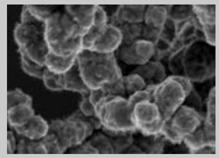
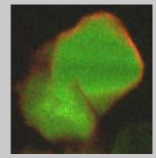
Exceptional service in the national interest

Sandia National Laboratories

M&M 2015 MICROSCOPY & MICROANALYSIS August 2-6 • Portland, OR





Pd
Rh

Quantitative EDS of Surface Modified Pd Powders for Hydrogen Storage

Joshua D. Sugar, Mark Homer, Paul G. Kotula, Patrick J. Cappillino, Markus Ong, and David B. Robinson

U.S. DEPARTMENT OF ENERGY NNSA

Pd Materials With Large Surface Area

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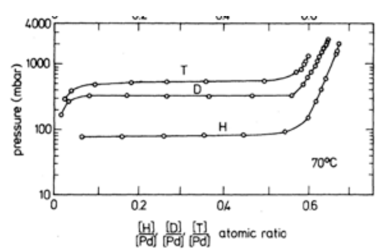
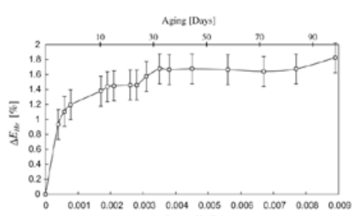
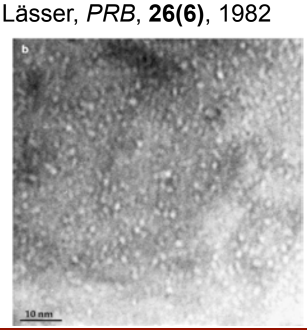
- Nanoporous materials have high surface areas
  - High surface area can improve surface-limited reaction rates (catalysis)
  - Provides an escape path for helium decay product (hydrogen storage)
    - He bubbles can cause stiffening of bulk Pd



Lässer, *PRB*, **26(6)**, 1982

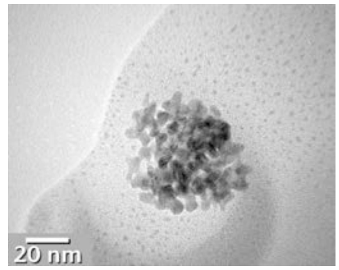


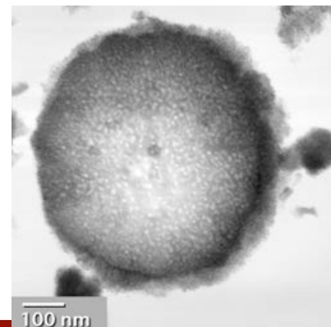


Fabre et al., *J Nuc Mat*, **342**, 2005

Pd Materials With Large Surface Area

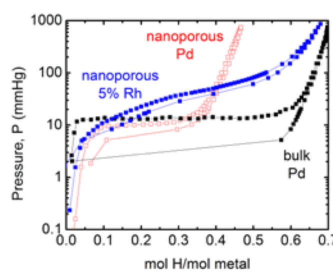
- Nanoporous materials have high surface areas
  - High surface area can improve surface-limited reaction rates (catalysis)
  - Provides an escape path for helium decay product (hydrogen storage)
    - He bubbles can cause stiffening of bulk Pd
- Goals
  - Uniform pore structure homogeneously distributed in material
  - Stable pore structure over wide T range



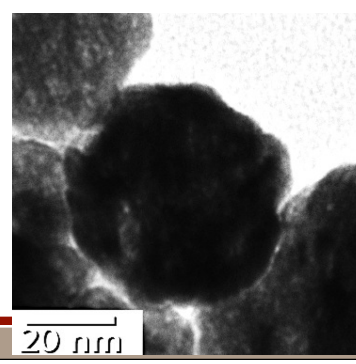


Nanoporous Pd/Rh alloys for H Storage

- Nanoporous Pd shows reduced capacity
- Nanoporous Pd has poor elevated temperature stability

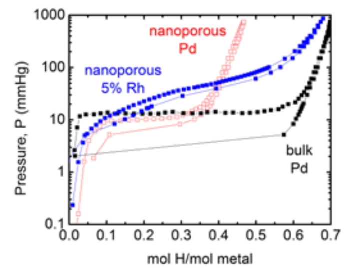


200 ° C
12 min

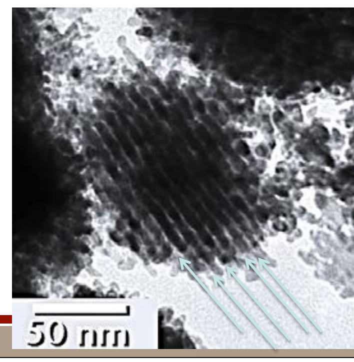


Nanoporous Pd/Rh alloys for H Storage

- Nanoporous Pd shows reduced capacity
- Nanoporous Pd has poor elevated temperature stability
- Nanoporous Pd/Rh alloys show promise for H storage
  - No reduced capacity
- Addition of Rh improves temperature stability
  - 10 at. % Rh-Pd has more stable pores
    - Stable up to 300°C
- Where is the Rh and is it uniform?
  - Pd/Rh overlap
  - Compositional variation at small length scales
  - Low count rates

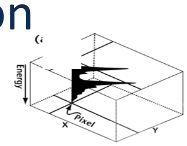


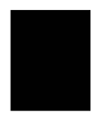
200 ° C
30 min

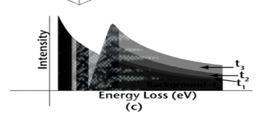


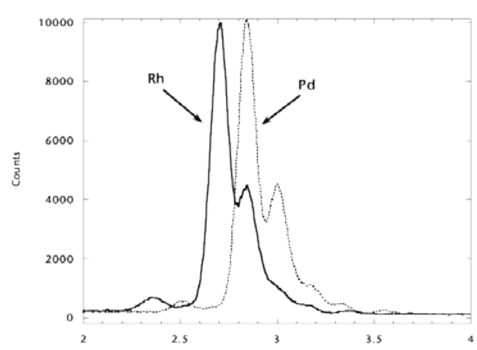
STEM-EDS Quantification

- EDS spectrum imaging
  - Spectrum at every pixel
  - Overlap of PdL and RhL



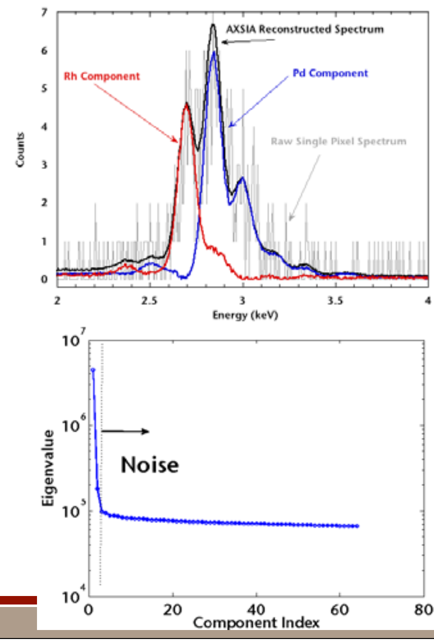






STEM-EDS Quantification

- EDS spectrum imaging
  - Spectrum at every pixel
  - Overlap of PdL and RhL
- Multivariate Statistical Analysis: AXSIA
  - Decomposition of data matrix
    - $D=C*S^T$
      - C is a matrix of spectral weight at each pixel
      - S are "pure" component spectra
    - Weighted for Poisson Statistics
    - Rotated for spectral simplicity
      - Kotula PG, et al. Microsc Miroanal 2003;9:1.
      - Keenan MR. Surf Interface Anal 2009;41:79.
  - Reconstruct the denoised data matrix D
  - Quickly identify Rh uniformity



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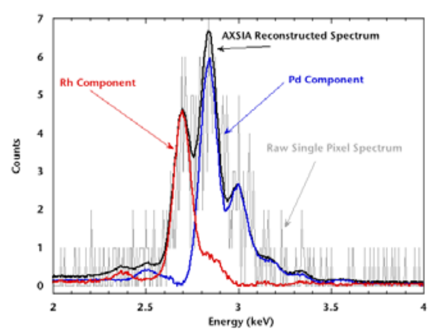
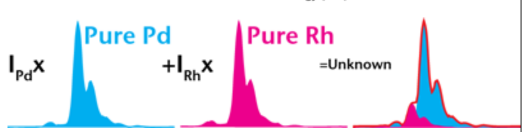
  - Reconstruct the denoised data matrix D
  - Quickly identify Rh uniformity
- Multiple Least Squares Fit-MLSQ
- Cliff-Lorimer Ratio
  - Cliff G, Lorimer GW. *J Microsc-Oxford* 1975;103:203.
  - From pure references and calibrated known standard (8 at.% Rh-Pd foil)





$$\frac{C_{Pd}}{C_{Rh}} = k_{Pd-Rh}\frac{I_{Pd}}{I_{Rh}}$$

$$C_{Pd}+C_{Rh}=1$$

$k_{\text{JEOL2010F}-200kV} = 0.99$

$k_{\text{Titan-200kV}} = 0.96$

$k_{\text{Titan-80kV}} = 1.11$

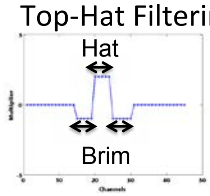
EDS Quant: Background Subtraction

- EDS Background Empirical Formula
  Lifshin, E. (1974). In *Proc. 9th Ann. Conf. Microbeam Analysis Soc.*, Ottawa, Canada, p. 53.
  - $N(E) = f_E P_E \overline{Z} \left[a\left(\frac{E_0 - E}{E}\right) + b\frac{(E_0 - E)^2}{E} \right]$

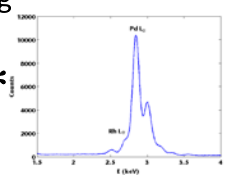
    f_E = absorption

    P_E = detector efficiency

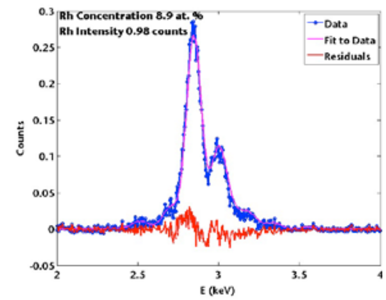
    $\overline{Z}$ = average atomic number
  - Computationally not straight forward
  - Difficult for 1000s of spectra
- Top-Hat Filtering

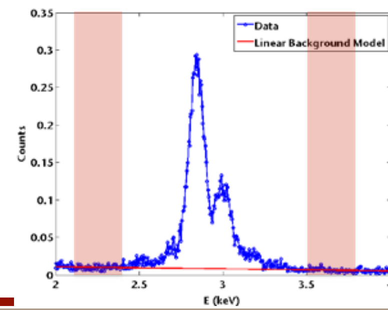


$*$



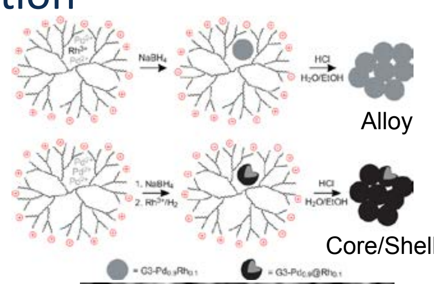
- Linear Interpolation

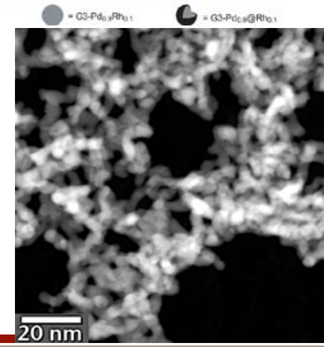




Method 1: Dendrimer-Encapsulated Nanoparticle Consolidation

- 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)

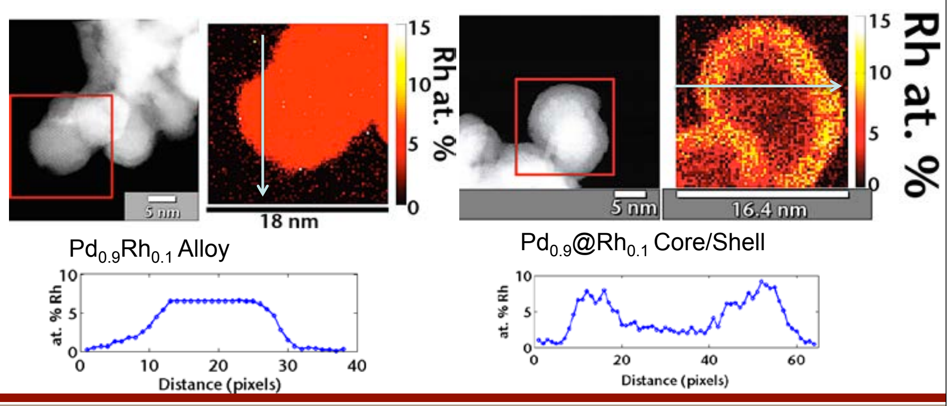




P.J. Cappillino, et al., *Journal of Materials Chemistry* **22** (2012)

Large Solid Angle Detector Finds Rh Shell

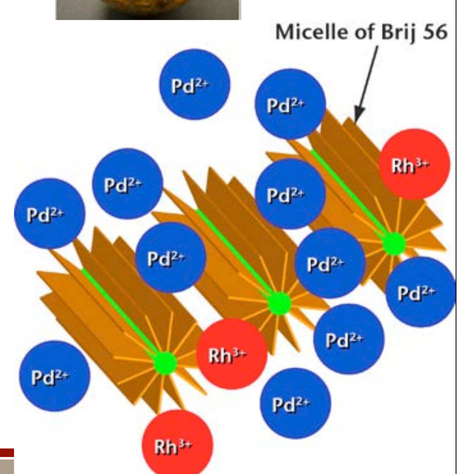
- FEI Probe-Corrected Titan G2 80-200 with 0.7 sr SDD detector array at 200 kV



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

Method 1: Surfactant Template Fabrication

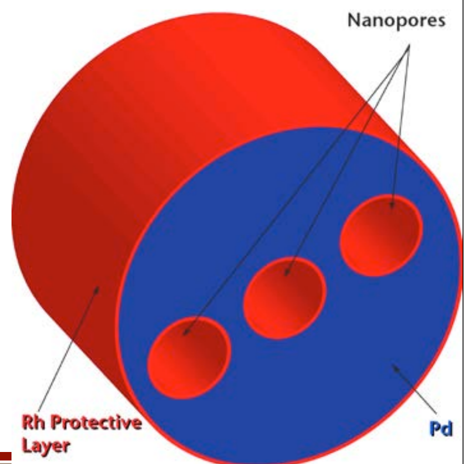
- Organic molecule, Brij 56, forms cylindrical micelle in water
  - Hydrophobic center
  - Solution of metal salts



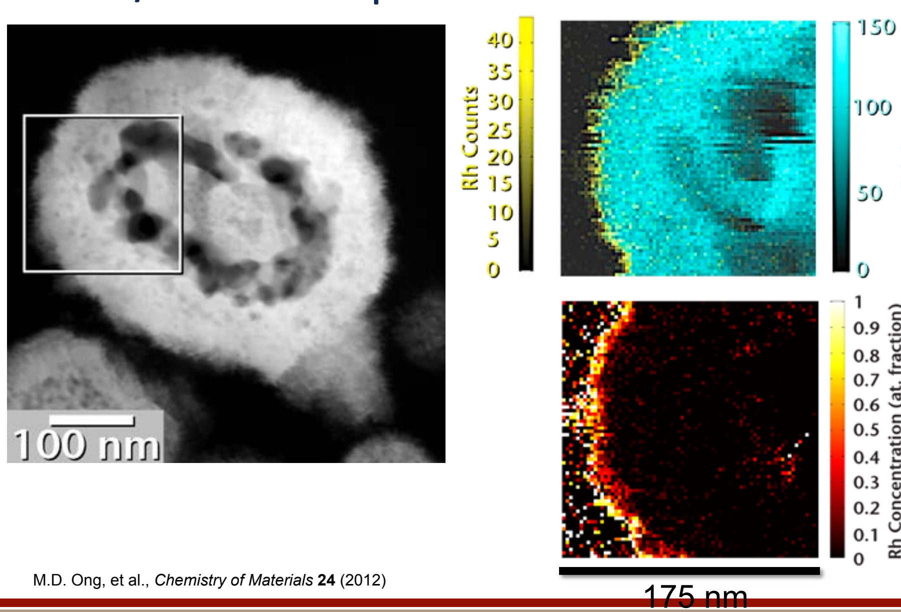
Robinson, D. et al., *IJHE*, **35** (2010).

Method 1: 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
- Did it work?



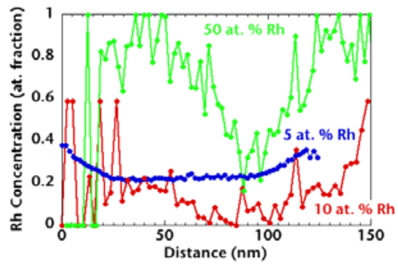
Core/Shell Compositional Distribution

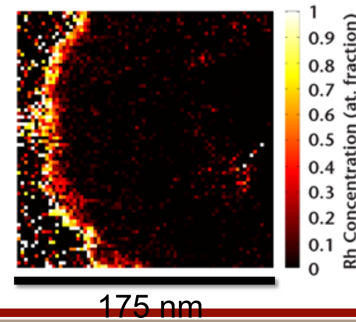


M.D. Ong, et al., *Chemistry of Materials* **24** (2012)

Core/Shell Compositional Distribution

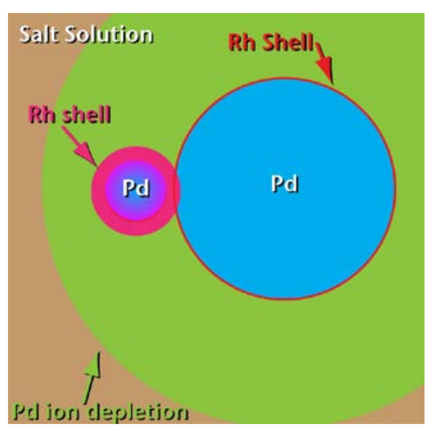
- Rh-rich shell
- Smaller (~100 nm diameter) particles have Rh concentration that is higher than the nominal concentration during synthesis
- Higher Rh content produces more uniform pore sizes
- Particle sections (ionmilling) show nonuniform pore-size distribution in larger particles





Kinetics Dictate Rh Distribution

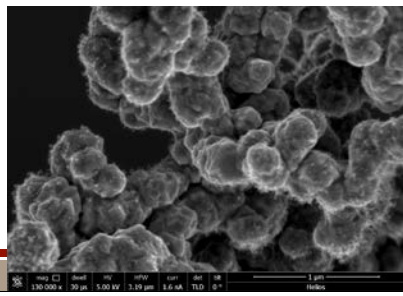
- Pd reduction faster than Rh
- Nucleation occurs throughout the reaction duration
- Large particles nucleate early in a Pd-rich environment
  - Creates a Pd-depleted zone
- All the Pd is consumed and reacted
  - Rh-rich shell on large particles then forms
- Can we get the Rh more uniformly distributed?

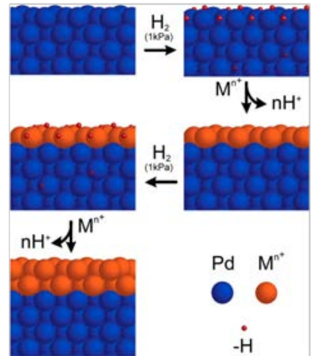


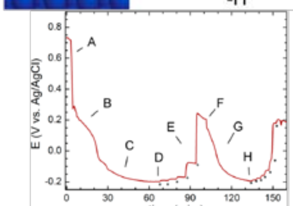
Atomic Layer Electroless Deposition

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

Wednesday Afternoon Poster: **Mark Homer**, *Preparation of Electron and X-Ray Transparent Inorganic Particles for Analytical Electron Microscopy*

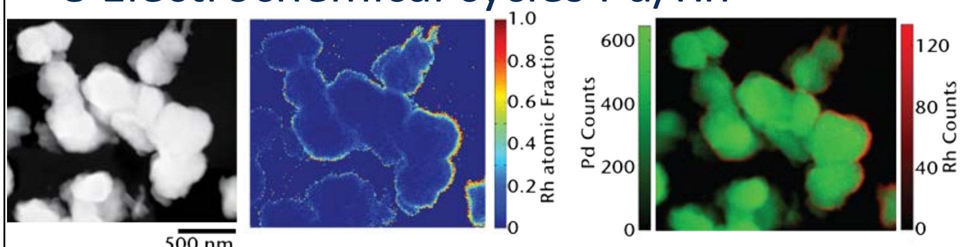






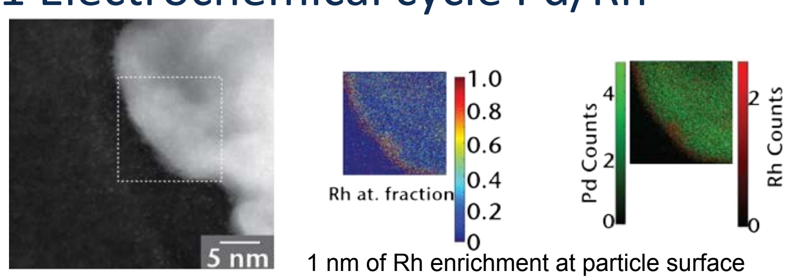
Cappillino, P. J., et al. (2014). "Atomic-Layer Electroless Deposition: A Scalable Approach to Surface-Modified Metal Powders." Langmuir **30**(16): 4820-4829.

8 Electrochemical cycles Pd/Rh



20-30 nm of Rh enrichment at particle surface

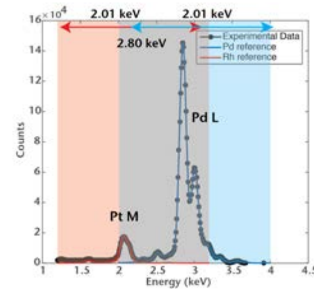
1 Electrochemical cycle Pd/Rh

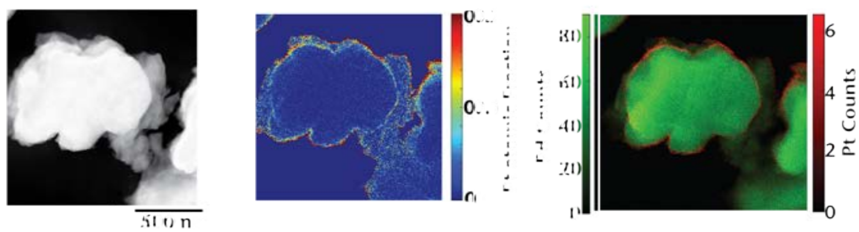


1 nm of Rh enrichment at particle surface

Pt Quantification Too

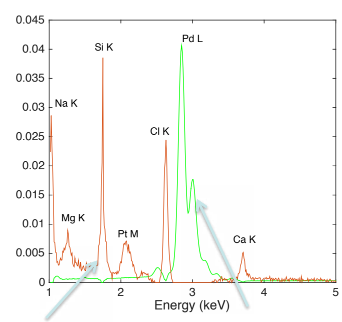
- Normalization Window for reference shapes is same energy width
- Cliff-Lorimer k-factor=0.96
- Electrochemically deposited Pt approximately 10 nm thick

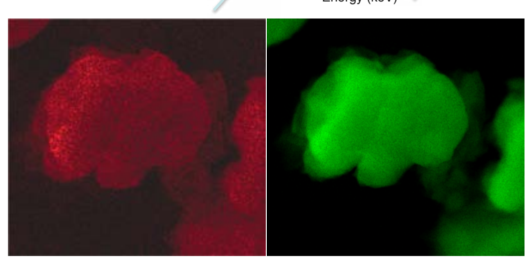




Surrounding Epoxy Causes Mixing in PCA

- Elements in surrounding epoxy resin mix with elements in coating layer
- Analysis using only MLLS yields the expected results
- Can we measure this material using FIB where no epoxy is required?



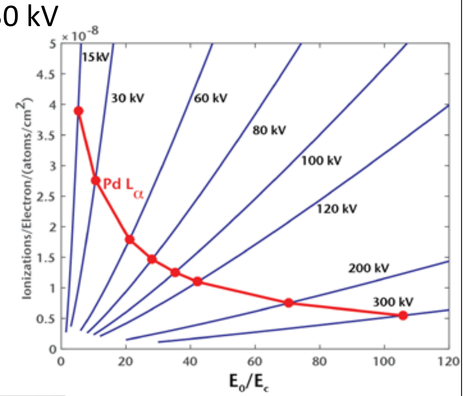


Are Thin Layers Observable at 30 kV

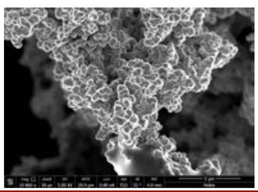
- Higher ionization cross-section at 30 kV

$$Q \propto \frac{\ln\left(E_0/E_c\right)}{E_0\ E_c}$$

Q = ionization cross section
E_0 =Accelerating Voltage
E_c = Ionization Energy for the shell in keV

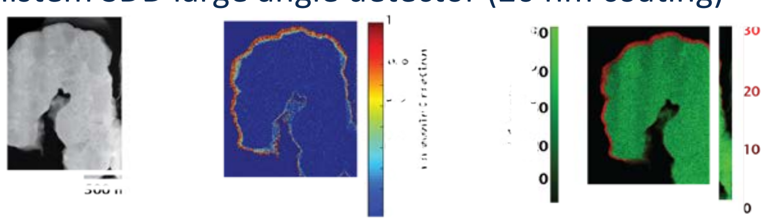


- Small interaction volume for thin samples
- FIB-thinned specimens

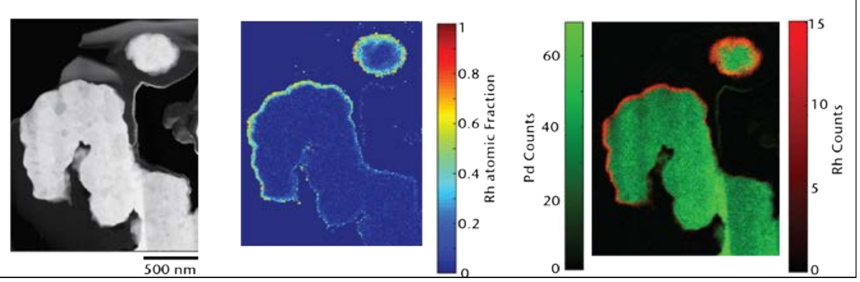


Expresslo

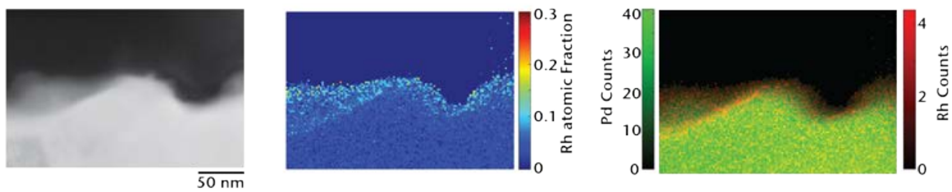
200 kV STEM on FEI Probe-corrected G2 Titan with Chemistem SDD large angle detector (20 nm coating)



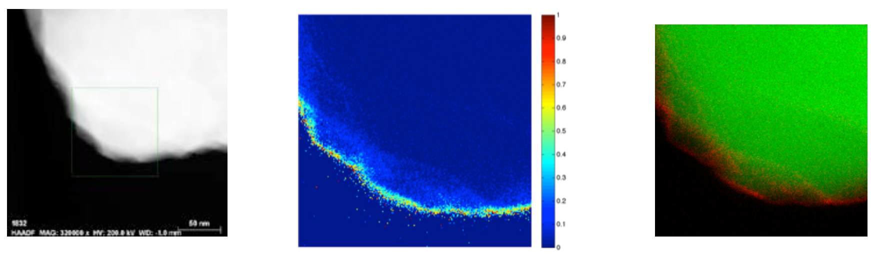
30 kV STEM on FEI Helios 660 with Oxford XmaX 80 SDD EDS Detector (assumed k-factor 1)



Thin (~1-2 nm) Layers at 30 kV

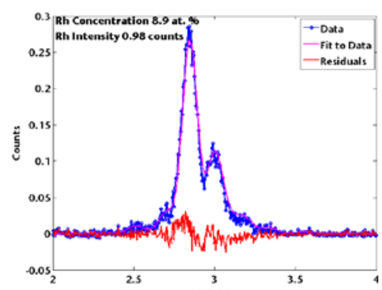


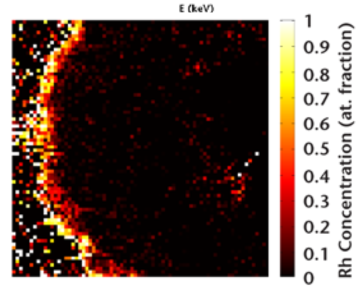
Thin (~1-2 nm) Layers at 200 kV



Summary

- EDS Quantification of Nanoporous Structures
  - MSA – denoising & quick inspect
  - MLSQ – linear background
  - Cliff-Lorimer





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- Multiple Sample processing routes with different character compositions and length scales
  - Surfactant Template
  - Dendrimer
  - ELAD

Summary

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- Multiple Sample processing routes with different character compositions and length scales
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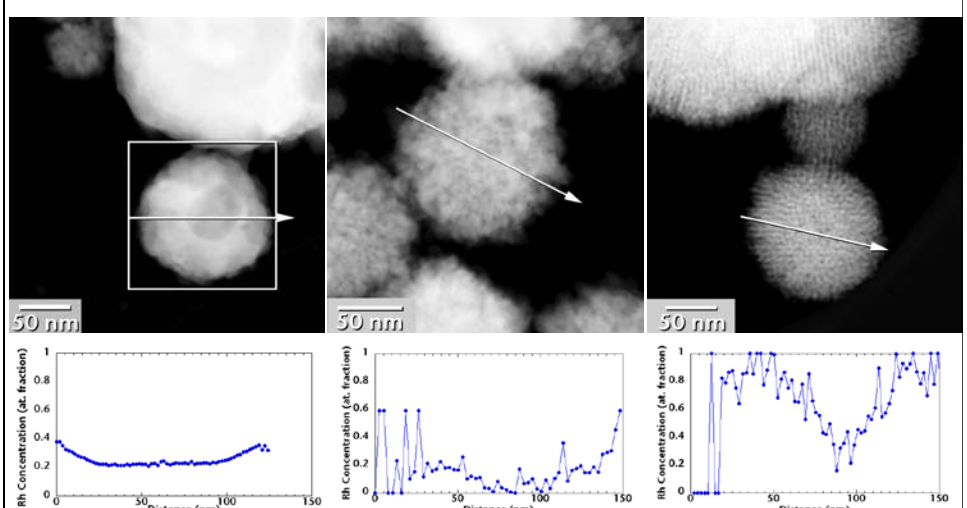
  - ELAD
- EDS at 30 kV is capable of observing layers with nanometer thickness

Conclusions

- Powerful tools available to quantify composition and morphology of nanostructures
  - Large area, large solid-angle detectors
  - Computational tools: MSA and MLSQ
  - Aberration-corrected microscopes with stable operation at a range of accelerating kV
  - Dualbeam platforms with STEM and EDS for preparation of thin samples and analysis of materials at 30 kV
- The available technologies for quantitative compositional analysis in complicated nano and sub-nanostructures is exciting because we can use our measurements to improve synthesis and processing parameters

Rh Quantification in Small Particles

5 at. % Rh-Pd | 10 at. % Rh-Pd | 50 at. % Rh-Pd



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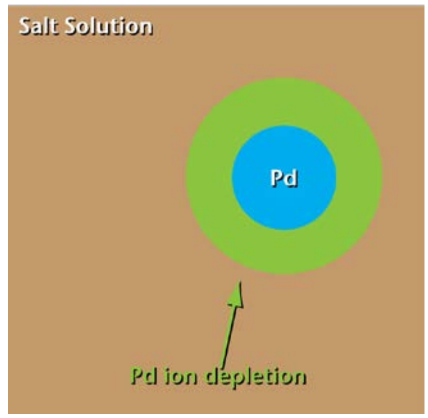

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Lifshin, E. (1974). In *Proc. 9th Ann. Conf. Microbeam Analysis Soc.*, Ottawa, Canada, p. 53.

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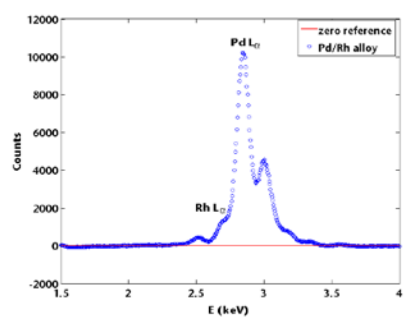


- Linear Interpolation

EDS Quant: Background Subtraction

- EDS Background Empirical Formula

Lifshin, E. (1974). In *Proc. 9th Ann. Conf. Microbeam Analysis Soc.*, Ottawa, Canada, p. 53.

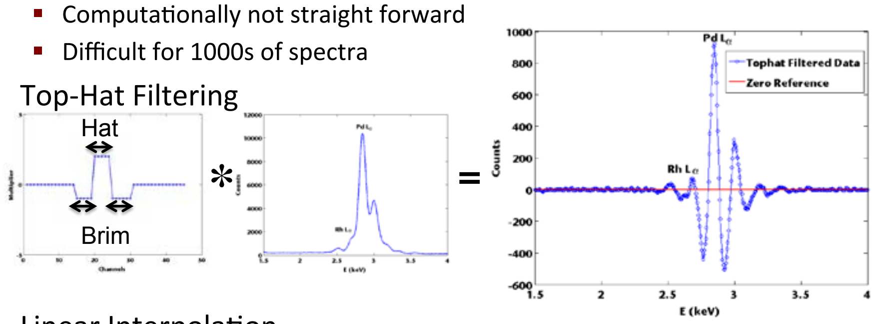
  - $N(E) = f_E P_E \bar{Z}\left[a\left(\frac{E_0 - E}{E}\right) + b\frac{(E_0 - E)^2}{E}\right]$

    f_E = absorption

    P_E = detector efficiency

    $\bar{Z}$ = average atomic number

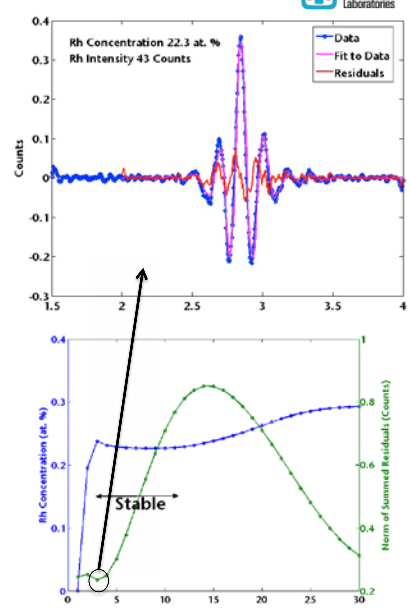
  - Computationally not straight forward
  - Difficult for 1000s of spectra
- Top-Hat Filtering



- Linear Interpolation

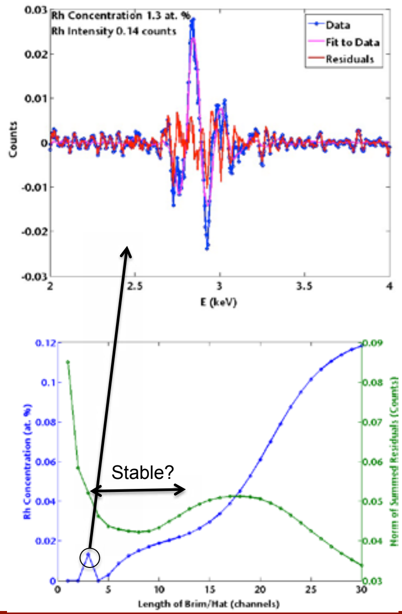
Tophat Filtering Unstable for Low-Count Rate Data

- Tophat Filtering
  - Fast and easy for large numbers of spectra
  - Separates peaks that overlap
  - Removes slowly varying background
- Surfactant Templated Nanoporous Materials
  - Input Count Rates ~1000 cps



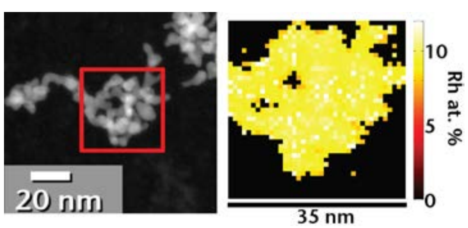
Tophat Filtering Unstable for Low-Count Rate Data

- Tophat Filtering
  - Fast and easy for large numbers of spectra
  - Separates peaks that overlap
  - Removes slowly varying background
- Surfactant Templated Nanoporous Materials
  - Input Count Rates ~1000 cps
- Agglomerated Dendrimer Encapsulated Particles
  - Input Count Rates ~100 cps
  - Optimizing tophat dimensions for every pixel is not feasible

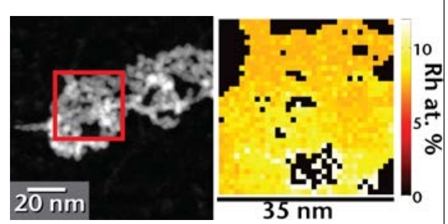


Core/Shell and Alloy Particles Still Indistinguishable

- JEOL 2010F & Oxford 0.1 sr SiLi Detector at 200 kV
  - MSA-denoise
  - MLSQ-linear background subtraction
  - Cliff-Lorimer



$Pd_{0.9}Rh_{0.1}$ Alloy

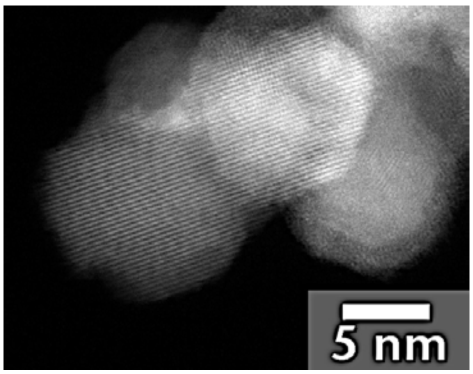


$Pd_{0.9}@Rh_{0.1}$ Core/Shell

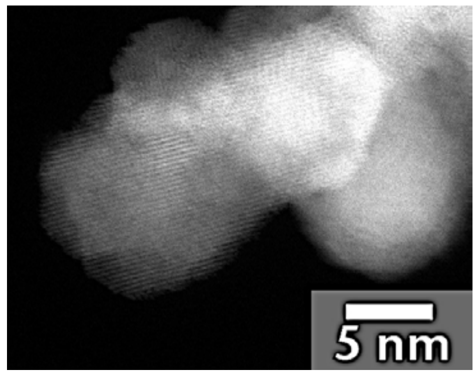
- Need More Counts!!!

Operate at 80 kV to Reduce Damage

- Evidence of damage before and after



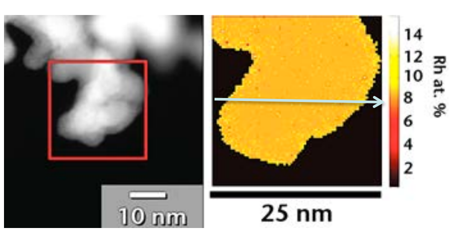
Before SI acquisition



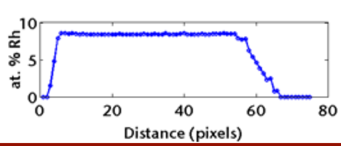
After SI acquisition

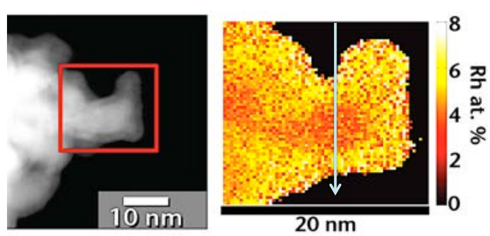
EDS Quant at 80 kV

- MSA-Denoise
- MLSQ-linear background subtraction
- Cliff-Lorimer
- Is it better?

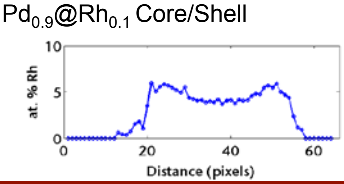


$Pd_{0.9}Rh_{0.1}$ Alloy



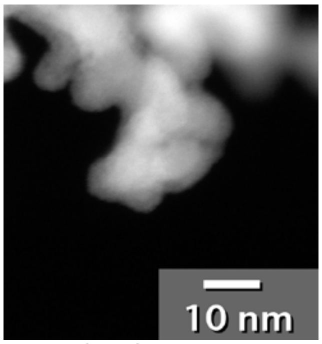


$Pd_{0.9}$@$Rh_{0.1}$ Core/Shell

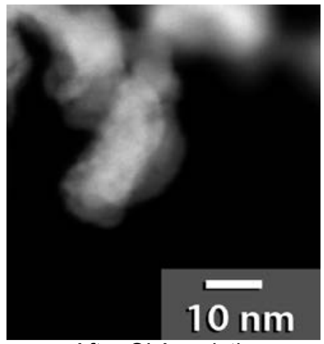


EDS Quant at 80 kV

- MSA-Denoise
- MLLSQ
- Cliff-Lorimer
- Is it better?



Before SI Acquistion



After SI Acquistion