


Spectroscopic Imaging of Core-Shell Structured Pt-Co Nanoparticles by Aberration-Corrected STEM

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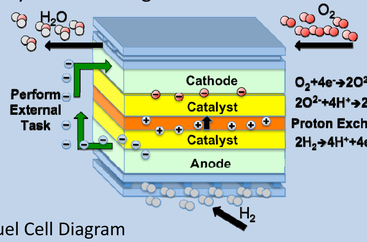
Motivations: Pt-Co Particles for Fuel Cells

One of the key challenges in developing Proton Exchange Membrane fuel cells as an effective means of energy conversion is improving the catalysis of the Oxygen Reduction Reaction in the cathode. Recent studies have found that replacing pure platinum with a platinum-3d metal alloycan produce up to a ten-fold increase in the catalytic activity[1]. We investigated a promising such candidate, Pt-Co alloyed nanoparticles. What follows is a summary of our findings.

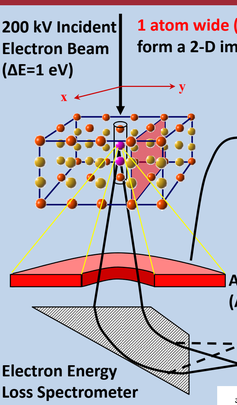


PEM Fuel Cell Diagram

Scanning Transmission Electron Microscopy & Electron Energy Loss Spectroscopy

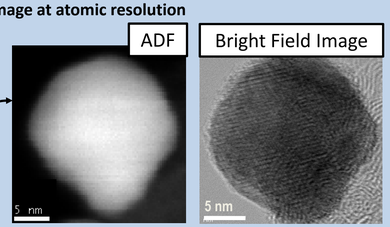
200 kV Incident Electron Beam (ΔE=1 eV)

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



Annular Dark Field (ADF) detector

Electron Energy Loss Spectrometer



Both direct and scattered beam can be used to form images.

EELS uses inelastic scattered electrons (electrons that have loss energy when they hit the sample) to produce a spectrum of energy loss for every point in an image.

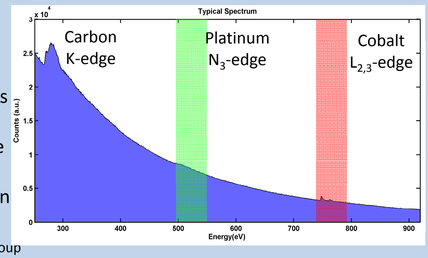


Diagram courtesy of the Muller Group

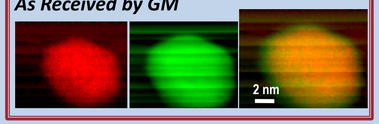
References

1. V. R. Stamenkovic et al. *Nature Mater.***6**, 41 (2007).
2. Y. Xu et al. *J. Am. Chem. Soc.***126,** 4717 (2004).

Summary of Particles Investigated

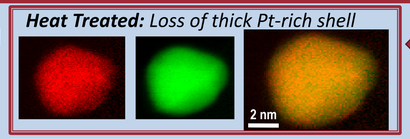
Heated at 800° C for 6 hours

As Received by GM

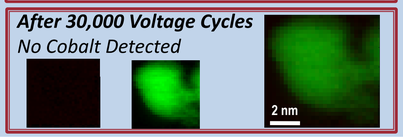


CCD was at room temperature during this acquisition. The streaks show the temperature variation. Data from this condition was not used in any quantitative analysis.

Heat Treated: *Loss of thick Pt-rich shell*

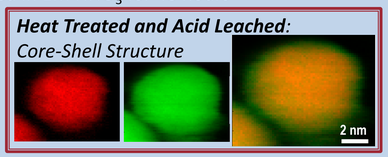


After 30,000 Voltage Cycles
No Cobalt Detected



Placed in 1M HNO_3 for 48 hours

Heat Treated and Acid Leached:
Core-Shell Structure

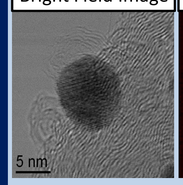


Legend: Co | Pt | Combined RG

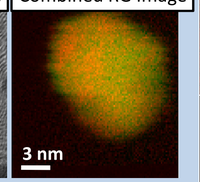
Heat Treated: Facet Dependence of Pt Shell

Typical acquisition

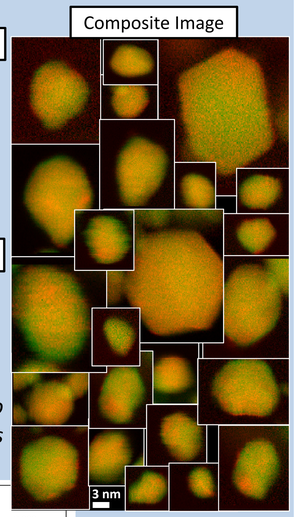
Bright Field Image



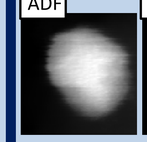
Combined RG Image



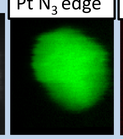
Composite Image



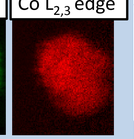
ADF



Pt N_3 edge

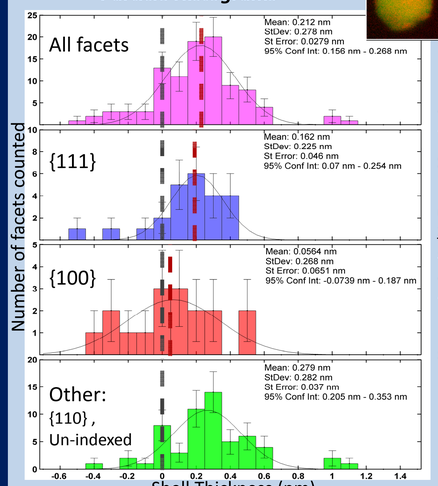


Co $L_{2,3}$ edge



Many particles investigated to build statistics

Particle Histograms



{111} Facet Shell Thickness:1.6 ± 0.5 *Å*
Statistically significant Pt-rich layer
(Agrees with calculations for Pt_3Co {111} terminated surfaces[2]).
{100} Facet Shell Thickness: 0.6 ± 0.7 *Å*
No statistically significant Pt-rich layer

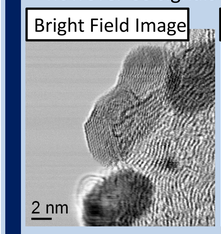
Heat Treated Particles Summary

- Weak Pt-rich layer seen on {111} facets but not {100} facets.
- 1st chemical observation of facet dependent Pt-rich shell in particles.

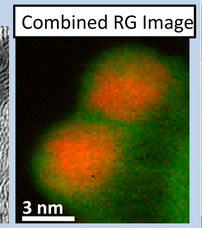
Heat and Acid Treated: Core-Shell Structure

ADF and Pt signals from neighboring particles shown touch however Co signals distinct illuminating Pt shell.

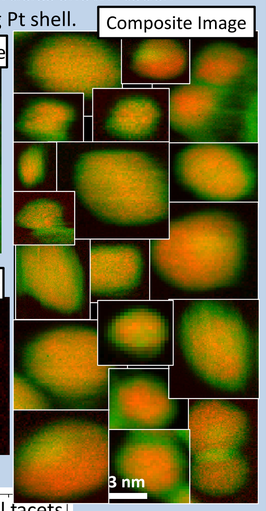
Bright Field Image



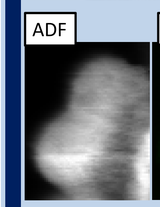
Combined RG Image



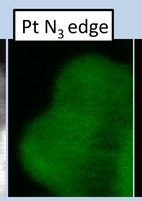
Composite Image



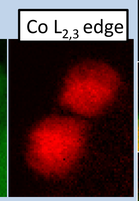
ADF



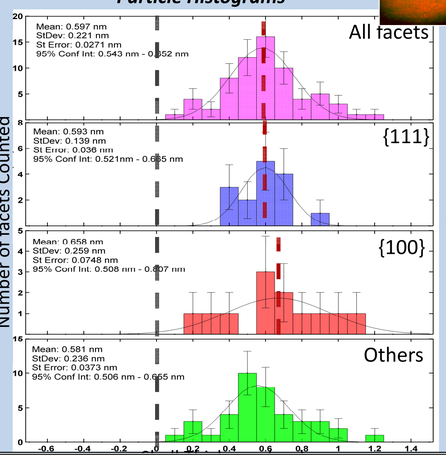
Pt N_3 edge



Co $L_{2,3}$ edge



Particle Histograms



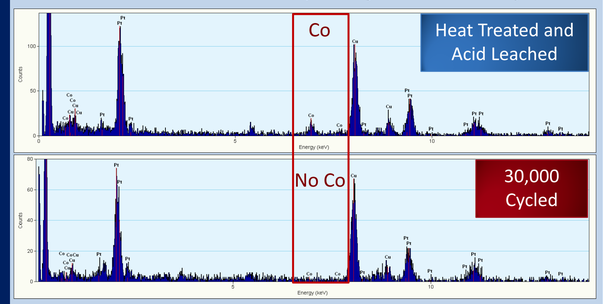
Shell Thickness:
6.0 ± 0.3 *Å*
No Statistically significant dependence of shell thickness on terminating facet

Heat Treated and Acid Leached Particles Summary

- Thick Pt-rich shell observed; no statically significant dependence of shell thickness on terminating facet.
- 1st direct observation of this Pt shell in EELS mapping.

After 30,000 Voltage Cycles

Heat and Acid Treated vs. 30,000 cycled EDX Composition

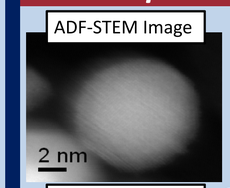


30,000 Cycled Particles Summary

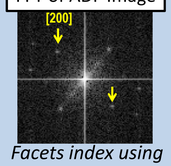
- No cobalt detected in particles by either EELS or EDX.

EELS Maps: Fitting Line Profile across facets

ADF-STEM Image

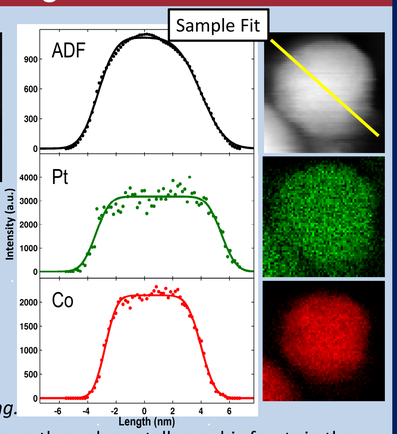


FFT of ADF Image



Facets index using diffractogram and known lattice spacing.

Sample Fit



Line profiles were drawn through crystallographic facets in the ADF, Pt and Co signals. The intensities extracted were then fit as shown above. From the fits, the width was determined.

Acknowledgments

I would like to acknowledge Professor David Muller for this unique opportunity to participate in cutting edge research; my graduate student mentors Julia Mundy and HuolinXin, thank you for your immense help; the entire Muller Group. Also John Grazul for a exceptional learning experience in the microscope; the Cornell Center for Nanoscale Systems, and the Ronald McNair Program, in particular its associated director Jason Hamilton.

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