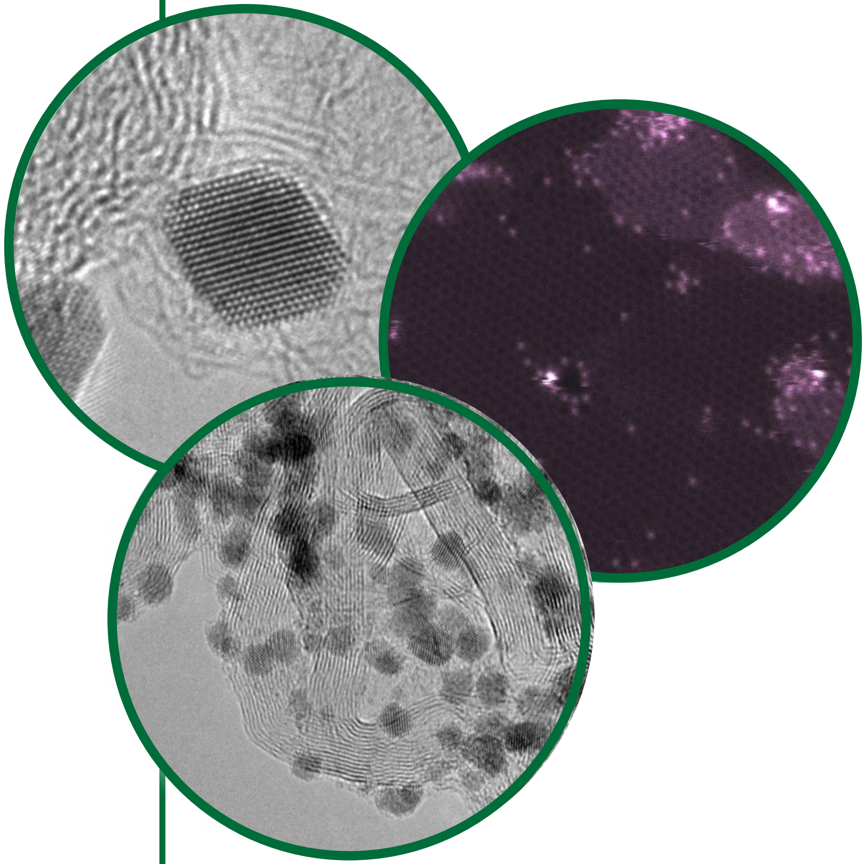
Characterization of Fuel Cell Materials

Project ID FC020



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Oak Ridge National Laboratory
Oak Ridge, TN

2012 DOE Annual Merit Review
May 17, 2012

U.S. DEPARTMENT OF ENERGY

OAK RIDGE NATIONAL LABORATORY
MANAGED BY UT-BATTELLE FOR THE DEPARTMENT OF ENERGY

Project Overview

Timeline

- Project initiated in FY2000
- *Continuous* - fundamental research on the microstructural characterization of fuel cell materials to improve durability

Budget

- Funding in FY11 - \$600k (~1.5 FTE)
- Funding in FY12 - \$600k (~1.5 FTE)

Barriers

- Fuel Cell Barriers Addressed
  - A: Durability
  - C: Performance

Partners

- Los Alamos National Laboratory
- Lawrence Berkeley National Laboratory
- GM
- Nissan Technical Center North America
- Nuvera Fuel Cells
- Naval Research Laboratory
- Proton OnSite
- Fuel Cell Energy
- Brown University
- University of Central Florida
- NREL
- UTC Power
- Additional DOE project collaborations: LANL, ANL, NREL, 3M, and UTC Power. Results from these studies are NOT included in this project summary

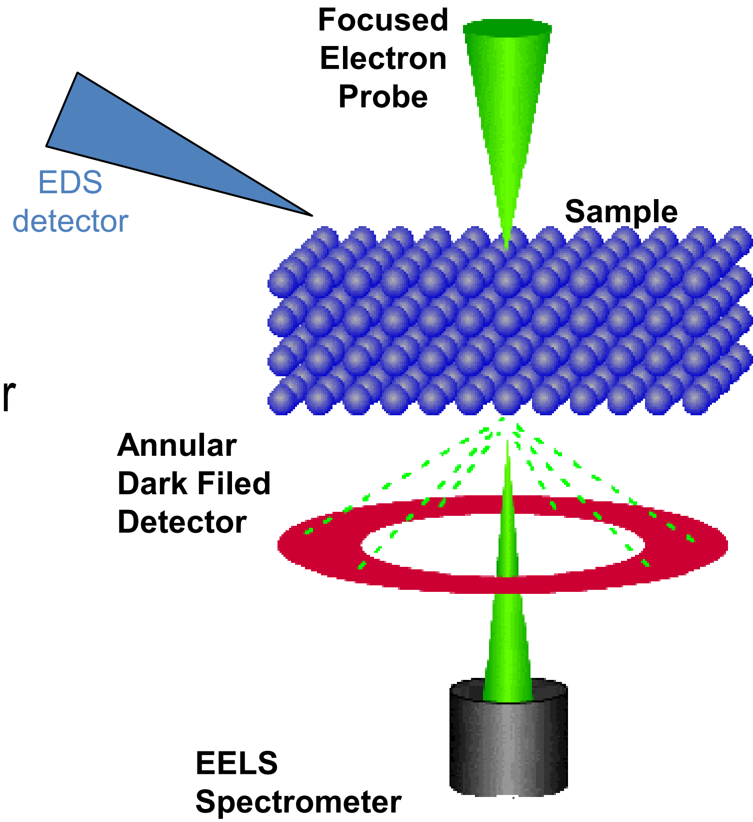
Relevance - ORNL Research Objectives

- Identify, develop, and optimize novel high-resolution imaging and compositional/chemical analysis techniques, and unique specimen preparation methodologies, for the μm-to-Å scale characterization of the material constituents comprising fuel cells (catalyst, support, membrane)
- Understand fundamental relationships between the material constituents within fuel cell MEAs and correlate these data with stability and performance as per guidance of the entire fuel cell community
- Integrate microstructural characterization within other DOE projects
- Apply advanced analytical and imaging techniques for the evaluation of microstructural and microchemical changes to elucidate microstructure-related degradation mechanisms contributing to fuel cell performance loss
- MAKE CAPABILITIES AND EXPERTISE AVAILABLE TO FUEL CELL RESEARCHERS OUTSIDE OF ORNL

Approach: Use Advanced Microscopy to Investigate Structure and Composition of Fuel Cell Materials and Correlate Observations With Performance

- Apply state-of-the-art electron microscopy techniques for the characterization of MEA material constituents:
  - Catalyst nanoparticles – composition, chemistry, size, and particle morphology
  - Polymer - membrane and electrode re-cast ionomer
  - Catalyst support materials
  - MEAs/GDLs/MPLs

- Collaborate with industry, academia, and national laboratories to make capabilities and microscopy expertise available to correlate structure/composition with MEA processing and/or life-testing studies



Milestone Schedule – FY11 and FY12

- FY11 Milestones:
  - Report results from a progressive study of the mechanisms of carbon corrosion as a result of transient FC operation. *Completed*
  - Report results of cathode corrosion monitored using the *in-situ* electrochemical cell for the HR-TEM/STEM *Completed*

- FY12 Milestones:
  - Report results from combined XPS/TEM/STEM study of ionomer degradation in PEM fuel cells MEAs as a function of aging protocol *Completed*
  - Publish results from fundamental study of Pt/graphene nucleation & growth as related to Pt supported on carbon blacks *On Track 8/12*

Technical Accomplishments and Progress Have Been Focused on Topics of Interest to the FC Community (Collaborators, Tech Team, and FY11 AMR Reviews)

Past AMR presentations have highlighted ORNL research specific to:

- Ionomer characterization
- Carbon support degradation
- Å-scale catalyst nanoparticle studies
- Electrode architecture optimization

ORNL has continued to focus resources on these topics, but has undertaken several new initiatives:

- Quantifying loss of Pt due to migration
- Characterization of ionomer films
- New technique development and application to FCs

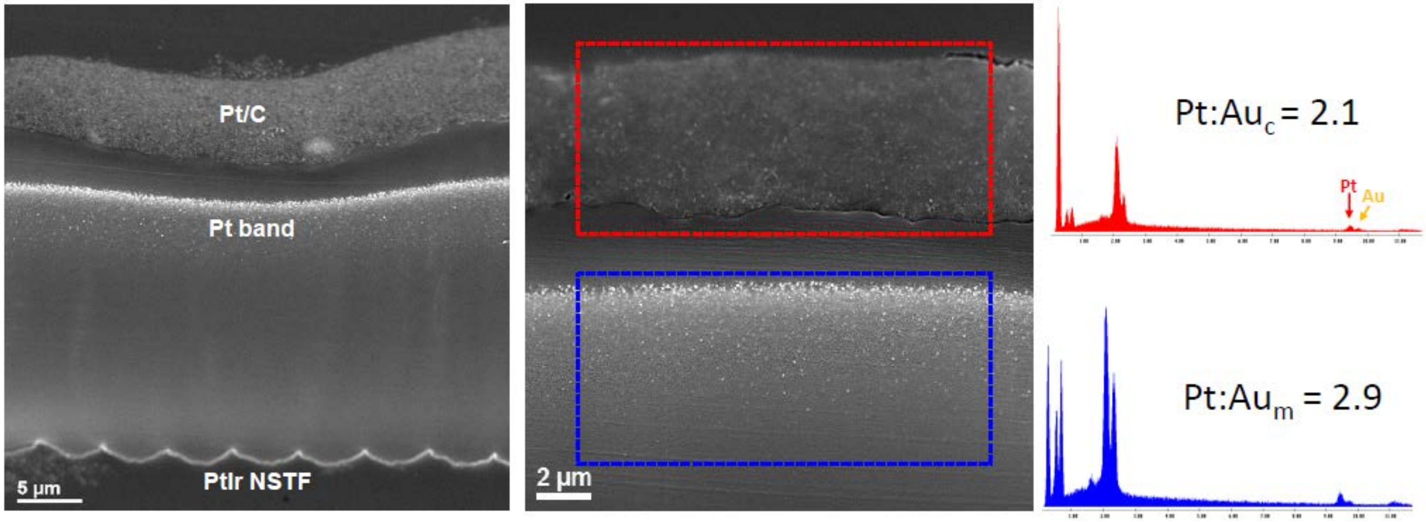
Technical Accomplishment: Quantifying Pt Loss Due to Dissolution and Migration Out of Cathode

Collaborating directly with several partners (3M and Nuvera Fuel Cells) to evaluate microscopy techniques to QUANTIFY the amount of Pt migration

- Bulk SEM-EDS of MEA cross-sections
- STEM-EDS of ultramicrotomed MEA cross-sections
- Extensive image analysis of particle distributions from TEM/STEM image series

Technical Accomplishment: Quantifying Pt Loss Due to Dissolution and Migration Out of Cathode

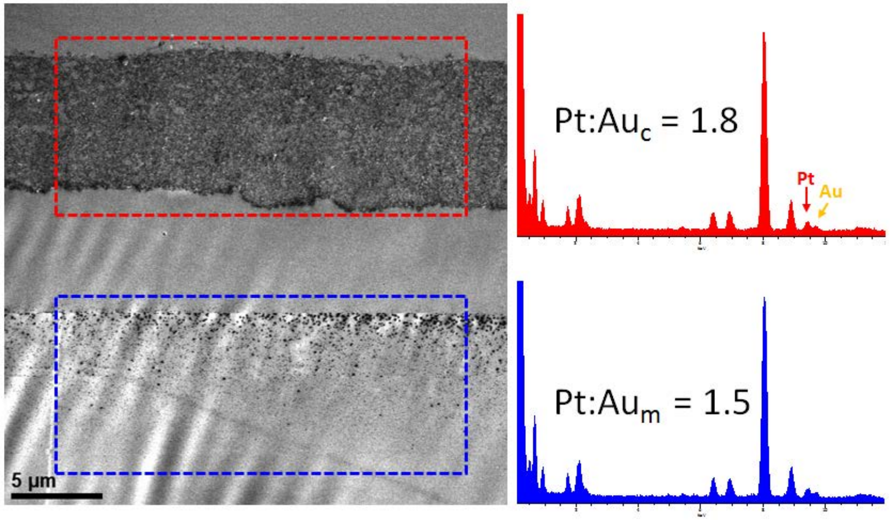
Bulk SEM-EDS Analysis:

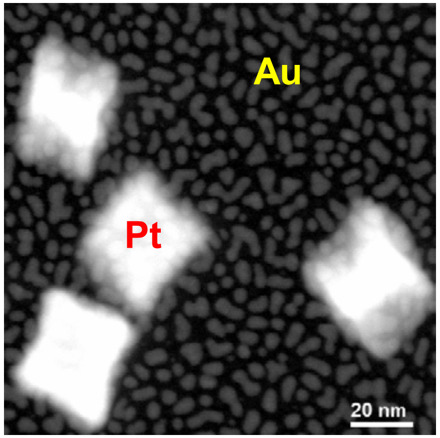


Samples coated with 5nm-Au - reference peak for quantification – Pt wt% in membrane calculated from SEM-EDS spectra.

W. Bi, G.E. Gray, and T.F. Fuller, *Electrochem. Solid St.* **10** (2007)

STEM-EDS Analysis:

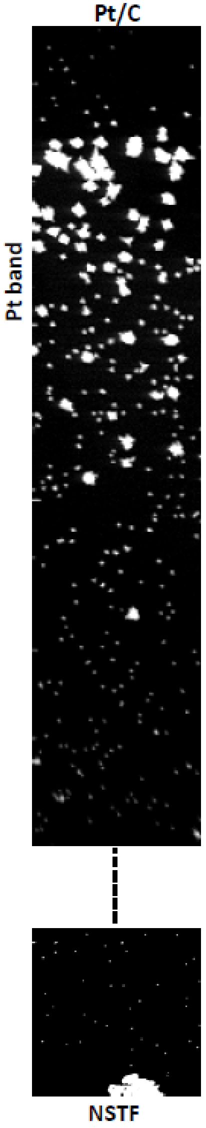


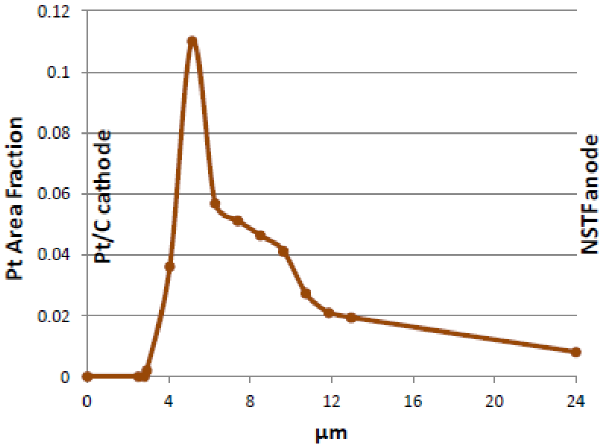


Au reference layer deposits as small particles on surface of MEA (background of the larger Pt particles).

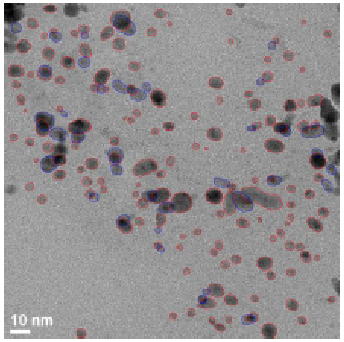
Technical Accomplishment: Quantifying Pt Loss Due to Dissolution and Migration Out of Cathode

Particle “counting”:

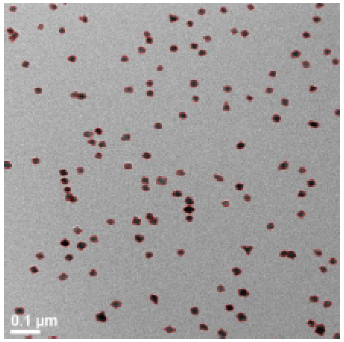




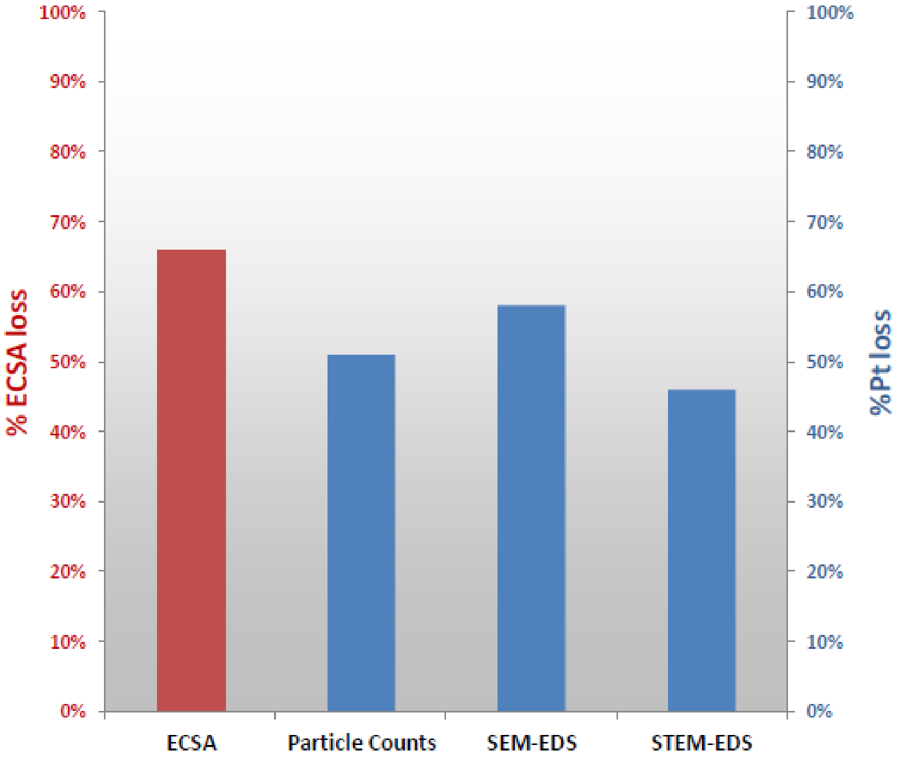
Pt loss can also be estimated by ‘simple’ particle counts - the Pt area fraction is calculated from TEM images of the cathode and membrane.



Cathode

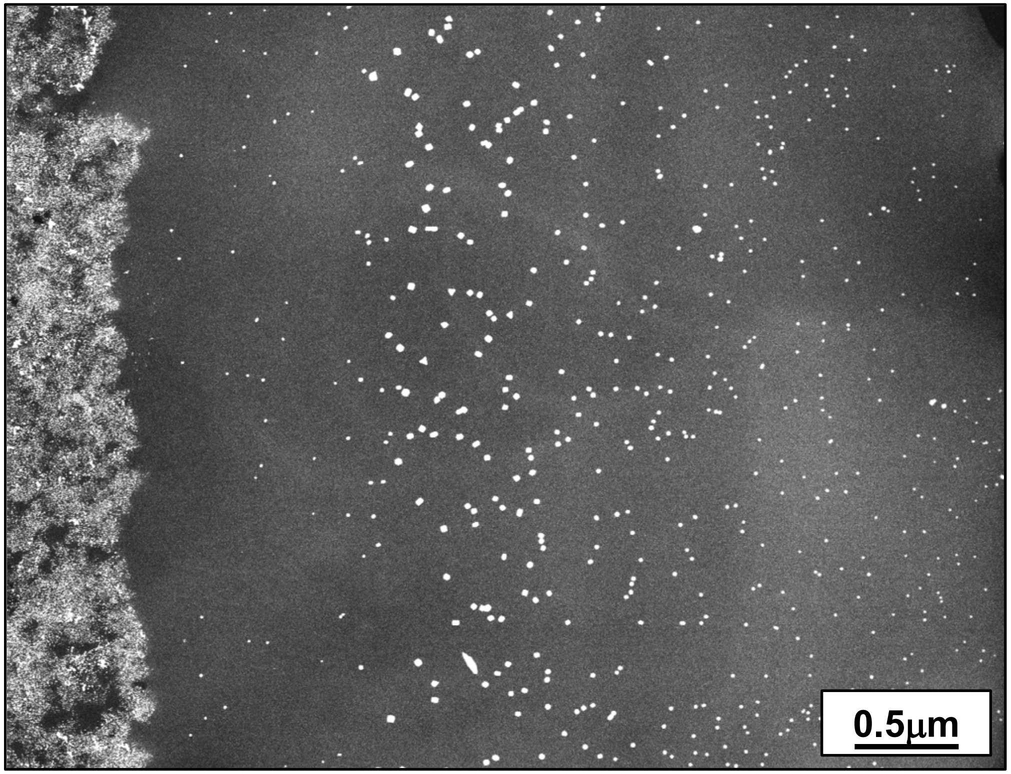


Membrane



Fairly good agreement between the three techniques – but is there a better technique?

Technical Accomplishment: Quantifying Pt Loss Due to Dissolution and Migration Out of Cathode

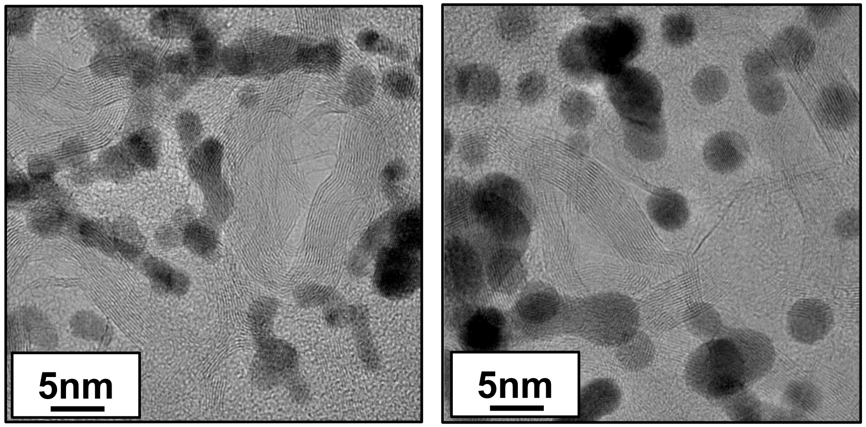


The formation of 'Pt band' in membrane during electrochemical aging/testing/use is well documented.

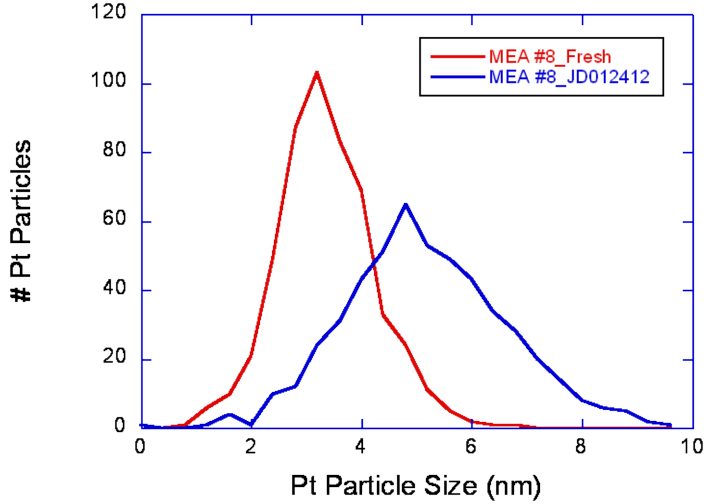
$\longrightarrow Pt^{2+} \longrightarrow Pt^{2+} + H_2 = Pt^0 + 2H^+$

What is the amount of Pt lost to migration?

The loss of Pt surface area in cathode due to particle coalescence/coarsening.



Pt particles before and after 1.2V hold for 400 hr in H_2/N_2



Technical Accomplishment: Quantifying Pt Loss Due to Dissolution and Migration Out of Cathode

Pt particle size change within cathode:

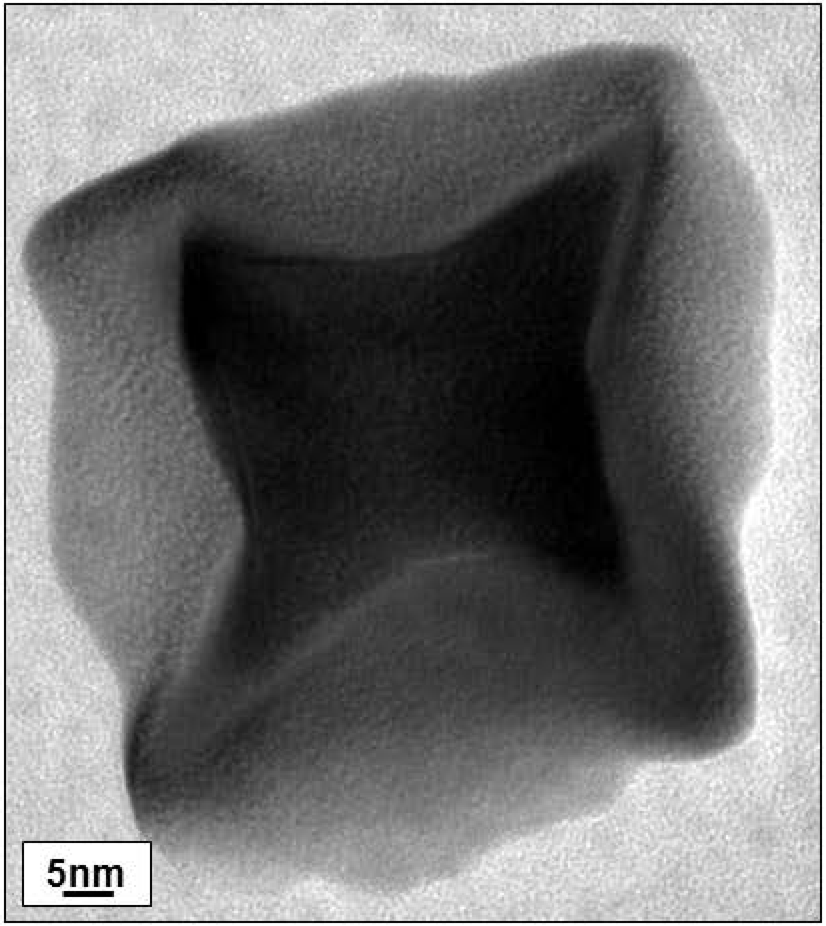
3.2nm → 5.0nm

$32 nm^2$ → $78 nm^2$

~940 Pt atoms → ~2500 Pt atoms

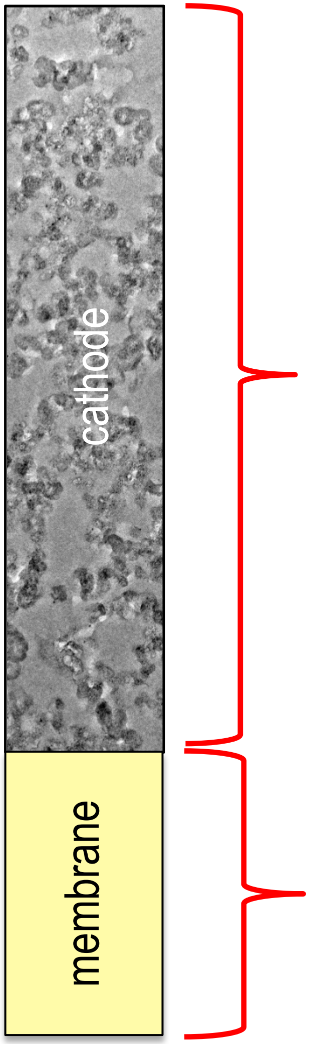
Nanoparticle coalescence results in fewer surface Pt atoms

Pt migration into membrane results in complete loss of Pt atoms



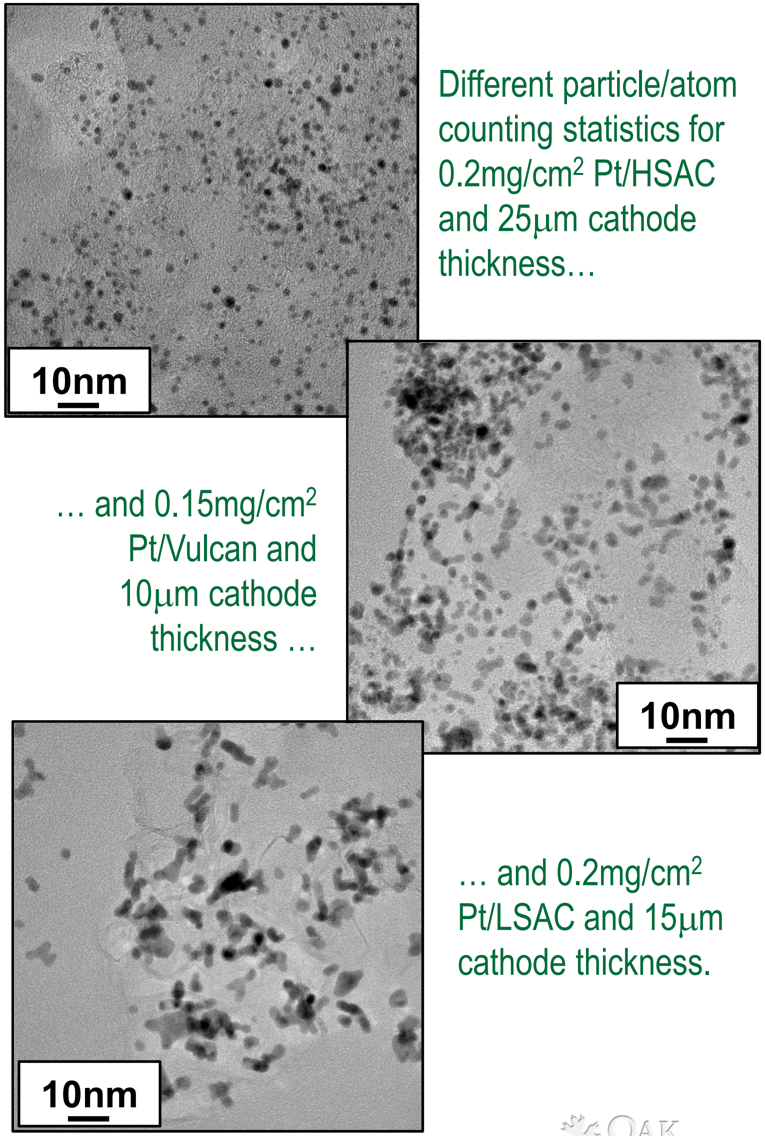
65nm Pt particle
~530,000 Pt atoms!

Technical Accomplishment: Quantifying Pt Loss Due to Dissolution and Migration Out of Cathode



Initial cathode thickness
Initial Pt loading
Initial Pt particle size/diameter
= # Pt atoms in cathode 'slab' of 1.5μm width that are available

Pt particle size distribution in membrane within 1.5μm X 5μm 'slab' after testing
= # Pt atoms that migrated into 'slab'

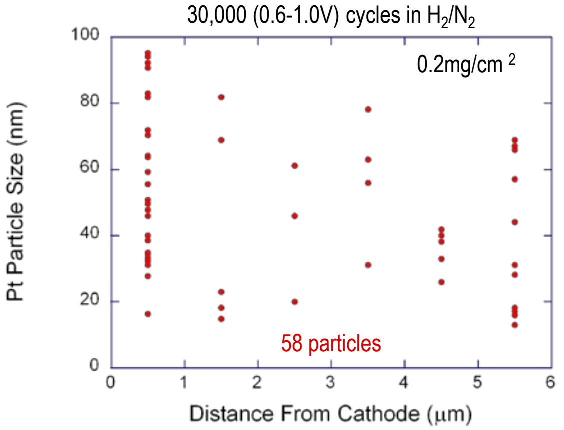


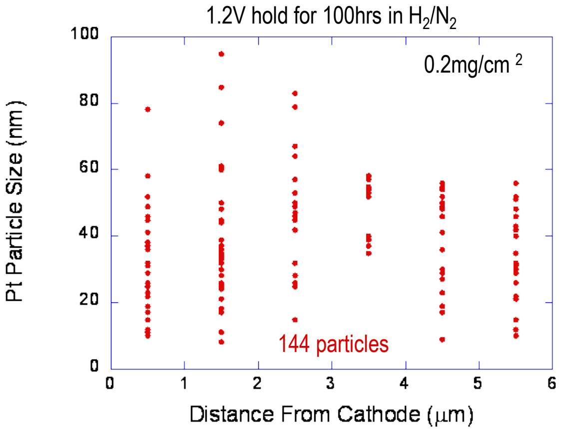
Different particle/atom counting statistics for 0.2mg/cm^2 Pt/HSAC and 25μm cathode thickness…

… and 0.15mg/cm^2 Pt/Vulcan and 10μm cathode thickness …

… and 0.2mg/cm^2 Pt/LSAC and 15μm cathode thickness.

Technical Accomplishment: Quantifying Pt Loss Due to Dissolution and Migration Out of Cathode


30,000 (0.6-1.0V) cycles in H_2/N_2


1.2V hold for 100hrs in H_2/N_2

$$\frac{\text{\# Pt atoms in membrane}}{\text{\# Pt atoms available initially in cathode}}$$

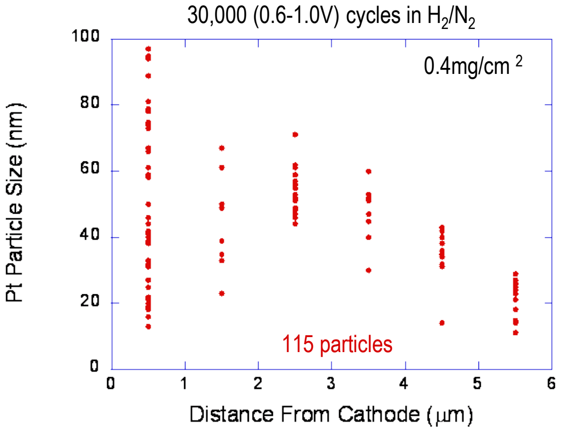
0.2mg/cm^2 Pt loading:
Cycled: Pt loss = 6%
1.2V hold: Pt loss = 9.5%

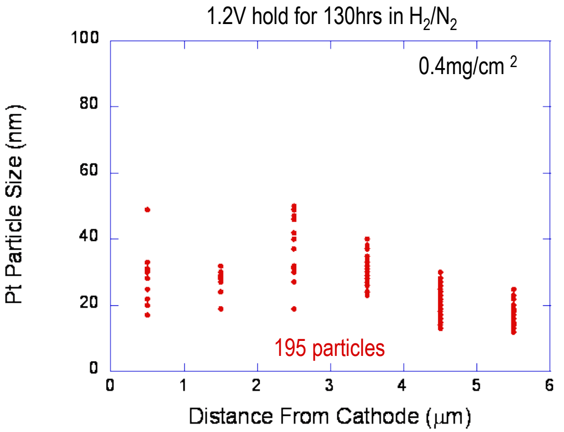
0.4mg/cm^2 Pt loading:
Cycled: Pt loss = 5%
1.2V hold: Pt loss = 1.8%

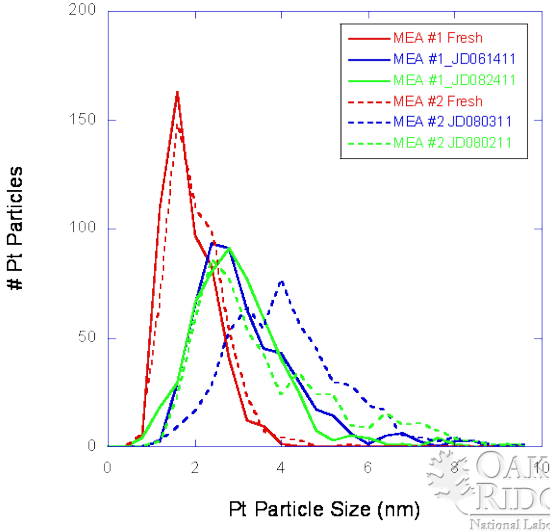
Pt/HSAC with 2X Pt loading (initial Pt size for both cases = 2nm)
Same test conditions yield different Pt migration profiles

Higher Pt loadings → *LESS* Pt migration

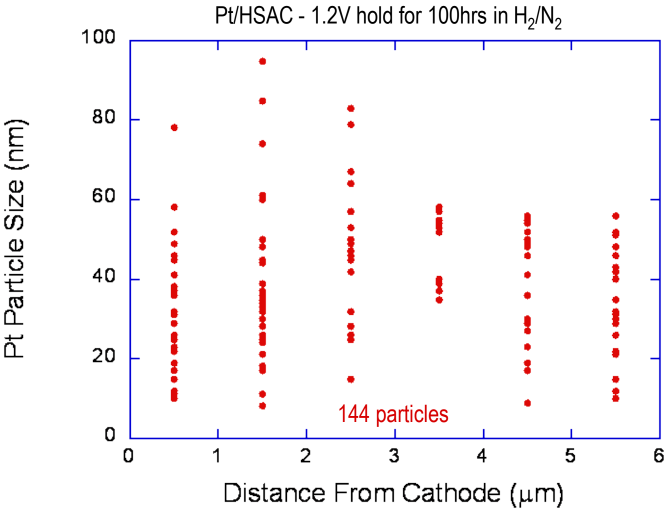
Higher Pt loading → *INCREASED* Pt coarsening


30,000 (0.6-1.0V) cycles in H_2/N_2

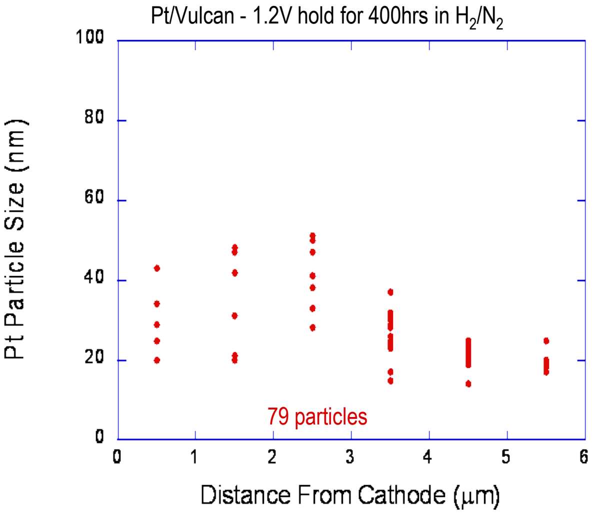

1.2V hold for 130hrs in H_2/N_2



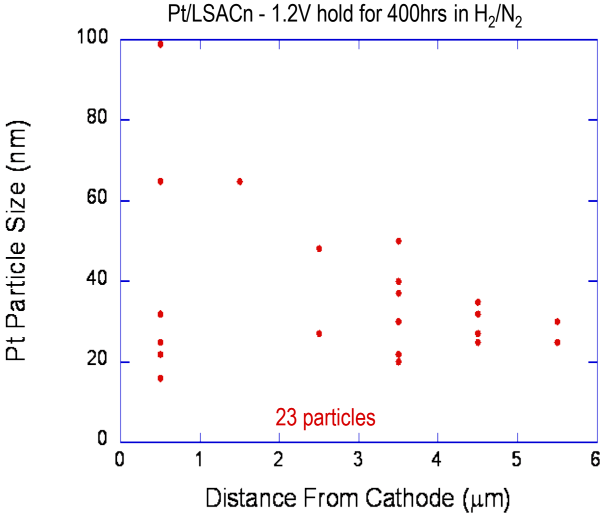
Technical Accomplishment: Quantifying Pt Loss Due to Dissolution and Migration Out of Cathode



Pt/HSAC:
1.2V hold for only 100 hr: Pt loss = 9.5%

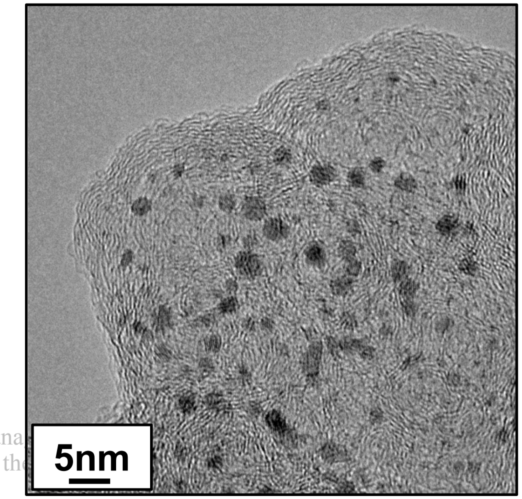


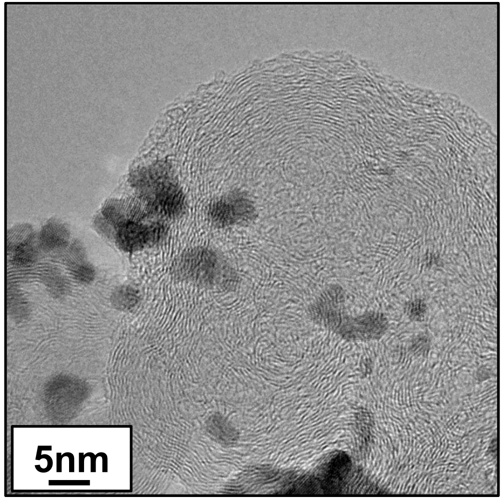
Pt/Vulcan:
1.2V hold for 400 hr: Pt loss = 2.4%

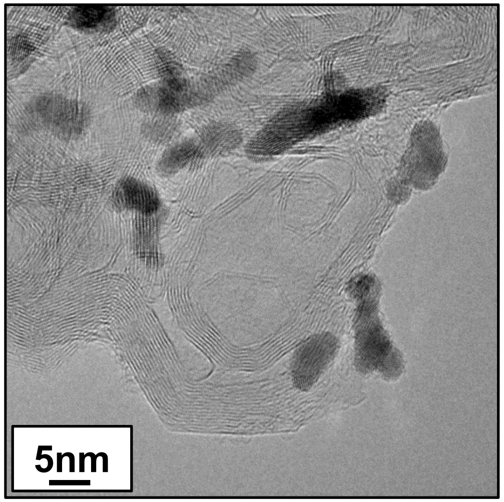


Pt/LSAC (graphitized HSAC):
1.2V hold for 400 hr: Pt loss = 1.3%

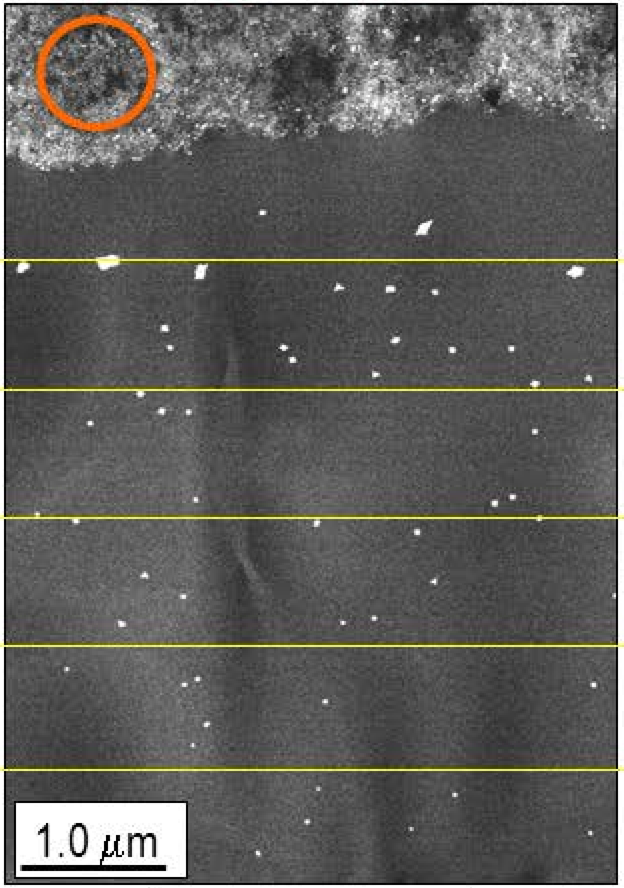
Pt stability during testing can be directly related to the *starting* Pt/C microstructures



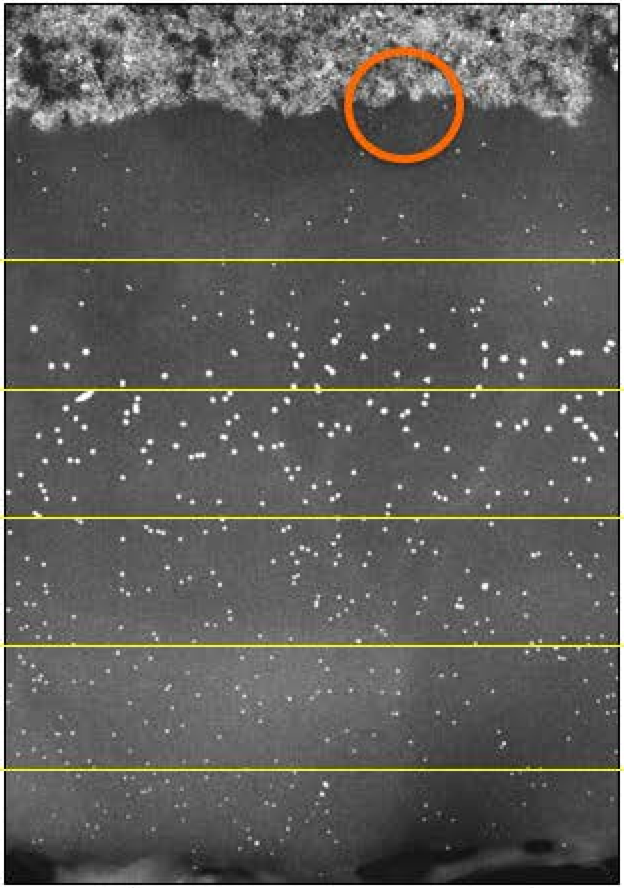




Technical Accomplishment: Quantifying Pt Particle Growth and Pt Loss Due to Dissolution and Migration (ongoing support for Nuvera's SPIRE Project)



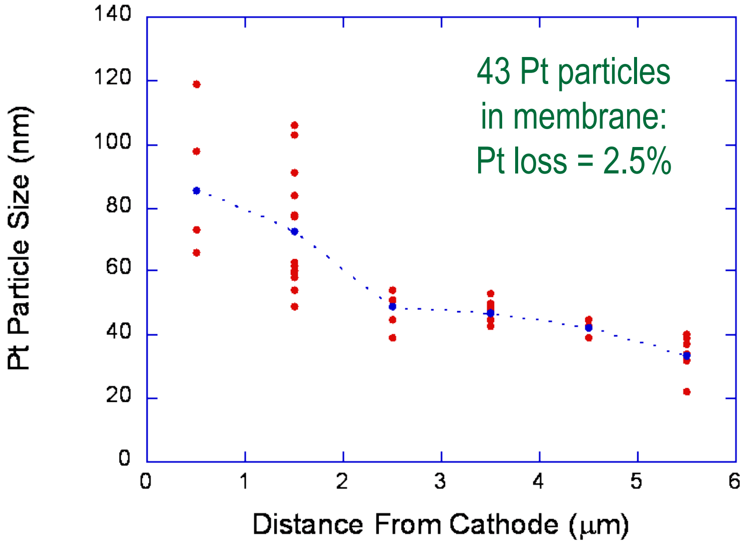
'standard' Pt loading
NST3A – 820 hours
Drive Cycle 0.586-0.886V



'standard' Pt loading
NST1A – 30,000 cycles
Triangle wave cycle
0.025-2.0A/cm^2

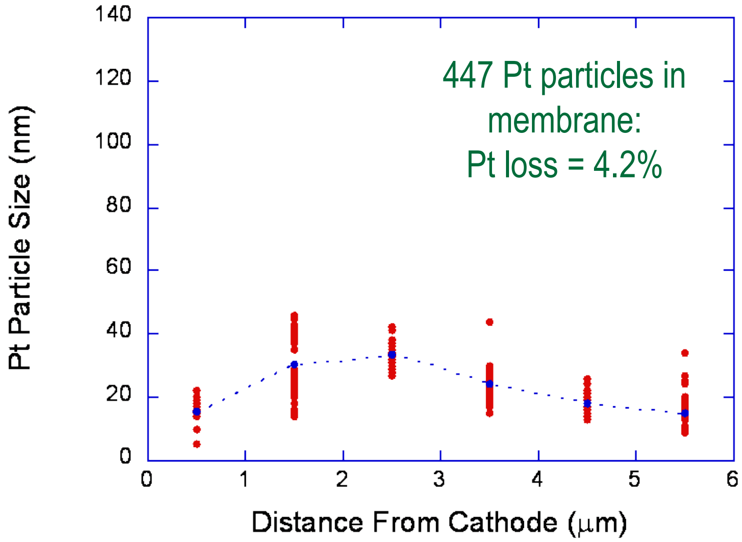
Technical Accomplishment: Quantifying Pt Particle Growth and Pt Loss Due to Dissolution and Migration (ongoing support for Nuvera's SPIRE Project)

Drive cycle covering 0.586-0.886V for 820 hours

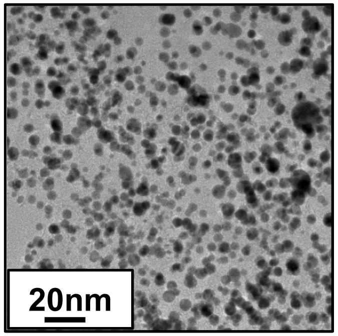


43 Pt particles in membrane: Pt loss = 2.5%

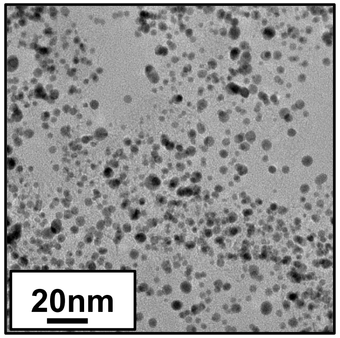
30,000 cycles 0.025-2.0A/cm^2 (triangle wave cycle)



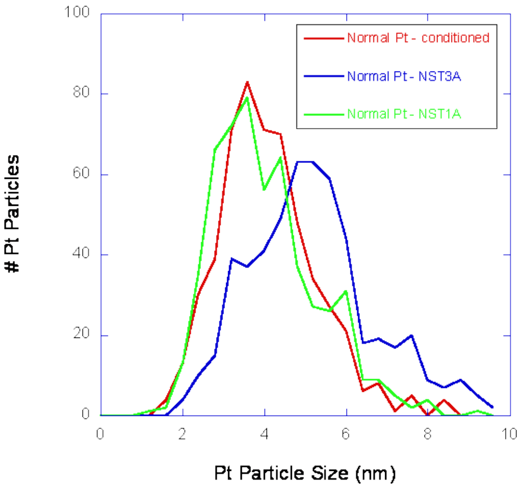
447 Pt particles in membrane: Pt loss = 4.2%



Drive cycle - 820 hr
4.3nm to 5.5nm



Triangle wave 30k cycles
4.3nm to 4.3nm (no change)

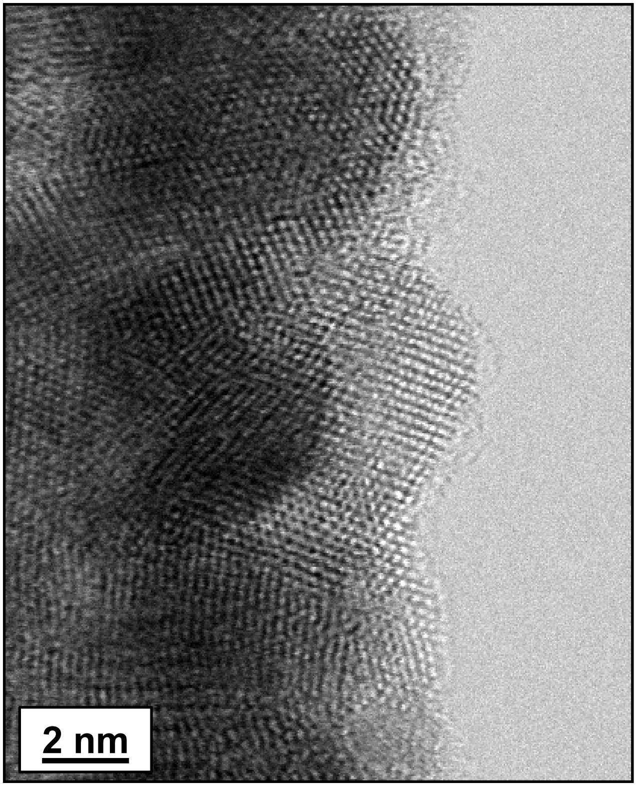


<u>LESS</u> Pt growth in cathode (NST1A)

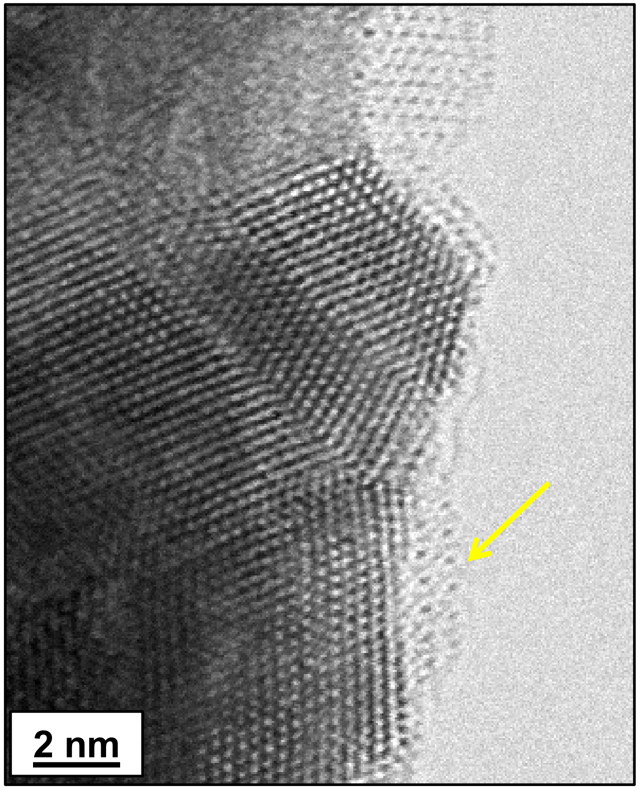
↓ ↓

<u>GREATER</u> Pt migration out of cathode (NST1A)

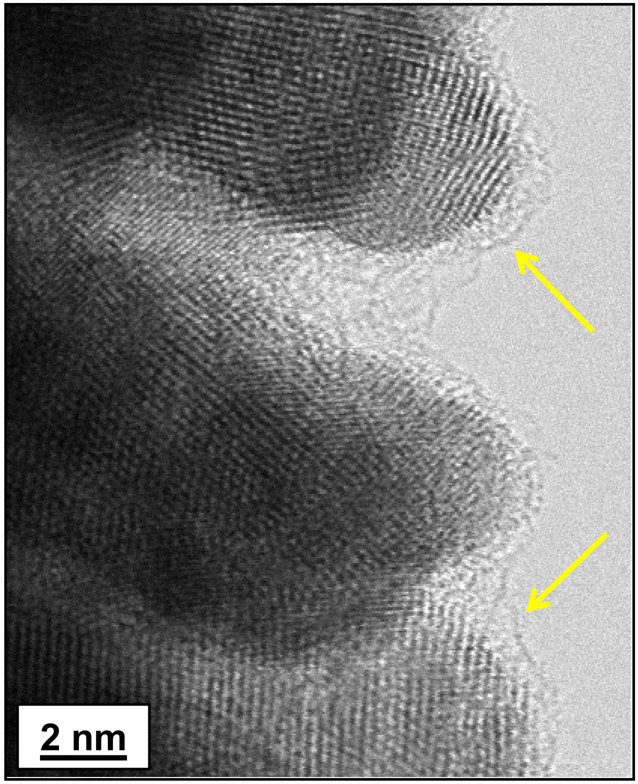
Technical Accomplishment: Characterizing Ionomer Interactions with Catalyst Layer Constituents (current/ongoing collaboration with GM)



No ionomer film



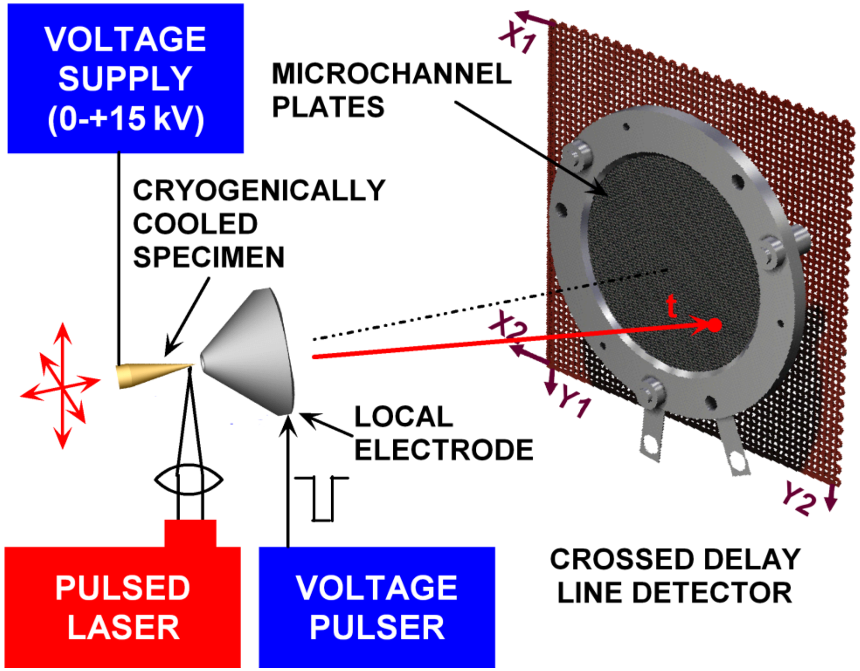
Discontinuous ionomer film



1-2nm continuous ionomer

Goal: "map" ionomer location and elemental distribution within ionomer films using ORNL's low-voltage Nion UltraSTEM/EELS

Technical Accomplishment: Atom Probe Tomography to Characterize NSTF Catalyst Compositions (recently initiated in collaboration with 3M)



VOLTAGE SUPPLY (0-+15 kV)

MICROCHANNEL PLATES

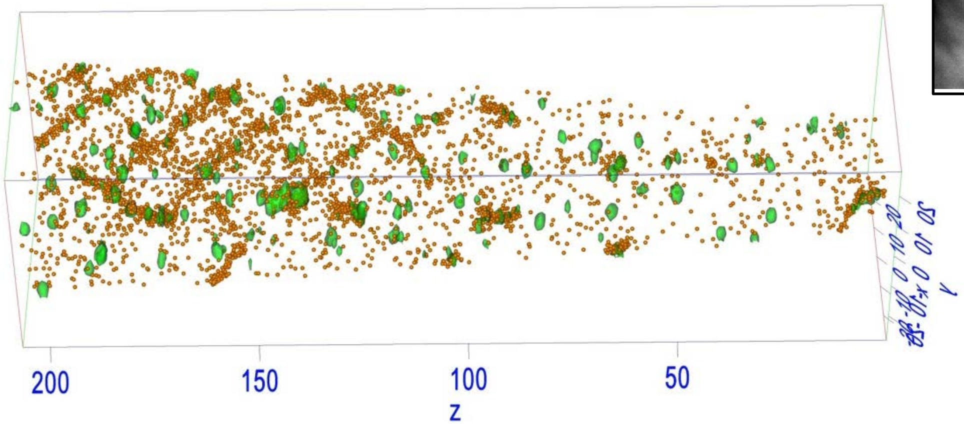
CRYOGENICALLY COOLED SPECIMEN

LOCAL ELECTRODE

PULSED LASER

VOLTAGE PULSER

CROSSED DELAY LINE DETECTOR



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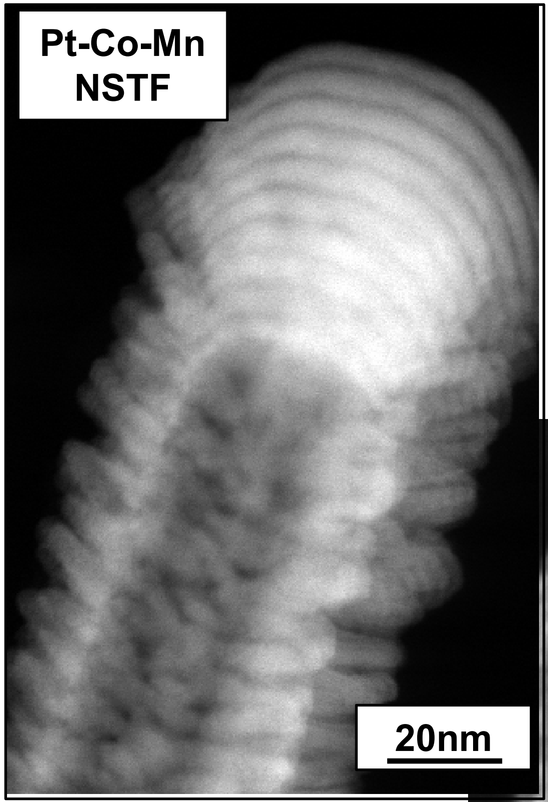
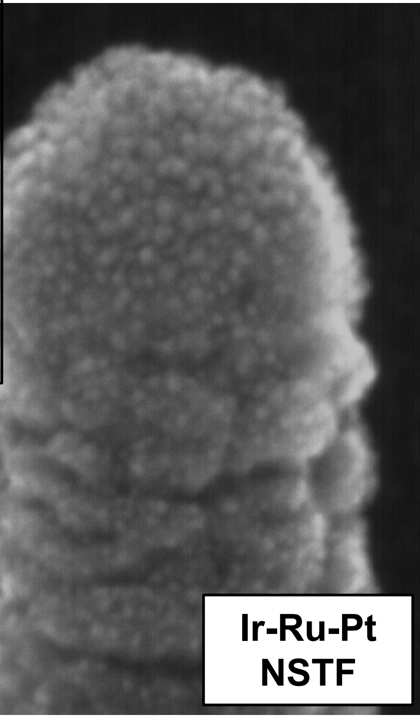


Pt-Co-Mn NSTF

APT can be used to characterize and quantify elemental partitioning, alloying, and clustering of atomic species.

NSTF whiskers may be the ideal shape for APT!



Ir-Ru-Pt NSTF

Established Collaborations On Baseline Project

Collaborations with ORNL are focused on (1) direct collaborations under baseline project to enable further understanding, (2) access via user programs, or (3) focused research under separate DOE projects.

- ***Los Alamos National Laboratory*** **–** durability studies (ASTs); FC materials for portable power applications; ionomer studies; alternative supports
- ***Lawrence Berkeley National Laboratory*** **–** membrane crystallization
- ***GM*** – high-resolution ionomer studies; in-situ liquid STEM catalyst studies; durability-tested MEAs to identify degradation mechanisms
- ***Nuvera Fuel Cells*** – SPIRE project support
- ***NREL –*** characterization of non-carbon catalyst supports
- ***Nissan Technical Center North America*** **–** characterization of TKK catalysts deposited on graphitized supports and durability studies
- ***Naval Research Laboratory*** **–** tantalum oxyphosphate + platinum catalysts
- ***Proton OnSite*** **–** MEAs/catalysts for electrolyzers
- ***Fuel Cell Energy*** **–** characterization of novel membrane structures
- ***UTC Power*** – GDL, support, and catalyst characterization
- ***University of Tennessee*** **–** ionomer studies
- ***Brown University*** – characterization of bi- and tri-metallic catalysts
- **Additional DOE project collaborations with LANL, ANL, NREL, 3M, and UTC Power. Results from these studies are NOT included in this project summary**

Proposed Future Work

- Correlate microstructural/compositional observations with AST protocols (automotive and stationary), especially related to catalyst coarsening & migration, carbon corrosion, membrane degradation – this is a continuing priority of this research program and has been part of ongoing and proposed “future” research each year.

- Steps have been taken to “re-establish” the development of in-situ liquid TEM/STEM as a priority for ORNL’s baseline project – this has already emerged as a future work topic because of community-wide interest and the fact that we have successfully demonstrated such capabilities for battery research.

- Expand on ionomer studies with GM to include interactions with carbons(s) using the low-voltage imaging/EELS capabilities of ORNL’s UltraSTEM® microscope.

- Continue to establish collaborations with industries, universities, and national laboratories (including access via ORNL User Facilities) to facilitate “transfer” of unique capabilities. This will include supporting new DOE projects with microstructural characterization and developing/applying advanced characterization techniques.

Project Summary

Relevance: ORNL's microscopy expertise and unique capabilities are integral to identifying materials degradation mechanisms, which are critical for developing mitigation strategies thereby enhancing stability and performance

Approach: Our approach is "unique" in that it is fully collaborative in nature and benefits the entire FC community – applying advanced microscopy methods to solve relevant FC problems is the primary goal of this project

Technical Accomplishments and Progress: We continue to listen to our partners and address important issues – during the past year we have focused on quantifying Pt migration, characterizing ionomer thin films, and implementing new techniques to characterize materials of interest. We continue to support the FC community with unique capabilities for microscopy evaluation of FC materials.

Collaborations: ORNL continues to establish new collaborations to provide access to unique imaging/analysis (microscopy) capabilities or to access lab (and expertise) for training.

Proposed Future Research: Our goal in the coming year will be to further establish ORNL's role as a leader in in-situ microscopy to characterize fuel cell materials, to further develop tomography (atom probe and electron techniques for 3D visualization), and to provide new insight regarding ionomer interactions with catalysts-supports.