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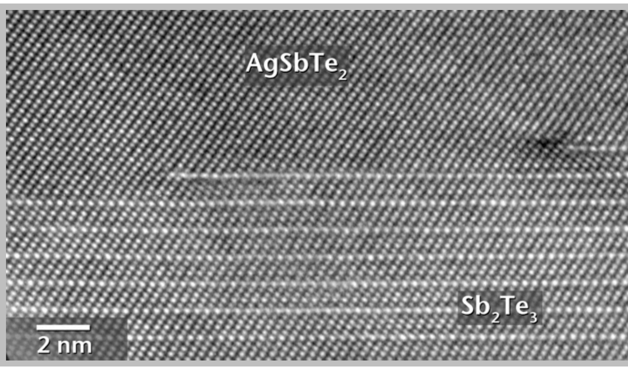

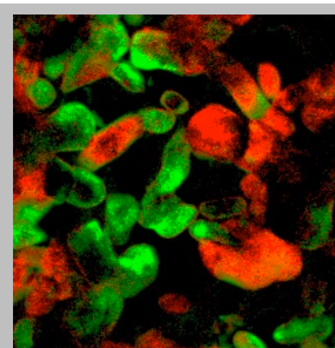

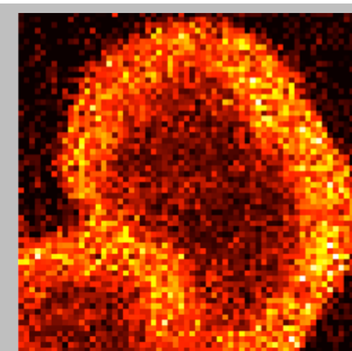

More Than Just a Picture: Answering Scientific Questions with Advanced Electron Microscopy

Joshua D. Sugar

Oct. 18, 2017

U.S. DEPARTMENT OF ENERGY

NNSA National Nuclear Security Administration

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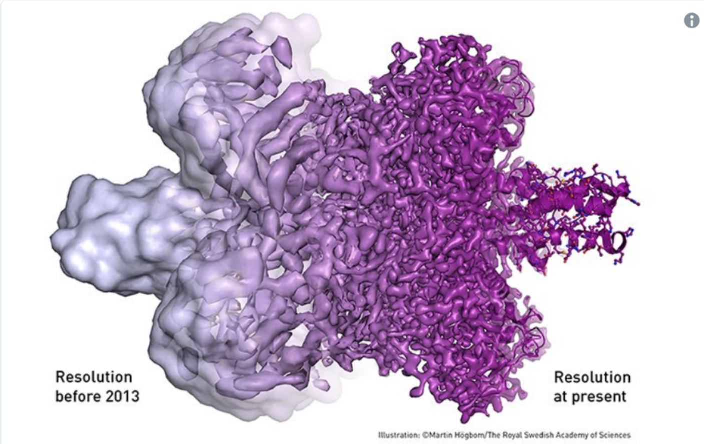
Speaking of Science

Three biophysicists win 2017 Nobel Prize in chemistry for imaging molecules of life

By Ben Guarino October 4 at 6:34 AM



The Nobel Prize
@NobelPrize
Follow

The final technical hurdle was overcome in 2013, when a new type of electron detector came into use.

2:56 AM - Oct 4, 2017 · Stockholm, Sweden

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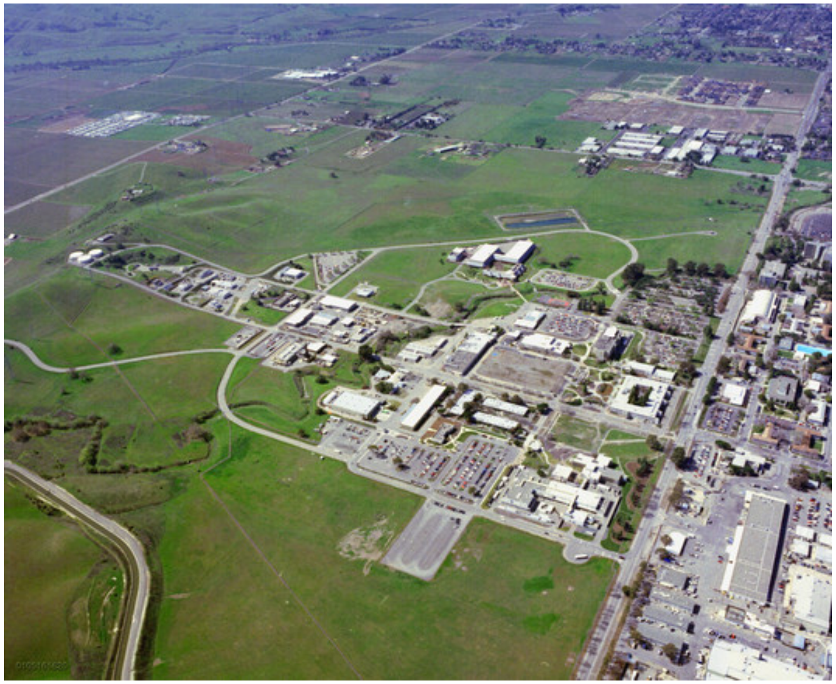
Quantitative information about bonding and structure leads to better understanding of biological function and the development of new therapies

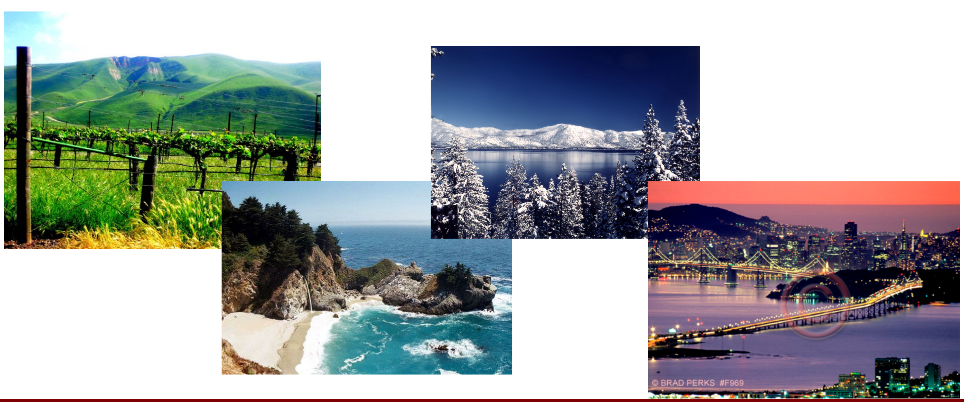
In materials science, we use microscopy to study structure, chemistry, and bonding so that we can understand transport phenomenon (mass, electron, ion, etc.) to develop new technology or make informed engineering decisions

Sandia National Labs Sites: National Security Complex



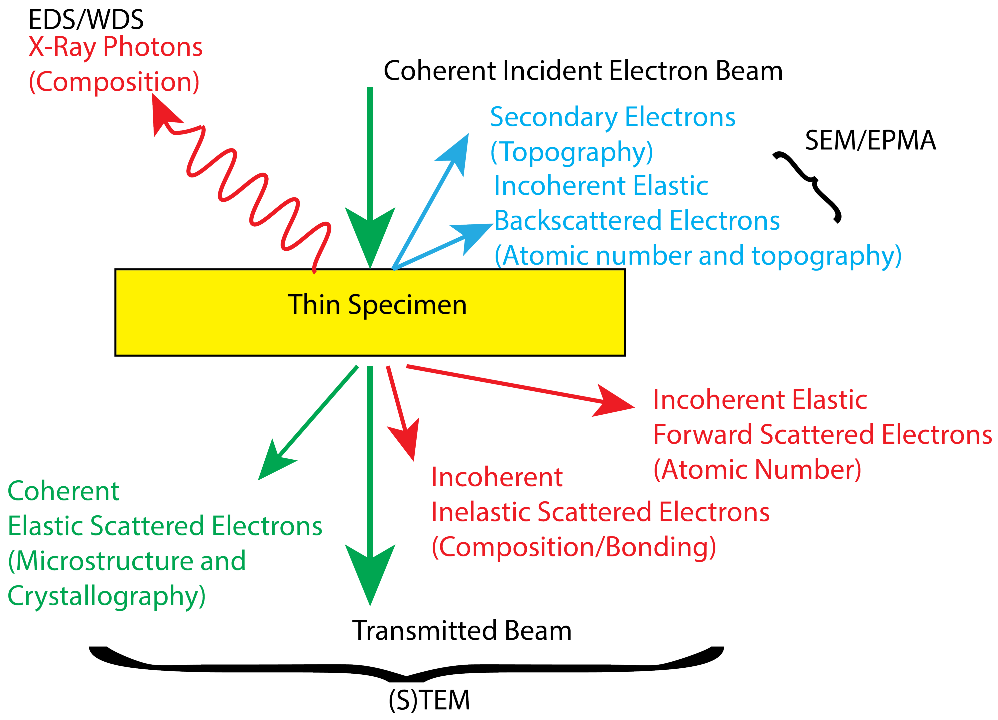
Livermore, CA

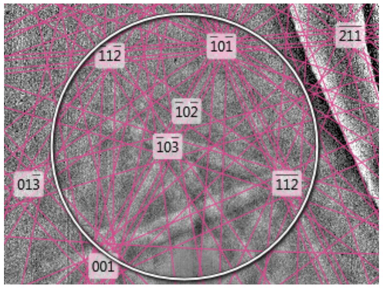
Albuquerque, NM

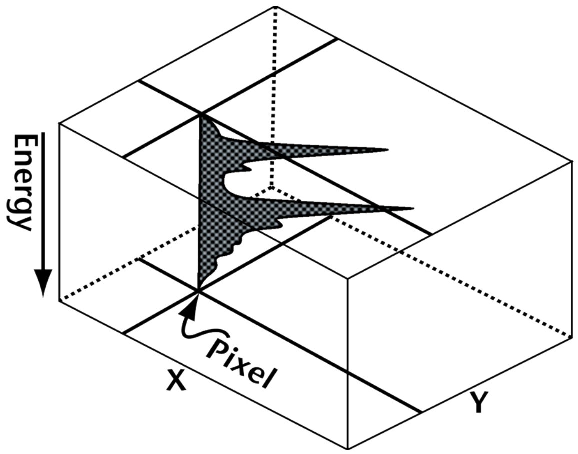


Available Signals for Microstructural Analysis

- Elastically Scattered Electrons
  - Energy is not lost from scattering process
  - Microstructural information from images
  - Crystallographic information from diffraction patterns
  - Atomic number (HAADF STEM)
- Inelastically Scattered Electrons
  - Energy is lost and converted into photons
  - Compositional and bonding/electronic structure information
    - Energy Dispersive Spectroscopy (EDS)
    - Electron Energy Loss Spectroscopy (EELS)







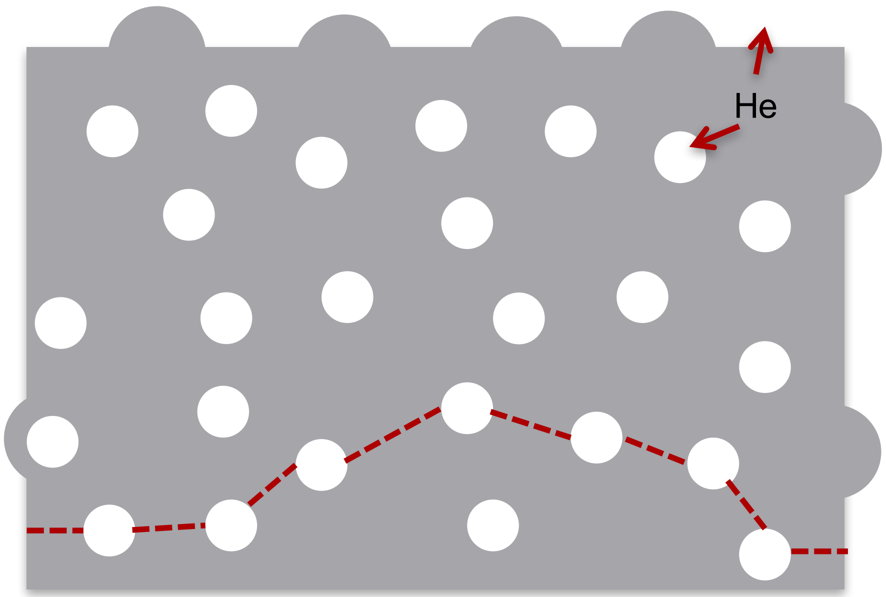
How do we use this information to understand materials synthesis and properties?

Linking Microstructural Measurements to Transport Phenomena

Sandia National Laboratories

- Helium bubbles formed by ^{3}H β decay, α decay, neutron (n, α) reactions
- Rh-ion transport during fabrication of nanoporous hydrogen storage materials
- Li-ion transport during charge/discharge of $LiFePO_4$ electrodes
- Electrical contact effects in device fabrication and transport

^{3}He causes bubbles in metal tritides

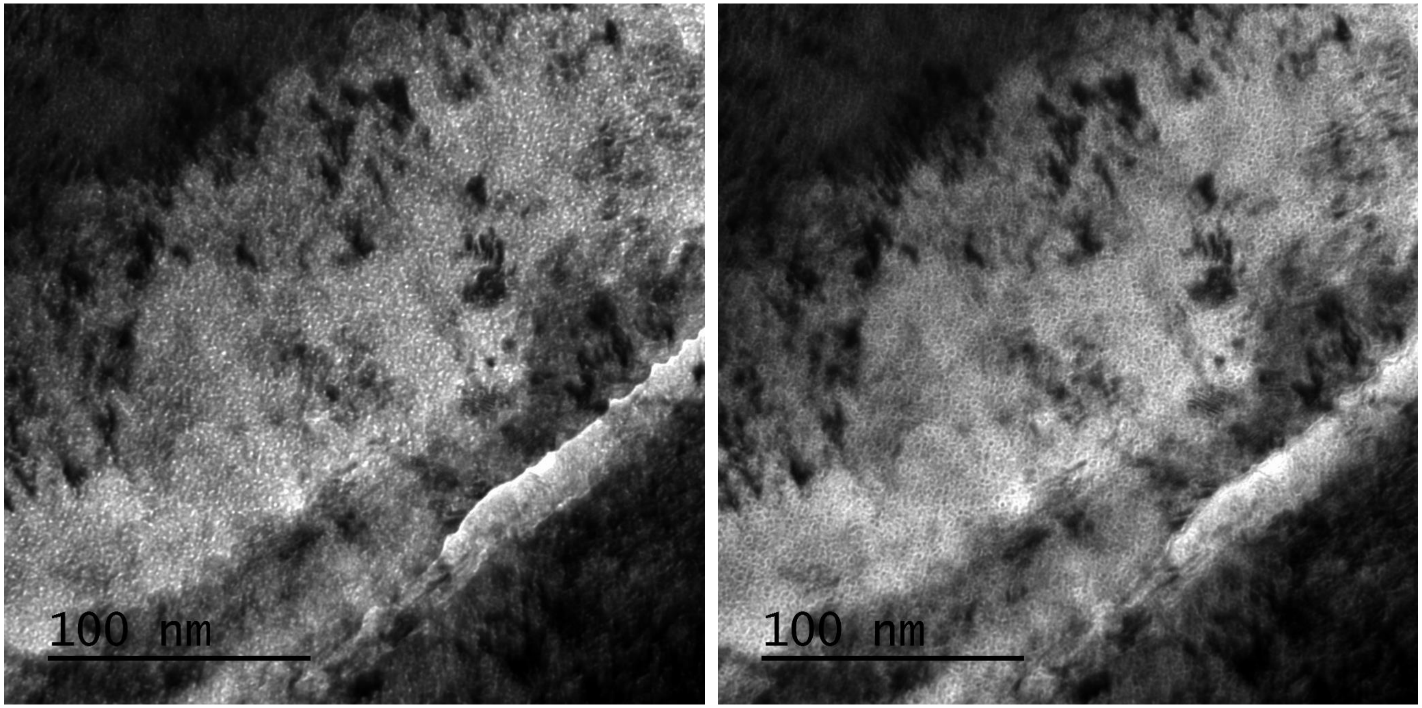


Early nucleation process is conventionally thought to define distributions, property evolution

- ^{3}H decays to insoluble ^{3}He.
- ^{3}He clusters push metal atoms, forming bubbles.
- Bubbles create fracture paths, swelling/deformation.
- ^{3}He may escape at surfaces (and fracture surfaces), through grain boundary paths.
- Properties are believed to depend on size and spacing distribution of bubbles

D.F. Cowgill, Fusion Sci. Tech. 28 539 (2005)
J.H. Evans, J. Nuc. Mater. 68 129 (1977)
F. Montheillet et al., Mat. Sci. Eng. A 494 407 (2008)

Helium Bubbles in Metals



100 nm

- Contrast reversal of bubble for over/under focus
- Bubbles are a few nm diameter, tens of nm apart

How do bubbles nucleate and grow?

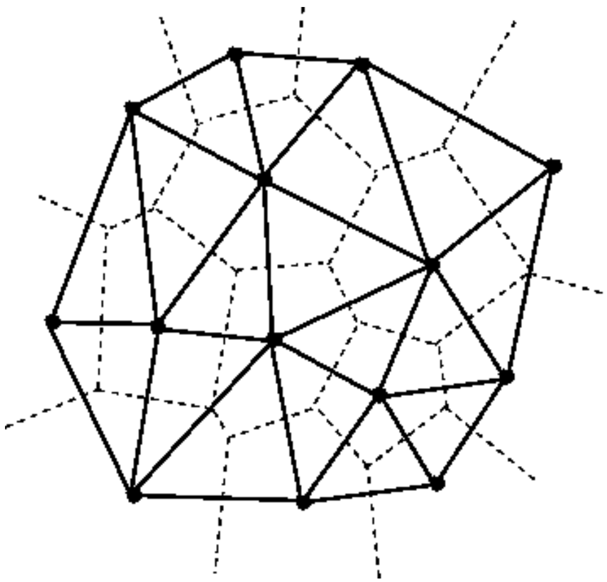
2D TEM Images

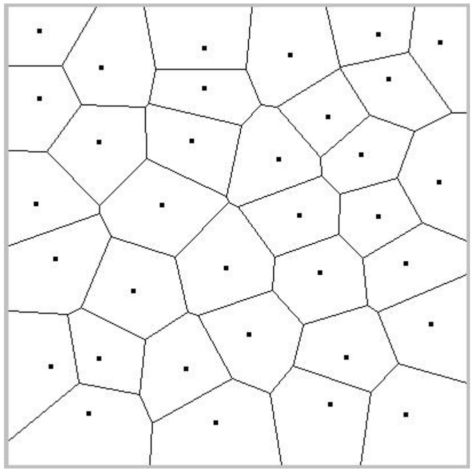
- No information on bubble spacing in z direction.
- Large bubbles may obscure small bubbles, skewing distribution.
- Smallest bubbles may be difficult to observe.

Capture Volume Theory

- Capture volume is described by Voronoi tessellation.

2D Voronoi tessellation





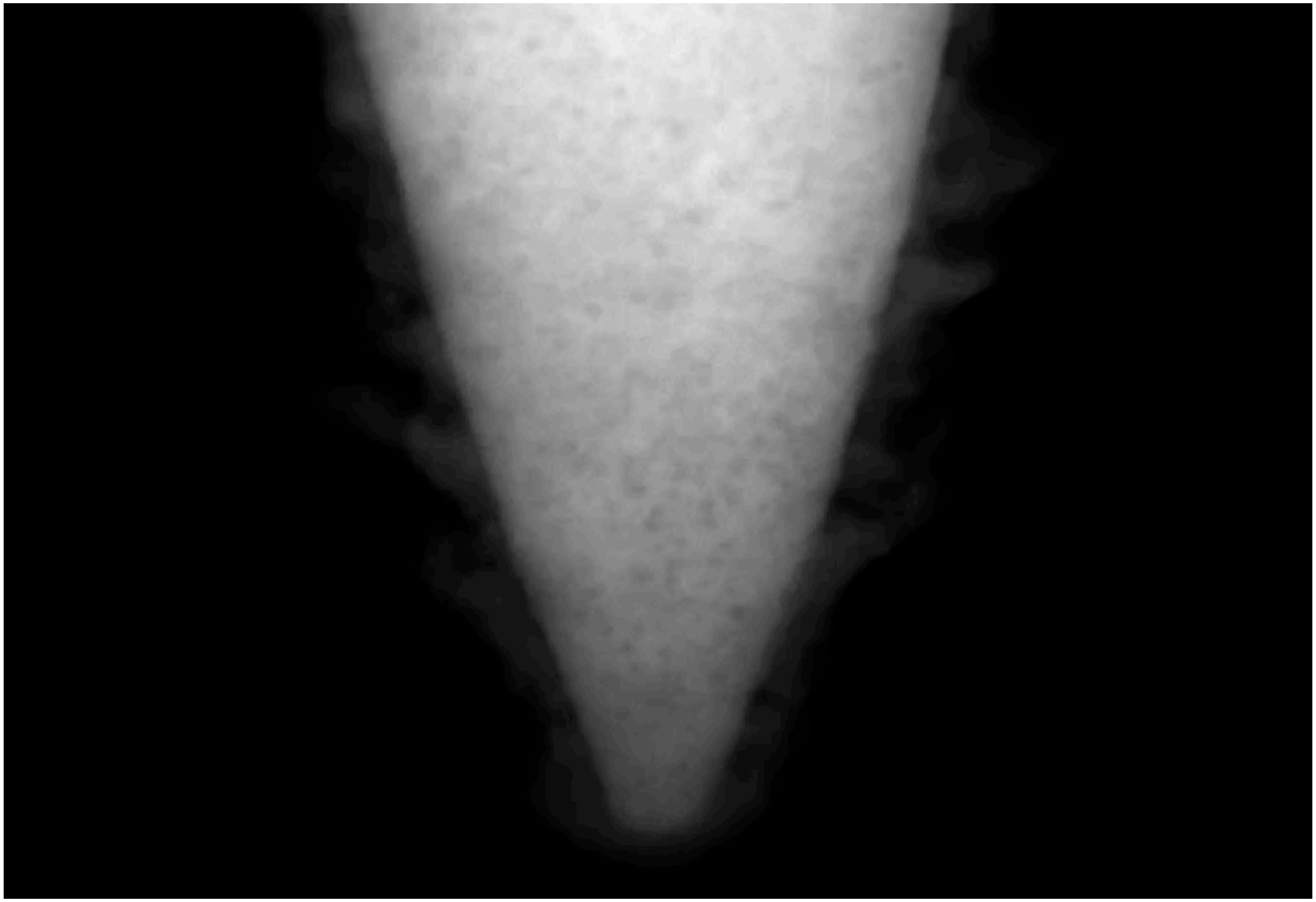
- Simultaneous early nucleation
- Diffusion-limited growth

Capture volume and bubble size should be correlated

We will measure 3D bubble distribution to validate theory and develop improved models of helium bubble nucleation and growth, and better predict swelling, fracture, and ^{3}He release.

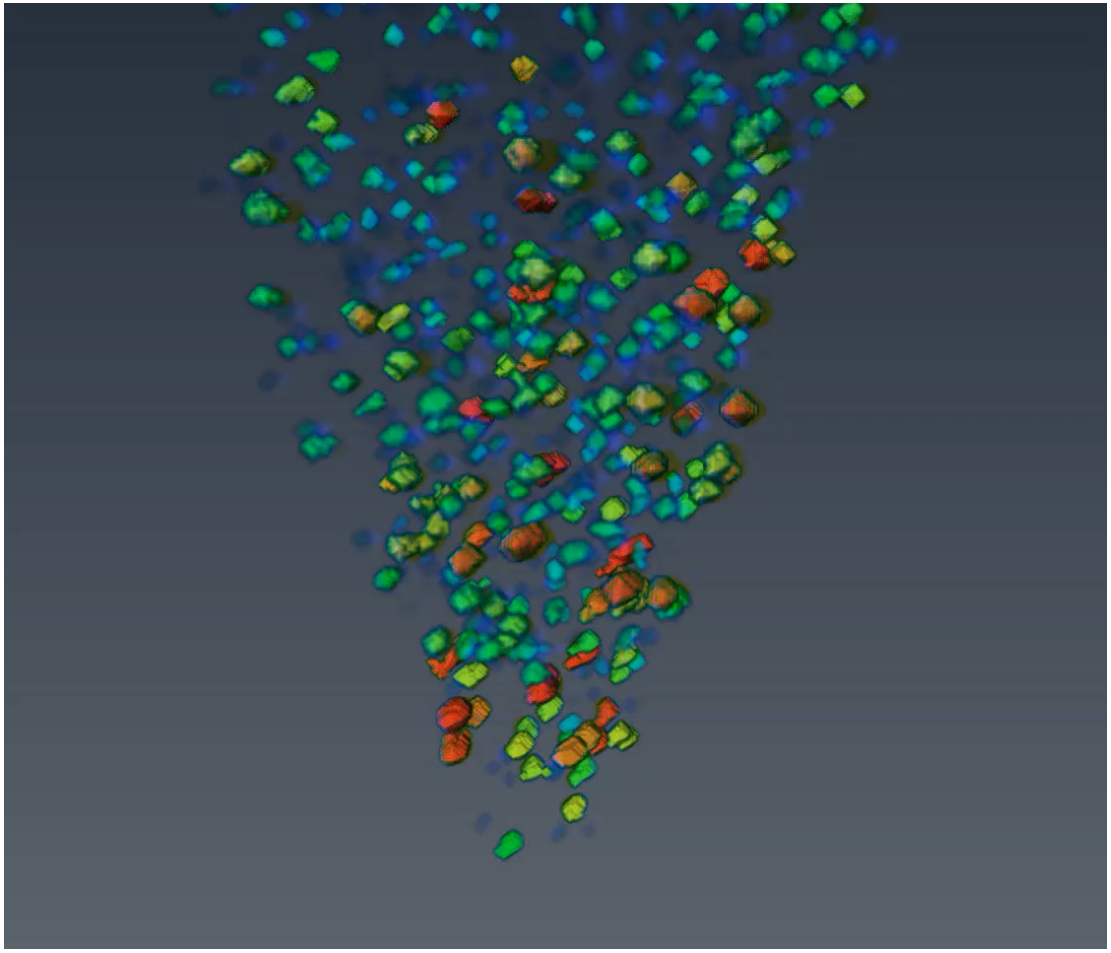
Dark field (HAADF) TEM Images

- Tritided for 3.8 years (from a SRNL Pd-5 at.% Ni ribbon).
- Single crystal (estimated He/Pd = 0.12).
- Bubbles are dark, ~2 nm diameters.
- Images taken from -70^o to 70^o (increment 1^o).



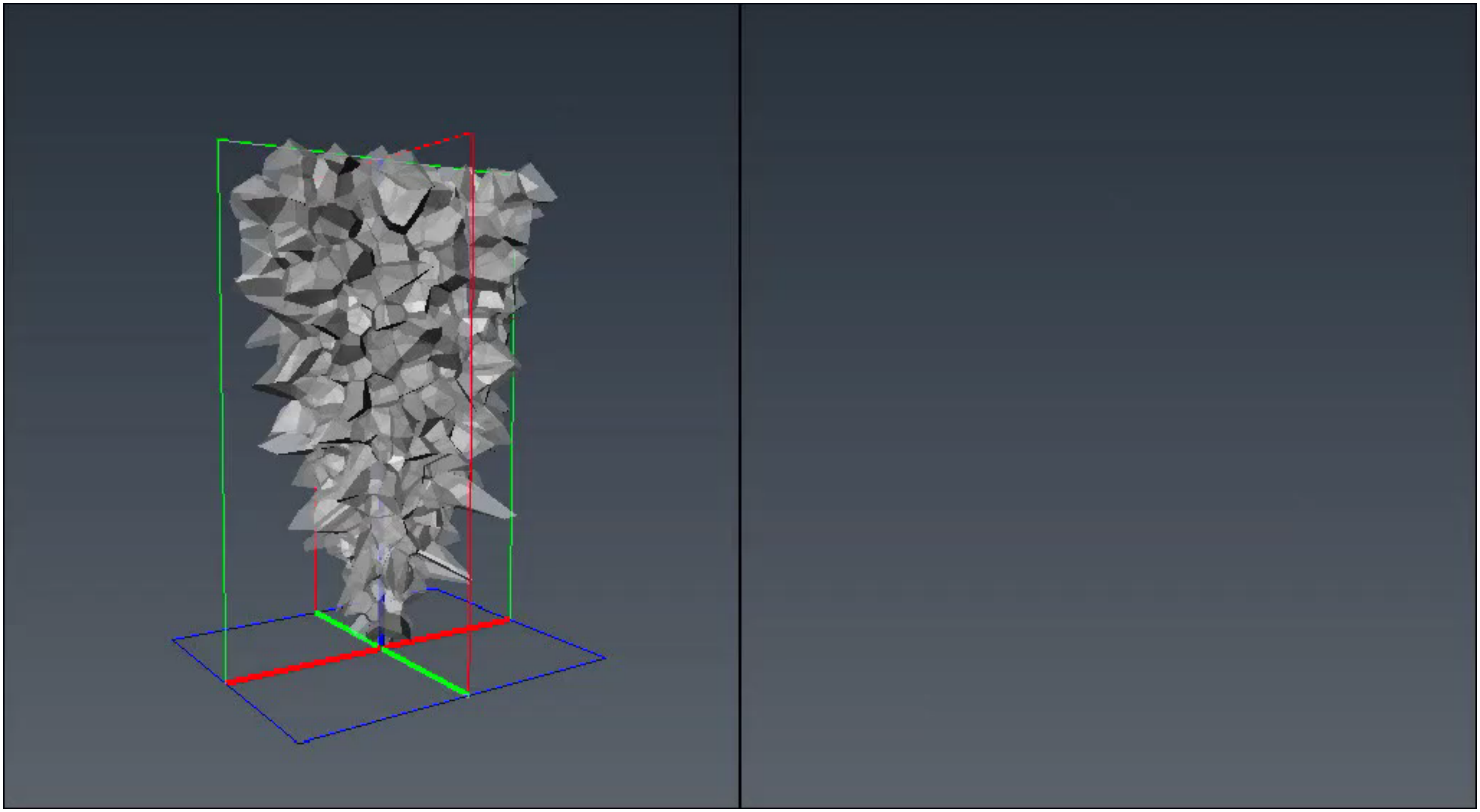
180 nm

Reconstruction of the 3D Bubbles



- 3D bubbles are iteratively matched to 2D experimental images using the "*Simultaneous Iterative Reconstruction Technique.*"
- ~1000 bubbles with average diameter 2 nm
- Bubbles can be elongated due to reconstruction artifacts
- Red bubbles are large, blue bubbles are small.

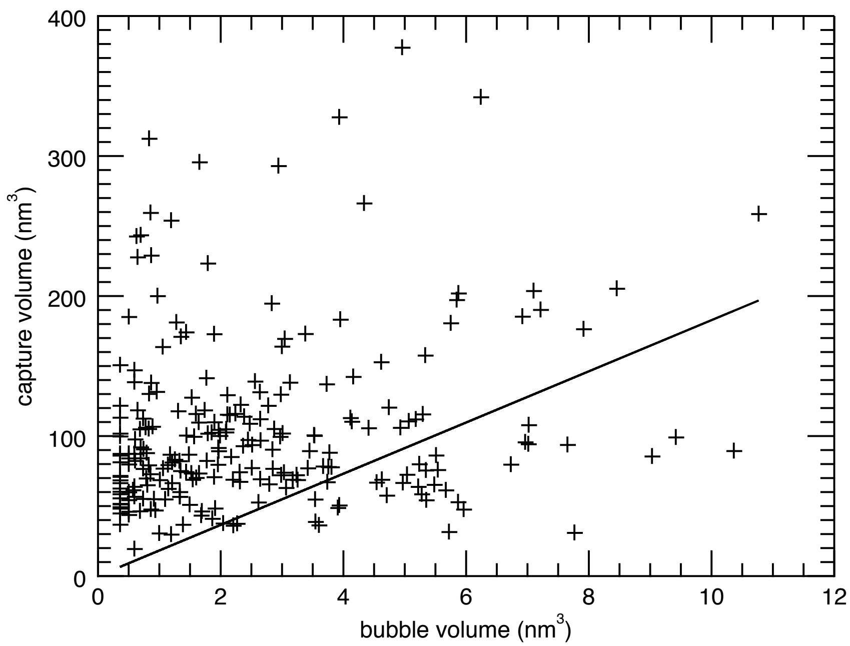
Reconstruction of capture volumes



- Determined by 3D Voronoi tessellation of bubbles
- Outer layer of surface-crossing volumes is omitted from further analysis

Bubble and Capture Volume Correlation

Individual Capture Volume



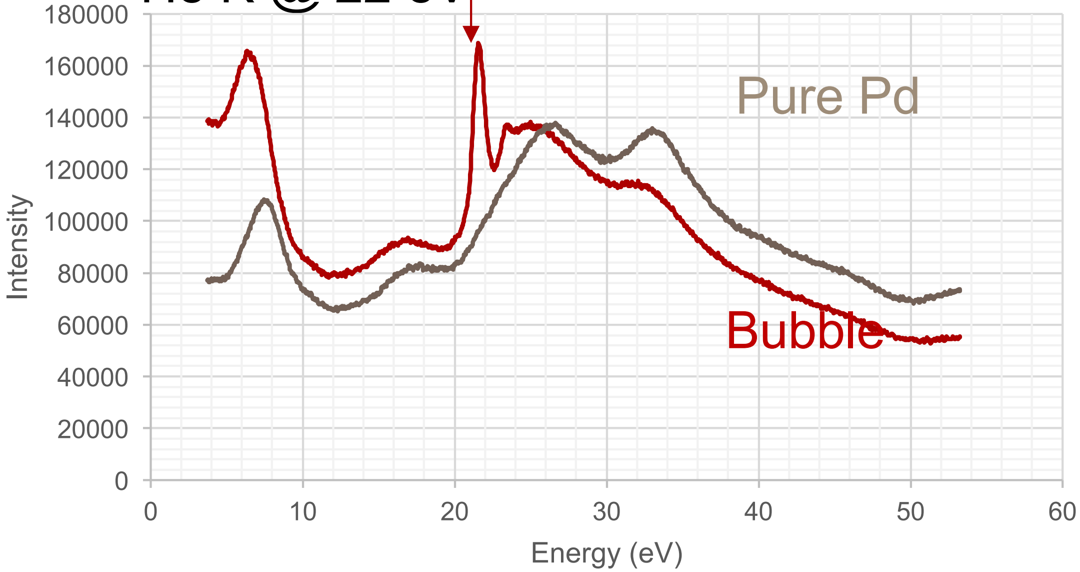
Solid line: expected for 3.8 year of tritium decay (He/Pd = 1.2) if bubbles have 5GPa pressure based on the loop punching growth

No bubble and capture volume correlation is found!

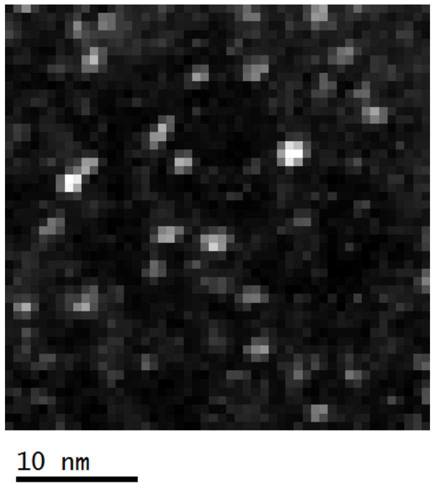
Bubbles can move or nucleation happens throughout aging process

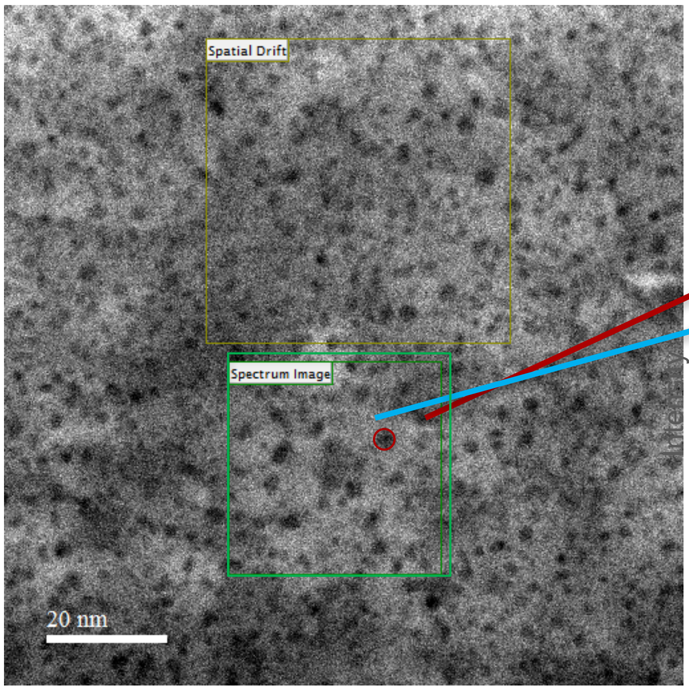
Next steps: measuring He pressure inside the bubbles

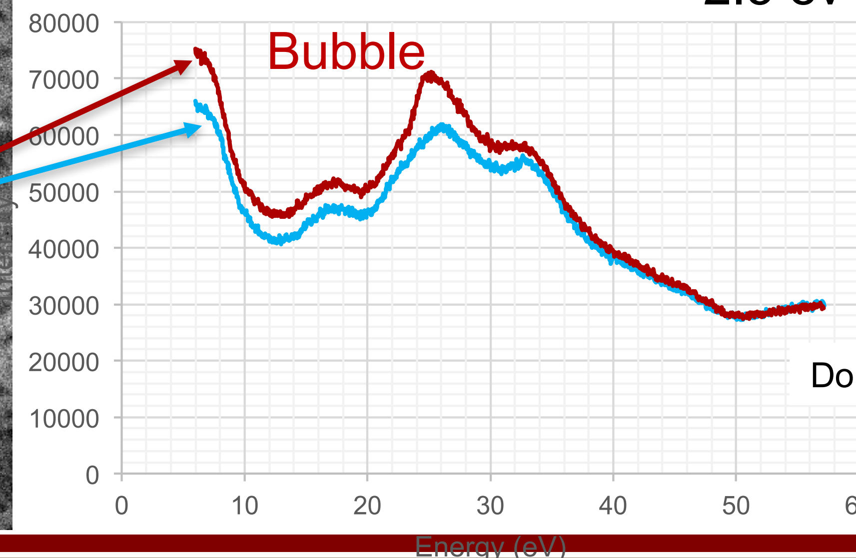
Measuring He Pressure with EELS



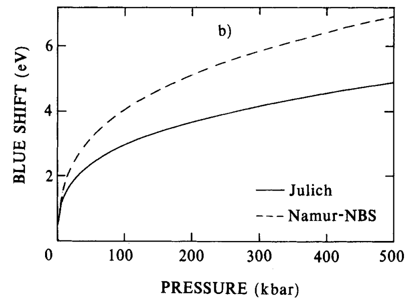
He fit Coefficient







2.5 ev shift → 2 – 5 GPa



Donnelly, SE, *Rad Eff*, **90**, (1985)

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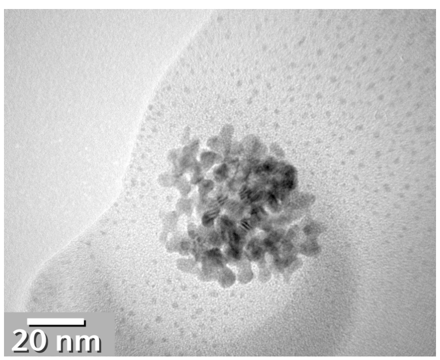
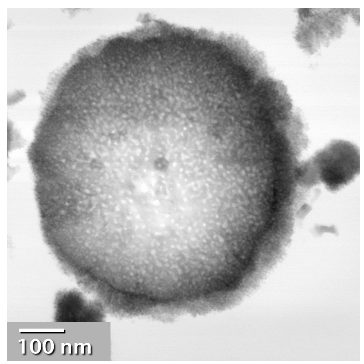
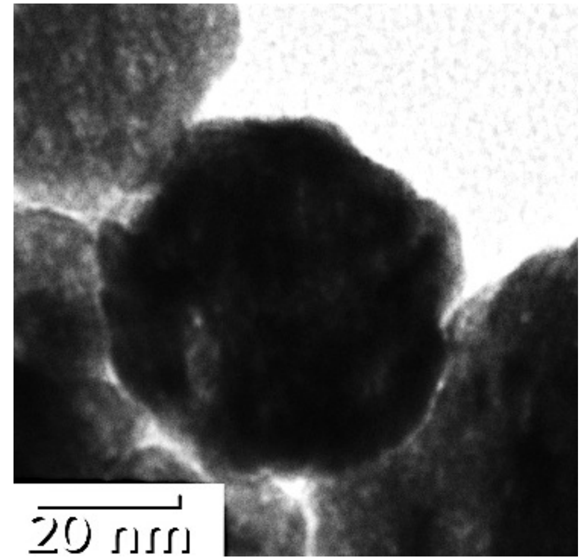
Pd Materials With Large Surface Area

- Nanoporous materials have high surface areas
  - Faster surface-limited reactions
  - He gas can escape
- Goals
  - Uniform pore structure homogeneously distributed in material
  - Stable pore structure over wide T range
- Addition of Rh increases T stability

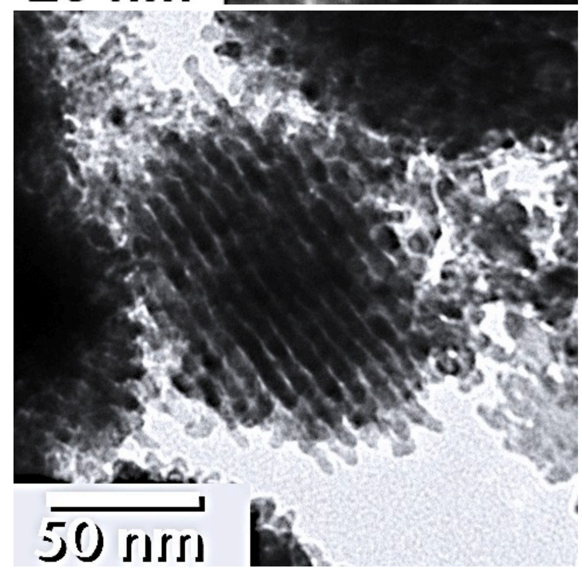




200 ° C
12 min
Pure Pd



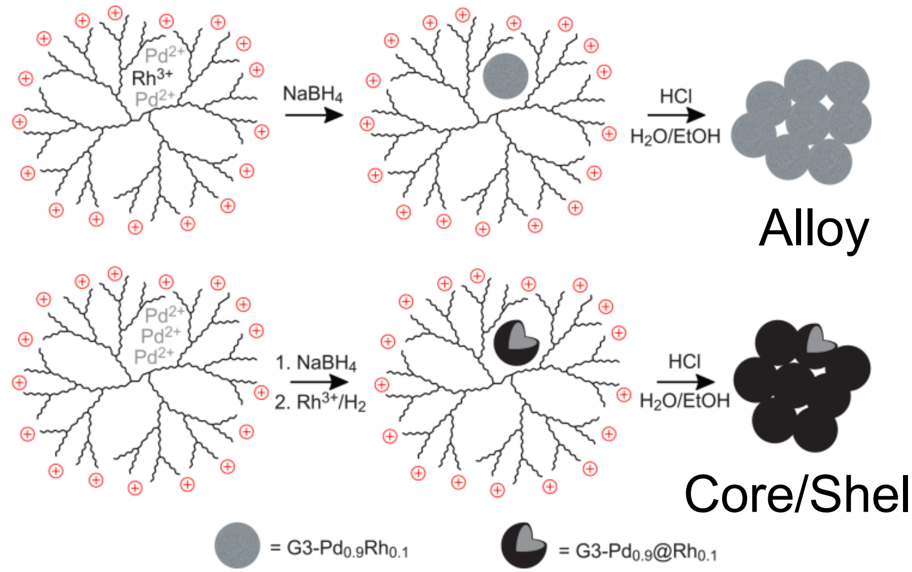
200 ° C
30 min
10 at.% Rh-Pd

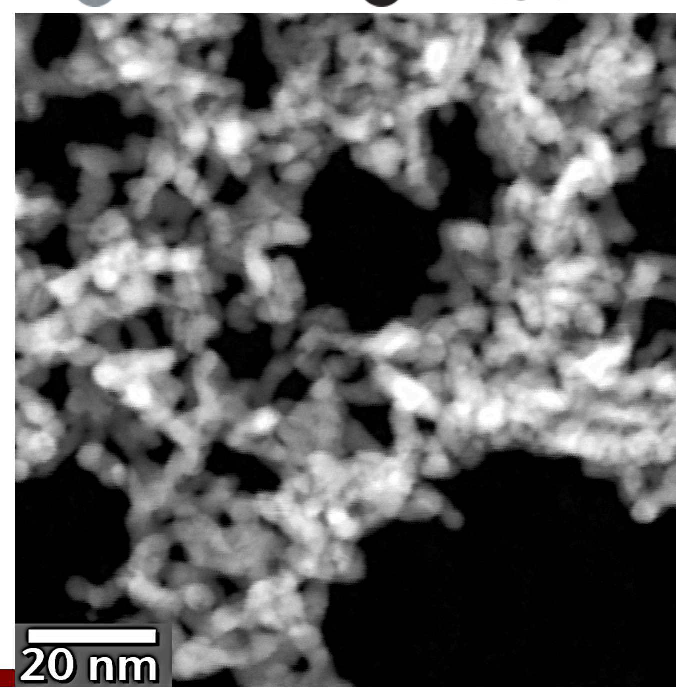


Where is the Rh and is it uniformly distributed?

Dendrimer-Encapsulated Nanoparticle Consolidation

- Pd/Rh Alloy particles: $Pd_{0.9}Rh_{0.1}$
  - Metal salts mixed with dendrimer and reduced together
- Pd/Rh Core/Shell particles: $Pd_{0.9}@Rh_{0.1}$
  - Pd salt reduced in first step
  - Rh salt reduced in second step
- Agglomerates of particles ~5 nm in diameter with pores between particles range in size (1 nm – 100 nm)

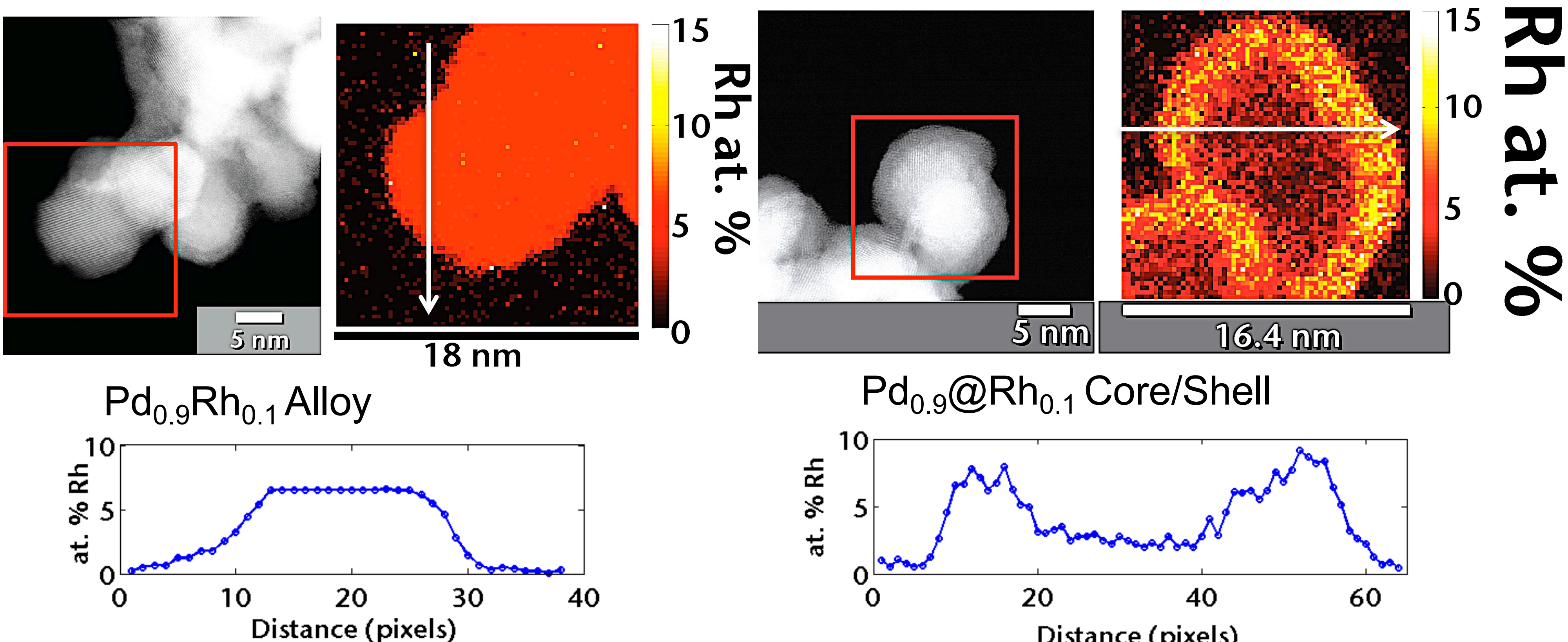




P.J. Cappillino, et al., *Journal of Materials Chemistry* **22** (2012)

Large Solid Angle Detector Finds Rh Shell

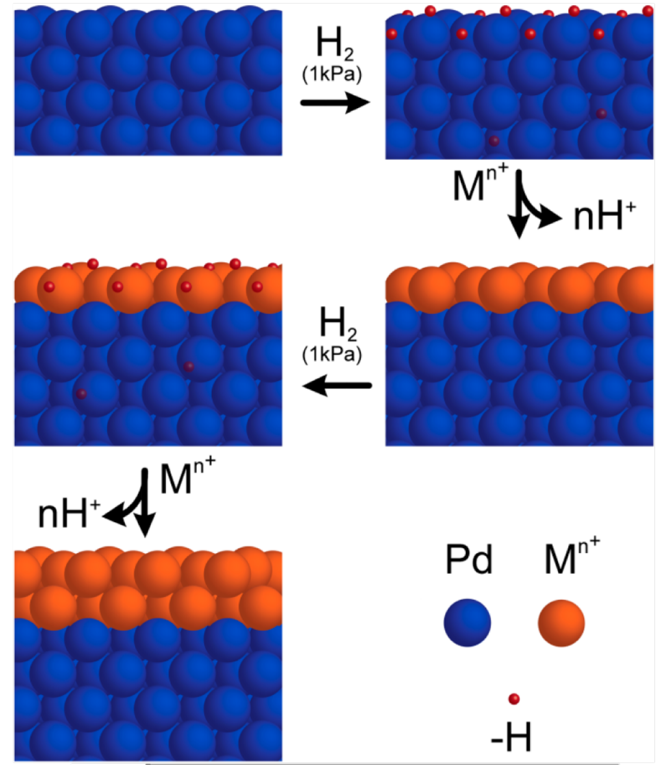
- FEI Probe-Corrected Titan G2 80-200 with 0.7 sr SDD detector array at 200 kV

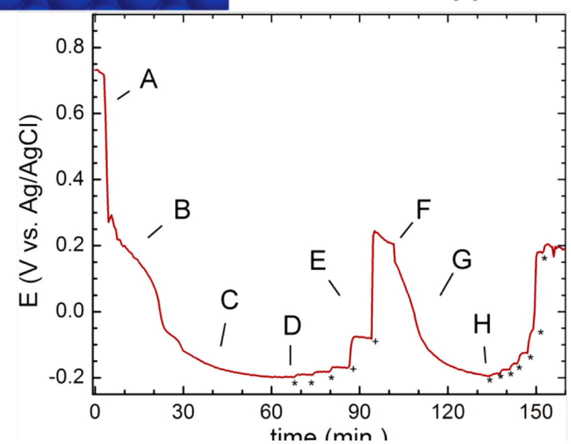


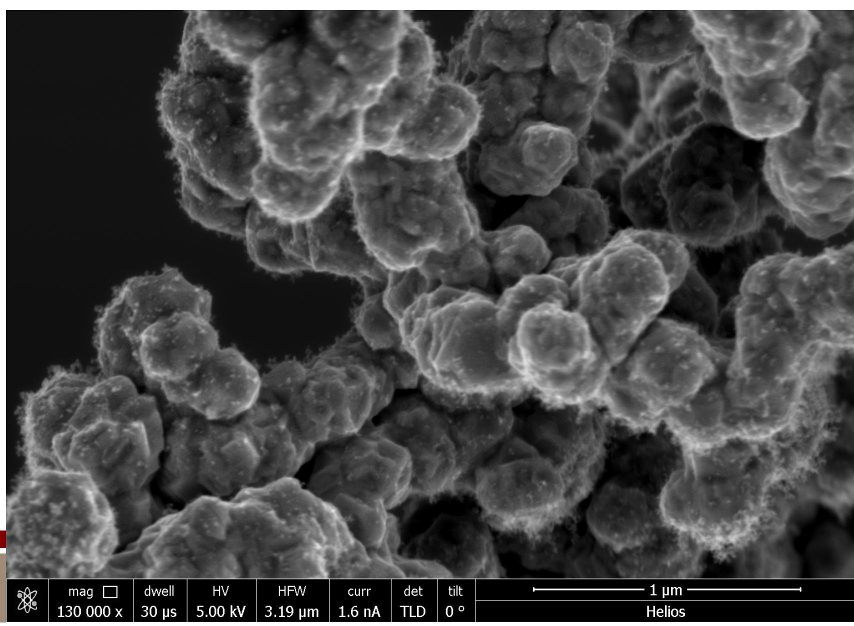
P.J. Cappillino, et al., *Journal of Materials Chemistry* **22** (2012)

Atomic Layer Electroless Deposition

- Precise control of thickness based on number of electrochemical cycles
- Deposition on high-aspect ratio structure
- Microtomed thin sections

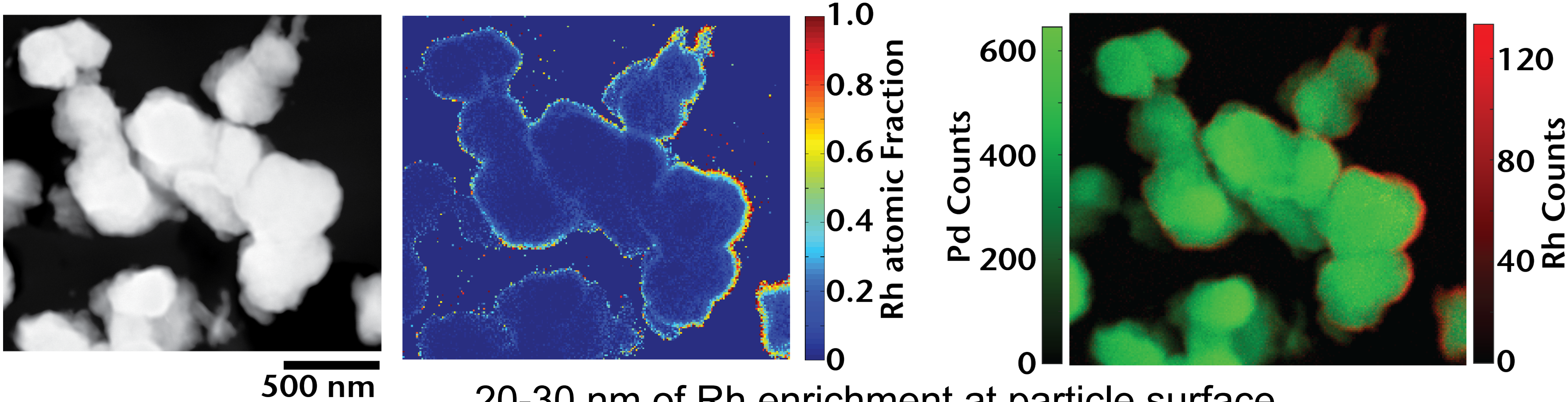






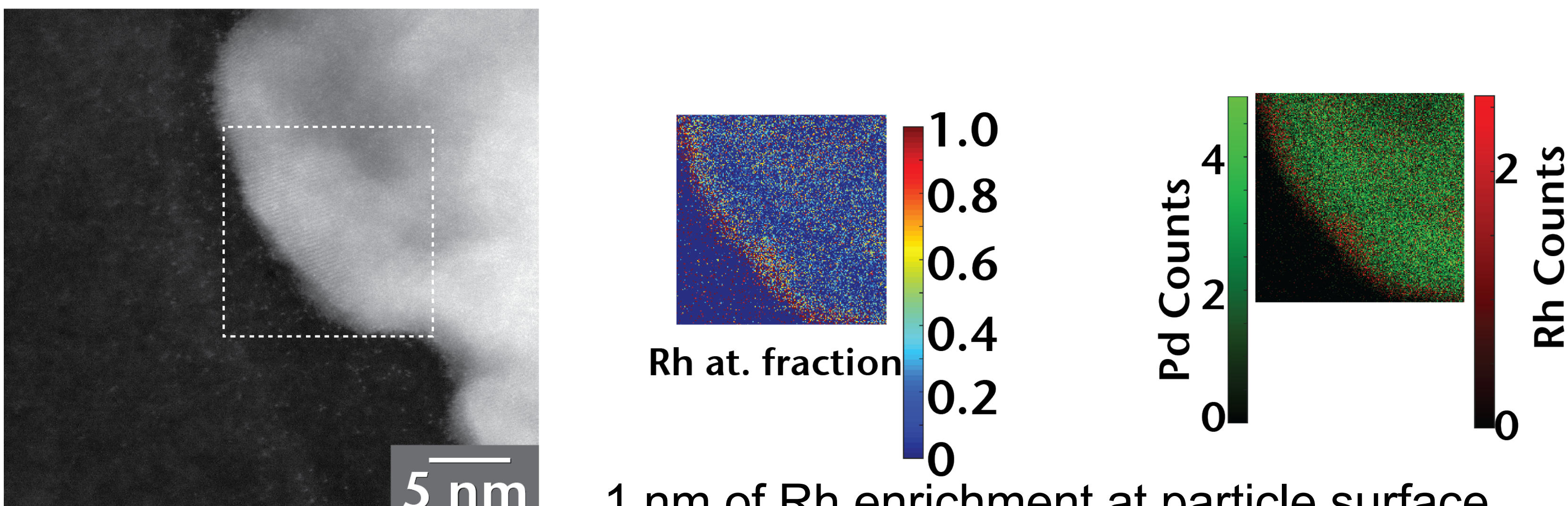
Cappillino, P. J., et al. (2014). "Atomic-Layer Electroless Deposition: A Scalable Approach to Surface-Modified Metal Powders." Langmuir **30**(16): 4820-4829.

8 Electrochemical cycles Pd/Rh



20-30 nm of Rh enrichment at particle surface

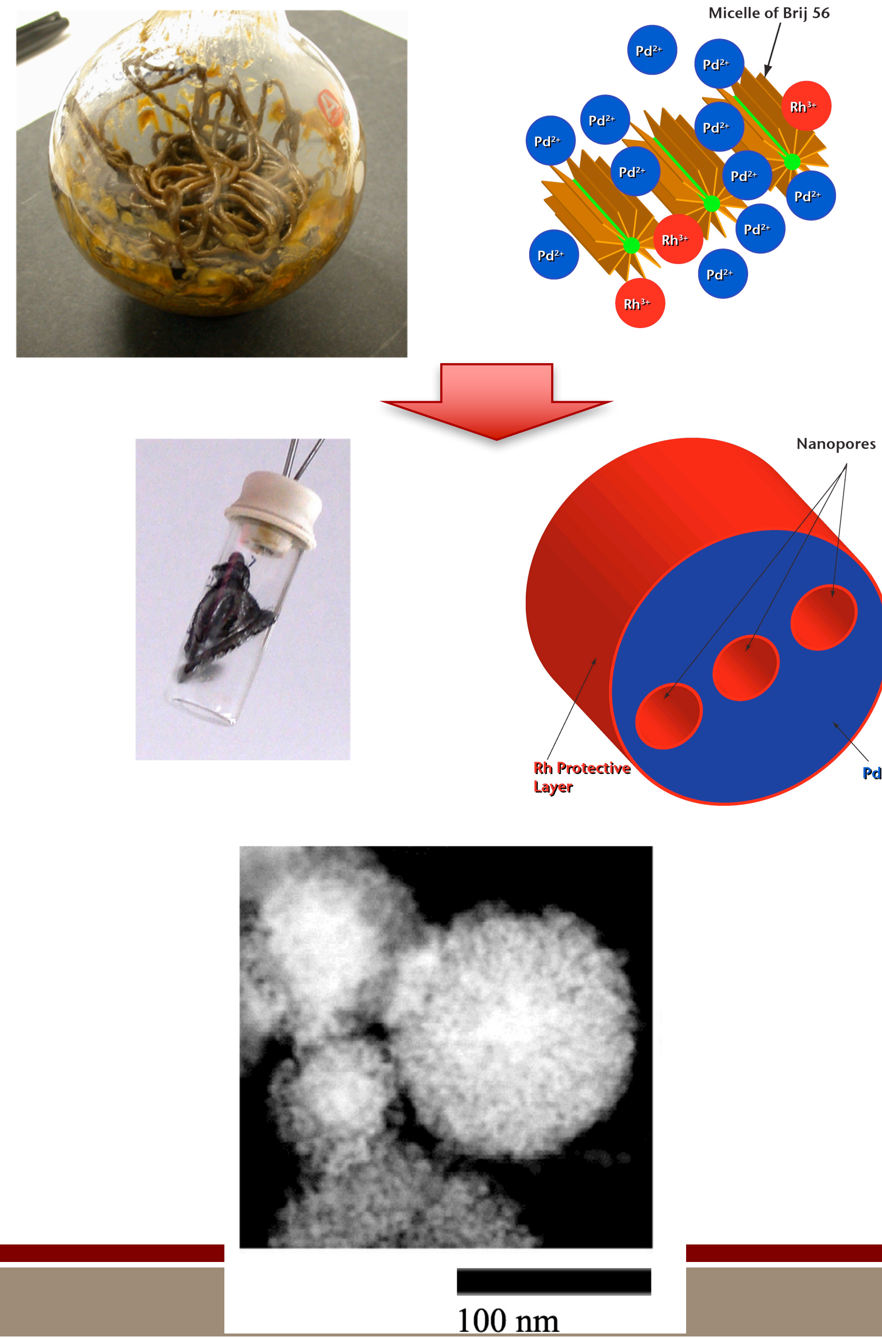
1 Electrochemical cycle Pd/Rh



1 nm of Rh enrichment at particle surface

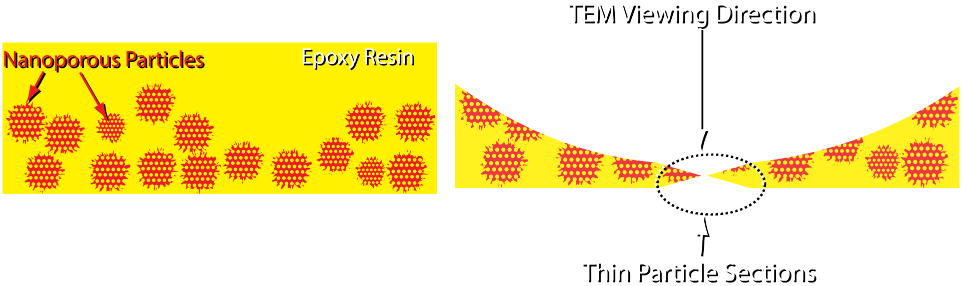
Surfactant Template Fabrication

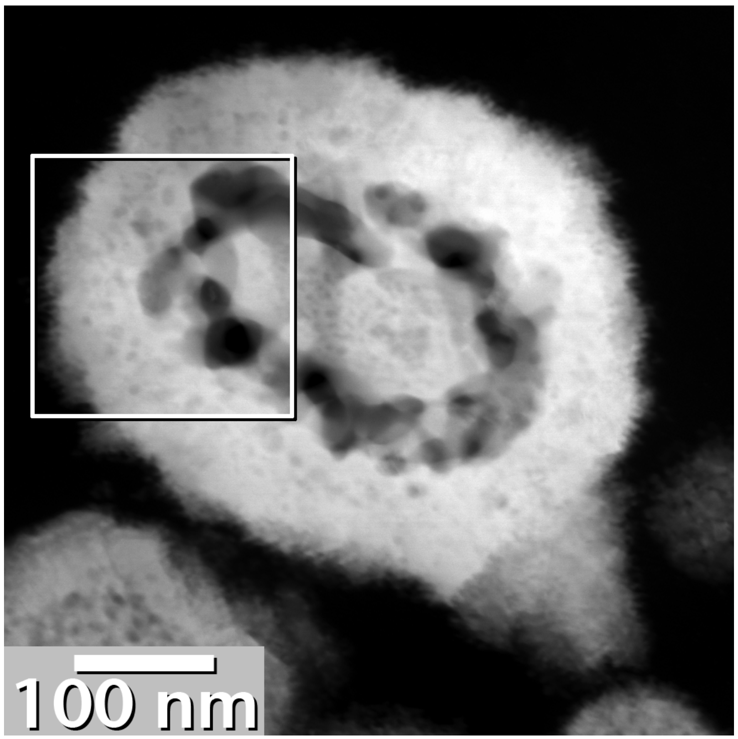
- Organic molecule, Brij 56, forms cylindrical micelle in water
  - Hydrophobic center
  - Solution of metal salts
- Reduce the metal salts in flowing gas
  - $(NH_4)PdCl_4 + H_2 \rightarrow Pd + NH_4Cl + 2HCl$
  - $2Na_3RhCl_6 + 3H_2 \rightarrow 2Rh + 6NaCl + 6HCl$
- Rinse off organic residue
- Nanoporous material

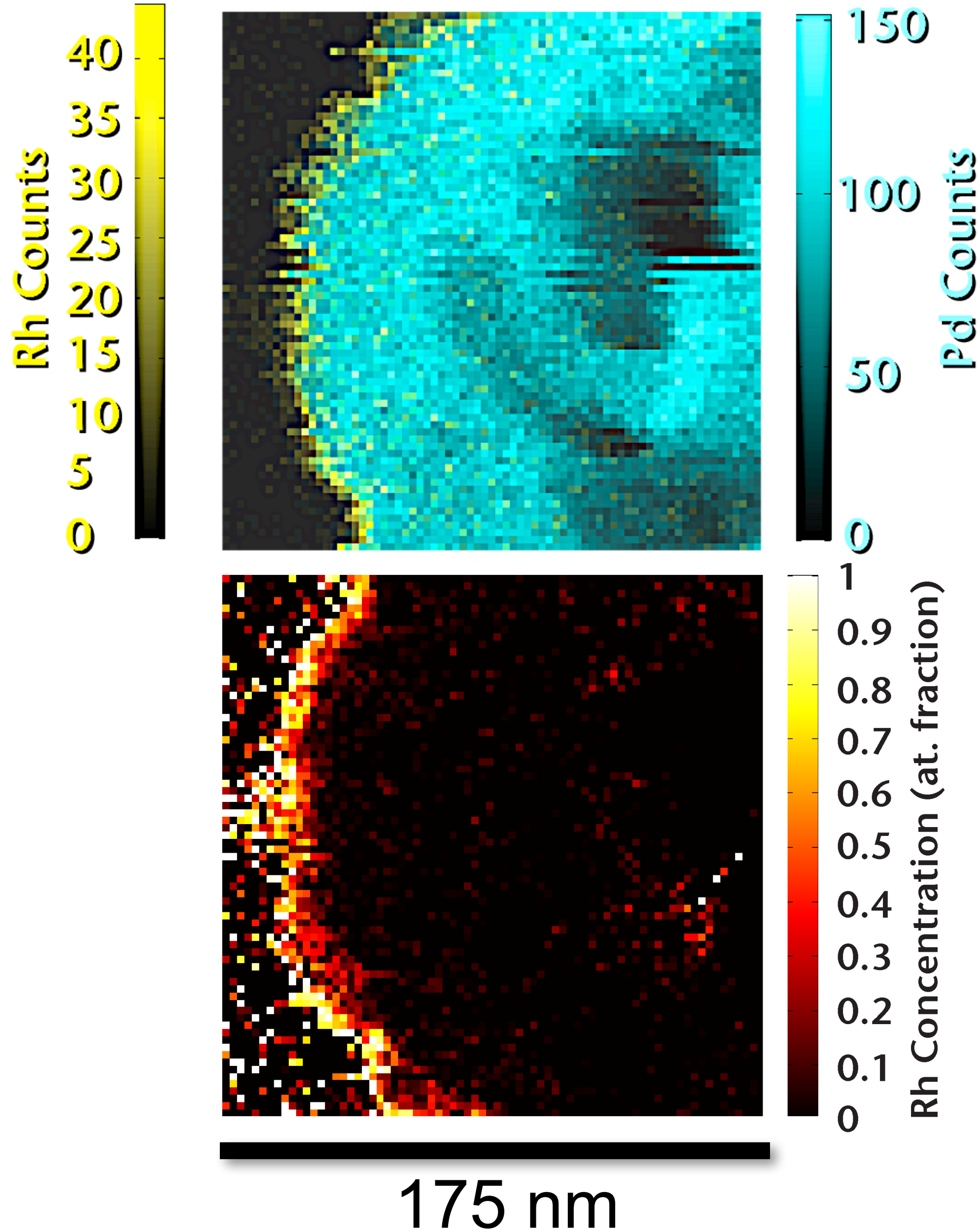


Robinson, D. et al., *IJHE*, **35** (2010).

Core/Shell Compositional Distribution



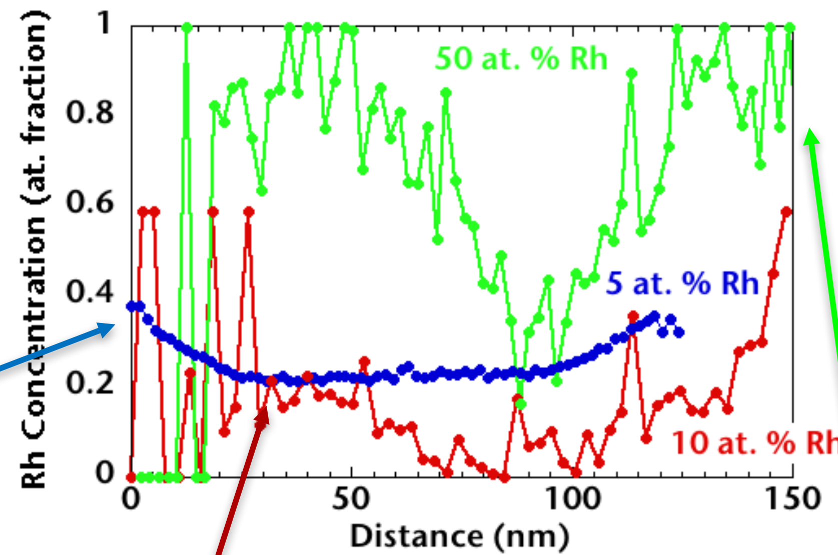


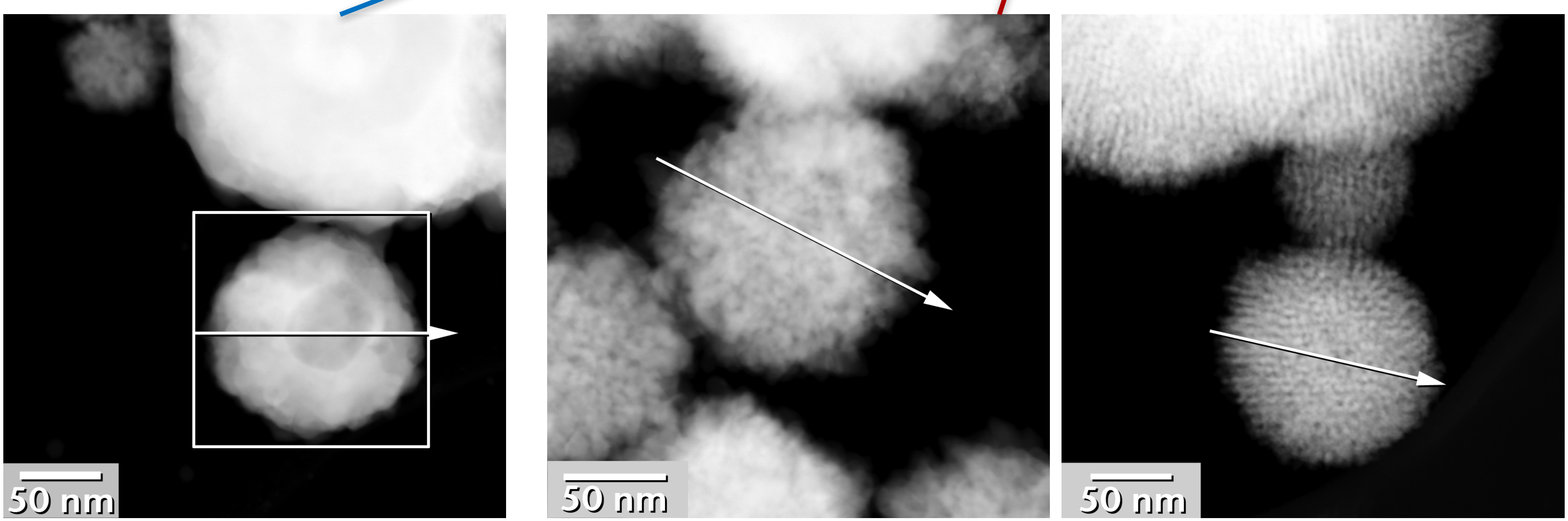


M.D. Ong, et al., *Chemistry of Materials* **24** (2012)

Core/Shell Compositional Distribution

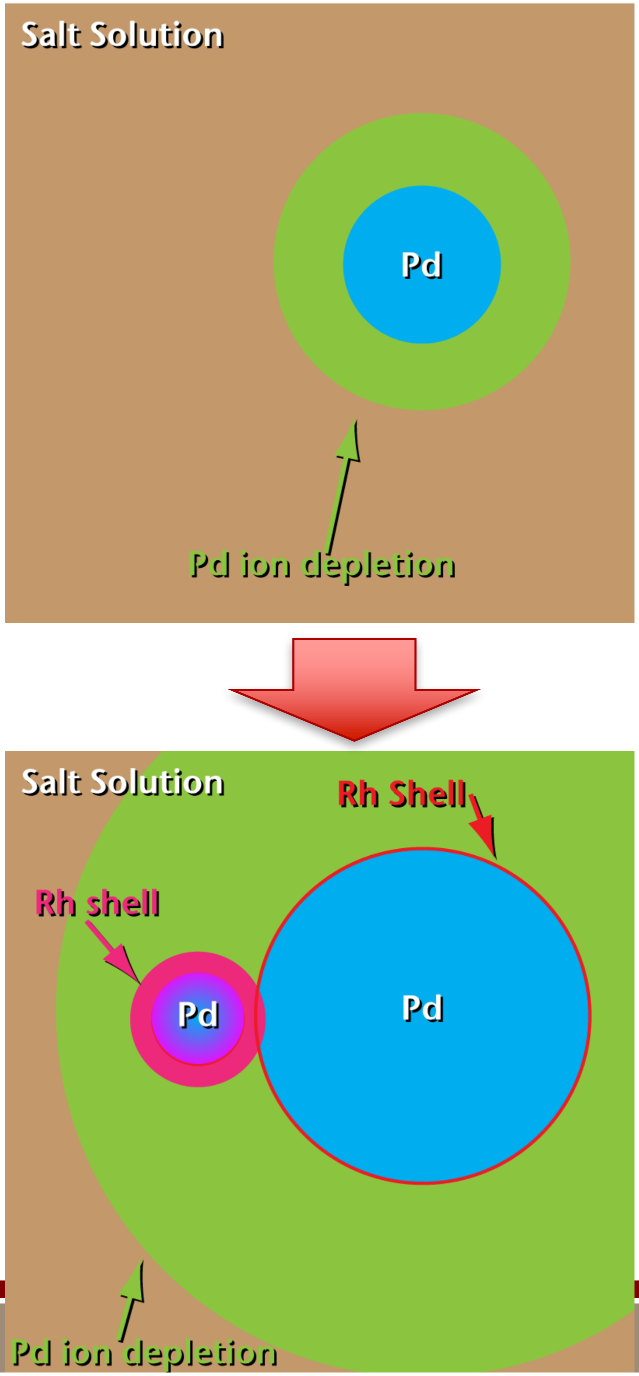
- Rh-rich shell
- Smaller (~100 nm diameter) particles have Rh concentration that is higher than the nominal concentration during synthesis
- Higher Rh content produces more uniform pore sizes





Kinetics Dictate Rh Distribution

- Pd reduction faster than Rh
- Nucleation occurs throughout the reaction duration
- Large particles nucleate early in a Pd-rich environment
  - Creates a Pd-depleted zone
- All the Pd is consumed and reacted
  - Rh-rich shell on large particles then forms
- Rh is distributed less uniformly than desired



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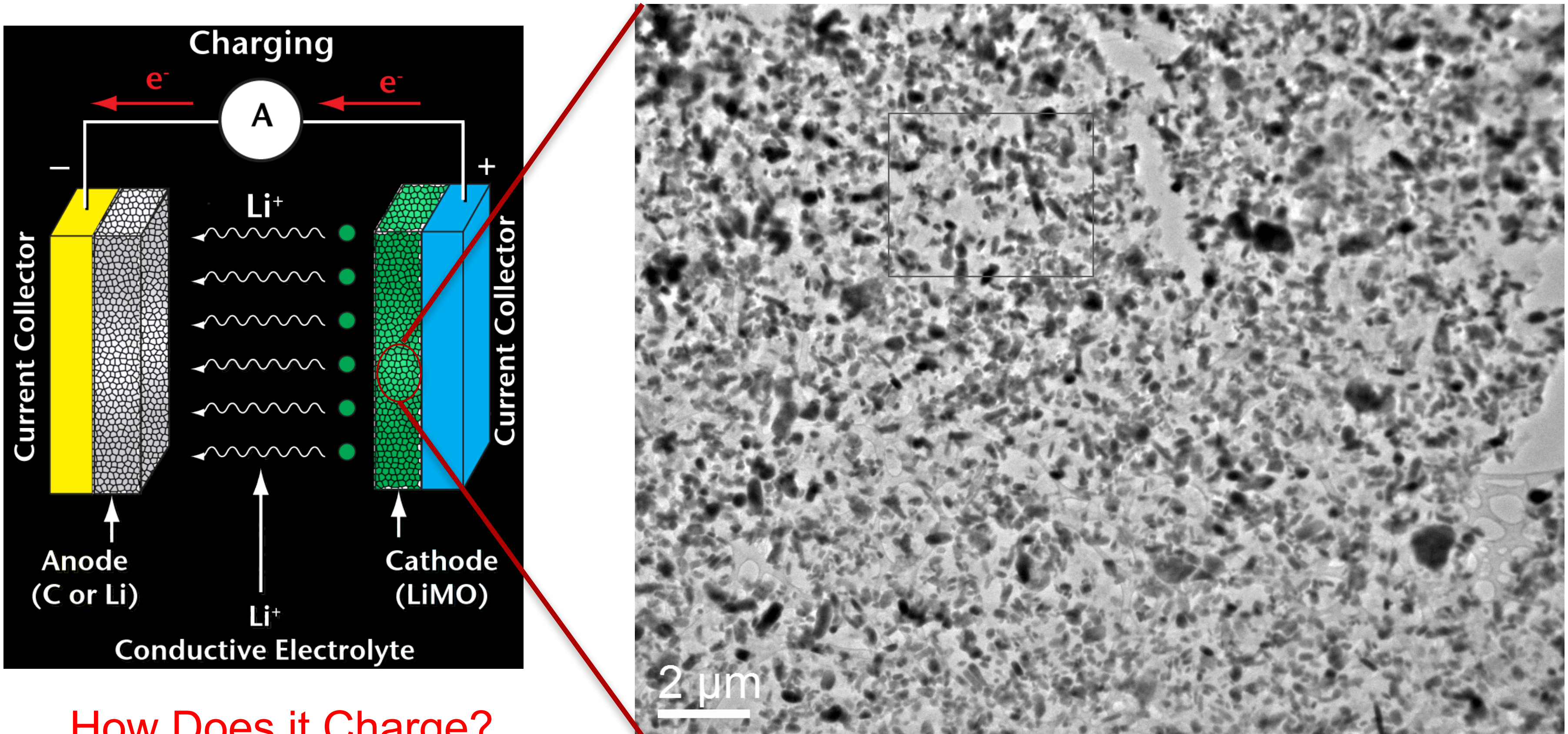
Electrochemical Energy Storage for Transportation

- Do particles charge at the same time?
- What limits the charging rate?

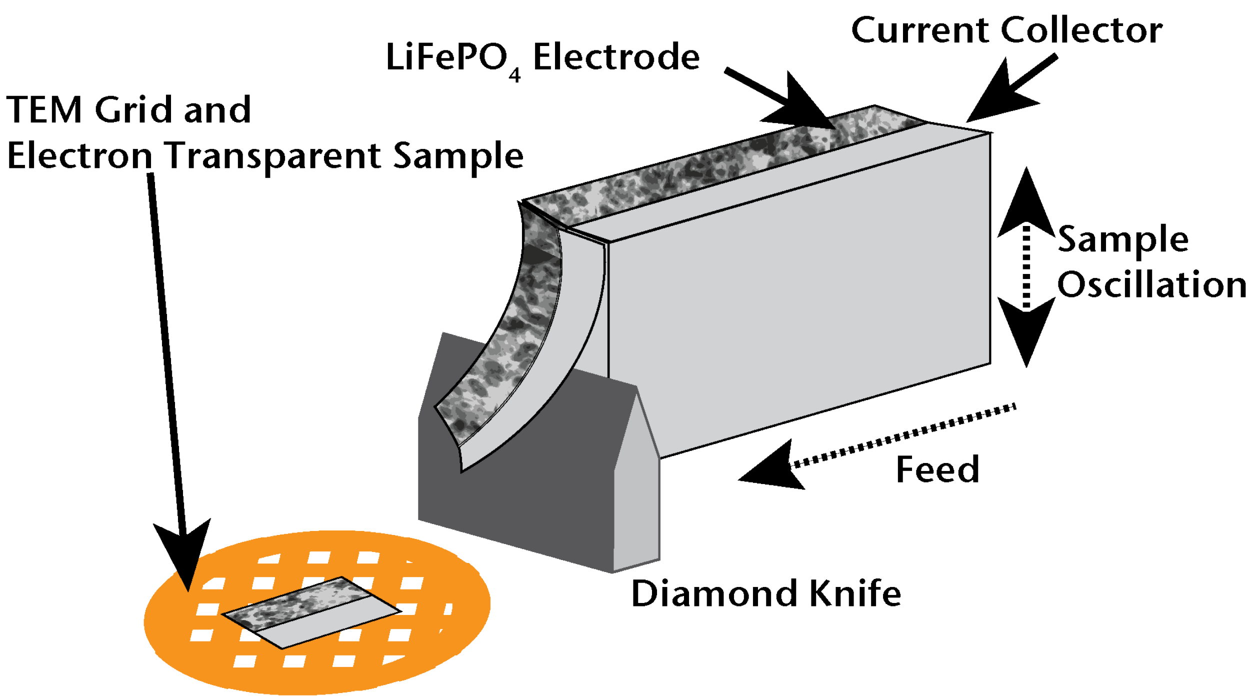


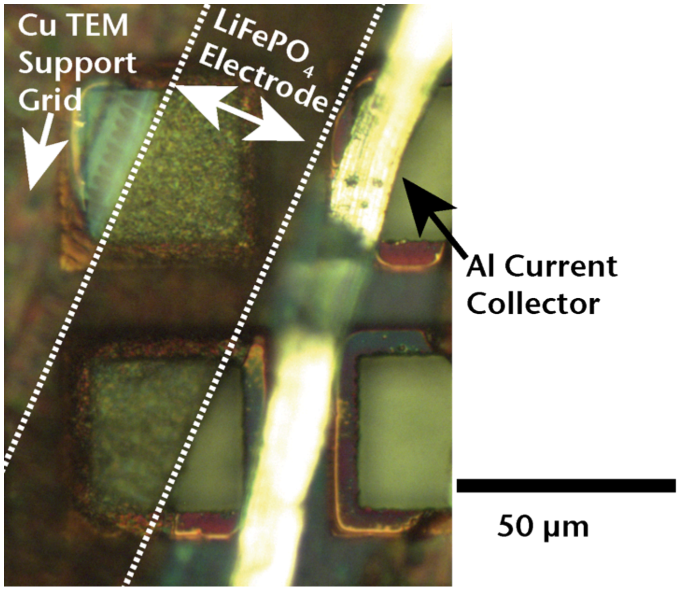
How Does it Charge?

We need a tool to be able to measure this

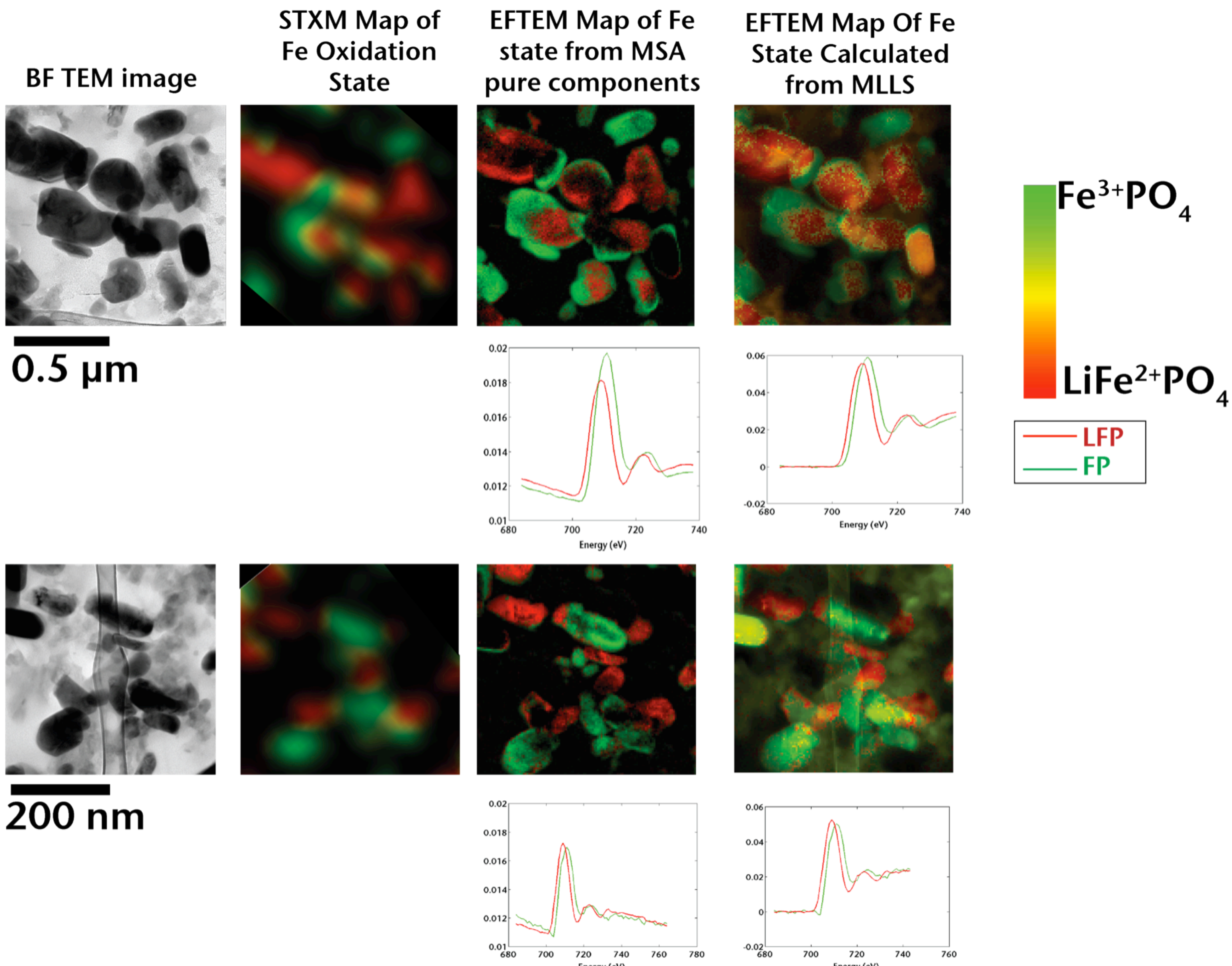
Making Thin Damage-Free Samples

- Sample Preparation Options
  - Particles on Grid – Too thick
  - Ion milling – Redeposition and too thick
  - FIB – Redeposition and damage
  - Ultramicrotome -Microstructure Preserved





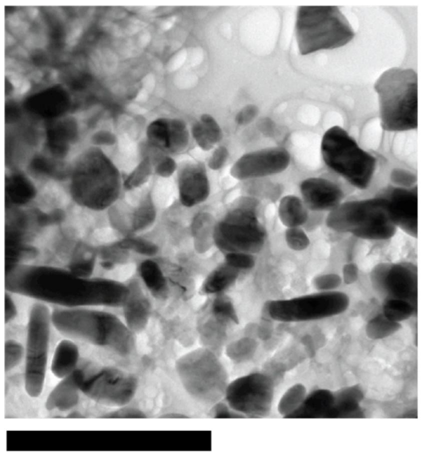
Validated Microtome Results



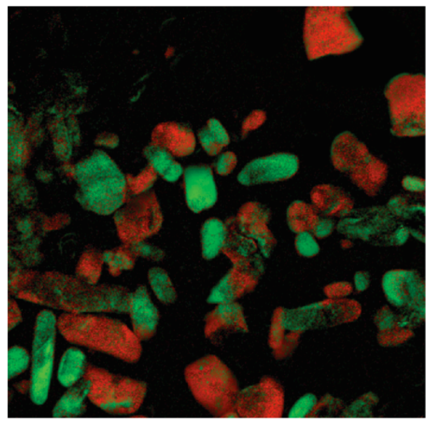
Sugar, J.D., et al., Journal of Power Sources, 2014. **246**(0): p. 512-521.

Large Areas Show Binary Phase Distribution

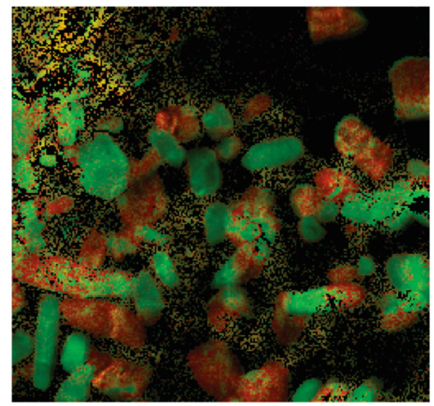
BF TEM image

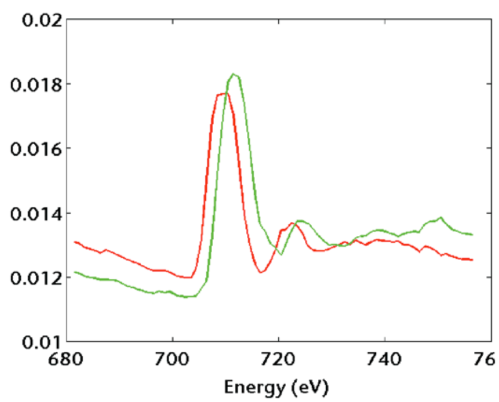


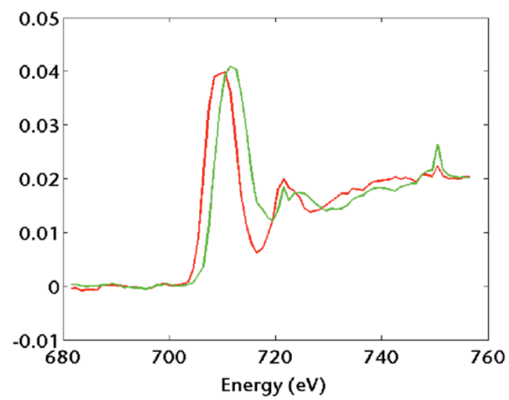
EFTEM Map of Fe state from MSA pure components



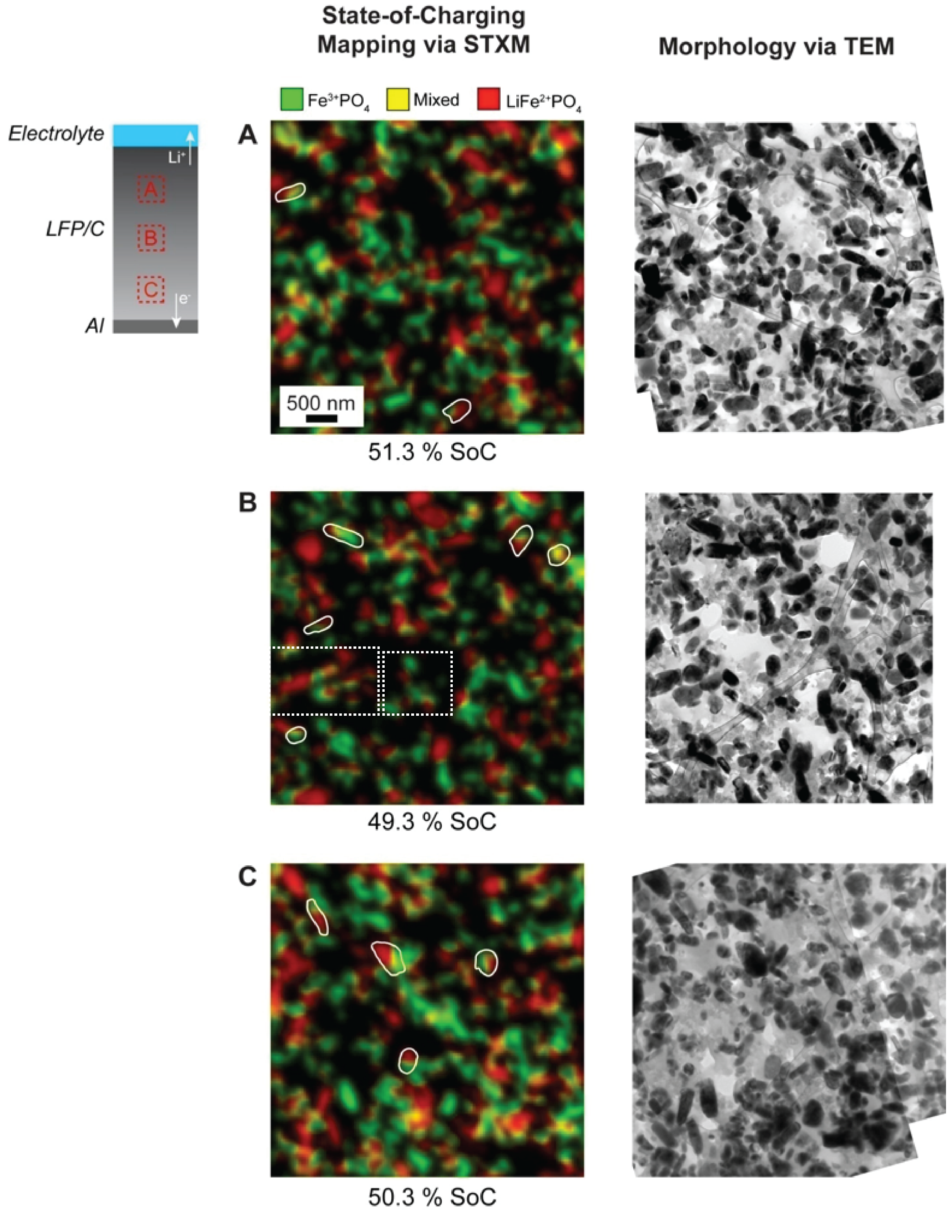
EFTEM Map Of Fe State Calculated from MLLS

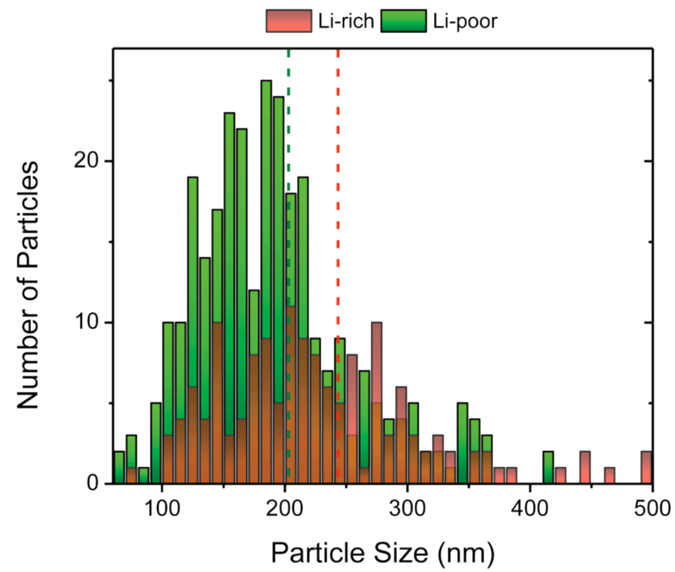






Large Statistical Information from combined STXM/TEM



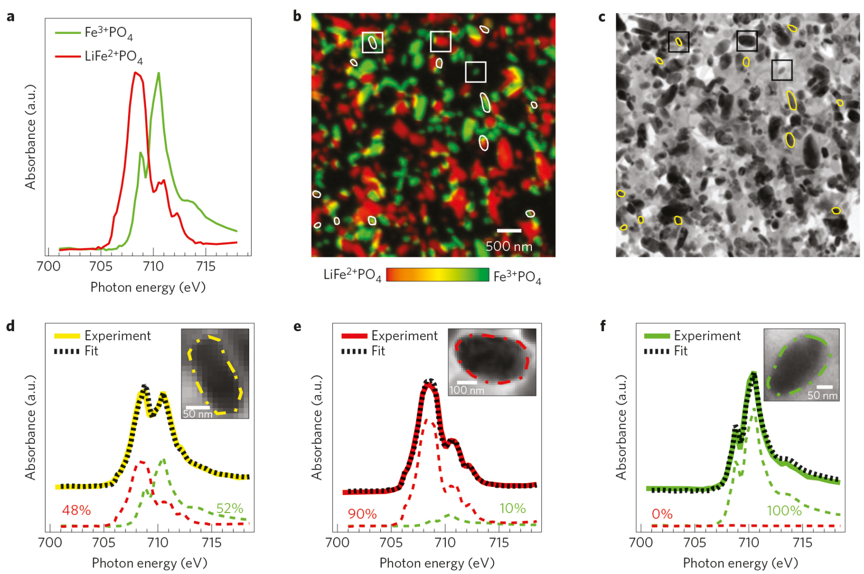


- Only 2% of particles are in a mixed state of charge (11/450)
- Particles that overlap can not be counted as one or the other
- There is a slight preference for smaller particles to transform first

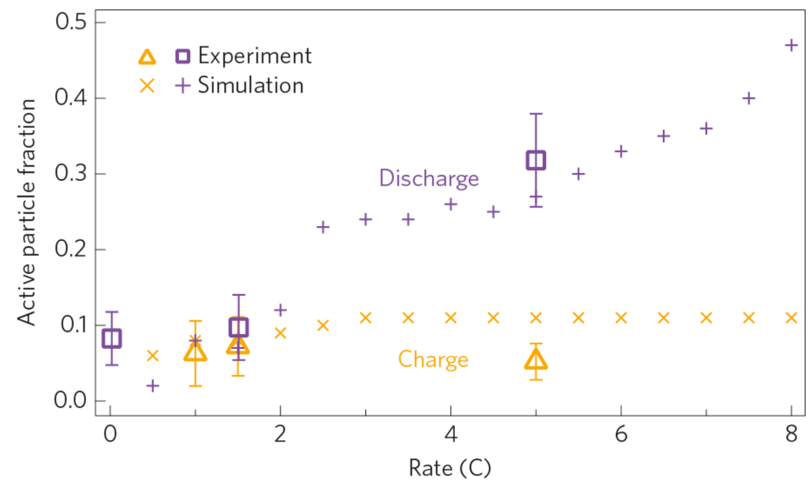
Once the transformation has started, it goes fast

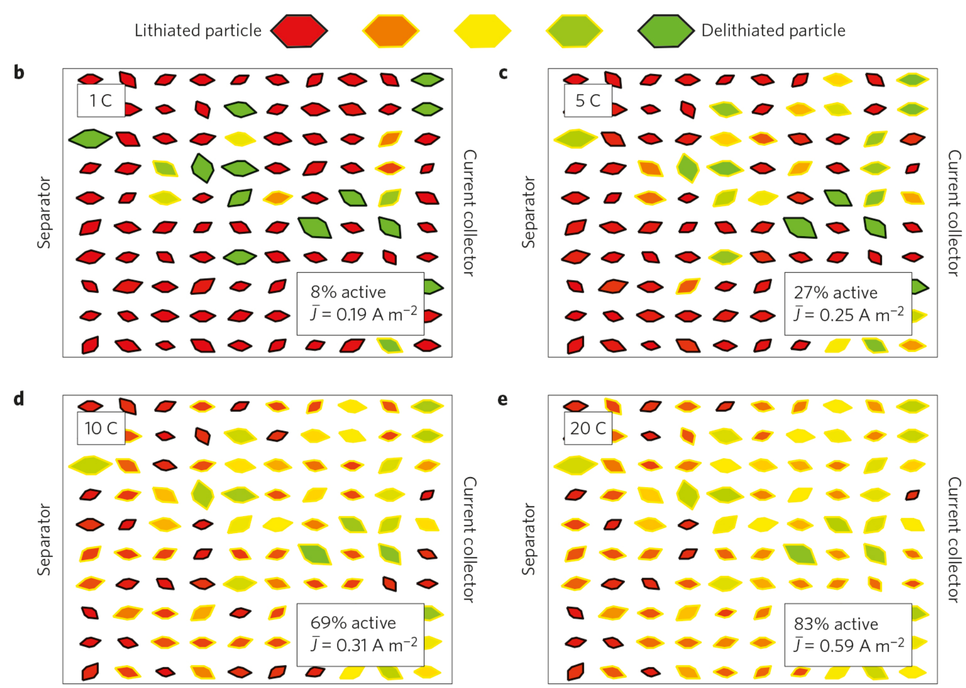
Chueh et al. *Nanoletters, 13, 2013, p.866*

At Large Overpotential More Nucleation of New Phase



5 C Charge rate



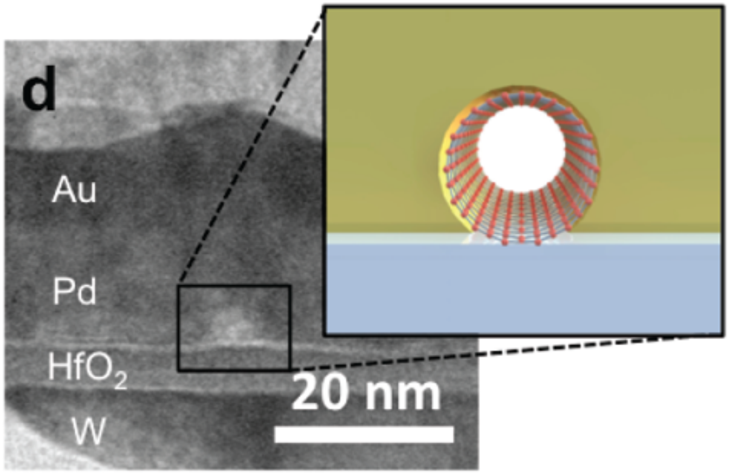


Faster charge/discharge rate more actively intercalating particles carrying the current, but the current/particle remains the same

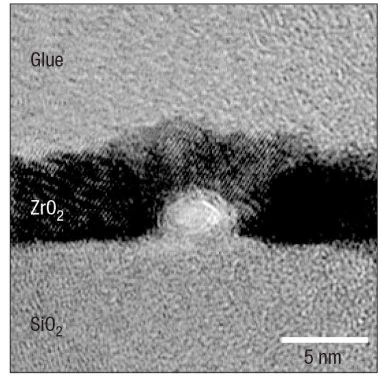
Linking Microstructural Measurements to Transport Phenomena

- Helium bubbles formed by ^3H β decay, α decay, neutron (n, α) reactions
- Rh-ion transport during fabrication of nanoporous hydrogen storage materials
- Li-ion transport during charge/discharge of $LiFePO_4$ electrodes
- Electrical contact effects in device fabrication and transport

The Contact Area and Chemistry Alters CNT Device Character

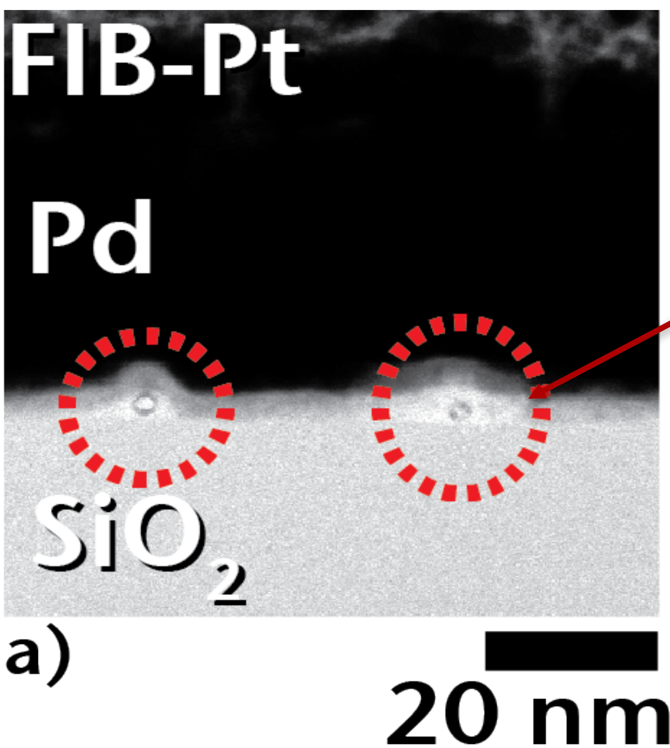


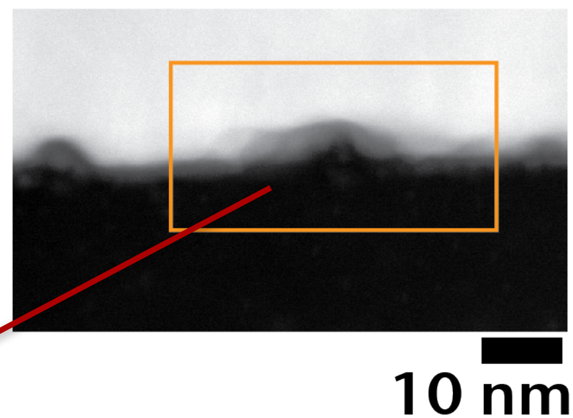
Franklin, A.D., et al., Nano Letters, 2012. 12(2): p. 758-762.

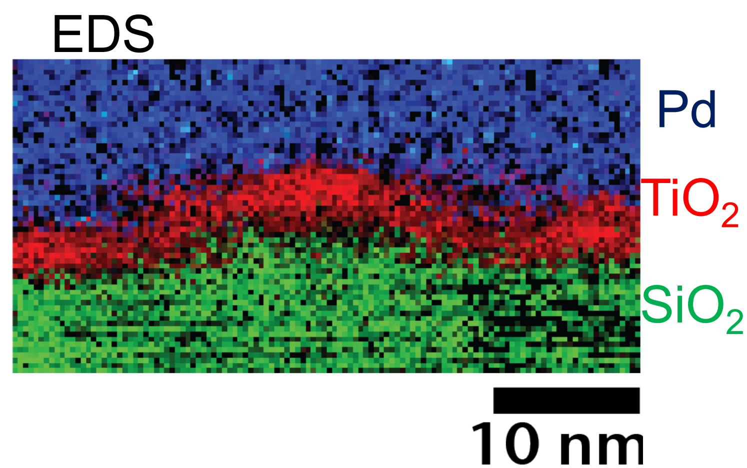


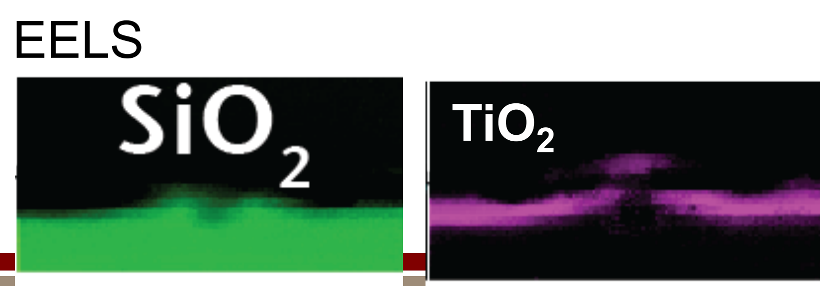
Javey, A., et al., Nature Materials, 2002. 1(4): p. 241-246.

Our contacts did not have expected Ohmic behavior because they were surrounded by a dielectric layer and had reduced contact area.

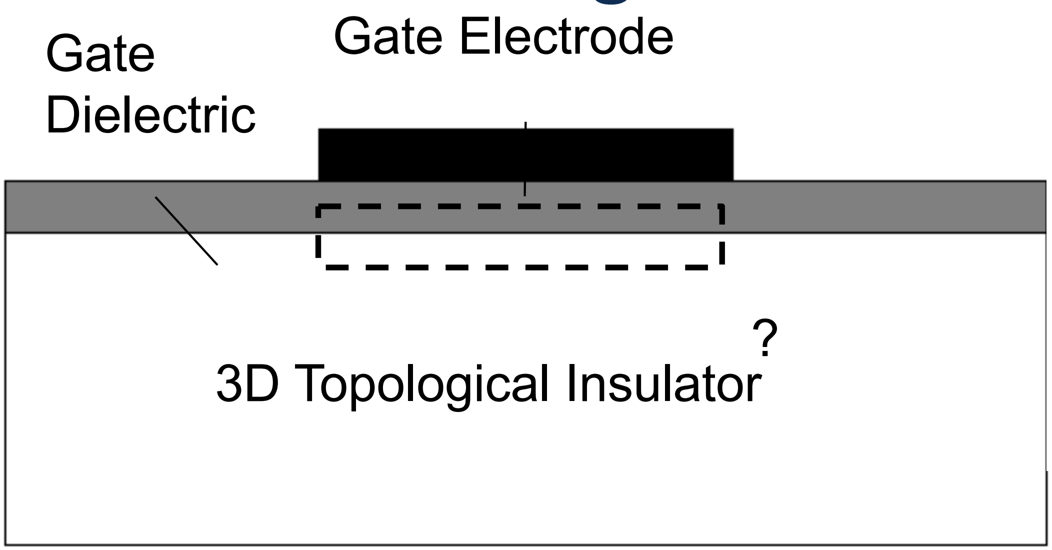


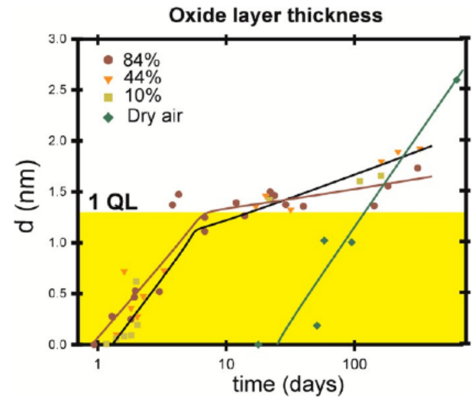




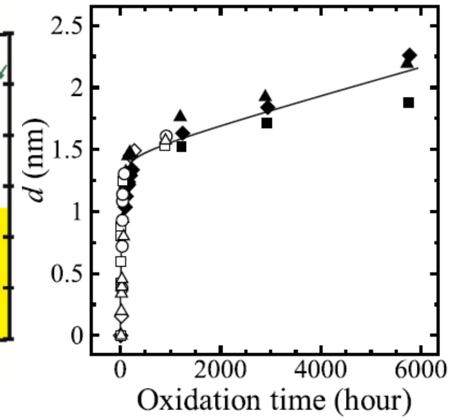


ALD Processing Can Result in "Dirty" Interfaces



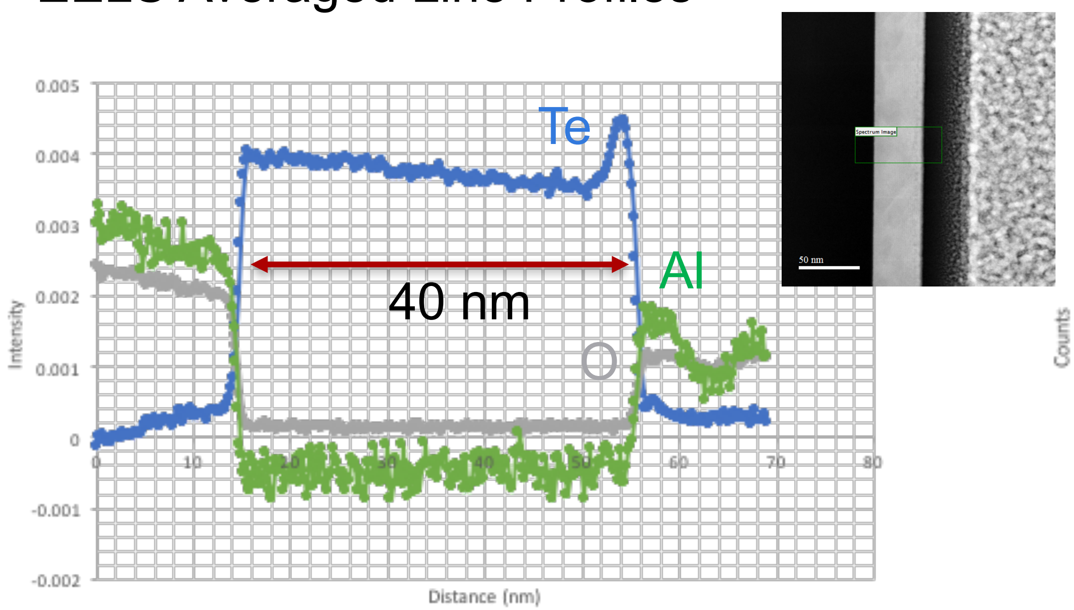


Yashina et al.
ACS Nano (2013)

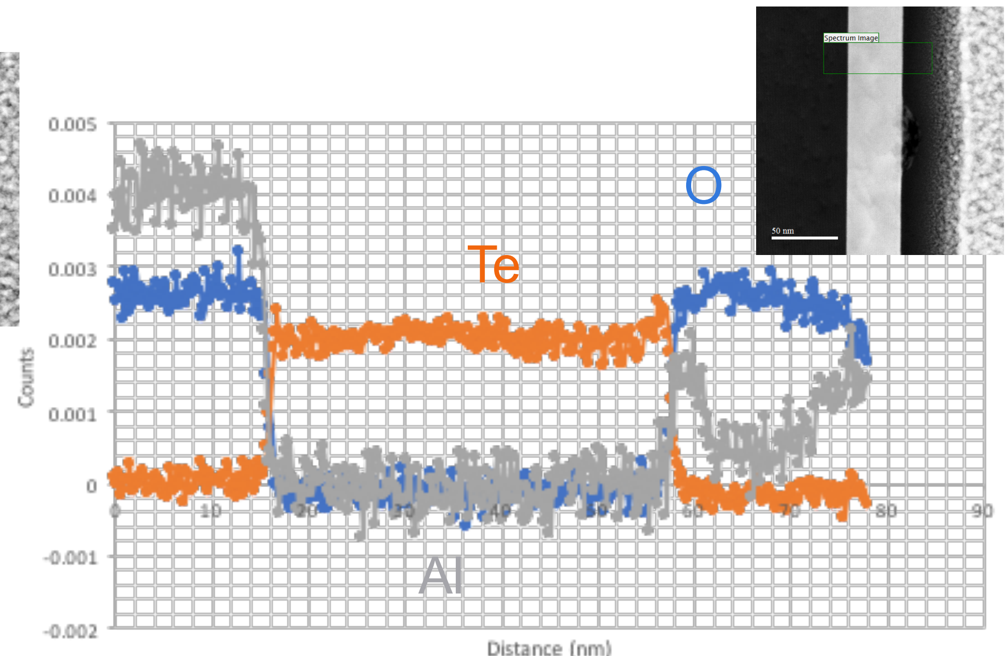


Bando et al. JPCS (2000)

EELS Averaged Line Profiles

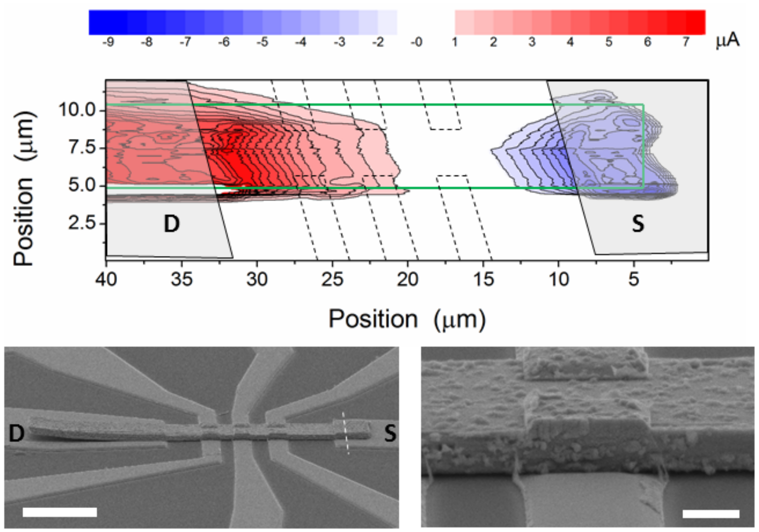


TMA/H_2O



TMA/Ozone

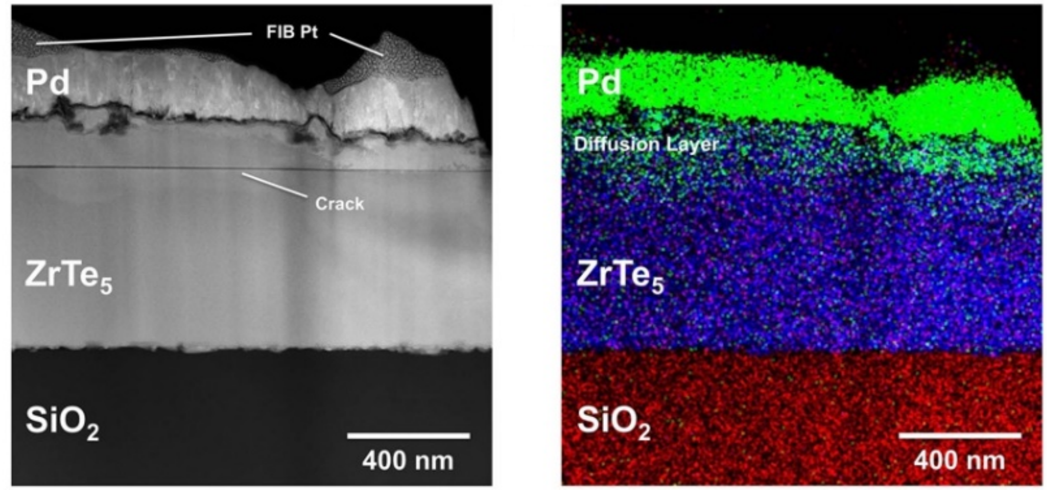
Understanding Transport in Exotic Devices is Limited by Contact Stability: Photothermal Electric Effect in $ZrTe_5$

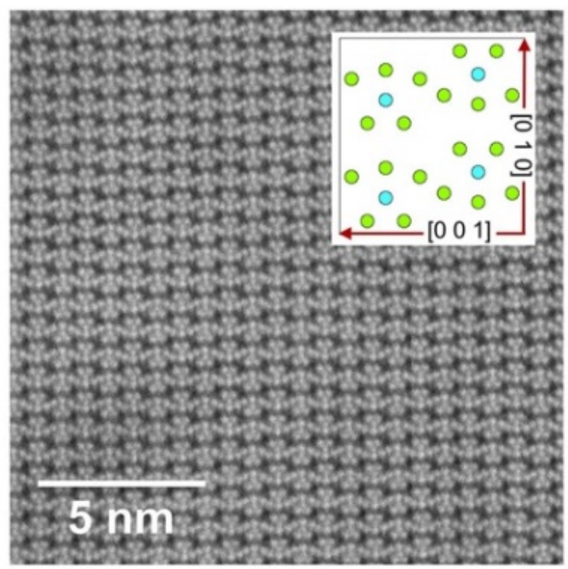


10 µm 1 µm

Scanning Photocurrent Microscopy of ZrTe5 nanoplatelet device showing photothermoelectric effect

François Léonard, Wenlong Yu, Kimberlee C. Collins, Douglas L. Medlin, Joshua D. Sugar, A. Alec Talin, Wei Pan, *ACS Applied Materials and Interfaces*, accepted 2017.

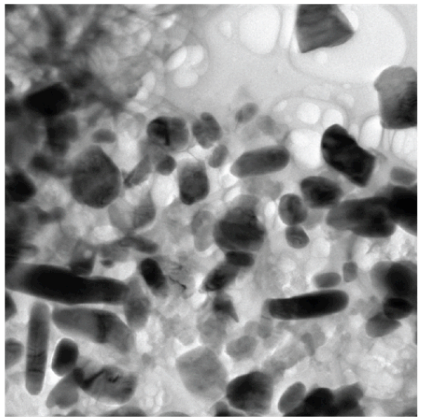




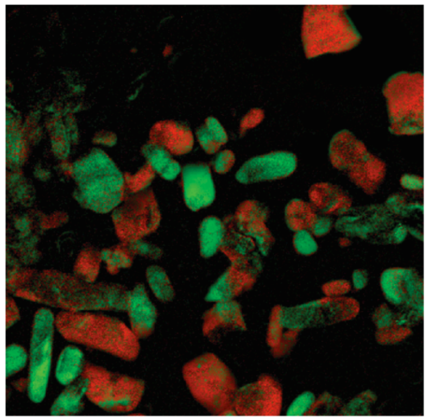
Reaction layer in contact shows reactivity of Te and need for a diffusion barrier

Summary

BF TEM image

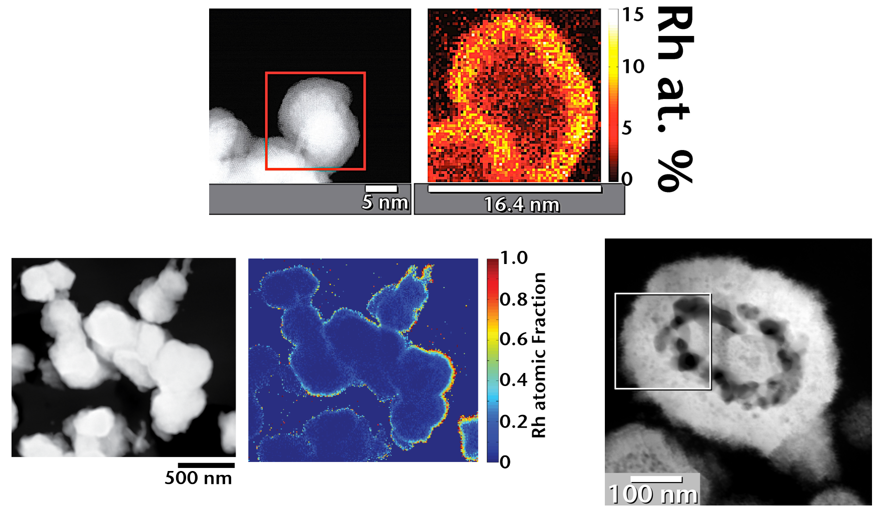


EFTEM Map of Fe state from MSA pure components



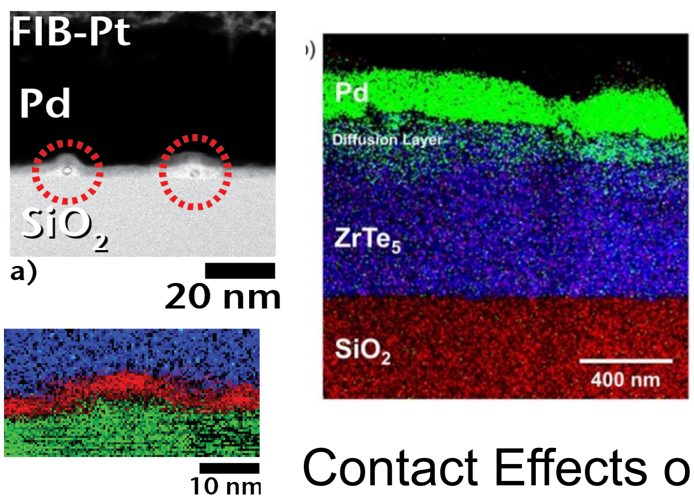
Fe^{2+}

Fe^{3+}

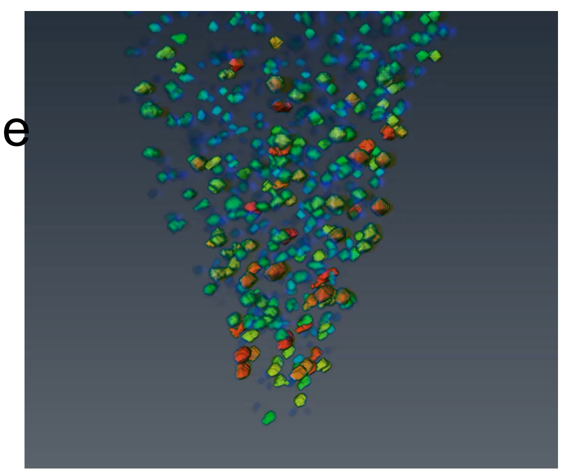


Rh transport in Nanoporous Pd

Li transport in LiFePO4



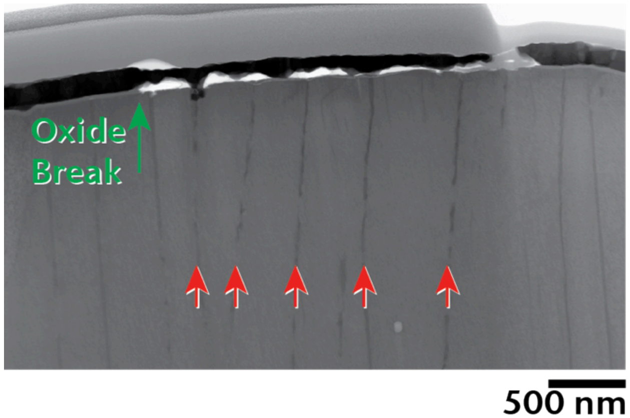
Tritium decay and He transport in Pd

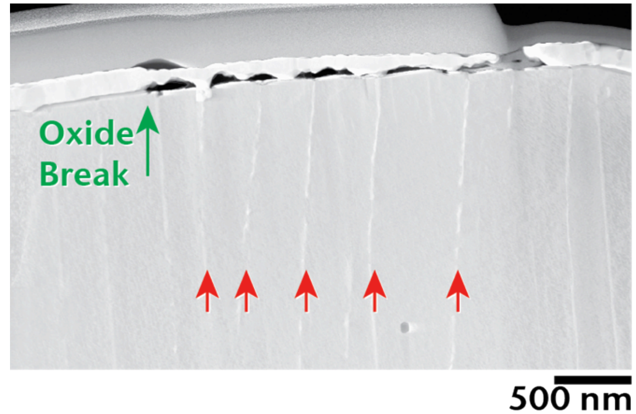


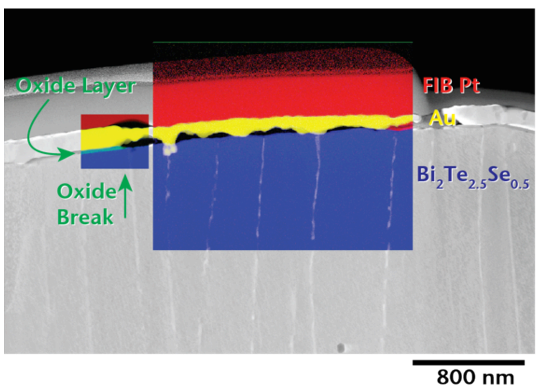
Contact Effects on Device Transport

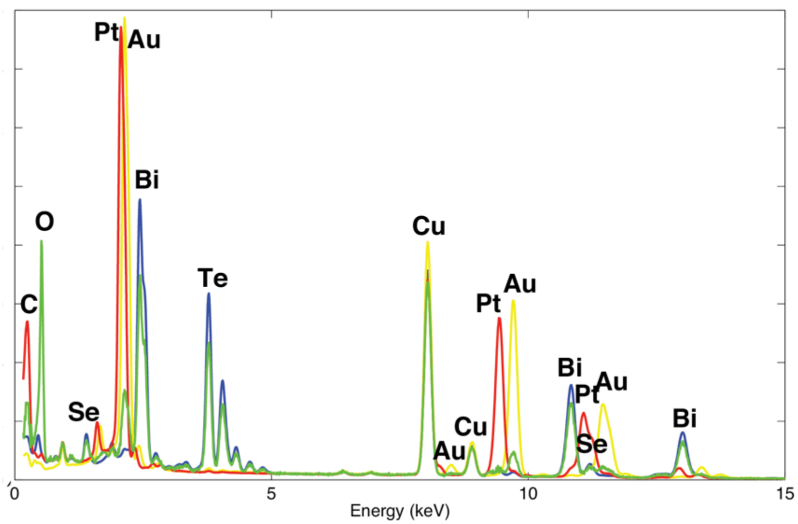
Conclusions

- By going beyond just the pictures that are obtained from electron microscopy we can learn a lot about transport and processing to further our understanding, discover new physical phenomena, develop new technology, and make informed engineering decisions
- New capabilities offered by these tools (stability, detectors, optics, etc.) have enabled high-throughput, high-quality data in 2D and 3D at all length scales, and provides access to new understanding that promotes progress in science and technology


Oxide
Break
500 nm


Oxide
Break
500 nm


Oxide Layer
FIB Pt
Au
$Bi_2Te_{2.5}Se_{0.5}$
Oxide
Break
800 nm


Pt
Au
Bi
O
C
Te
Se
Cu
Au
Pt
Cu
Au
Bi
Pt
Au
Se
Bi
0
5
10
15
Energy (keV)