Microstructural Characterization Of PEM Fuel Cell MEAs

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This presentation does not contain any proprietary or confidential information

Project ID# FC27

Program Overview

Timeline

- Initiated in FY2000
- *Goal:* Project provides for fundamental research and industrial support for MEA durability studies

Budget

- ~$200k each FY through FY04
- ~$300k base funding in FY05 and FY06
- Additional $75k for Arkema membrane characterization
- Scheduled through FY07

Barriers

- A. Durability - 5000h for transportation application
- B. Cost - ≤$15/kW
- C. Electrode Performance
- D. Thermal, Air, and Water Management

Primary Interactions

- Los Alamos National Lab
- Argonne National Lab
- Gore Fuel Cell Technologies
- PlugPower
- FuelCell Energy
- Arkema Inc.

ORNL Research Objectives

- ***Technique Development*** to structurally and chemically characterize the different MEA components and correlate microstructure with performance
- ***Collaborate on fundamental durability studies*** to elucidate MEA degradation mechanisms using post-mortem evaluation:
  - Have been limited since lengthy testing times are required
  - Interacting degradation mechanisms involving multiple MEA/GDL/MPL components
  - Inability to perform in-situ or non-destructive evaluation of individual MEA components during testing
  - primary issue with regard to successful commercial implementation of FCs

→ ***reduce system cost per hour of life by improving the stability/durability of individual MEA components***

Approach: Use Advanced TEM And SEM Characterization Techniques To Evaluate Relevant nm-Scale MEA Changes

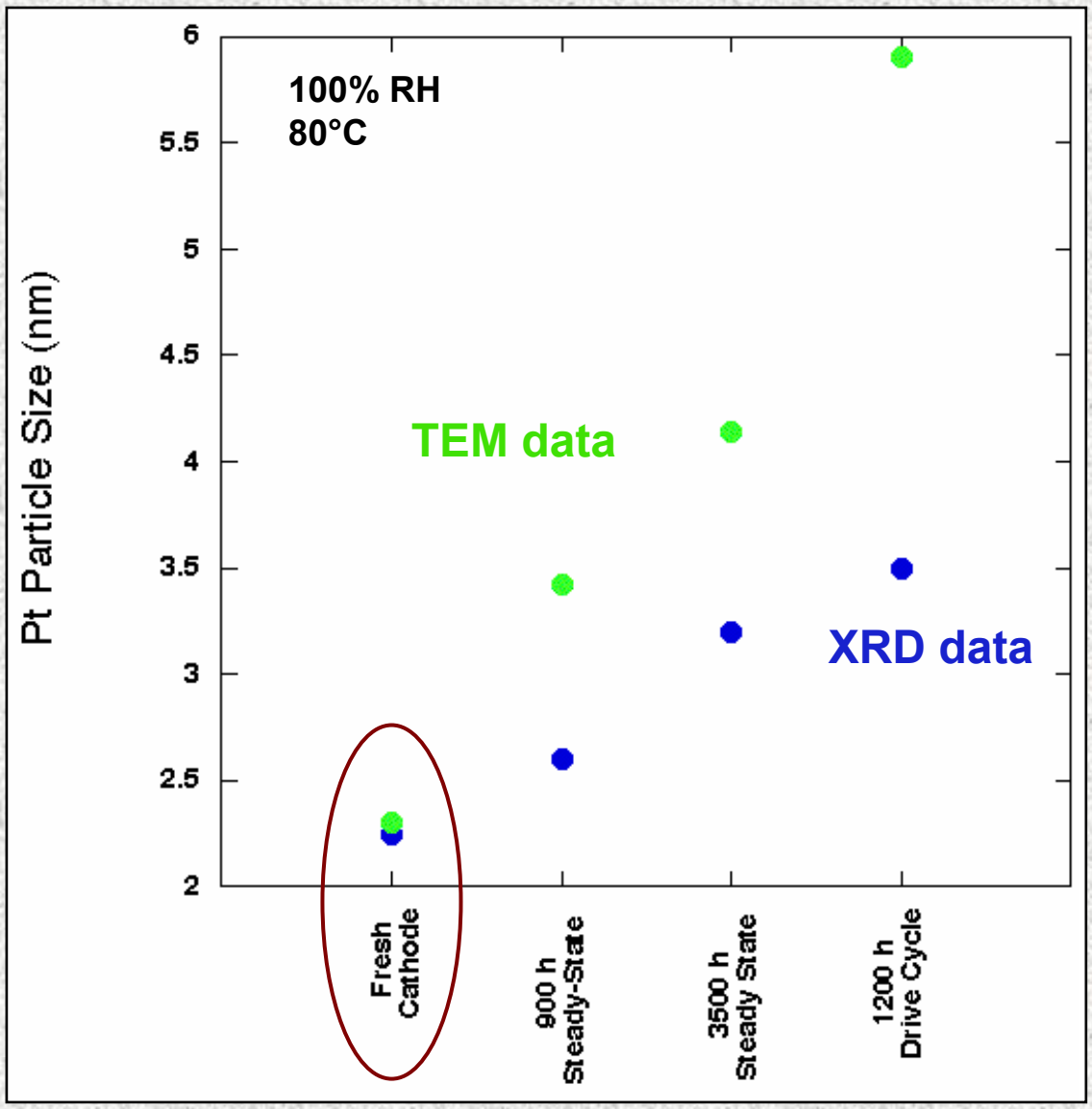
- Develop the appropriate SEM and TEM *sample preparation* methodologies for evaluating the constituents comprising layered MEAs
  - recast ionomer within porous catalyst layer
  - polymer membrane
  - carbon support
  - electrocatalyst
- Apply these techniques to fully evaluate changes to individual MEA constituents as a result of *electrochemical aging* and elucidate degradation and failure mechanisms contributing to performance loss via high-resolution imaging and microchemical analyses

→ **design materials with improved durability**

Technical Accomplishments And Progress
ORNL/LANL Collaboration

- *Effect of potential cycling, temperature, and %RH on cathode Pt catalyst and N112 membrane durability:*
  - *5 cm² MEAs cycled 10mV/sec @ 60°C, 80°C, 120°C and 50% RH and 100% RH*
    - *0.1-0.96 V, 1500 cycles*
    - *0.1-1.2 V, 1500 cycles*
    - *1200 h, 2000 h, 2350 h drive cycle*
  - *Steady-state operation 0.6 V for 900 h and 3500 h*
  - *Correlate X-ray scattering data with TEM data*
- *MEA structural/compositional changes during electrochemical aging*
- Stability of alternative bi- and tri-metallic catalysts (not limited to LANL collaboration)

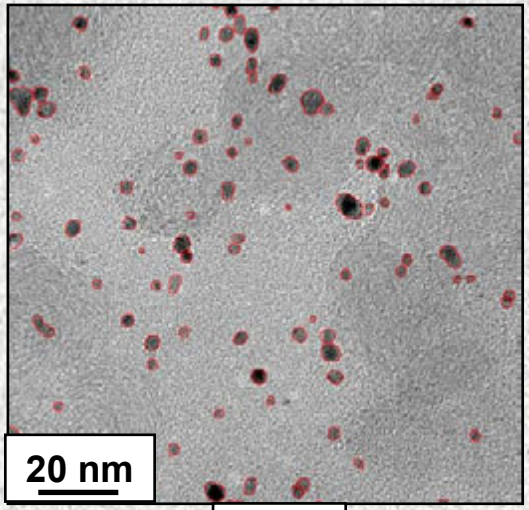
Growth Of Pt Particles Determined By X-Ray Diffraction (LANL) and TEM (ORNL)



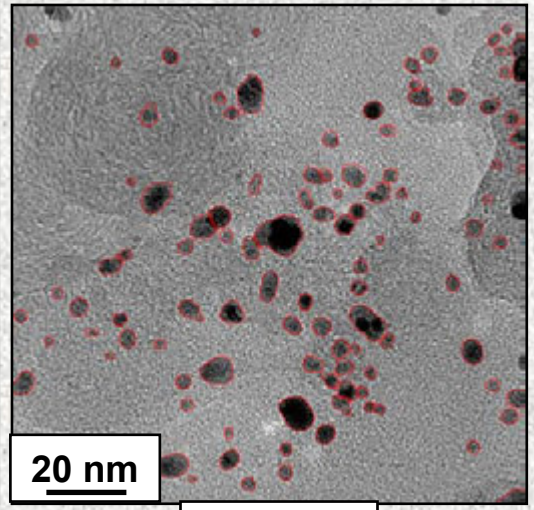
Cathode Pt particles

Discrepancy between Pt size data measured using XRD and TEM techniques

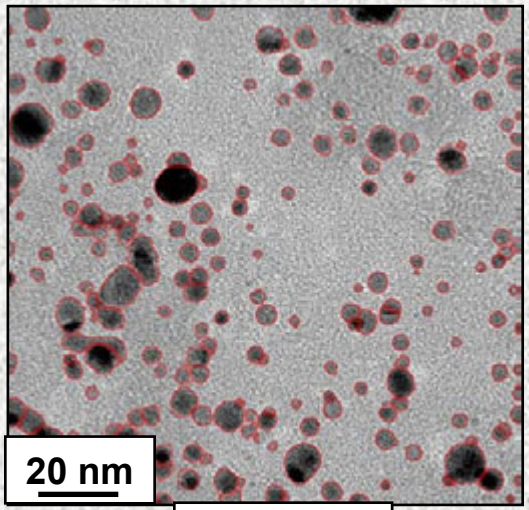
Cathode Pt Particle Size Distributions Are Measured From TEM Images Of Intact MEA



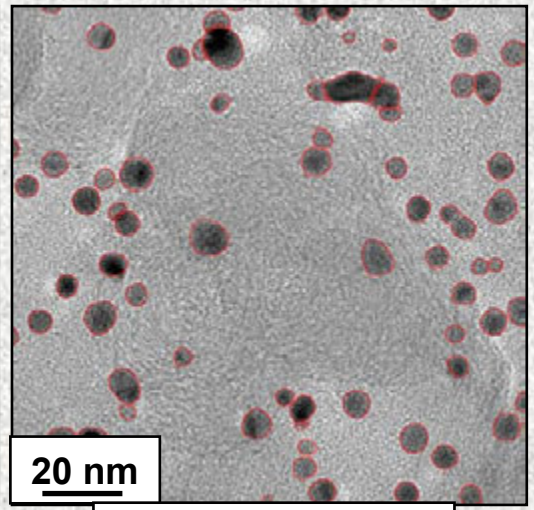
fresh



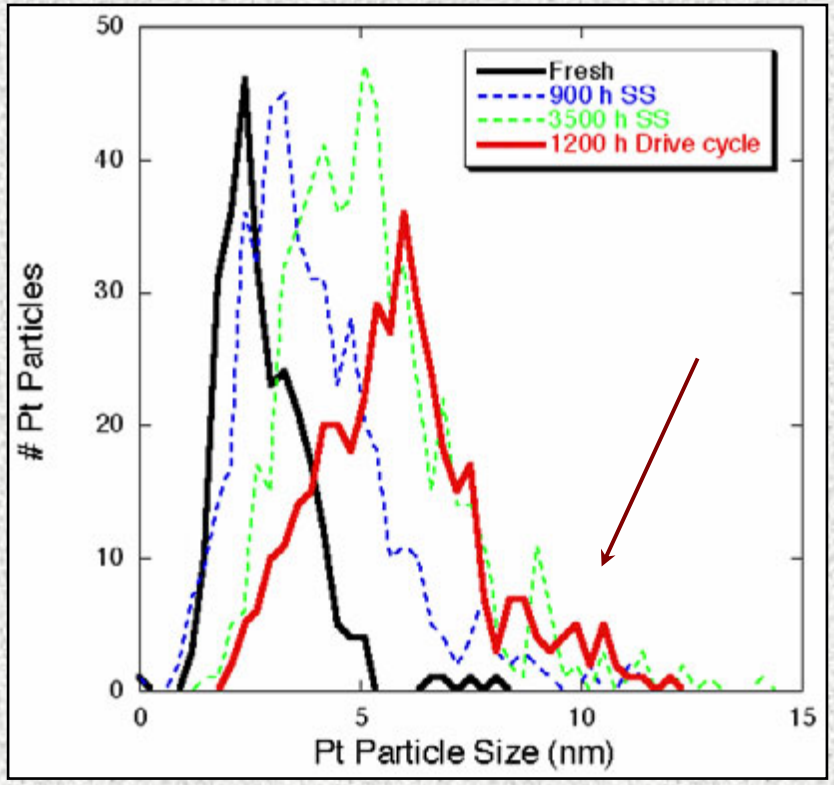
900 h SS



3500 h SS

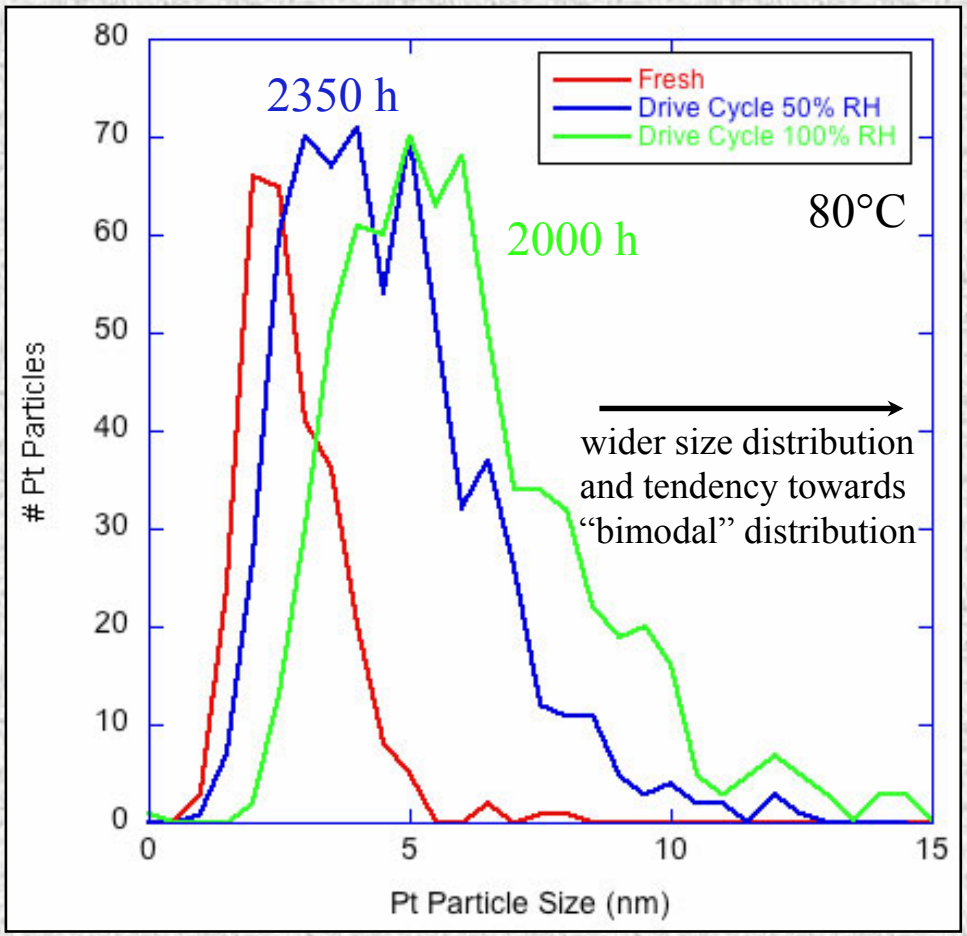


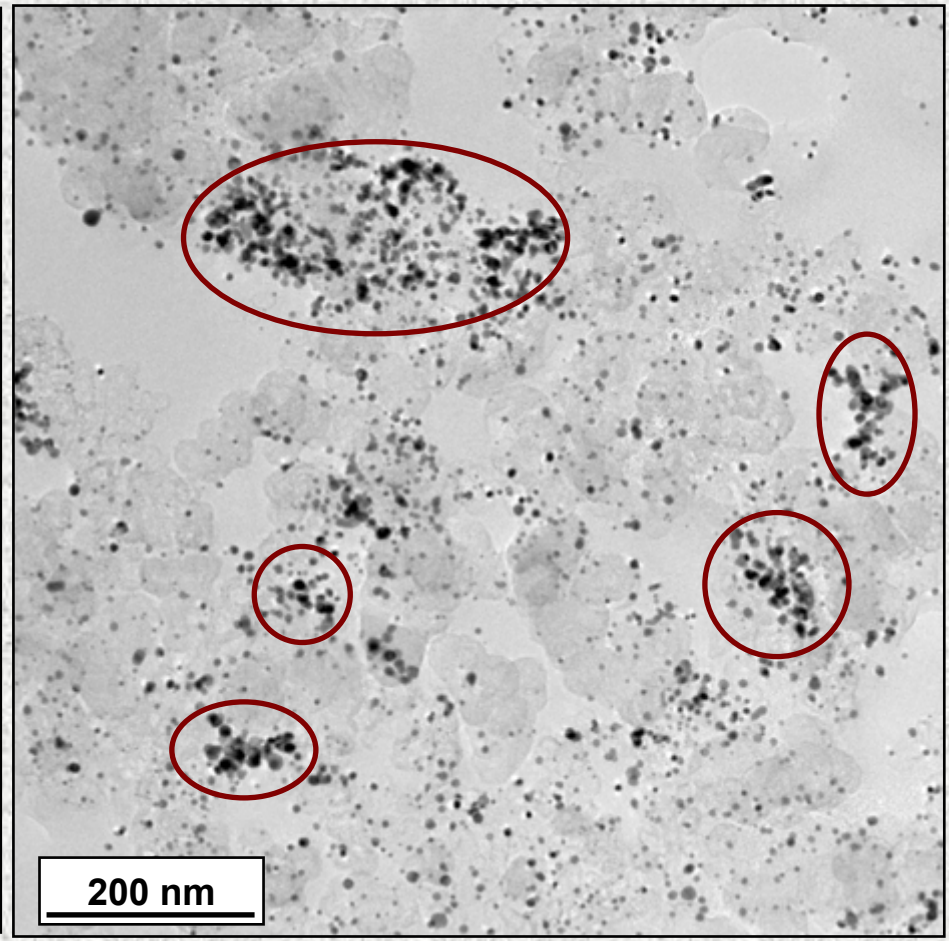
1200 h drive cycle



TEM data clearly shows how Pt size DISTRIBUTION changes

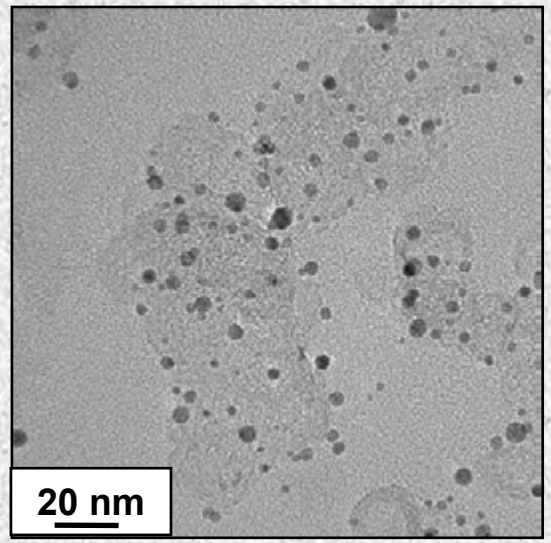
Pt Particle Size/Distributions Changed As A Function Of US06 Drive Cycle - % RH

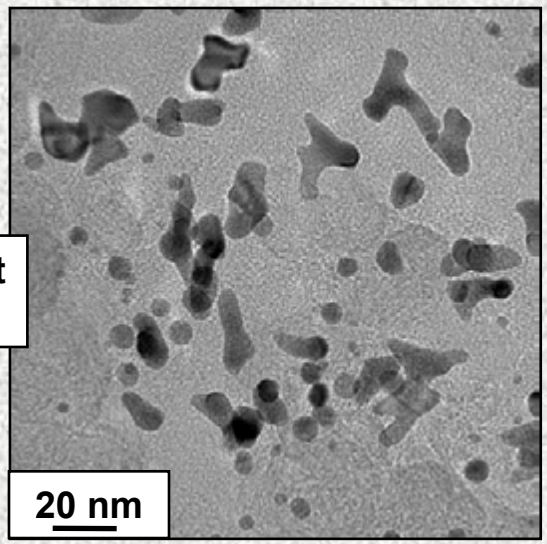




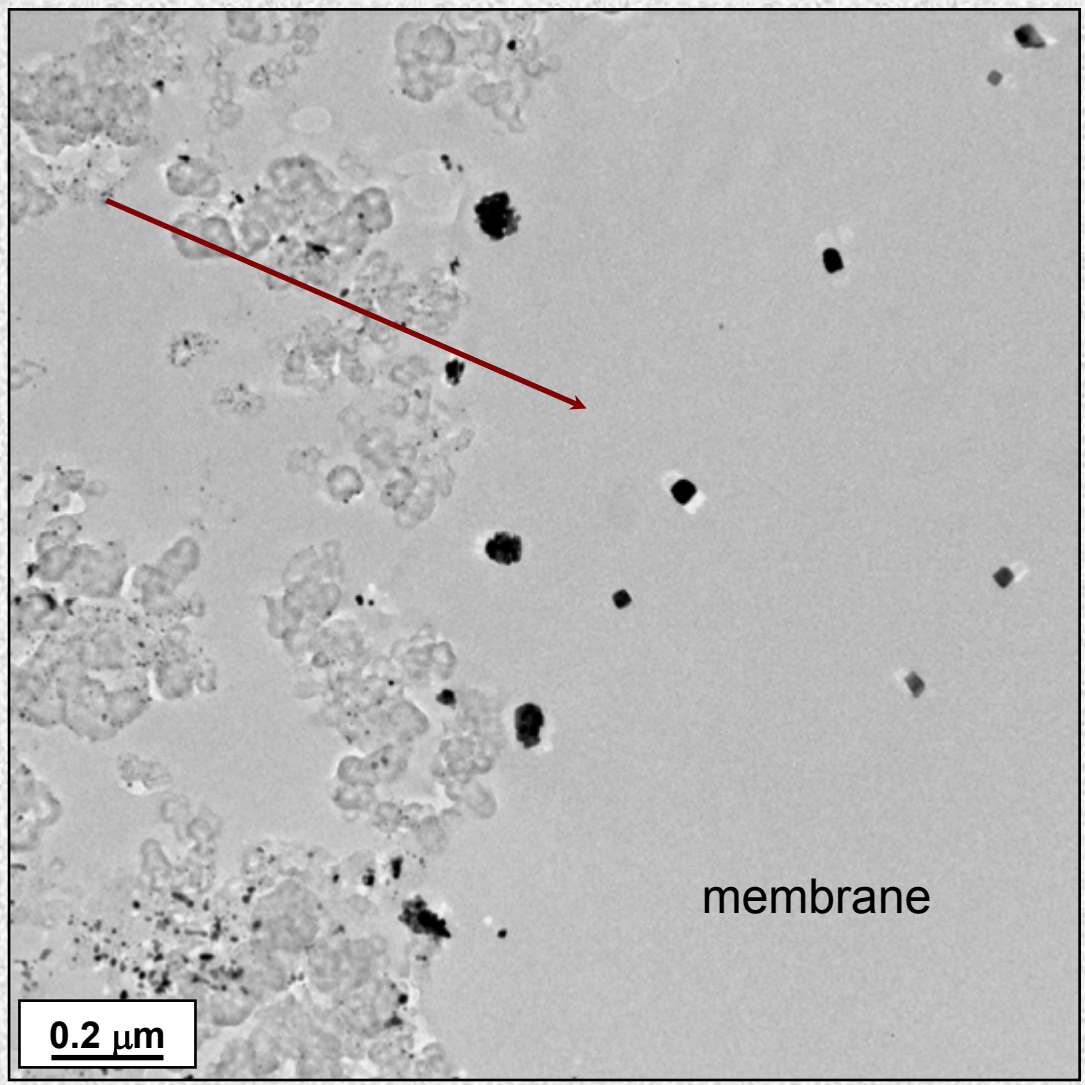
Larger Pt particles are clustered together in localized regions of cathode

If MEA Is Cycled 0.1-1.2V (1500h/50% RH), Pt Migrates To Cathode/Membrane Interface And Well Into Membrane

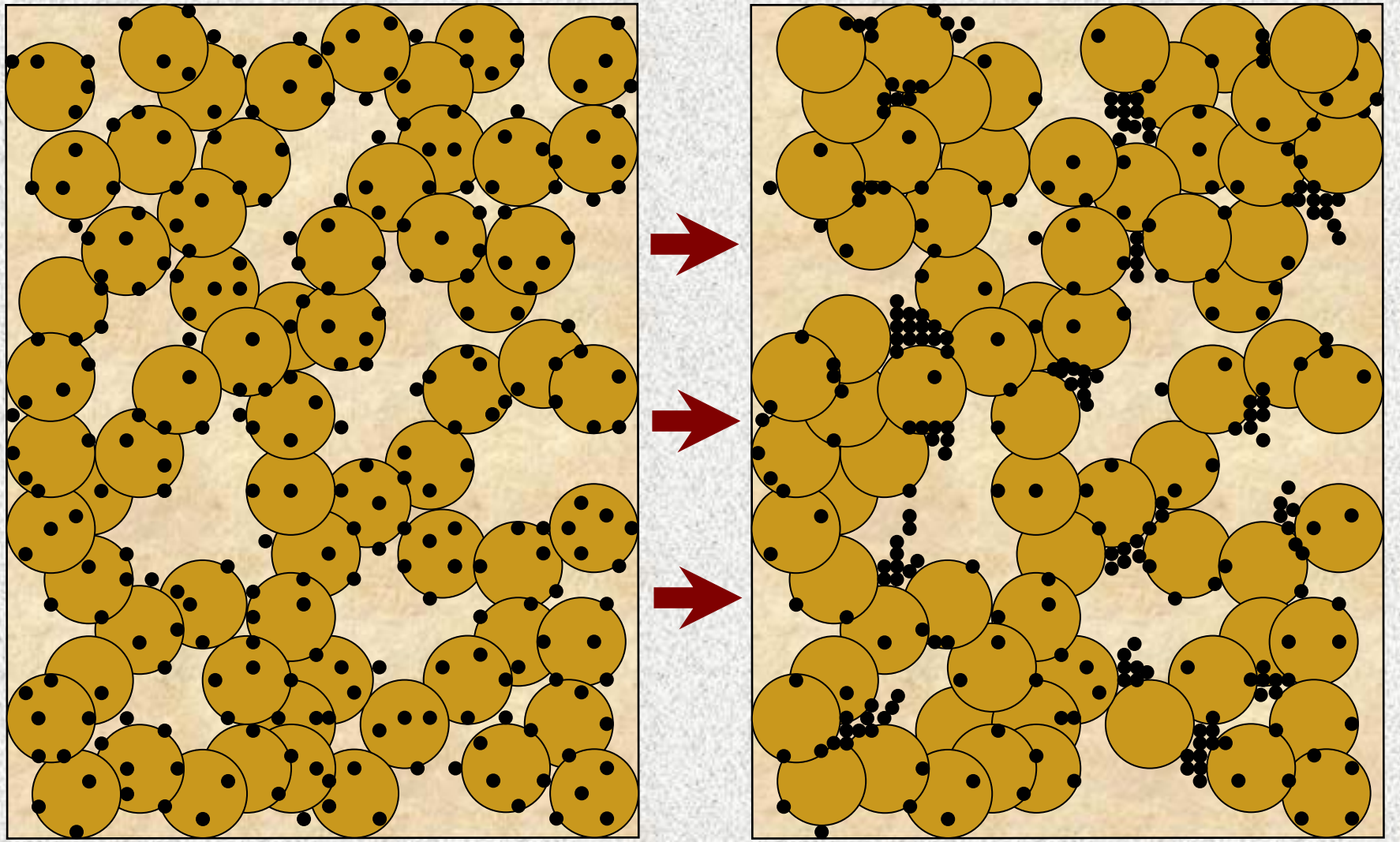




localized Pt coarsening



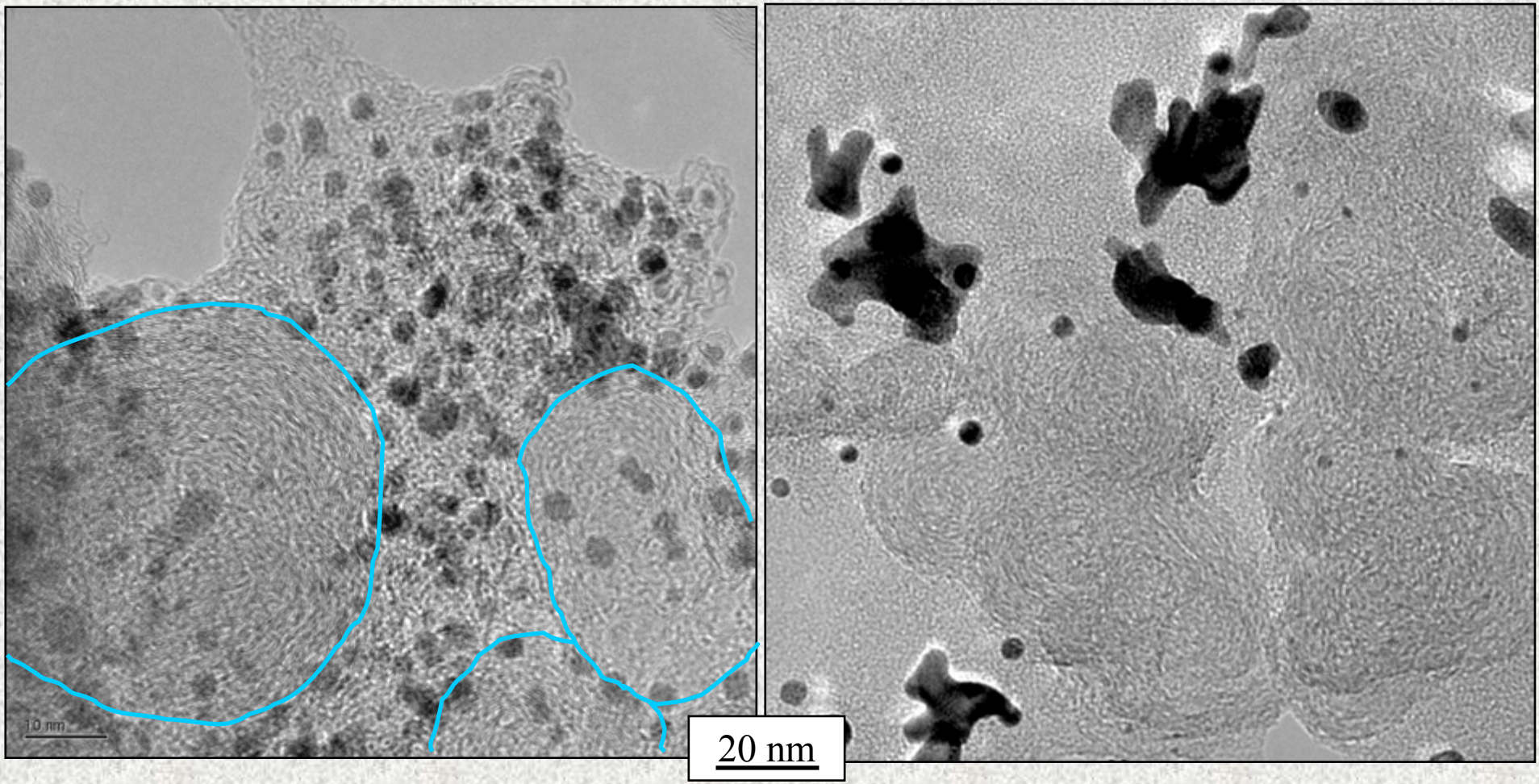
Schematic Comparing Homogenous Vs. "Real" Electrode Constituent Distribution



Prior To Mixing Pt/C With Ionomer

After Mixing Pt/C With Ionomer

Increased Pt Coarsening Associated With Higher-Density Of Pt Concentrated Within Ionomer "Pockets"



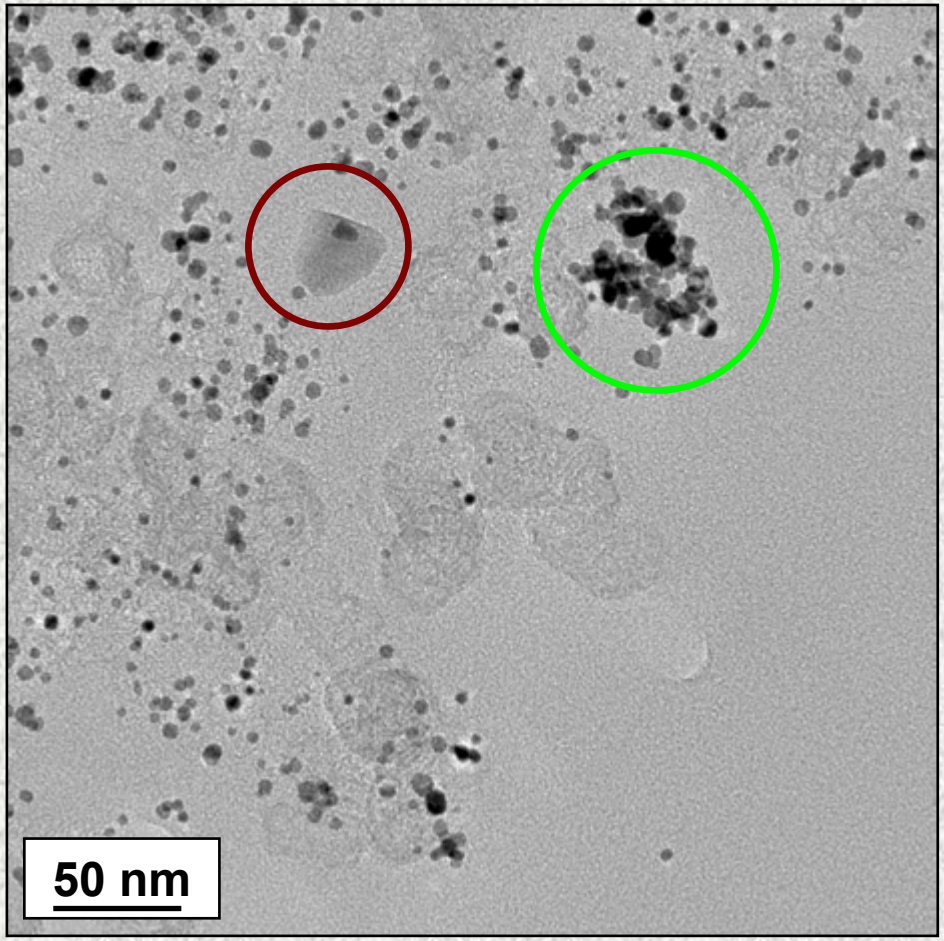
Fresh cathode Pt catalyst particles

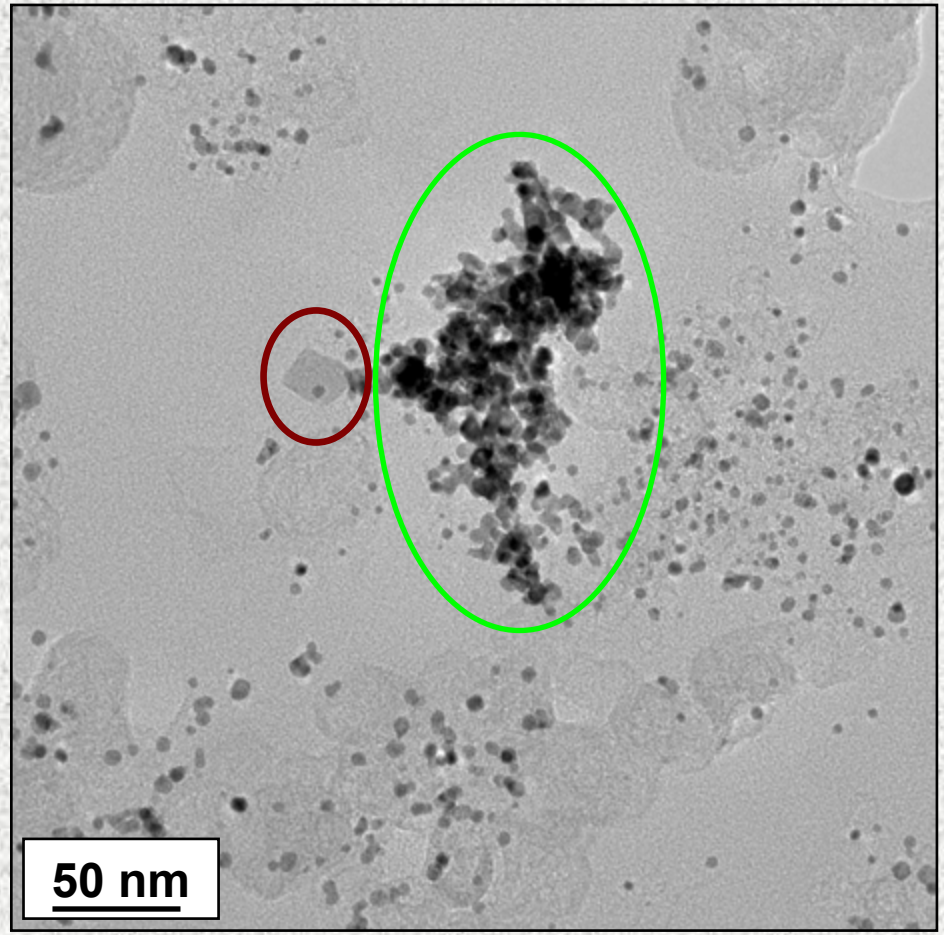
Pt particles after 100% RH, 80°C, 1500 cycles 0.1-1.2 V

Technical Accomplishments And Progress
ORNL/LANL Collaboration

- Effect of potential cycling, temperature, and %RH on cathode Pt catalyst and N112 membrane durability:
  - 5 cm^2 MEAs cycled 10mV/sec @ 60°C, 80°C, 120°C and 50% RH and 100% RH
    - 0.1-0.96 V, 1500 cycles
    - 0.1-1.2 V, 1500 cycles
    - 1200 h, 2000 h, 2350 h drive cycle
  - Steady-state operation 0.6 V for 900 h and 3500 h
  - Correlate X-ray scattering data with TEM data
- *MEA constituent structural/compositional changes during electrochemical aging*
- *Stability of alternative bi- and tri-metallic catalysts (not limited to LANL collaboration)*

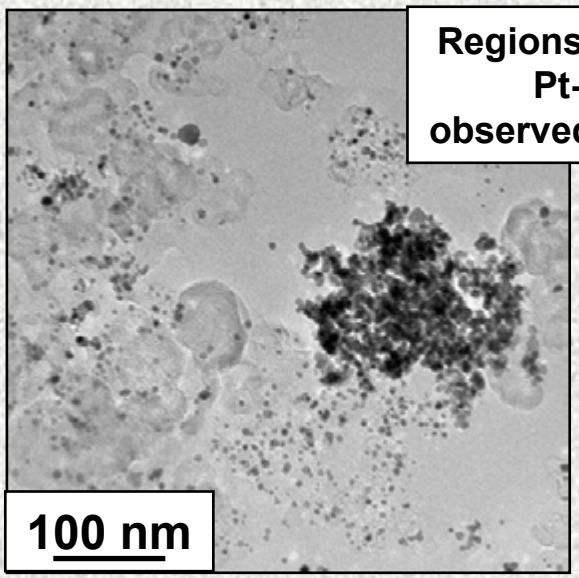
Commercial Pt_3Cr Cathode Electrocatalysts Have Been Used In LANL MEAs



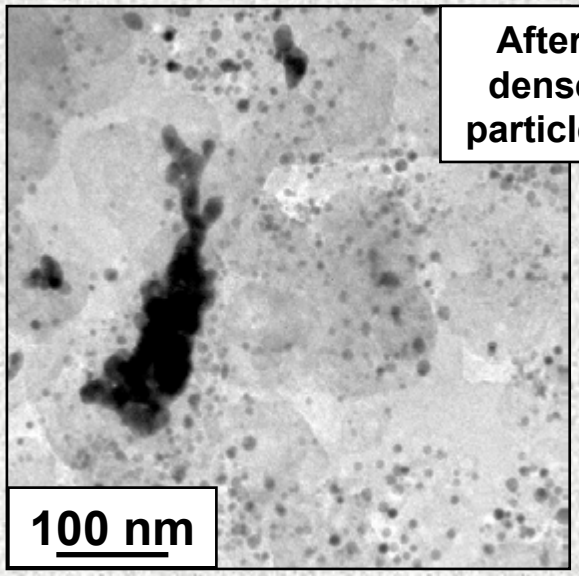


The individual Pt-Cr particle size distribution was fairly uniform (~4-5 nm), but extensive *particle agglomeration* was observed.
Residual, large *Cr_2O_3 particles* remained from catalyst processing.
Particle composition closer to $Pt_{10}Cr$ than Pt_3Cr.

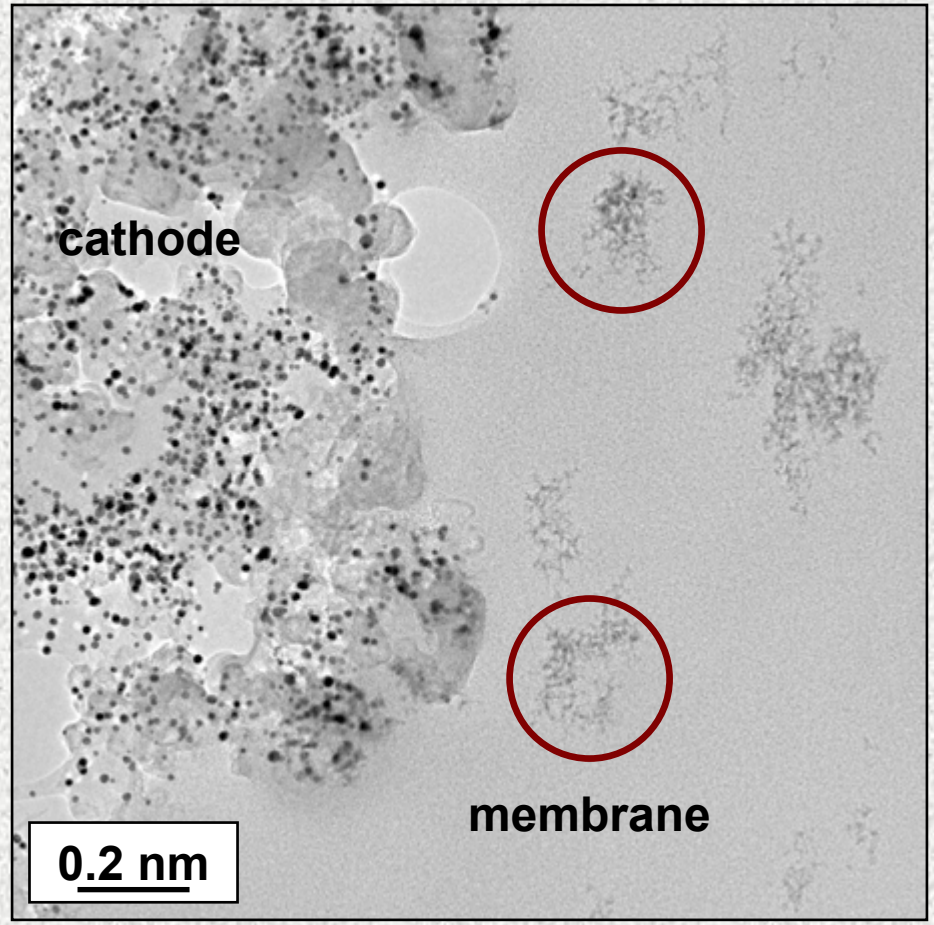
Inhomogeneously Dispersed Pt-Cr Particles Characterized By Instabilities During Aging



Regions of agglomerated Pt-Cr particles observed in fresh cathode

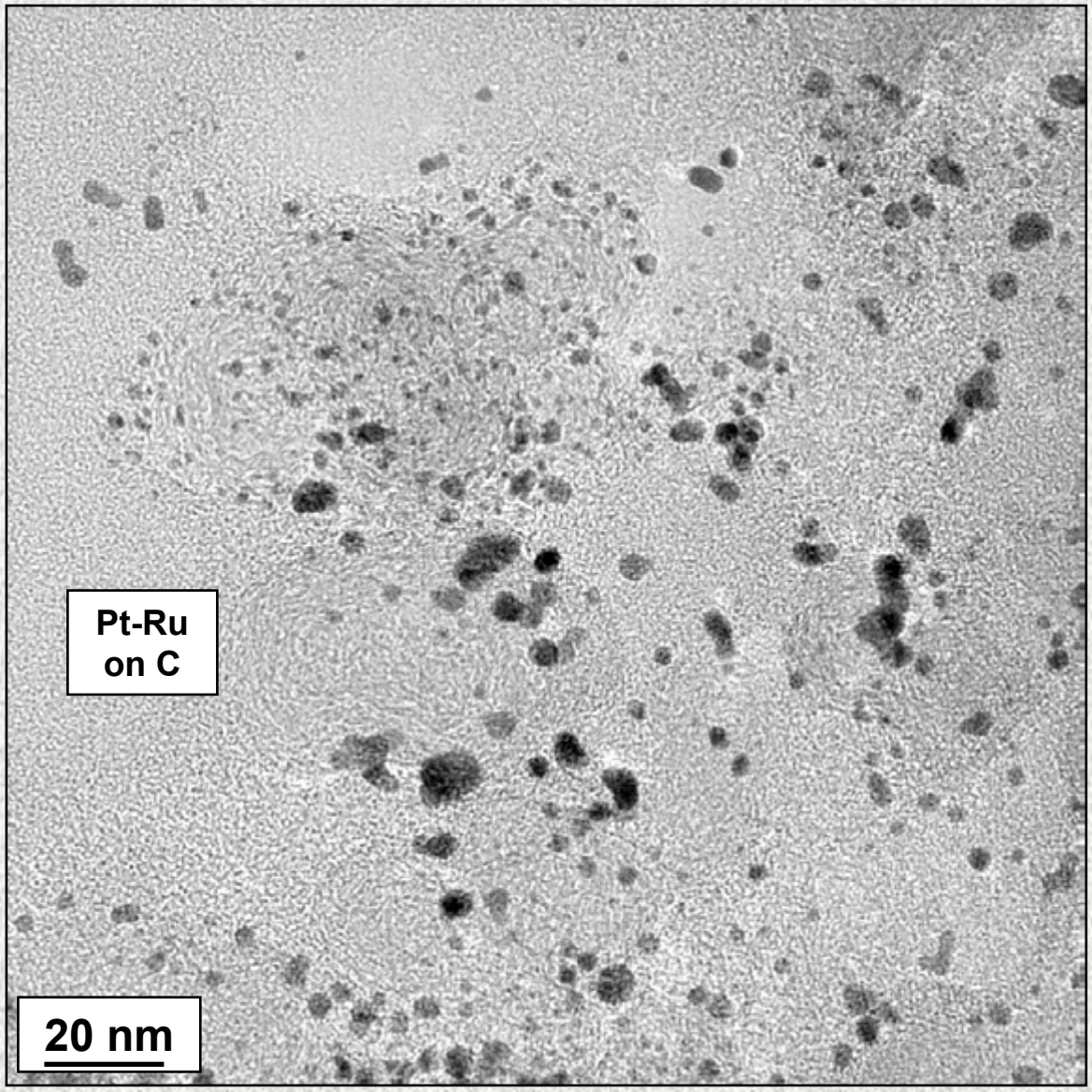


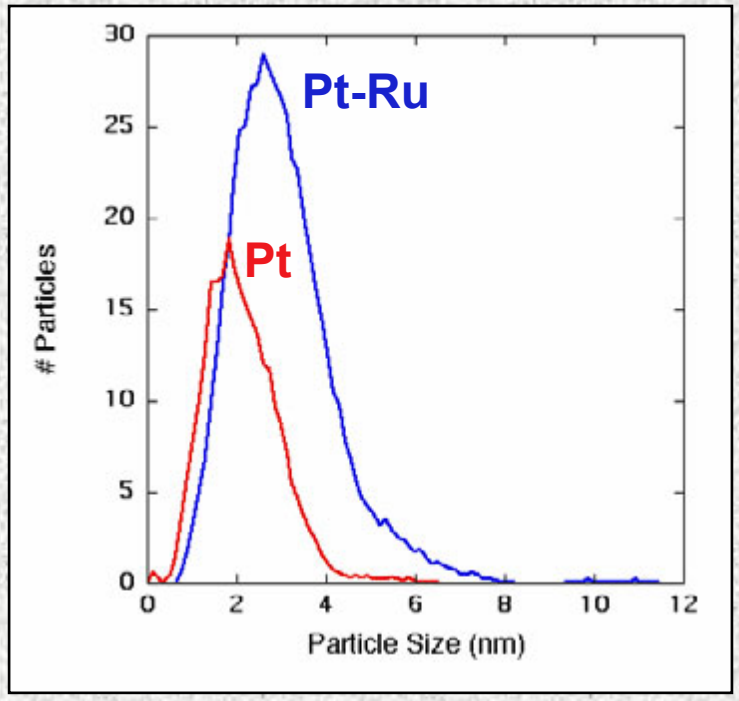
After aging for 500h, densely packed Pt-Cr particles sinter together



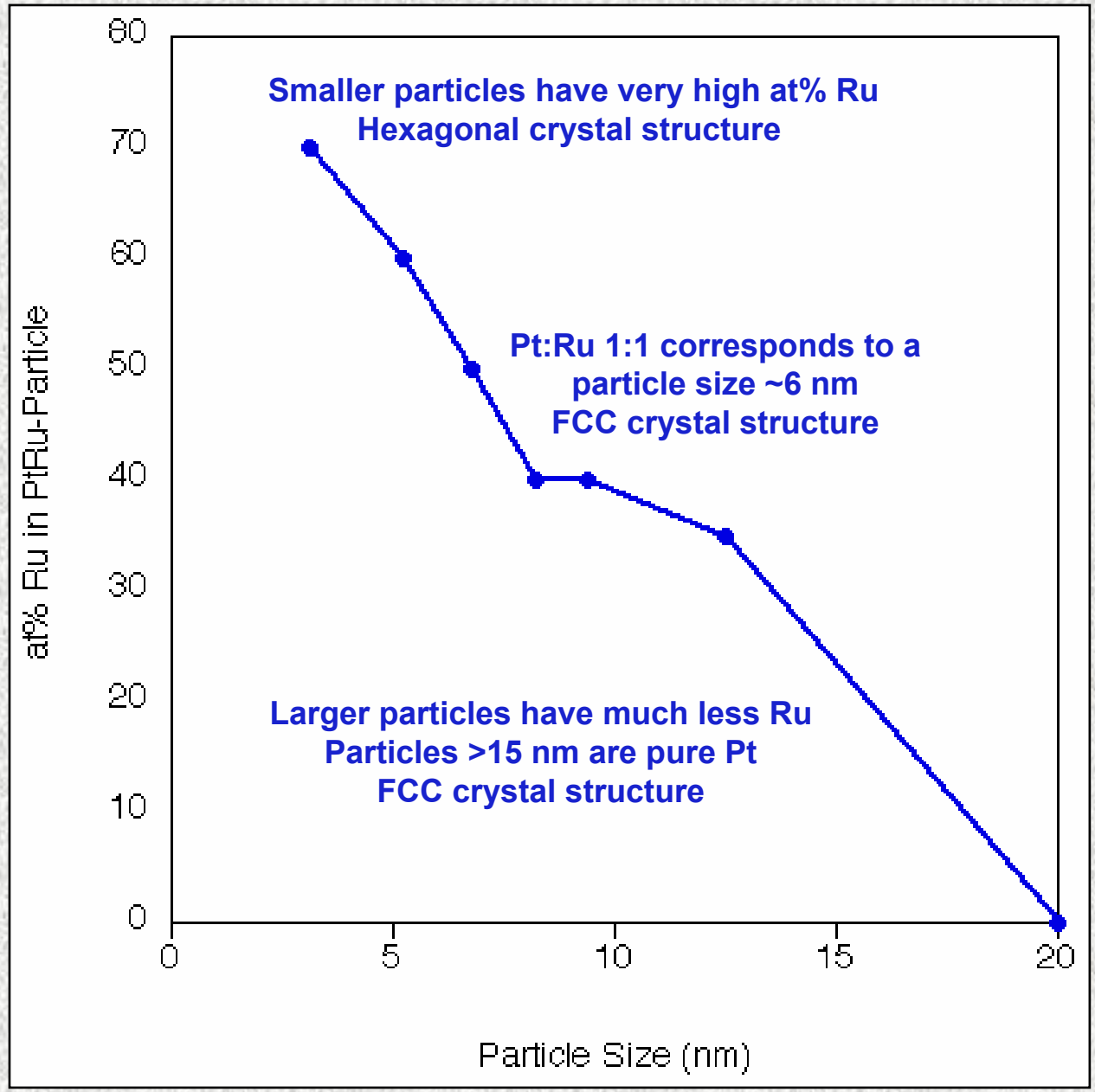
Dissolution of Cr_2O_3 particles in cathode and migration and re-precipitation of smaller Cr_2O_3 particles in membrane observed after aging for 500 h.

Typically, PtRu Anode Catalysts Have A Wide Size Distribution Compared With Pt

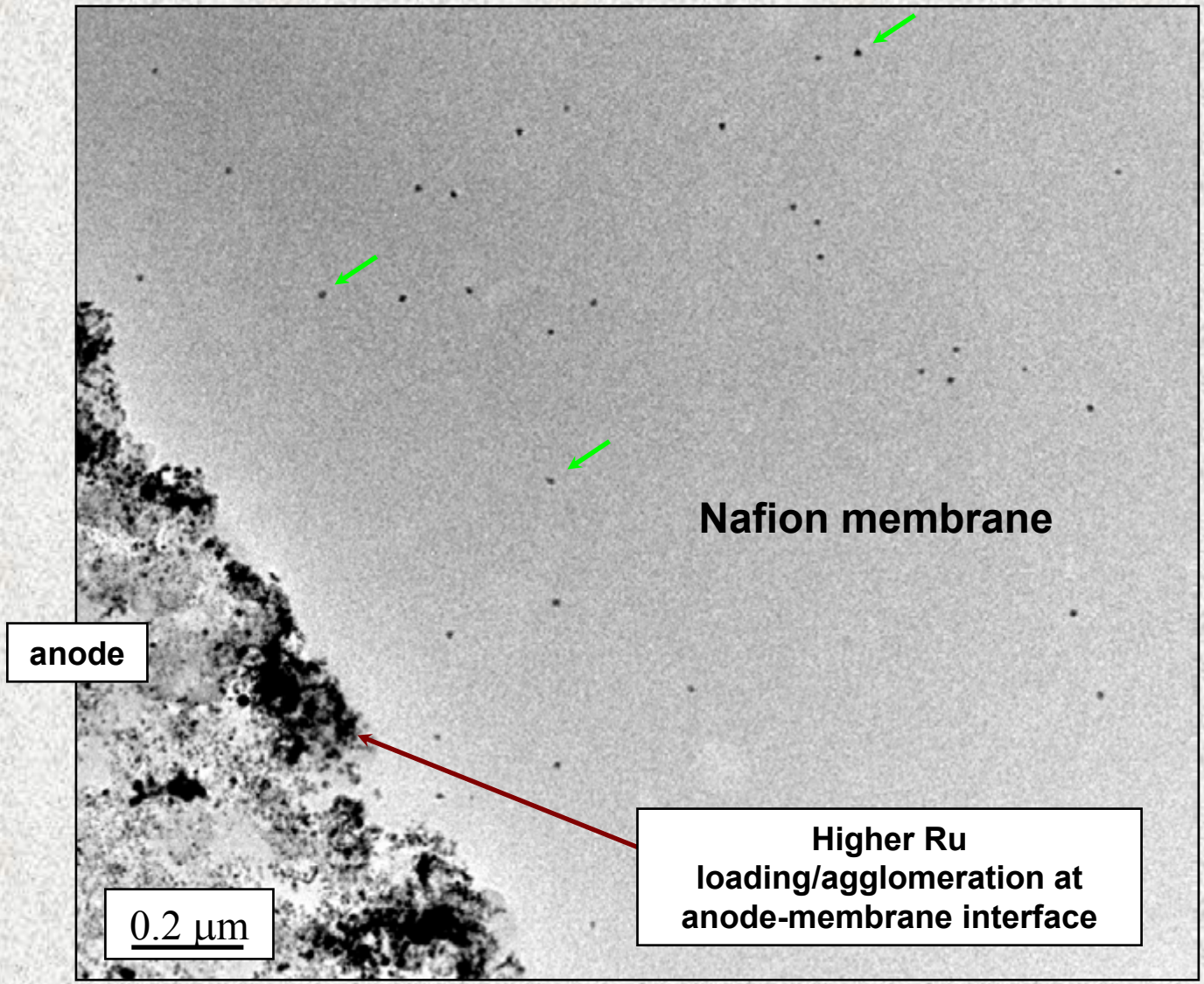




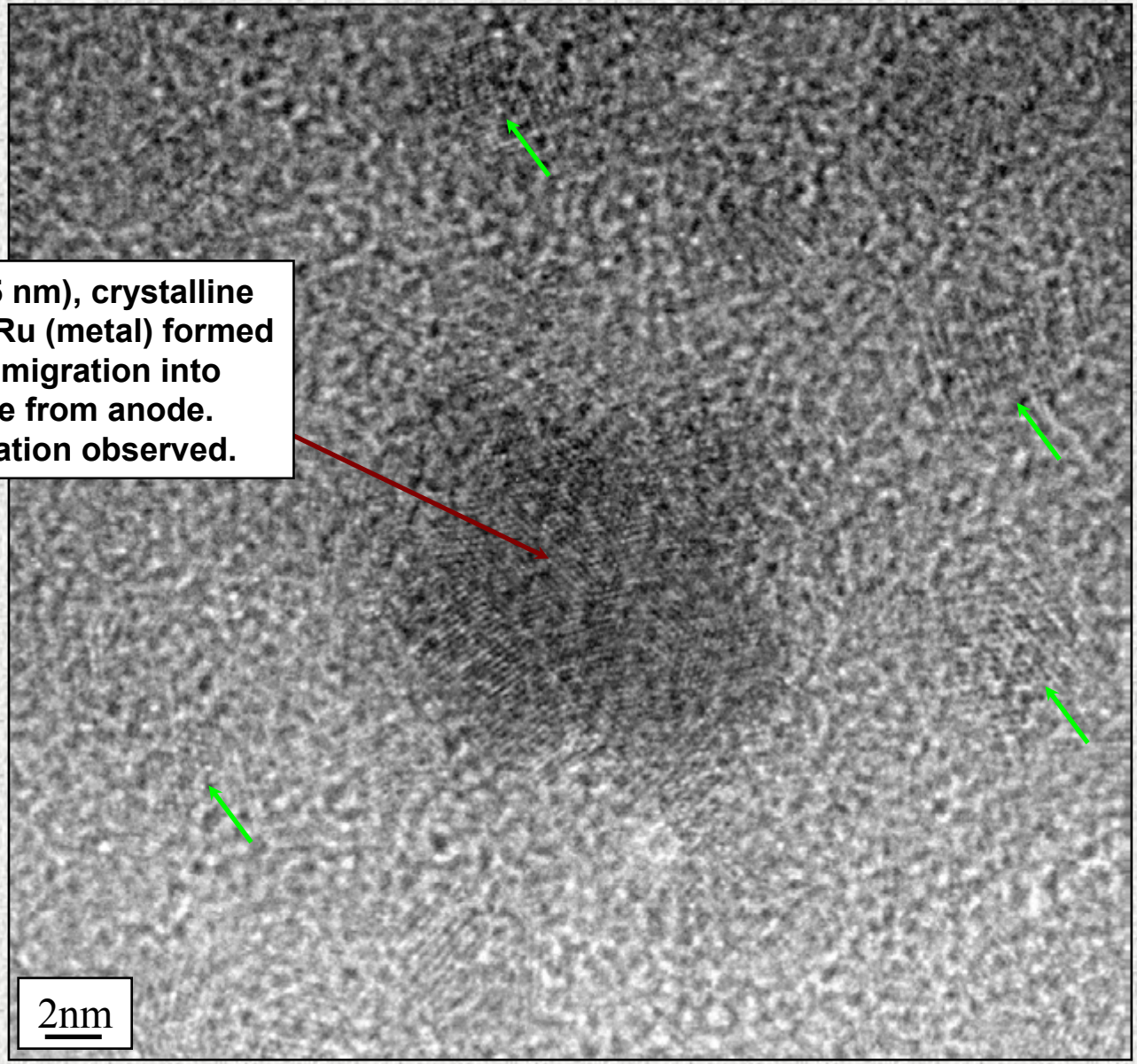
Pt:Ru Changes With Particle Size



Following Long-Term Stack Testing, Ru-Containing Particles Were Identified Within Nafion Membrane Close To Anode



Particles Within Membrane Were Identified as Pure Hexagonal Ru Clusters

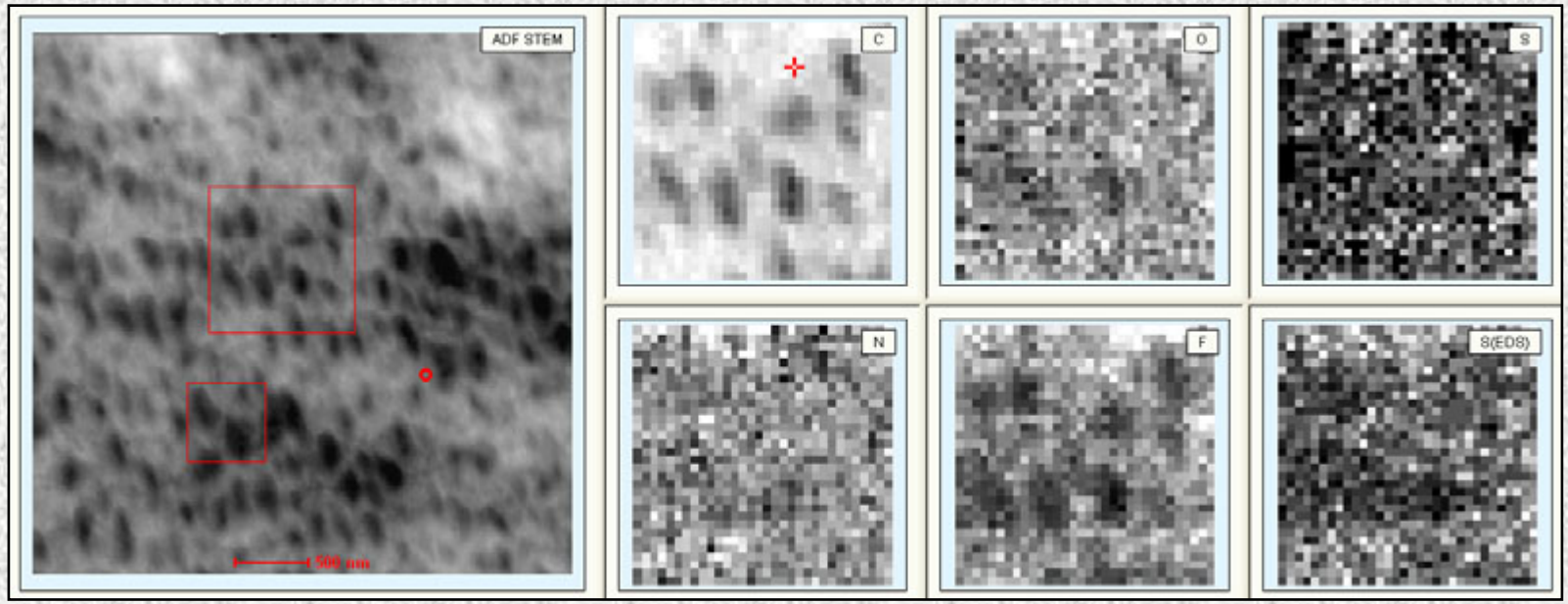


Large (12-15 nm), crystalline particles are Ru (metal) formed by Ru ion migration into membrane from anode.
No Pt migration observed.

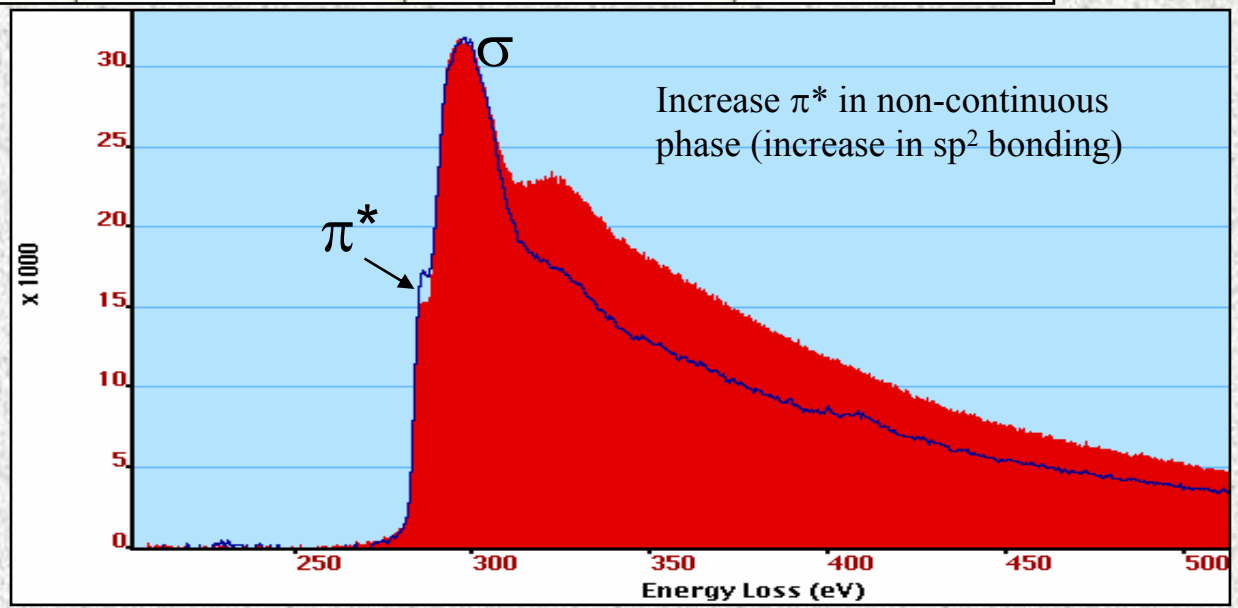
Technical Accomplishments And Progress
ORNL/Arkema Collaboration

- *Characterize the fine-scale morphology (phase separation) in differently-processed Arkema membranes*
- *Relate observed microstructural features to processing conditions used and performance (properties) of membrane*
- *Use the microstructural, compositional,and chemical data to "optimize" processing parameters for membranes with improved proton conductivity, durability, etc.*
- *Phase 2 of this project is currently underway at ORNL*

Typical Analyses Conducted On As-Processed Arkema Membranes



Phase-separation evident - non-continuous second phase aligned parallel to membrane surface (elliptical-shaped isolated (dark) phase ~0.2-0.4 μm long). Carbon map indicates a change in mass thickness (density) and F,O-depletion associated with small phase-separated regions.



Future Work

- ***Remainder of FY 2006***
  - Continue working with LANL and ANL on fundamental MEA research and initiate new studies on MEA component durability (focus on Carbon support degradation).
  - Further evaluate the chemical/compositional properties of recast ionomer and membranes using advanced electron microscopy techniques such as EELS and EXELFS (Arkema collaboration).
- ***Goals for FY 2007***
  - Continue collaborative work with MEA developers and manufacturers to provide relevant microstructural characterization regarding MEA degradation, performance, and failure.
  - Expand fundamental non-proprietary research with LANL and ANL.

Summary

- *High-resolution TEM microstructural and compositional analyses have been conducted on intact LANL MEAs subjected to US06 drive cycle conditions, as well as steady state and potential cycling conditions*
- *Statistically relevant Pt particle sizes and distributions have been determined from TEM images and show "true" distributions with respect to Pt placement within cathode*
- *Final particle size distributions can be directly related to initial dispersion of catalyst on carbon support and within ionomer*
- *Stand-alone membranes (Arkema and LANL) have been successfully prepared using microtomy techniques and have been analyzed via TEM and SEM*
- *The instability of bi-metallic catalyst particles during electrochemical aging can, in many circumstances, be directly related to compositional inhomogeneity of the "fresh" catalyst particles*

Response To 2005 Reviewer Comments

- ***Emphasis is more based on analytical methods than on solving fuel cell problems.***

  One of the primary goals of this project is to *develop* the necessary tools for conducting the high-resolution TEM and SEM analyses of MEA constituents and to then apply these tools to relevant FC issues. The actual application of these techniques depends on forming collaborations with other labs and industry.

- ***Need to team with those who are working with commercial MEA designs - LANL materials may not be relevant.***

  ORNL has always encouraged collaborations with external developers and manufacturers! In most cases, the LANL MEAs are used as the standards for technique development and these techniques are then applied to industrial MEA designs, the results of which are generally considered proprietary.

- ***Need to establish experiments to elucidate decay mechanisms.***

  The microstructural characterization work *depends* on the manufacture and testing of relevant MEA systems by industry and other national laboratories. ORNL provides the nm-scale microstructural information, which can then used to optimize the particular MEA design. Conducting fundamental and systematic aging tests on a series of relevant MEAs has long been a goal of the ORNL work, but achieving this goal has been difficult!

Publications/Presentations

- J. Xie, D.L. Wood, K.L. More, P. Atanassov, and R.L. Borup, "Microstructural Changes of MEAs During PEFC Durability Testing at High Humidity Conditions," *J. Electrochem. Soc.* **152**(5) A1011-20 (2005)

- K.L. More and K.S. Reeves, "Partial Embedding of 3-Layer MEAs for Ultramicrotomy" in Microscopy & Microanalysis **11**(2) (2005).

- K.L. More and K.S. Reeves, "Understanding MEA Structure from Evaluations Using Electron Microscopy," Abstract #316, presented at the 2005 Fuel Cell Seminar, Palm Springs, CA, November 14-18, 2005.

- K.L. More, J. Bentley, and K.S. Reeves, "Microstructural Characterization of PEM Fuel Cell MEAs," presented to the Fuel Cell Tech Team, USCAR, Southfield, MI, January 18, 2006.

- J.T. Goldbach, K.L. More, and A.L. Manheim, "Nano-Scale Investigation of Morphologies in Polymer Electrolyte/PVDF Blend Membranes," presented at the 06 AIChE Spring National Meeting, Orlando, FL, April 24-28, 2006.

- K.L. More, "Microstructural Evaluation of MEA Material Constituents to Elucidate PEMFC Degradation Mechanisms," invited presentation at the 2006 Gordon Research Conference on Fuel Cells, to be held in Smithfield, RI, July 23-28, 2006.

Collaborations With PEMFC Manufacturers Are Critical To Success Of This Program

- ***Los Alamos National Laboratory***
  - Electrochemical aging conditions on MEA microstructure and durability

    ORNL/LANL non-proprietary collaboration is ongoing
- ***Argonne National Laboratory***
  - Systematic study of processing effects and aging on MEA microstructure and durability

    ORNL/ANL non-proprietary collaboration recently initiated
- ***Additional Proprietary Collaborations With:***
  - Gore Fuel Cell Technologies (*as-processed & aged MEAs*)
  - PlugPower (*as-processed & aged MEAs*)
  - FuelCell Energy (*as-processed & aged MEAs)*
  - Arkema Inc. *(membranes & MEAs, initiated May 2005)*