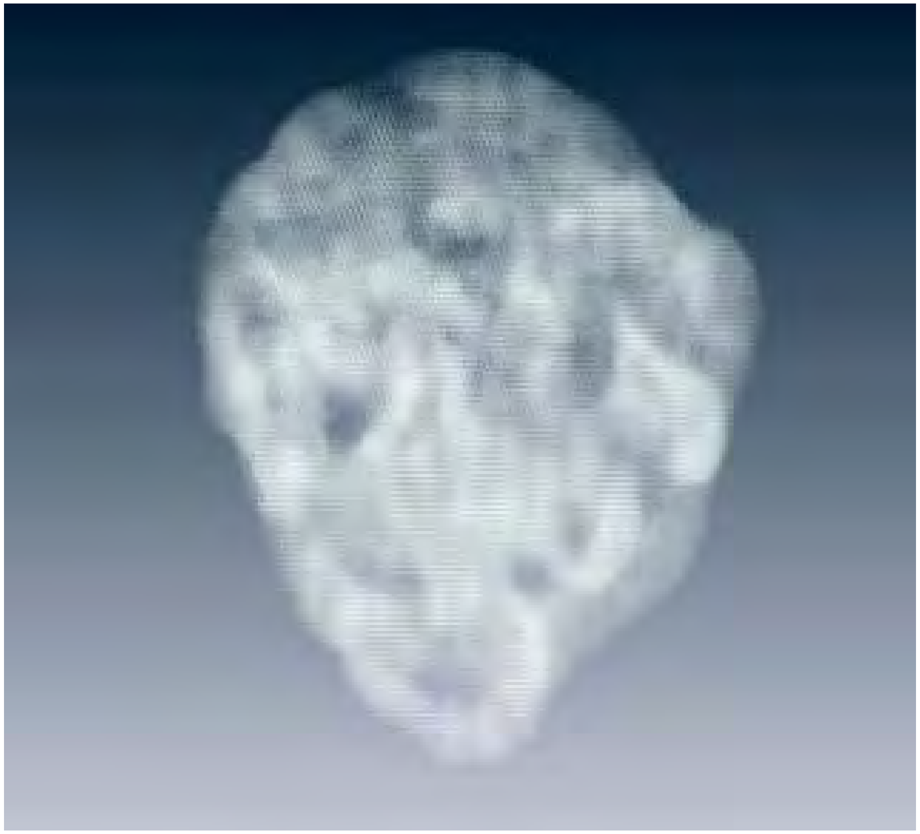
Porous, acid-leached $PtCu_3$



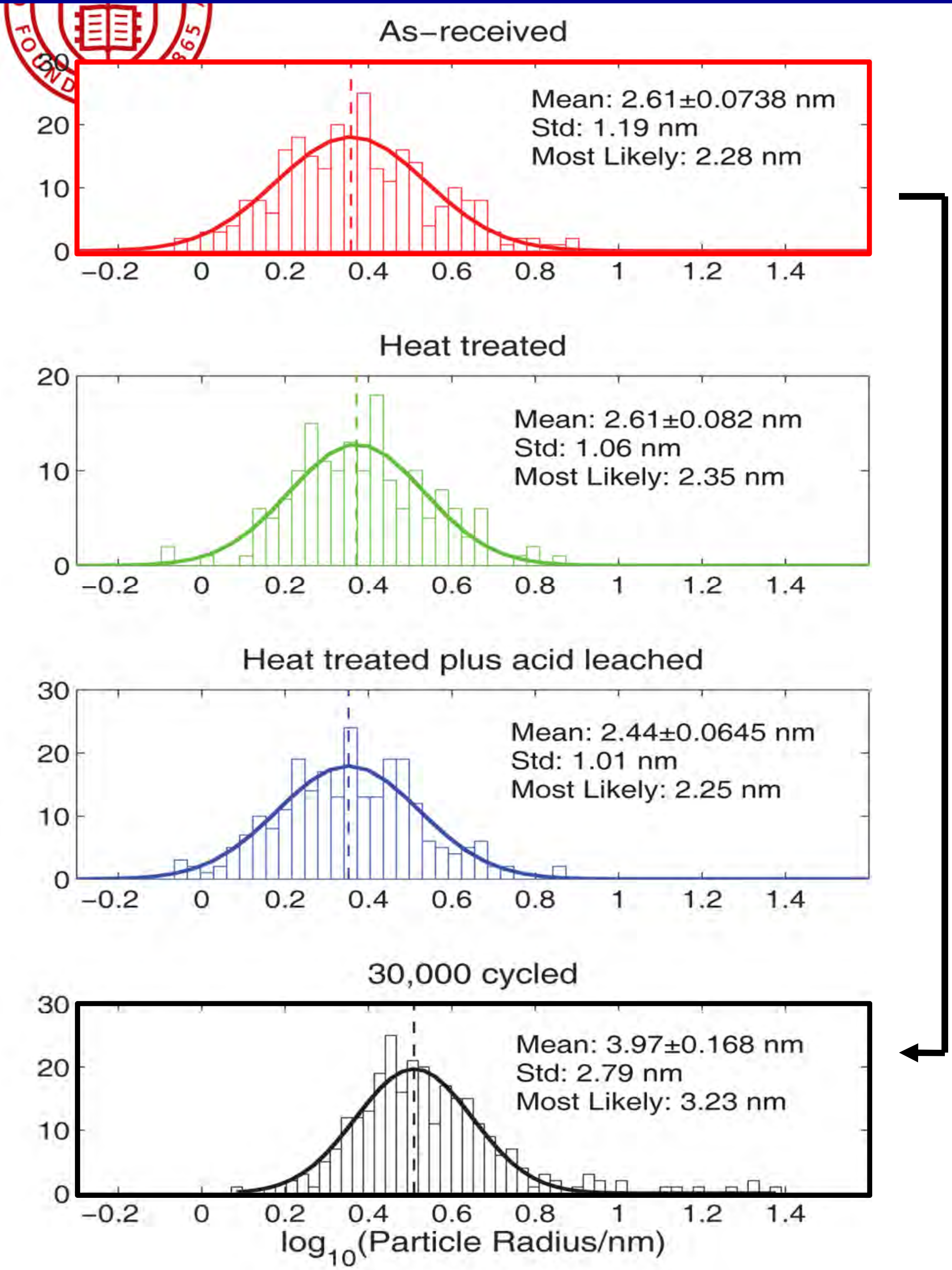


EST Reconstructed $PtCu_3$ Nanoparticle
(Equal-Slope Tomography, John Miao, Mary Scott, UCLA)





Particle Size Distributions (radius not diameter)



Reactivity loss

60%

Can this number be explained by the loss of surface area?

Surface area loss

Assume no loss of cobalt

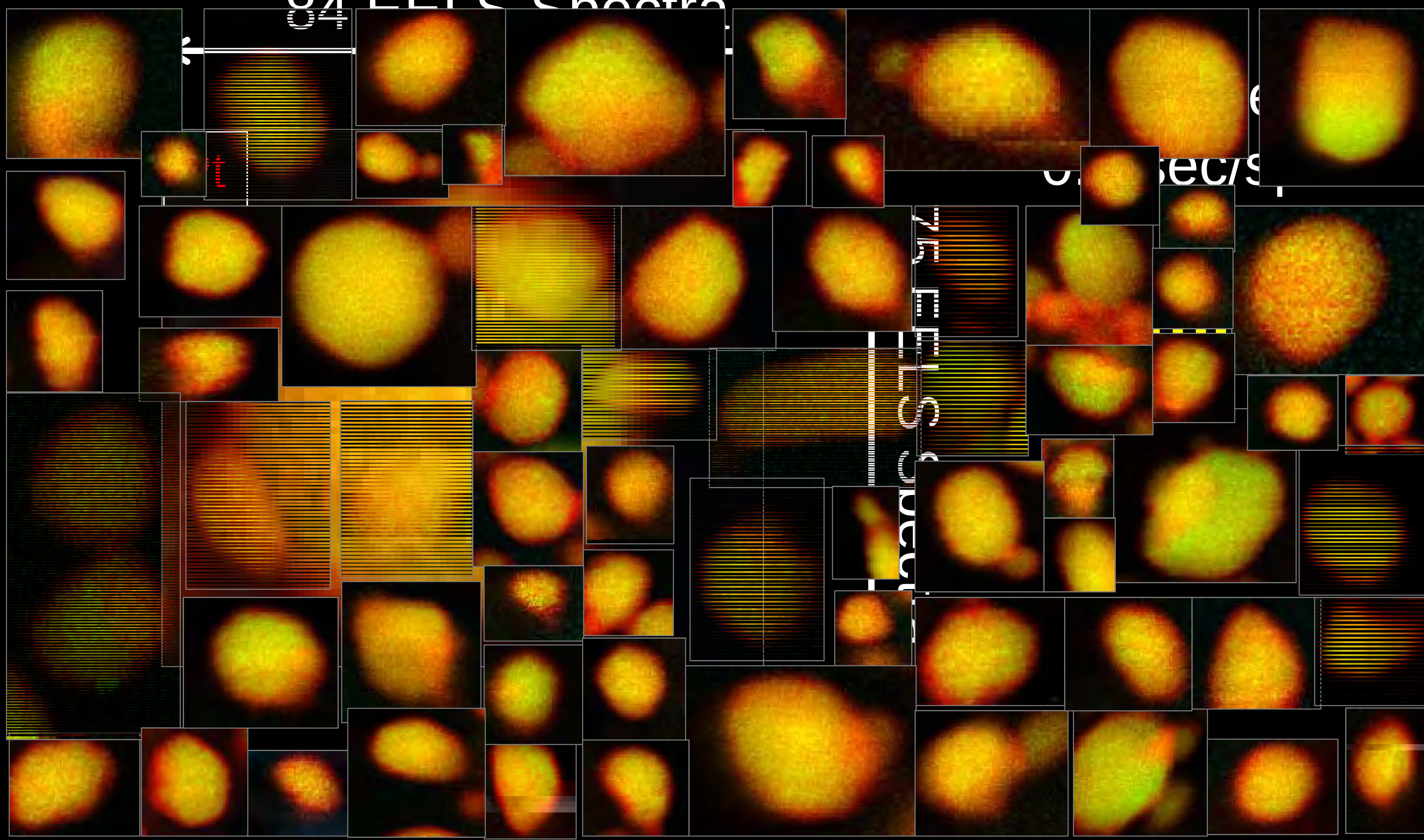
Surface loss: 15.8%

Assume all Co lost (volume loss of ~25%)

Surface loss: 36.8%

Bigger particles have lower reactivity per unit area. Why?

Pre-voltage Cycling Particles: Pt Rich Shell

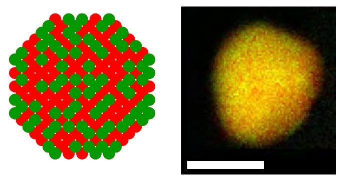


H. L. Xin *et al.*, *Nano Letters* **12** 490 (2012)

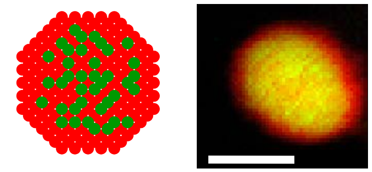
Heat Treated and Acid Leached:
From Pt-rich {111} surface → 3 ML Pt shell on all surfaces

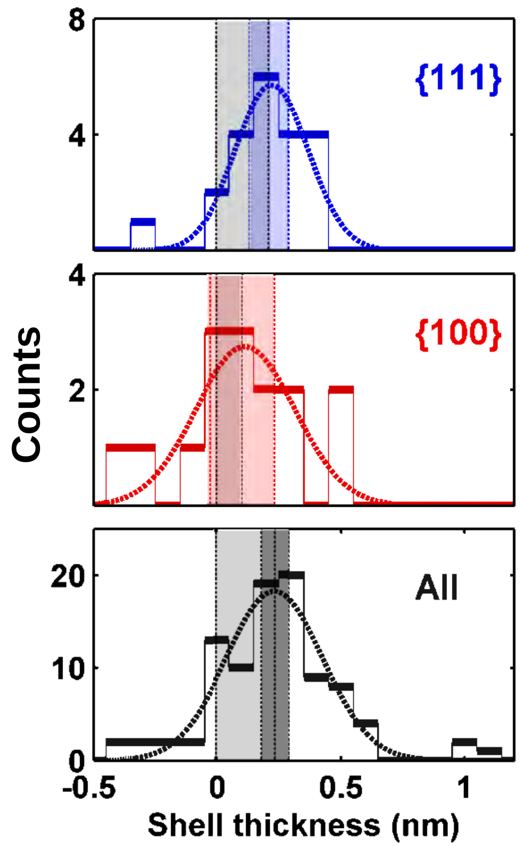
Scale bar:
5 nm

Heat Treated:



Heat Treated and Acid Leached:

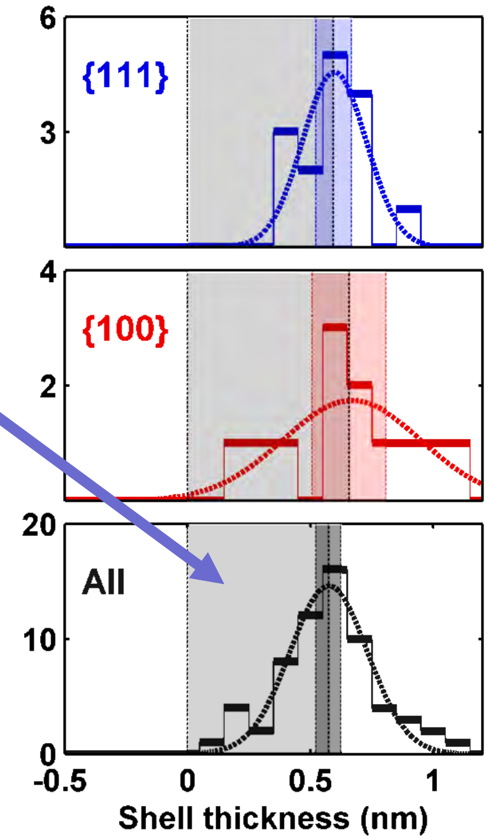




Pt segregation on {111} only

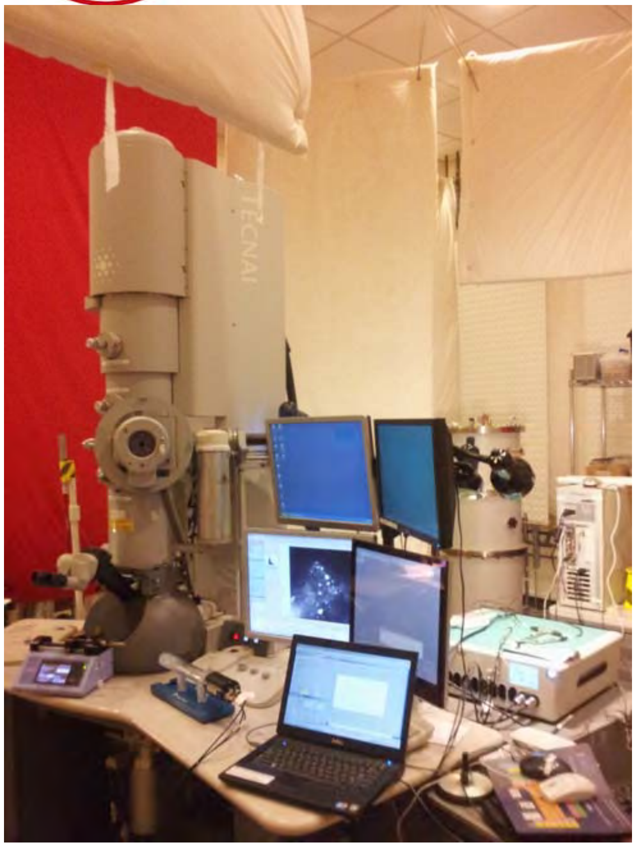
3 ML Pt-shell:
- No Co neighbors
- No Co 2nd neighbors
- No Co-Pt bonding

Yet:
- Enhanced activity over pure Pt.

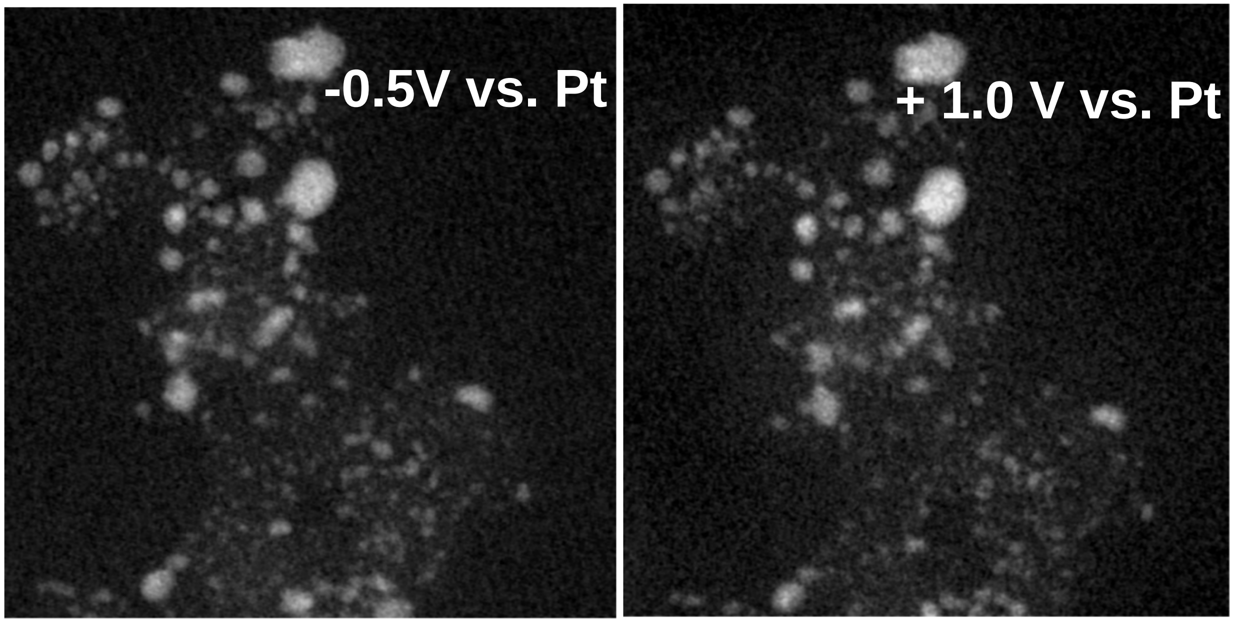


No statistical correlation between facet and shell thickness

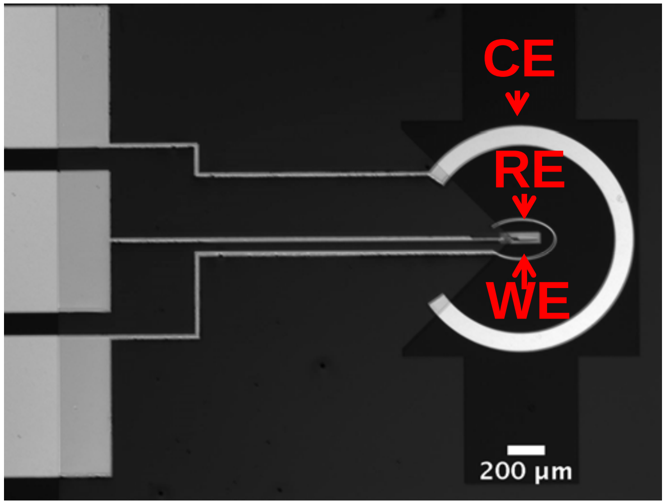
In-situ Electrochemical Cycling of Fuel Cell Catalysts

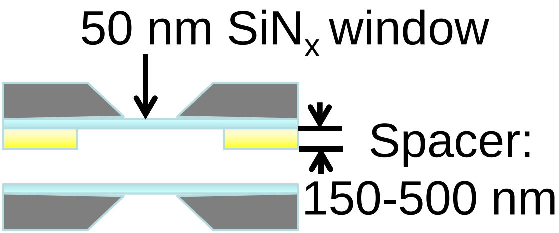


Protochips Electrochemical Holder

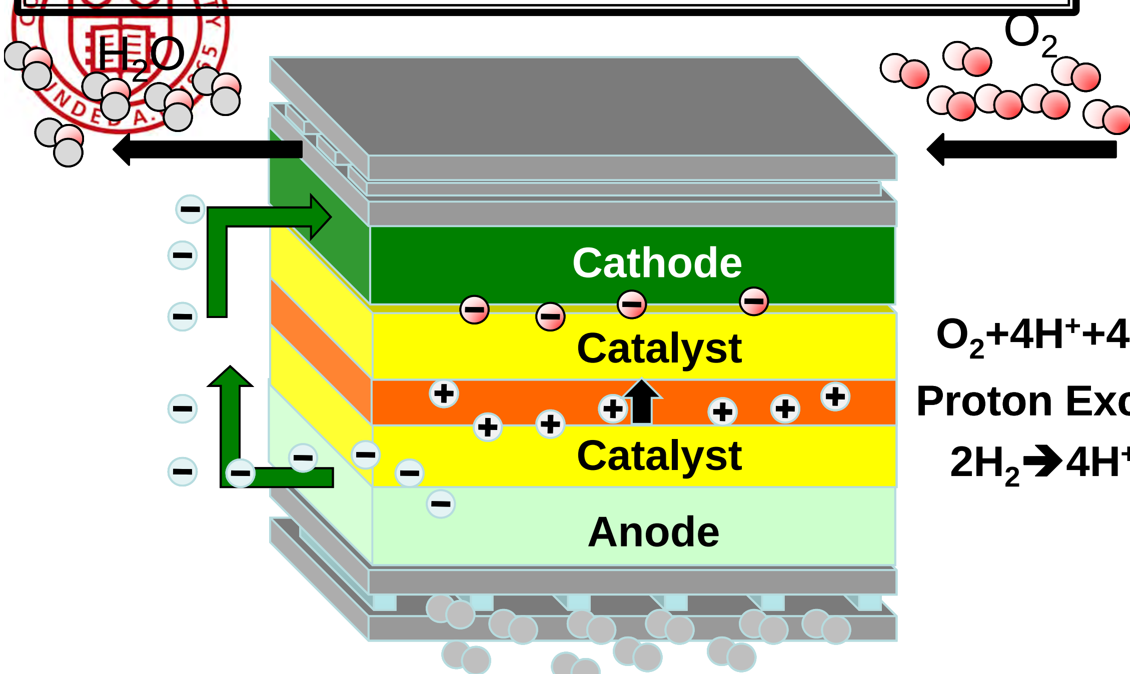


Pt_3Co/C in 0.1 M Perchlorate Acid





Proton Exchange Membrane Fuel Cell



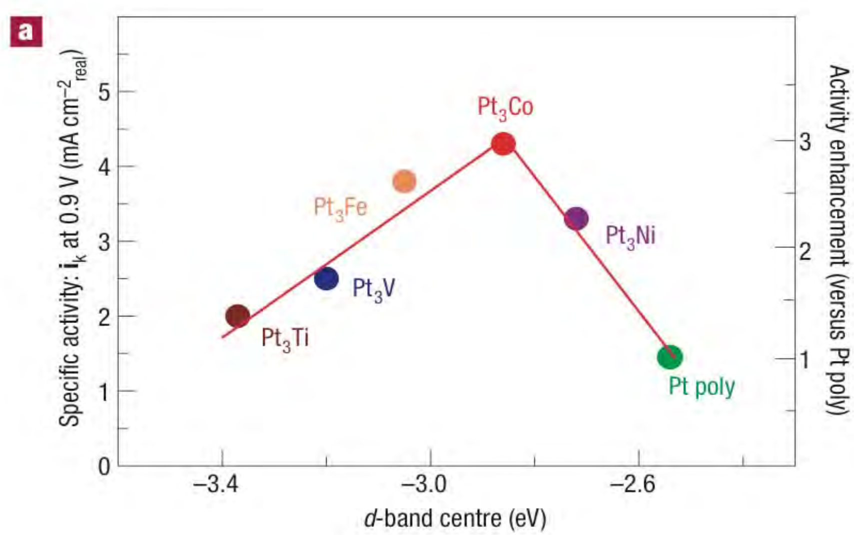
$O_2 + 4H^+ + 4e^- \rightarrow 2H_2O$

Proton Exchange Membrane

$2H_2 \rightarrow 4H^+ + 4e^-$

Limiting Step:
Oxygen Reduction Reaction in Cathode

Improved Catalytic Activity v. Pure Pt Metal

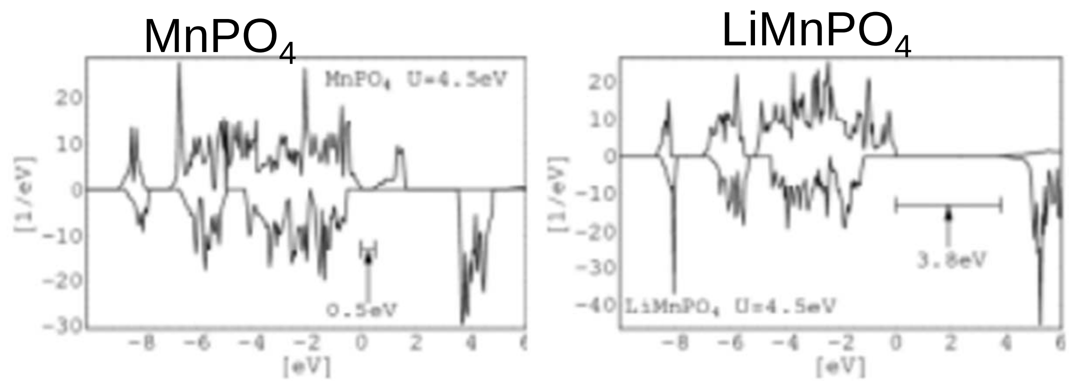


V. R. Stamenkovic et al. *Nature Mater.* **6**, 241 (2007).

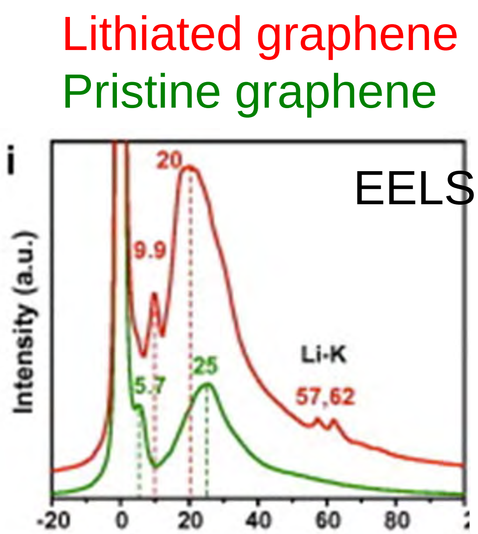
Pt_3Co catalyst particles:

- What is the atomic distribution of Pt and Co in these particles?
- How durable are these alloys?

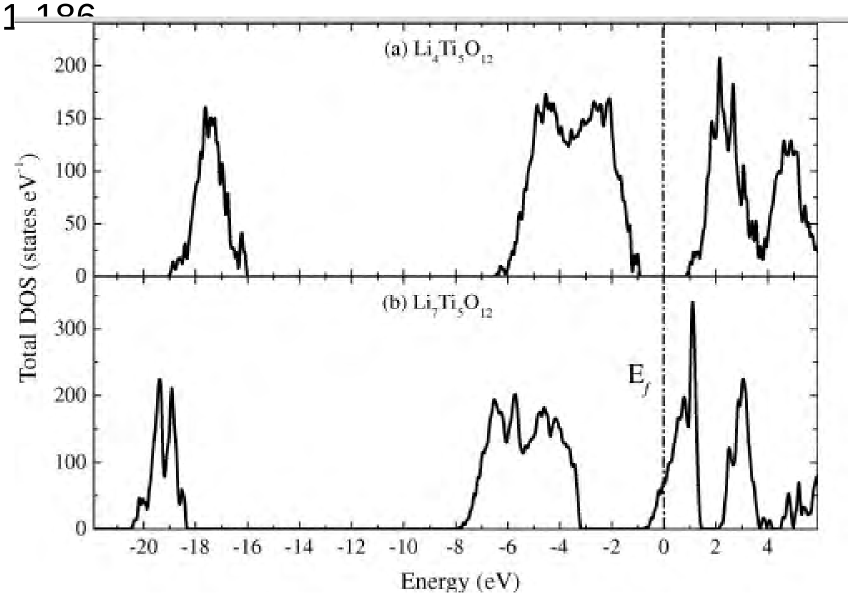
Liquid cell EFTEM technique with new battery materials



Fei Zhou, et. al. Solid State Communications 132.3 (2004): 181-186

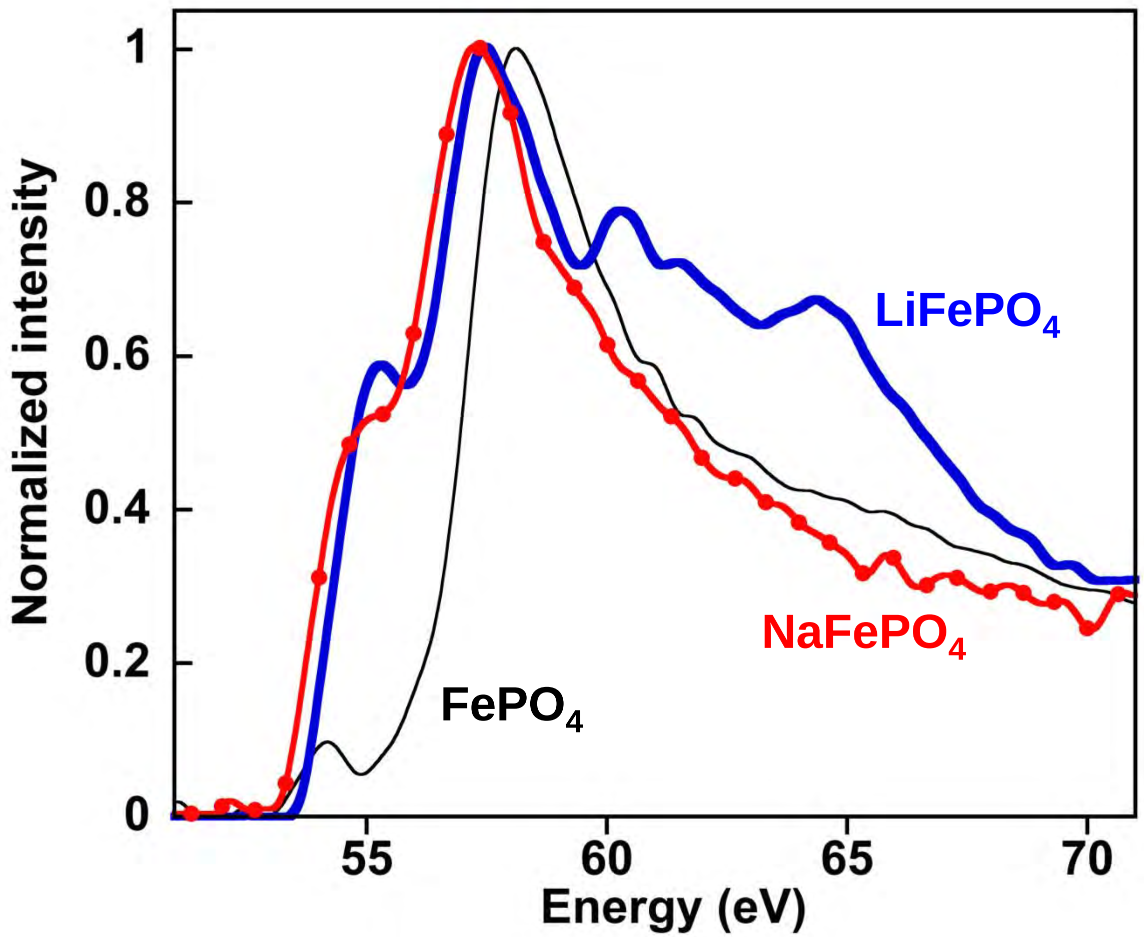


Xiao Hua Liu, et al. Carbon, **50** 10, (2012) 3836–3844



Ouyang C.Y, et. al. Echem Comm. **9** 5 (2007): 1107-1112

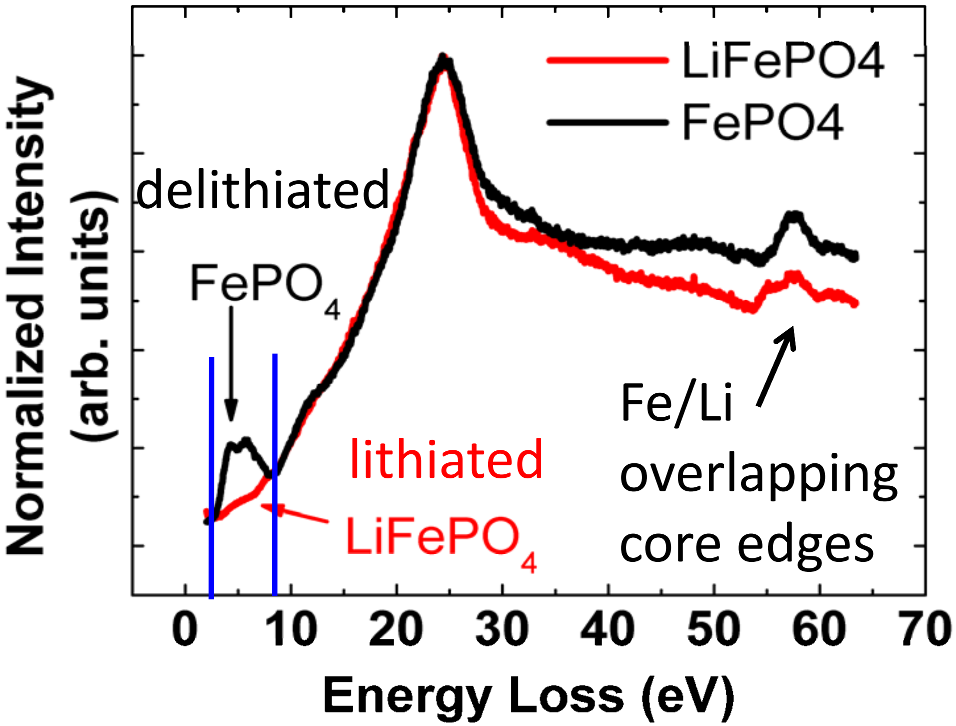
Li-K Edge Problems II



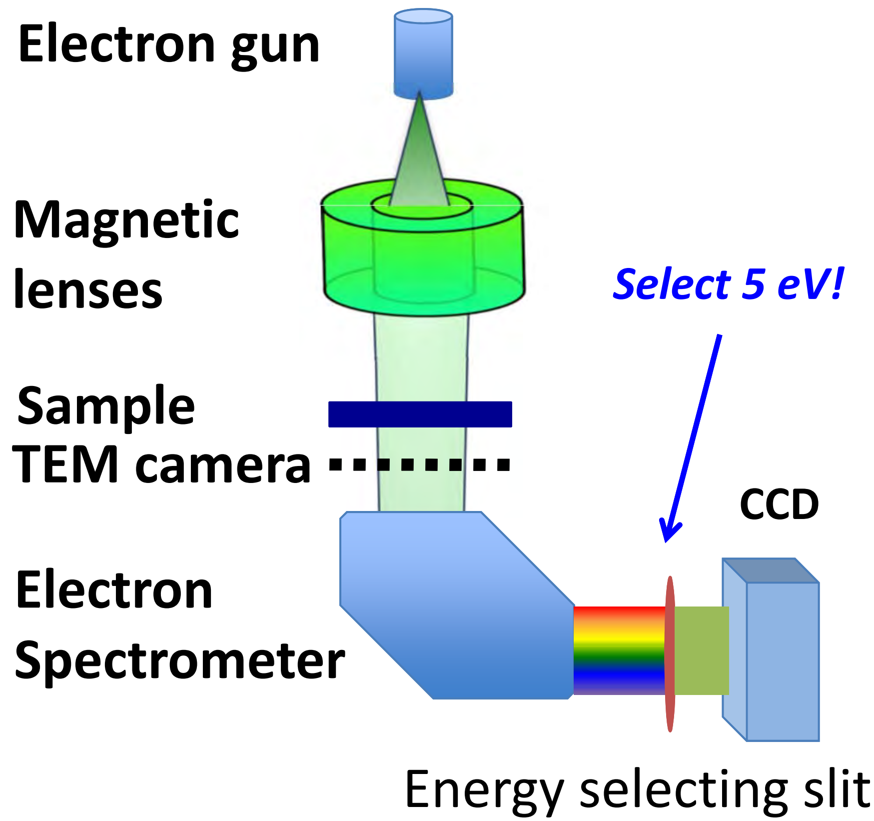
P. Moreau, Micron **43** (2012) 16

Valence EELS for Batteries

Monochromated EELS, 0.2 eV resolution



Transmission Electron Microscope (TEM)

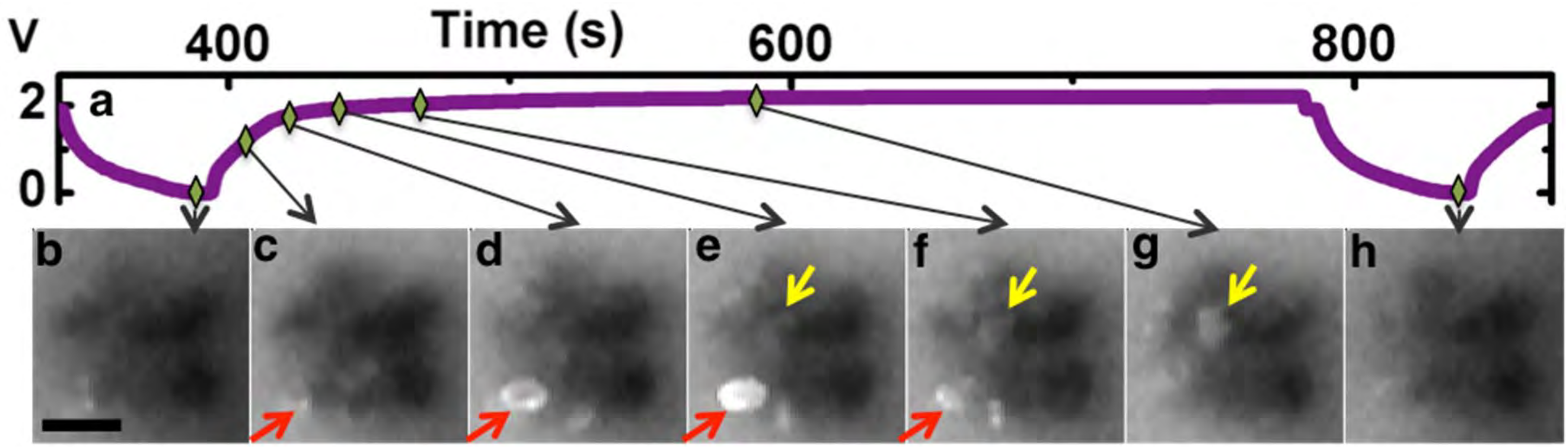


Energy-Filtered TEM (EFTEM)

Want *rapid* spectroscopic images of the 5 eV signal!

EFTEM imaging!

Mechanism of Lithiation



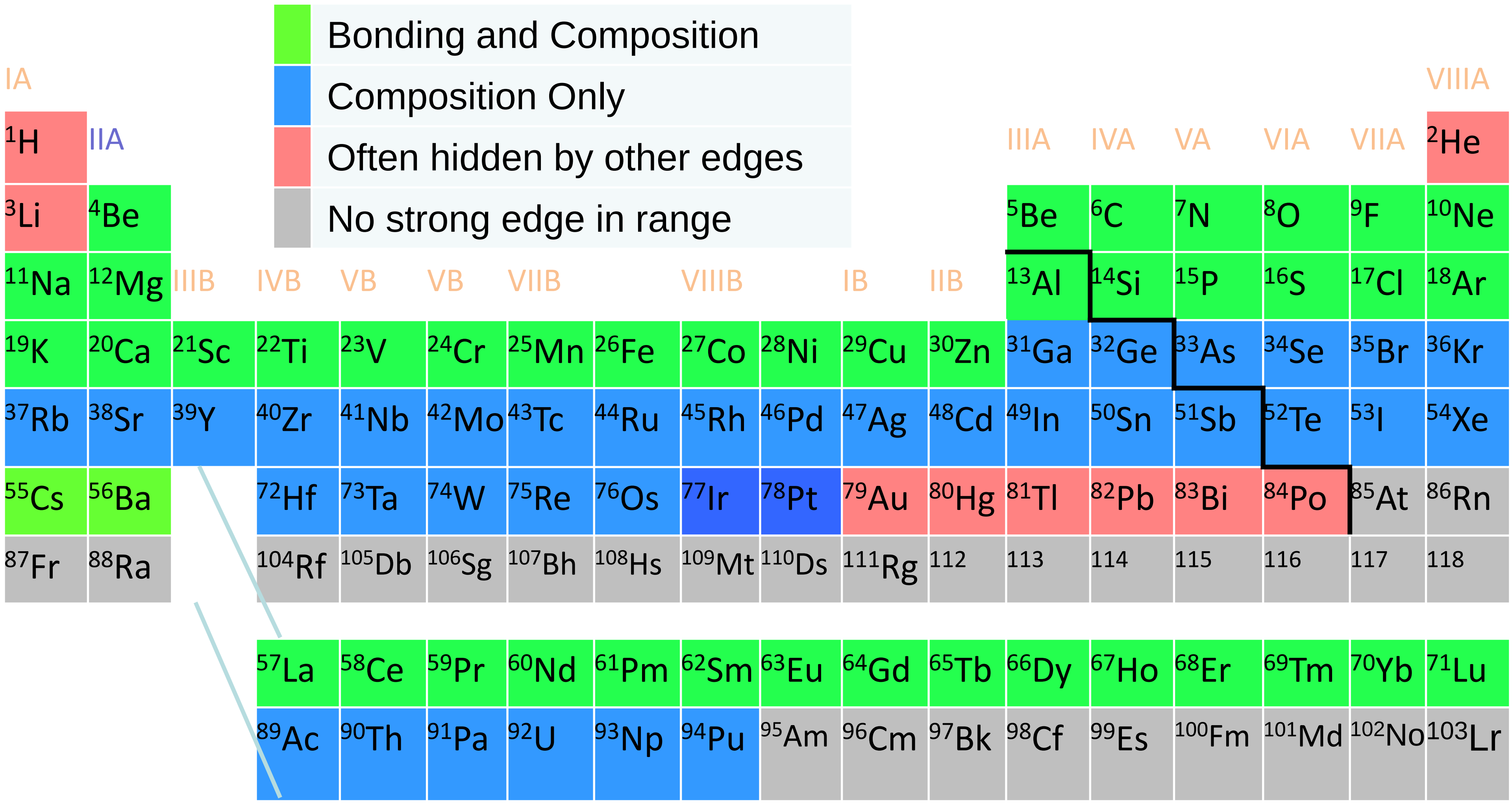
2 dominant modes of lithiation for this experiment:

We see core-shell type structures during growth of the $FePO_4$

Slow nucleation for domino cascade

Highly dependent on particle size and experimental conditions: further investigation necessary

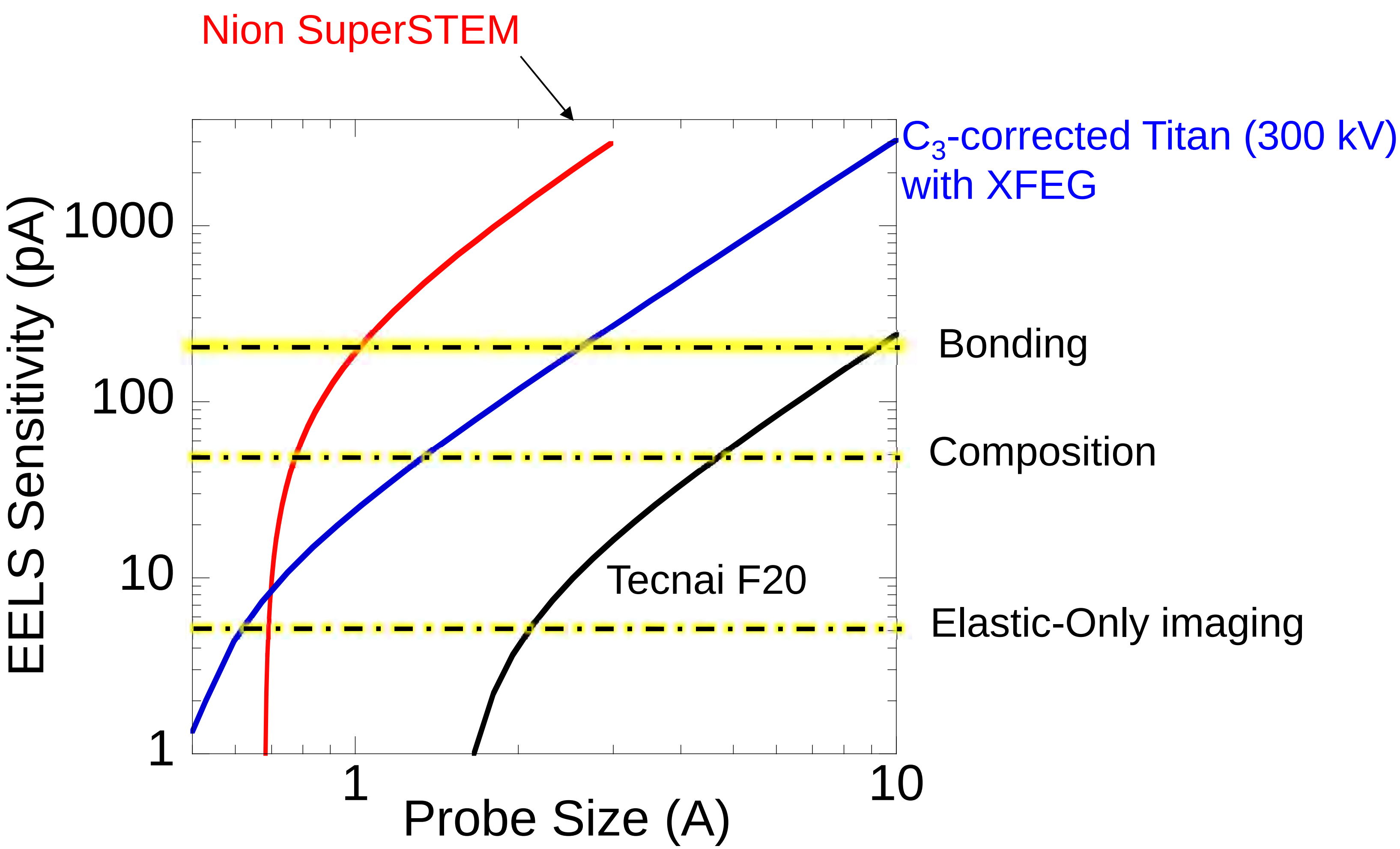
Elements Accessible by EELS



Imaging Pt: P. Cueva et al, *Microscopy and Microanalysis* **18**, 667 (2012).

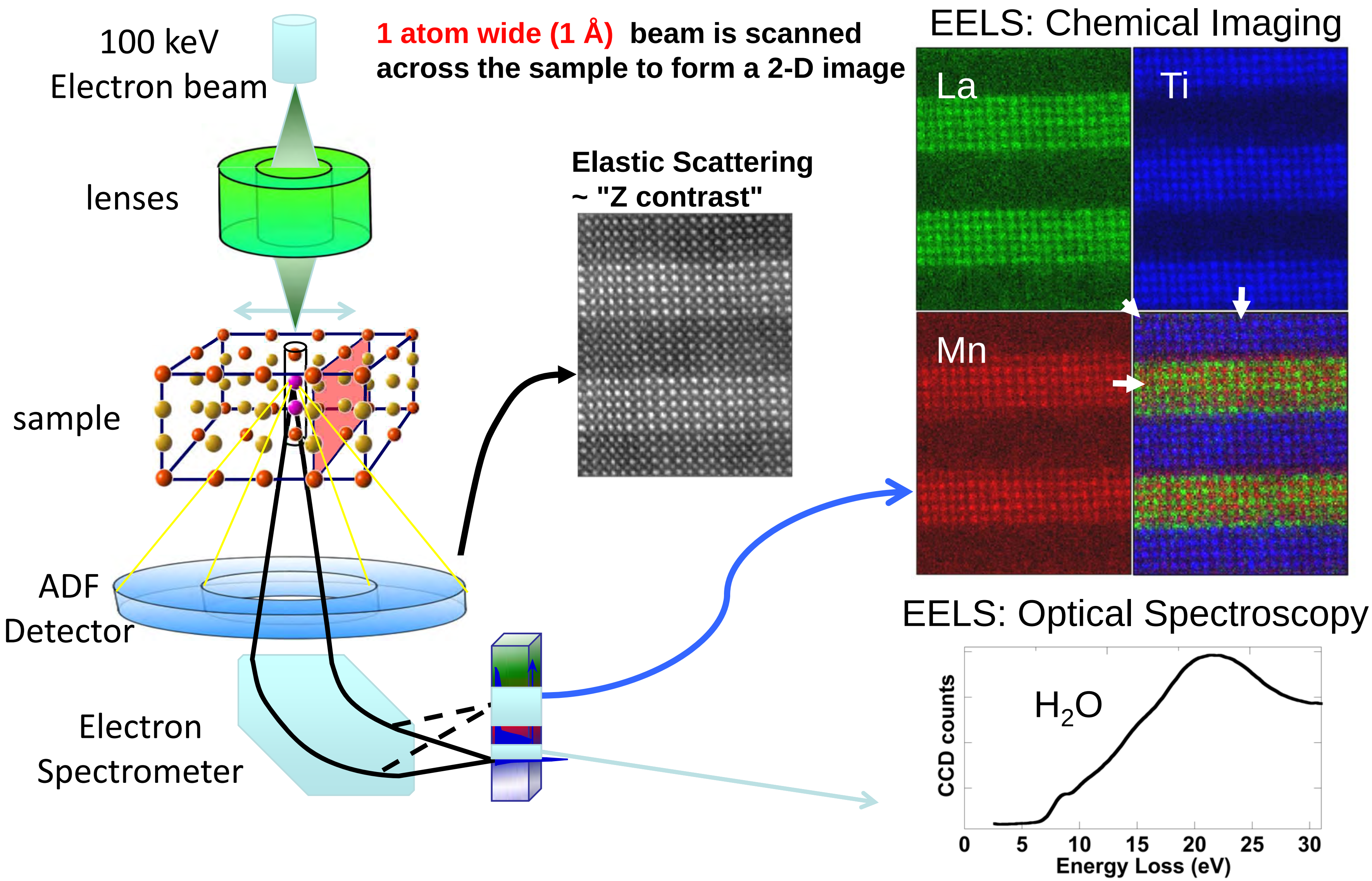
Tradeoff: Probe Size for Beam Current

I_{coll} = β x (Probe Area) x (Probe Solid Angle) x (Collection Efficiency)



D. A. Muller, *Nature Materials*, **8**, 263 (2009)

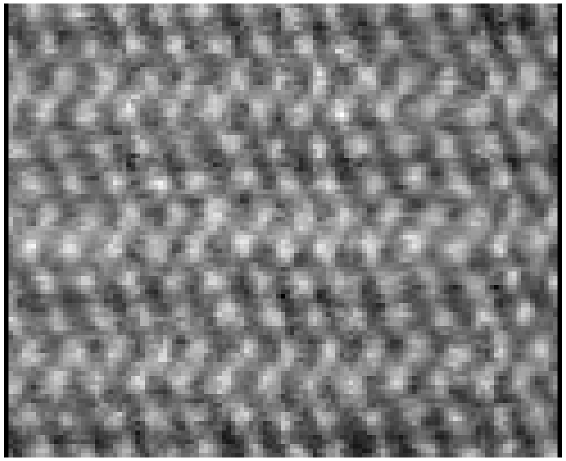
Scanning Transmission Electron Microscopy



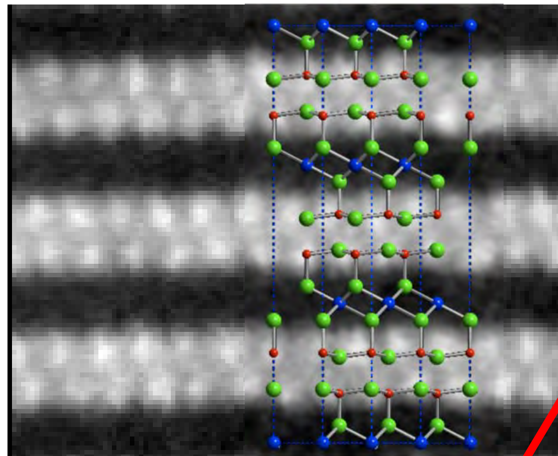
Muller, Kourkoutis, Murfitt, Song, Hwang, Silcox, Dellby, Krivanek, *Science* **319**, 1073 (2008).

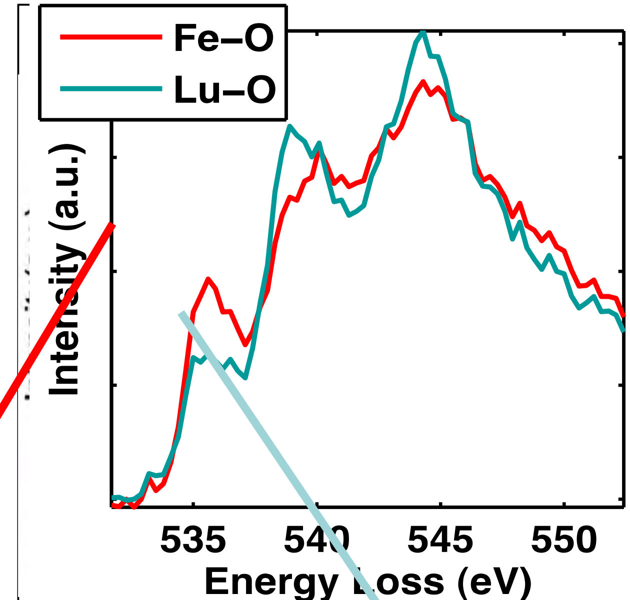
Mapping Chemical Environment of O atoms in $LuFe_2O_4$

O K-edge

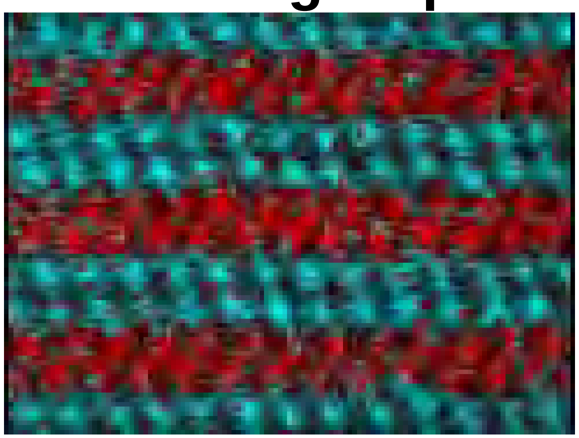


Fe $L_{2,3}$ - edge

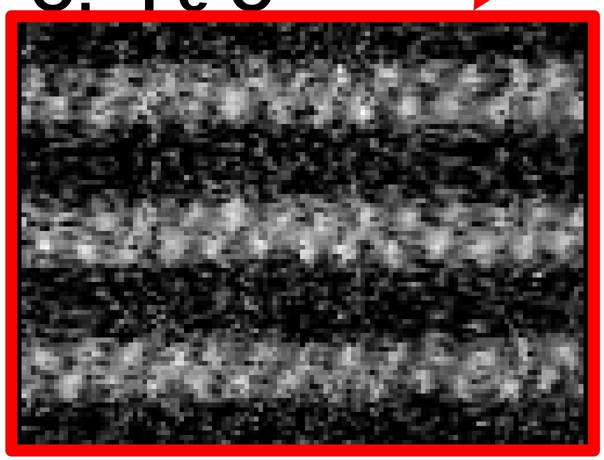




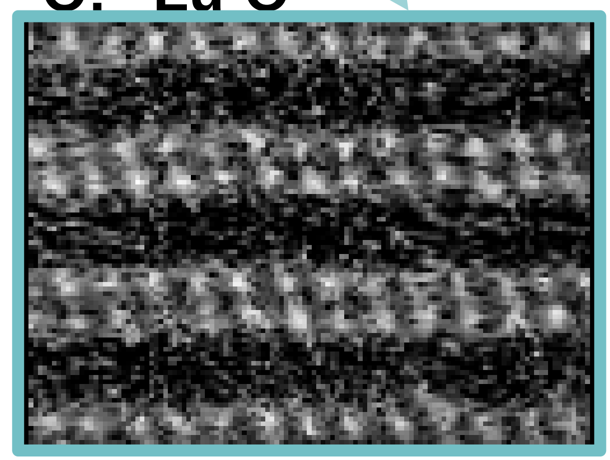
O Bonding Map



O: “Fe-O”

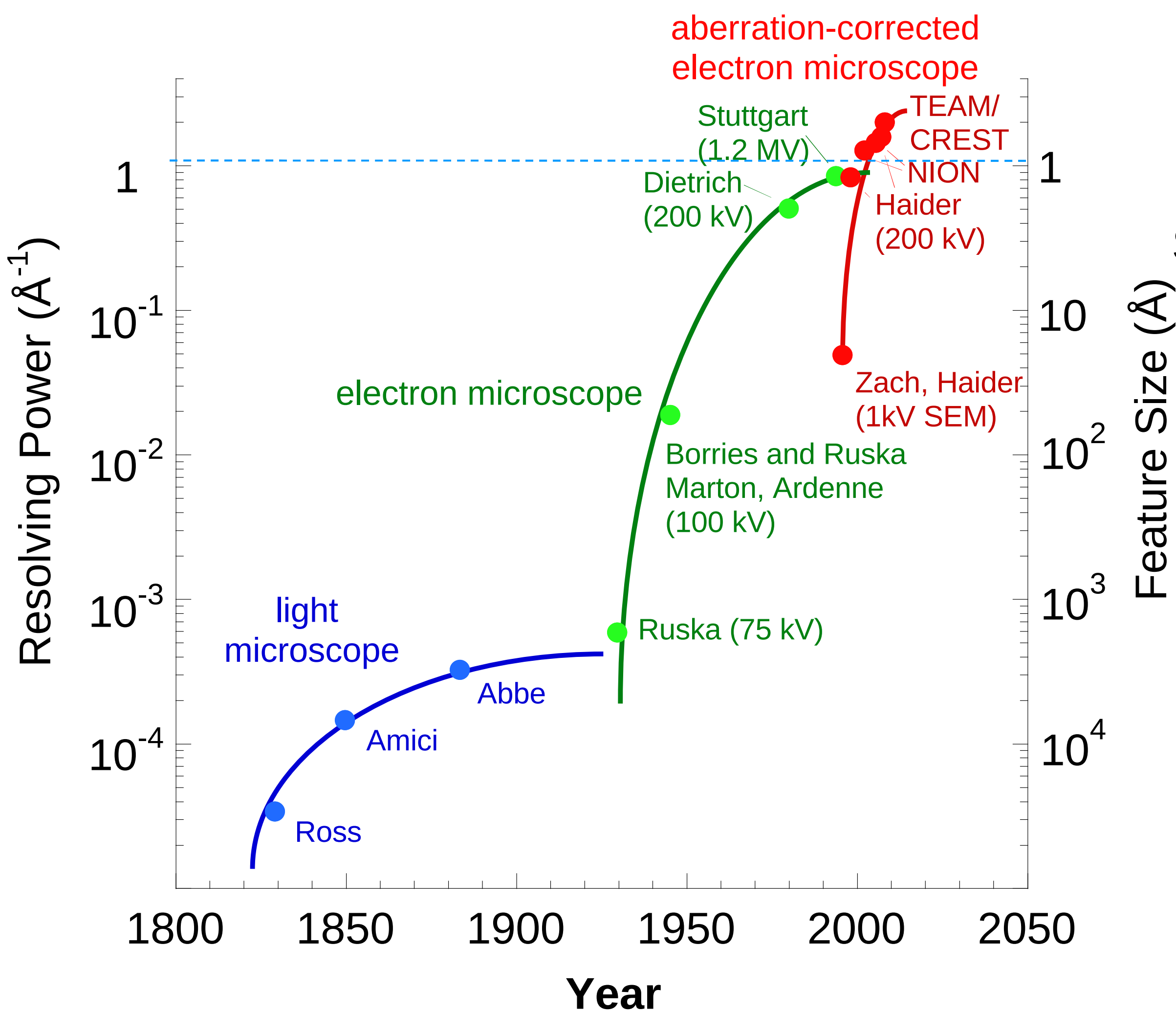


O: “Lu-O”



J. A. Mundy et al, *Appl. Phys. Lett.* **101**, 042907 (2012).

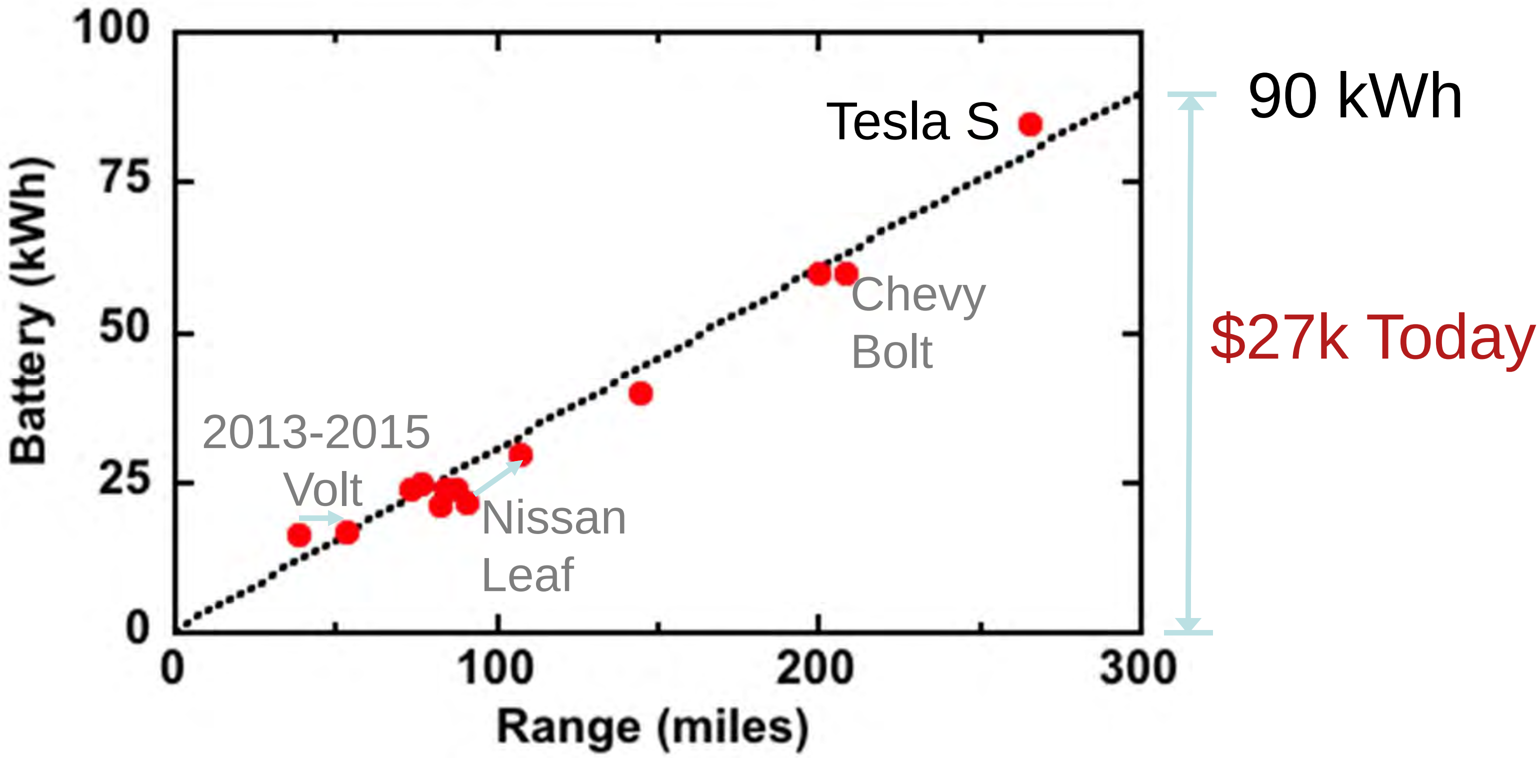
Hardware Advances in Microscopy



Corrected optics have enabled practical Sub-Angstrom resolution

Muller, Nature Materials, (2009), Adapted from Rose (2009)

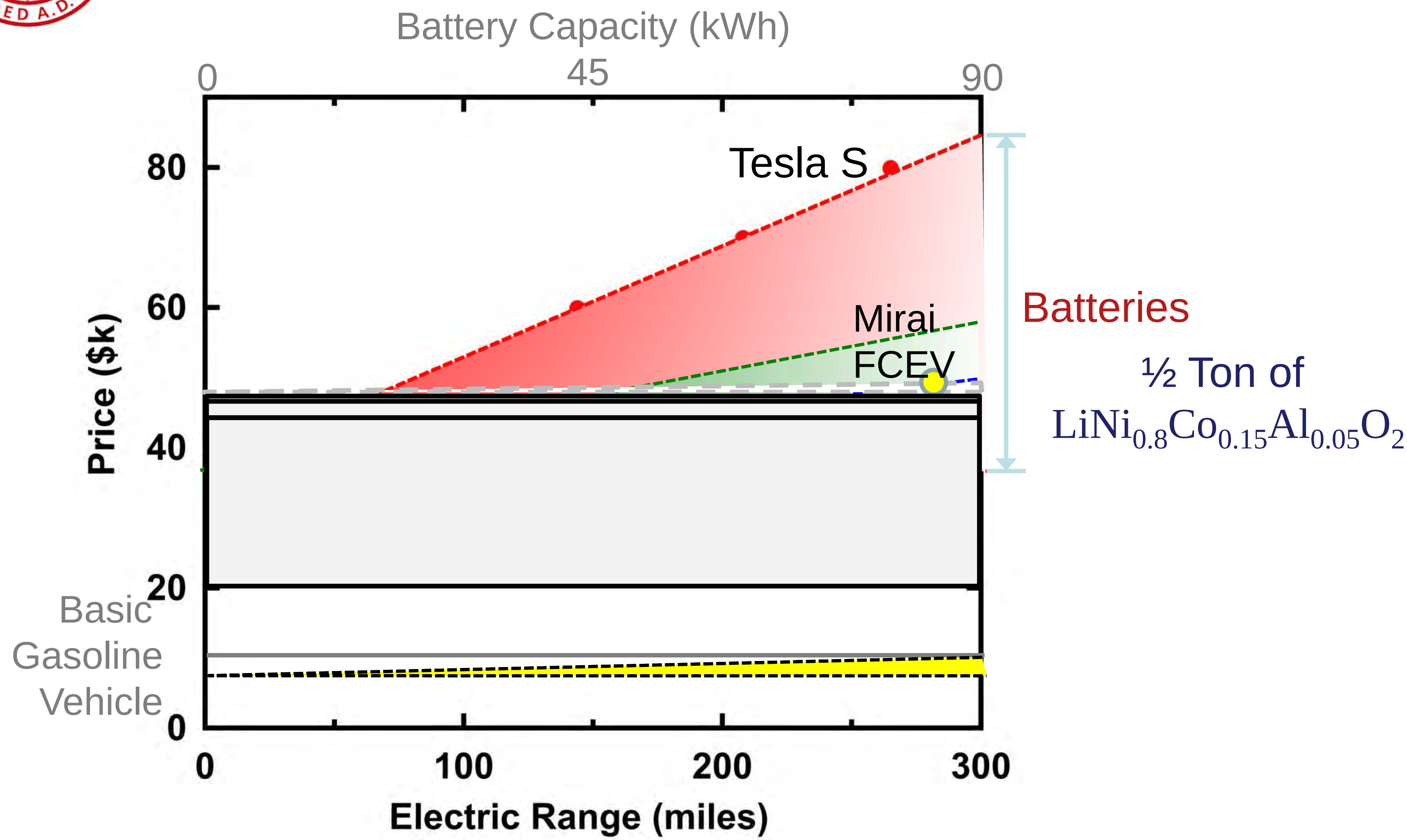
Electric Vehicle Range is Set by Size of Battery



How much does 90 kWh cost?

- Tesla : $27,000 (inc. ½ ton of $LiNi_{0.8}Co_{0.15}Al_{0.05}O_2$)
- Future Li-ion : $13,500 - $20,000
- To beat Gas : $1,000-$3,000 → **New Materials (<33 $/kWh)**

Electric Vehicle Price & Range Dominated by Battery

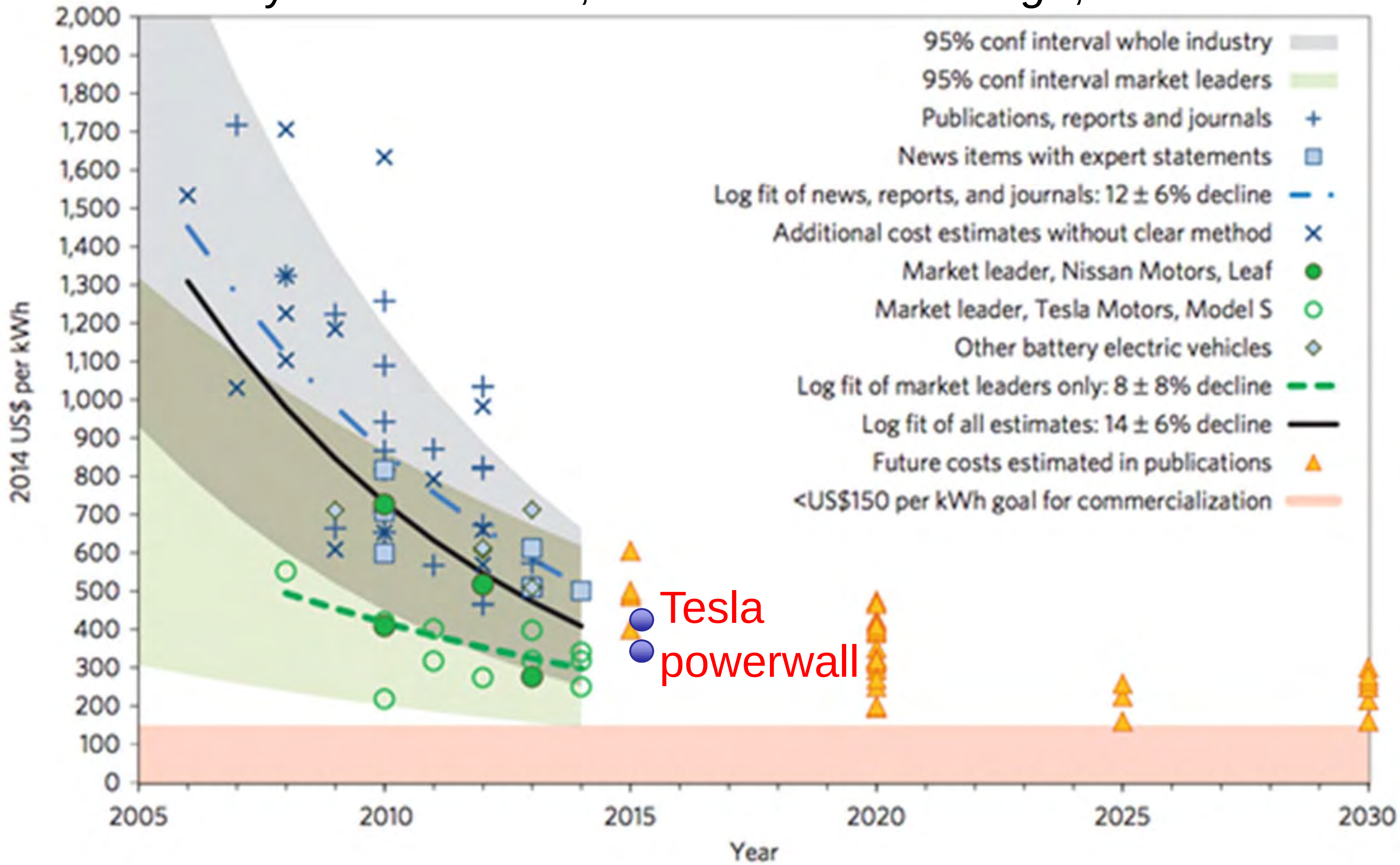


To beat Gasoline: Need 90 kWh Battery for < $3000

(or Fuel cell)

Battery Cost is Reducing Exponentially

Nykvist & Nilsson, *Nature Climate Change*,2015



$150/kWh * 90 kWh = $13,500