Microstructural Characterization Of PEM Fuel Cell MEAs

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This presentation does not contain any proprietary or confidential information

Project ID# FC39

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
- ~$230k received in FY05
- Scheduled through FY07

Barriers

- O. Stack Materials ($30/kW)
- P. Durability - 5000 h
- Q. Electrode Performance

Primary Interactions

- Los Alamos National Lab
- Gore Fuel Cell Technologies
- PlugPower
- FuelCell Energy
- Arkema Inc.
- Battelle Memorial Institute

Research Objectives

- ***PEMFC durability*** primary issue with regard to successful commercial implementation of FCs

  → *reducing system cost per hour of life*
- ***Fundamental durability studies*** are required to understand MEA degradation mechanisms
  - Lengthy testing times required
  - Interacting degradation mechanisms involving multiple MEA/GDL/MPL components
  - Inability to perform in-situ or non-destructive evaluation of the components during testing
- ***Elucidate*** contributing MEA degradation mechanisms for different aging conditions

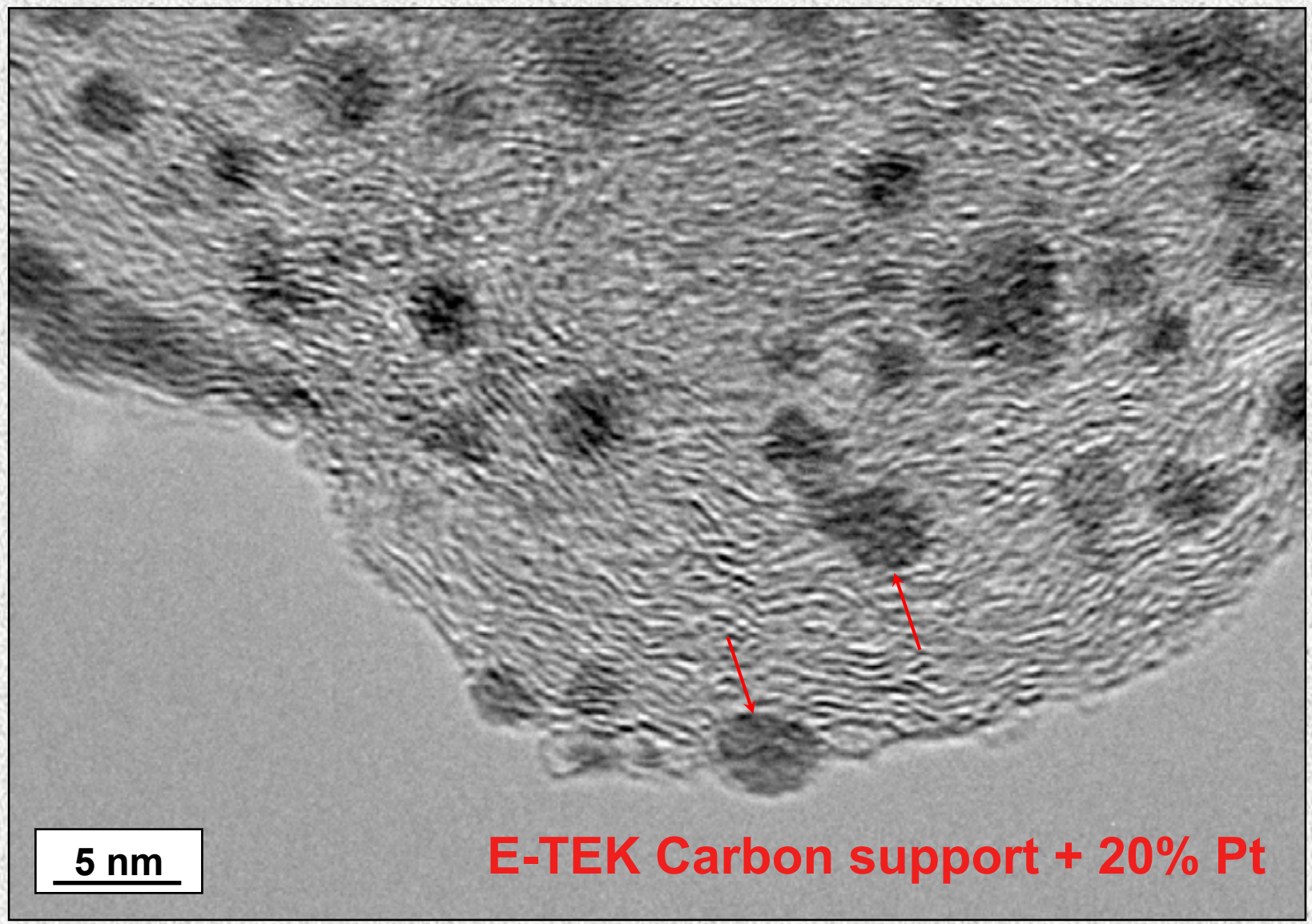
Approach: Use Advanced TEM And SEM Preparation And Imaging Techniques To Evaluate nm-Scale MEA Constituents

- Develop improved SEM and TEM *sample preparation* methodologies for evaluating different structural aspects of layered MEAs
  - recast ionomer within porous catalyst layer
  - GDLs
- Evaluate microstructural changes to MEA during *electrochemical aging* and determine contributing degradation/failure mechanisms via high-resolution imaging and microchemical analyses
  - MEAs characterized to date have been single cell and stack tested

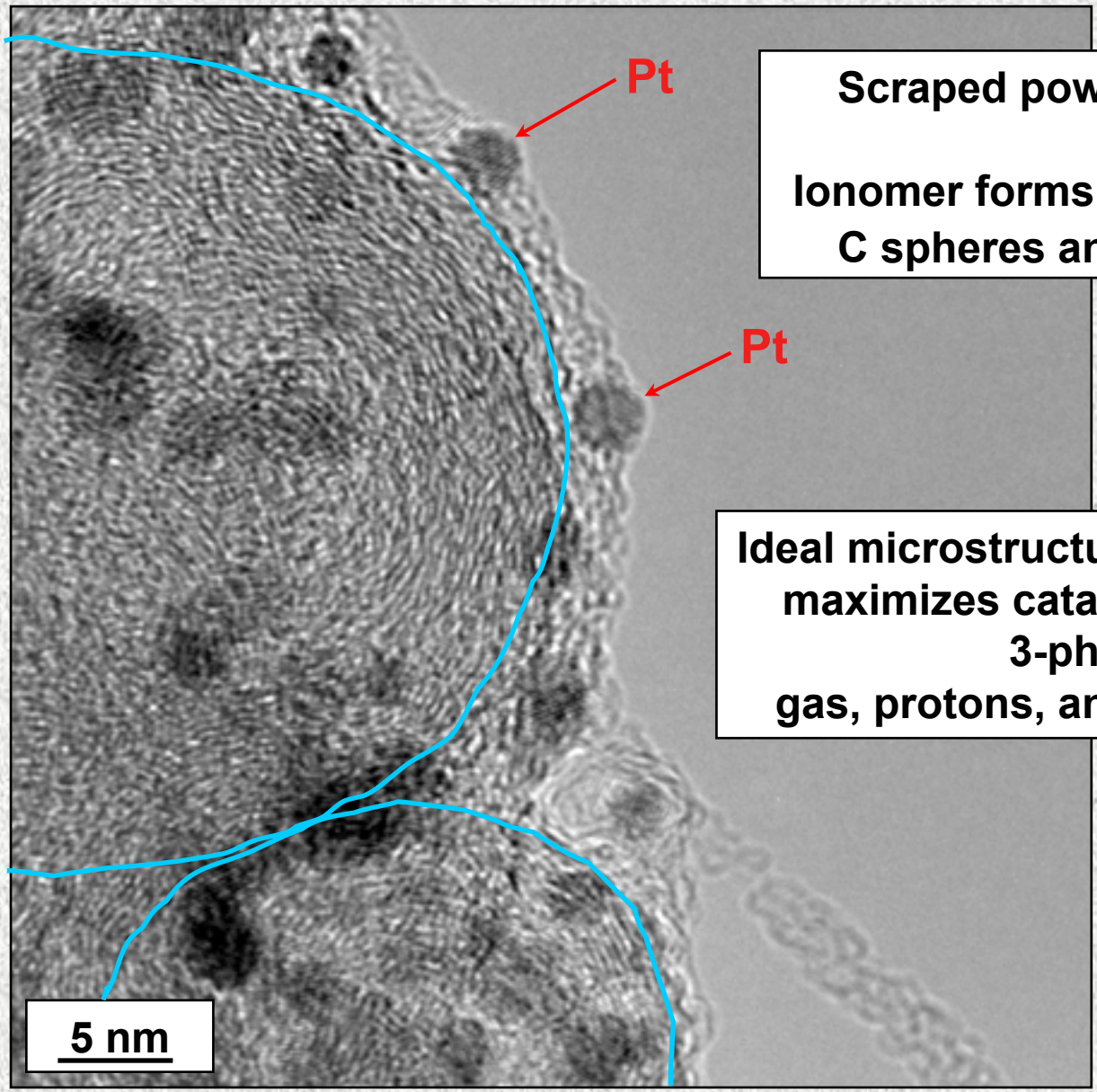
Technical Accomplishments And Progress

- A new ultramicrotomy TEM sample preparation technique, *"partial" electrode embedding*, was successfully demonstrated
- Direct imaging of intact recast ionomer, carbon/Pt, and pore network surfaces within MEA porous catalyst layers
- Several durability studies were initiated/completed with external collaborators:
  - Significant progress made on characterization of LANL-produced, electrochemically-aged MEAs (non-proprietary research)
  - Proprietary durability studies were initiated with:
    - Gore Fuel Cell Technologies
    - PlugPower
    - FuelCell Energy

TEM Imaging - Surface Of Non-Processed Powder Specimens



TEM Imaging Surfaces Of Cathode Powder

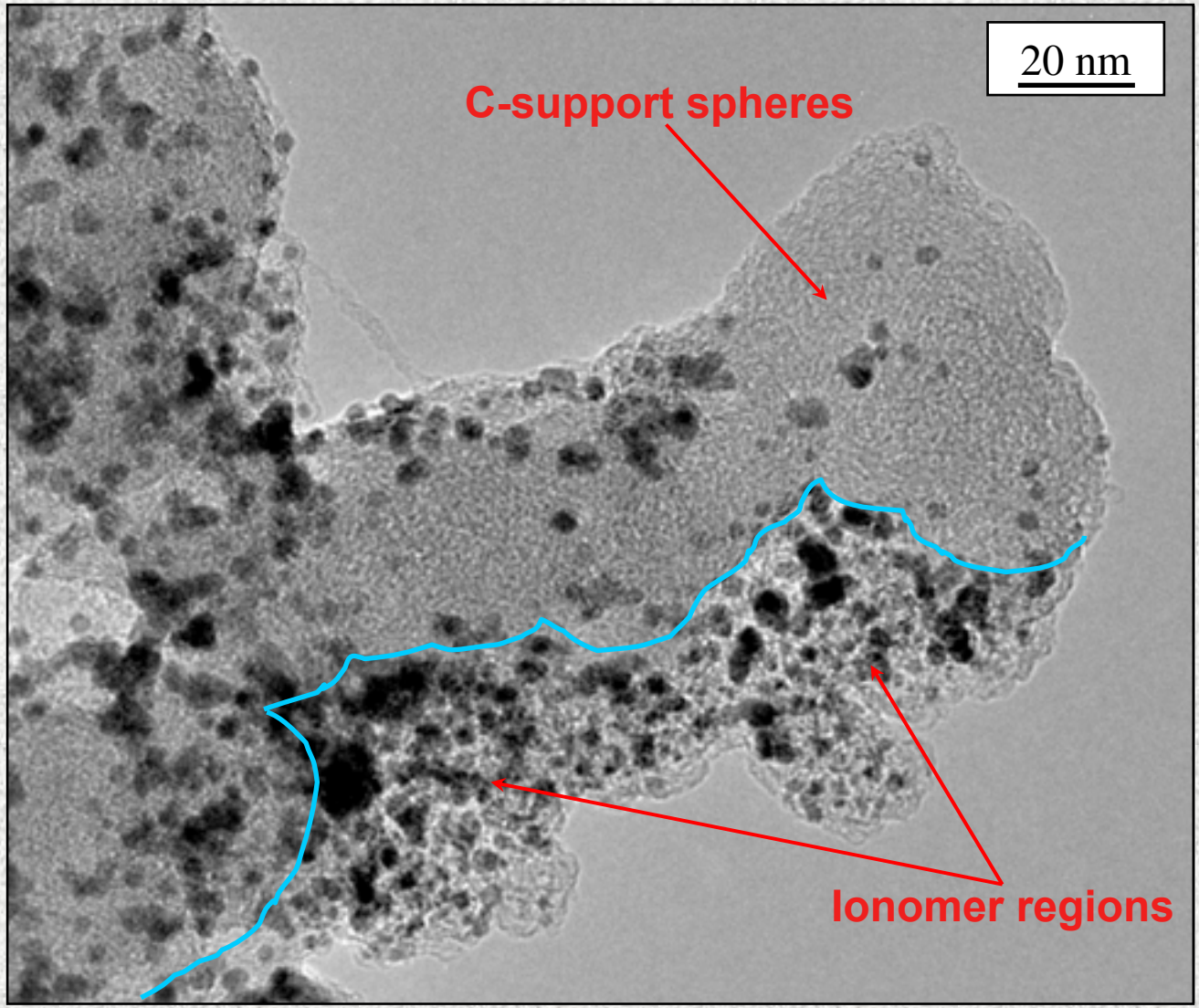


Scraped powder from processed MEA

Ionomer forms web-like structure between C spheres and coats some C surfaces

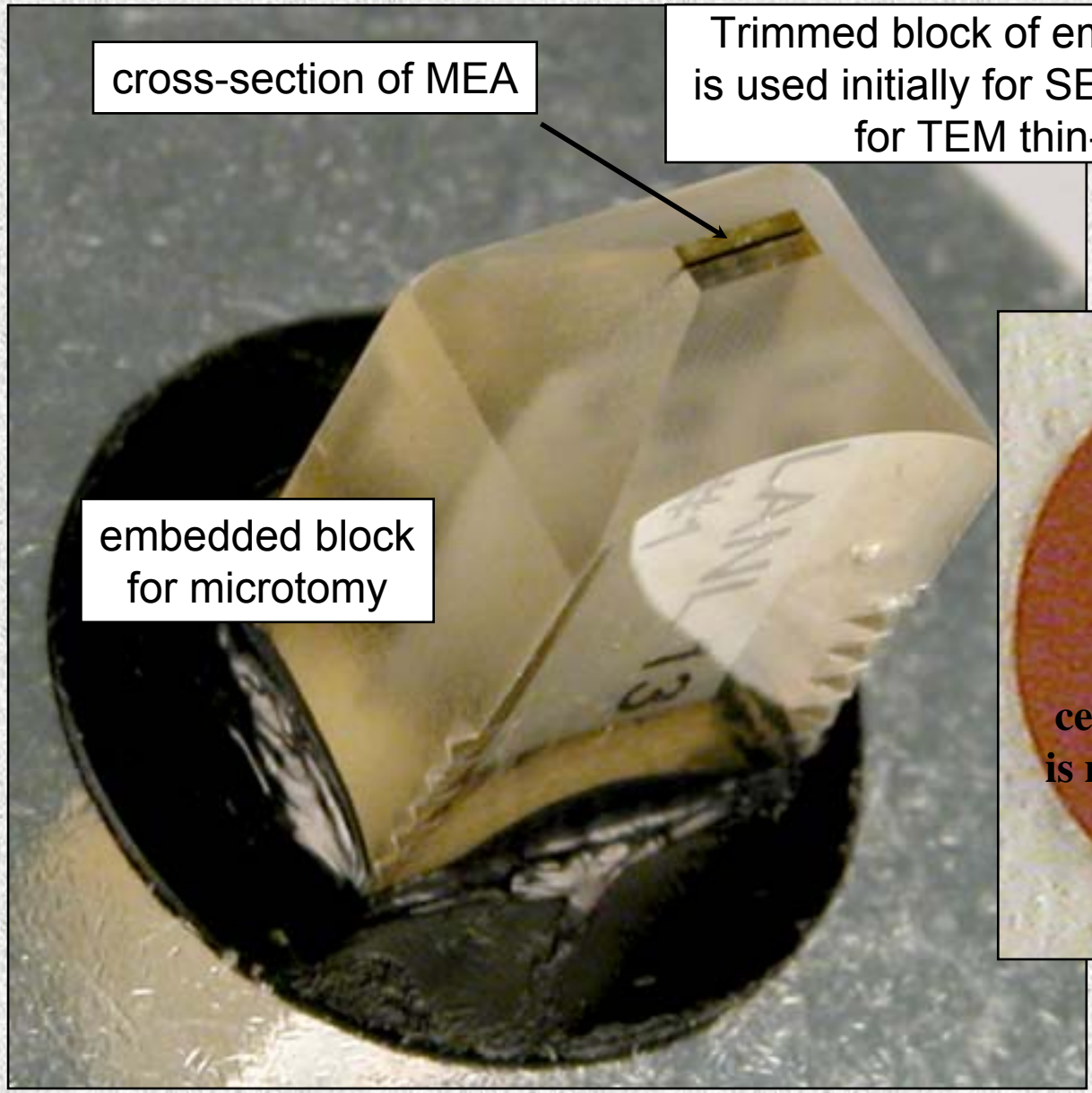
Ideal microstructure within porous electrodes maximizes catalyst utilization by creating 3-phase interfaces: gas, protons, and electrons to active sites

However, Overall Structure Is Not Ideal

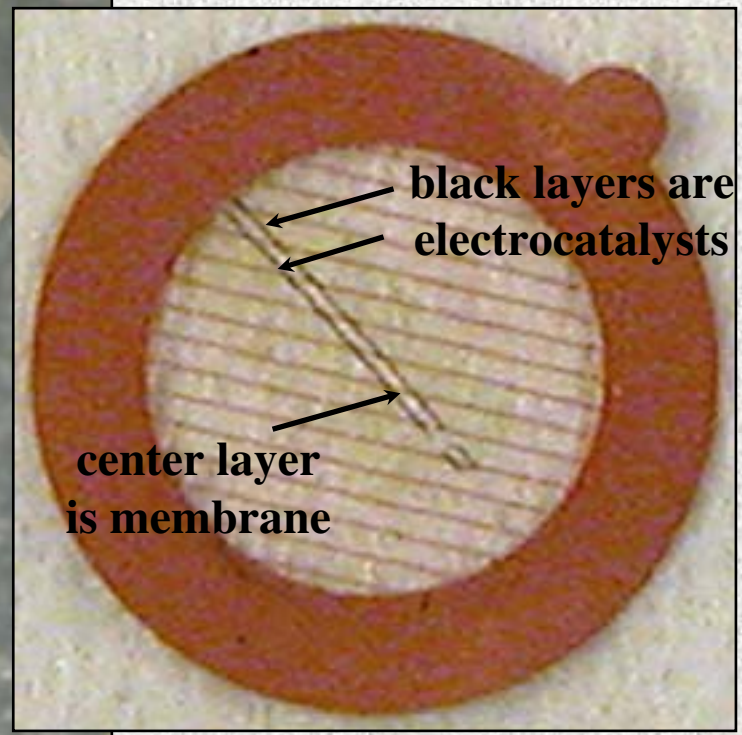


The ionomer (1) tends to "clump" around and between the C-support rather than homogeneously coating the spheres and (2) "picks up" much of the Pt during ink preparation and redistributes it such that the ionomer regions have a very high Pt concentration

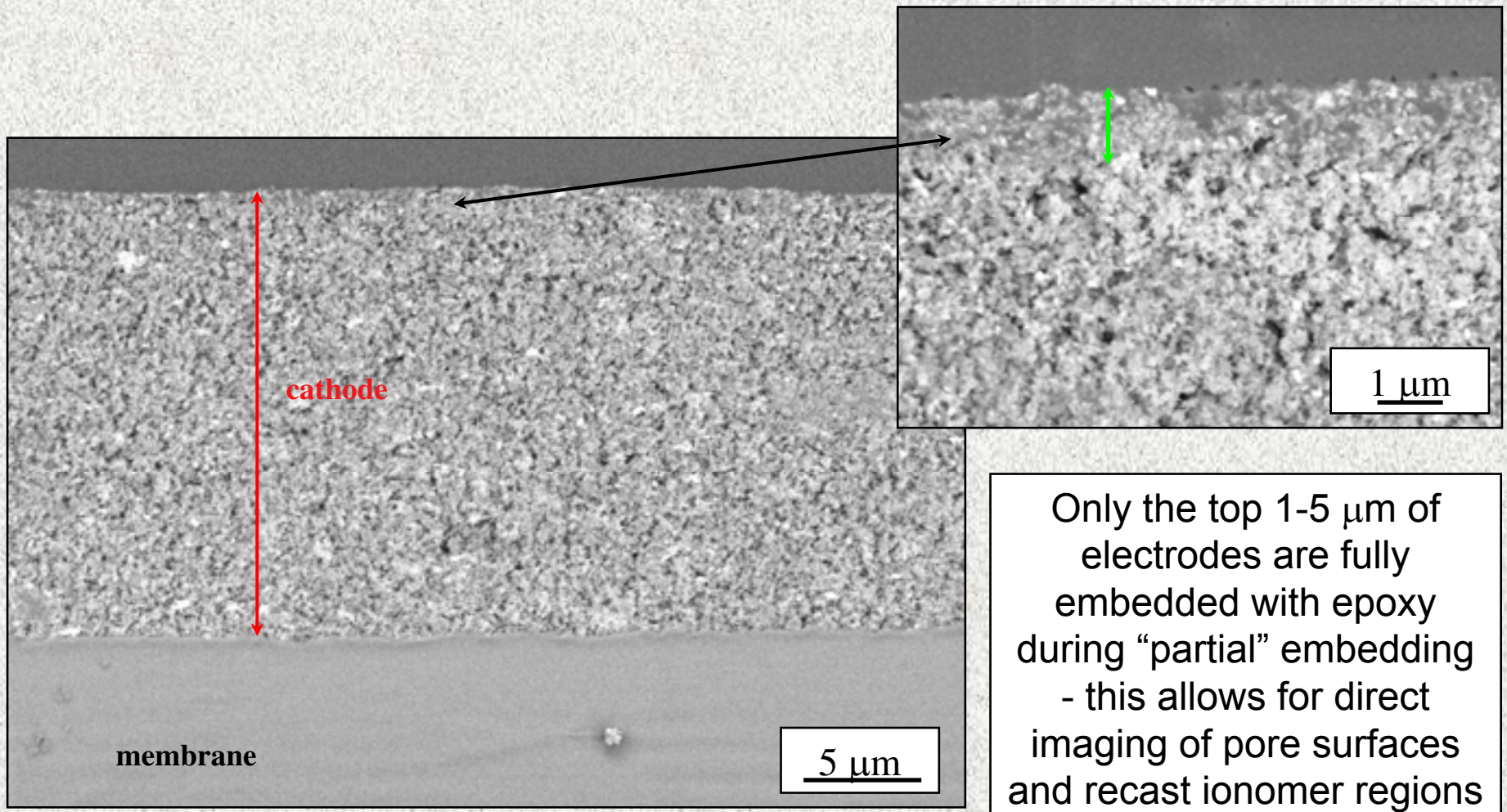
Ultramicrotomy Is Used To Prepare MEA Cross-Sections For SEM & TEM Analysis



Trimmed block of embedded MEA cross-section is used initially for SEM imaging and is then ready for TEM thin-section preparation.

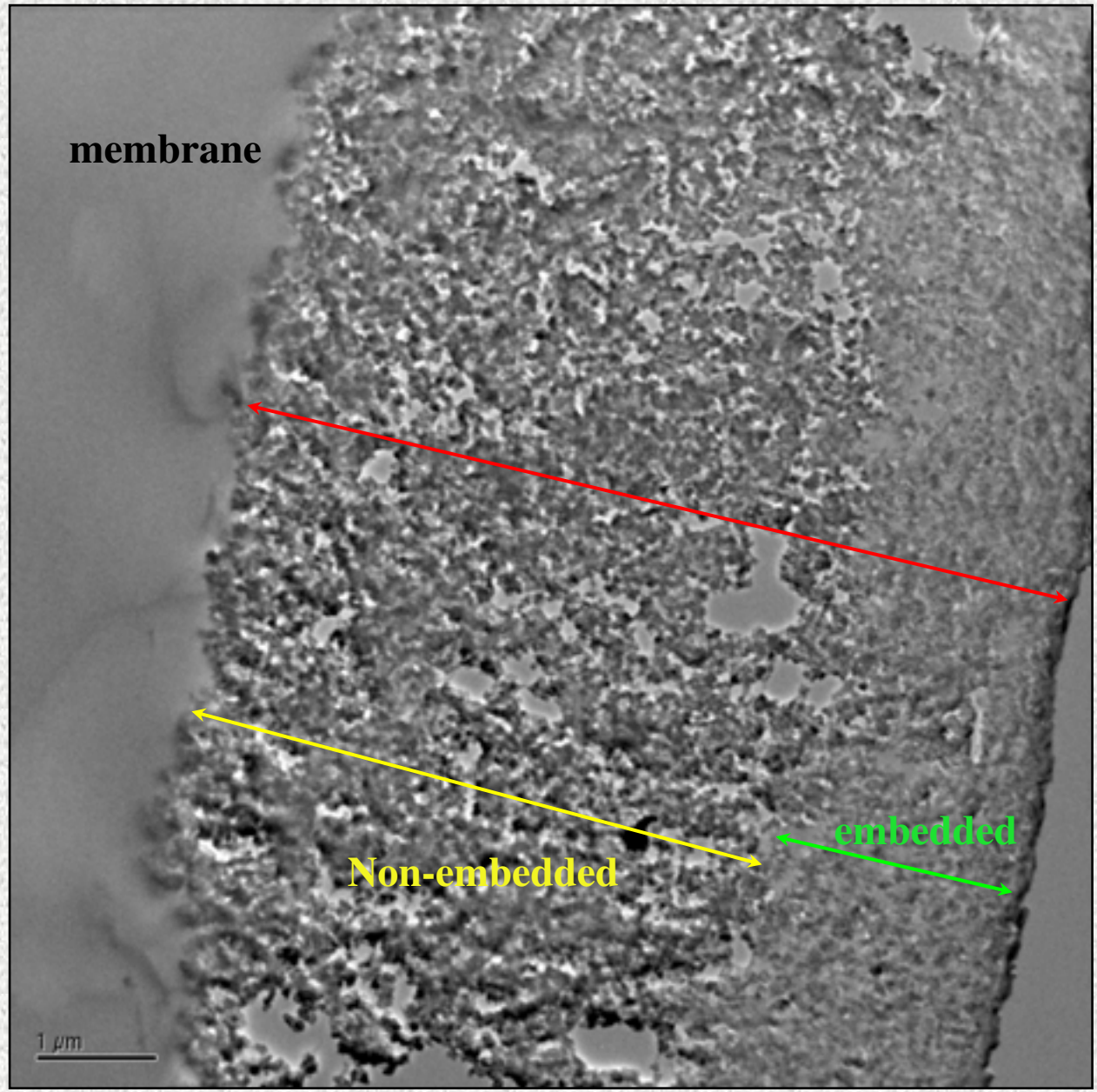


MEA Is "Partially" Embedded To Image Ionomer Regions Within Porous Electrode

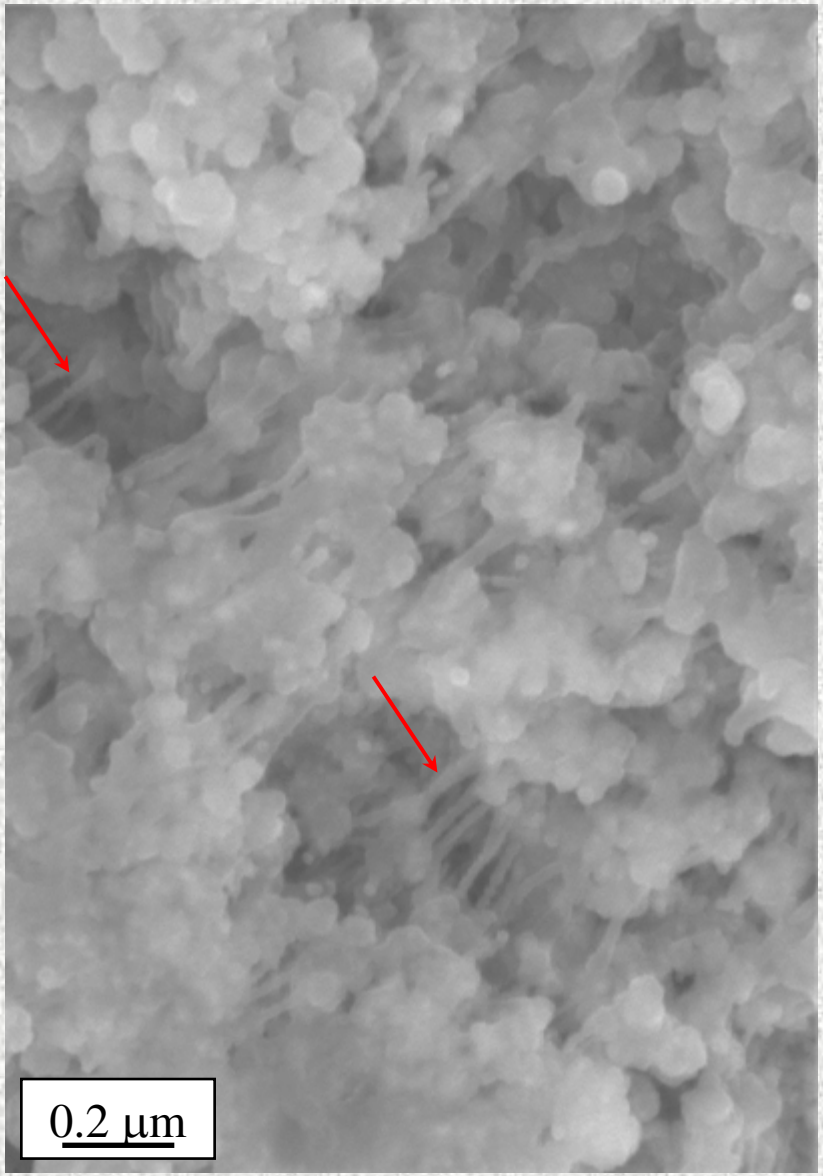


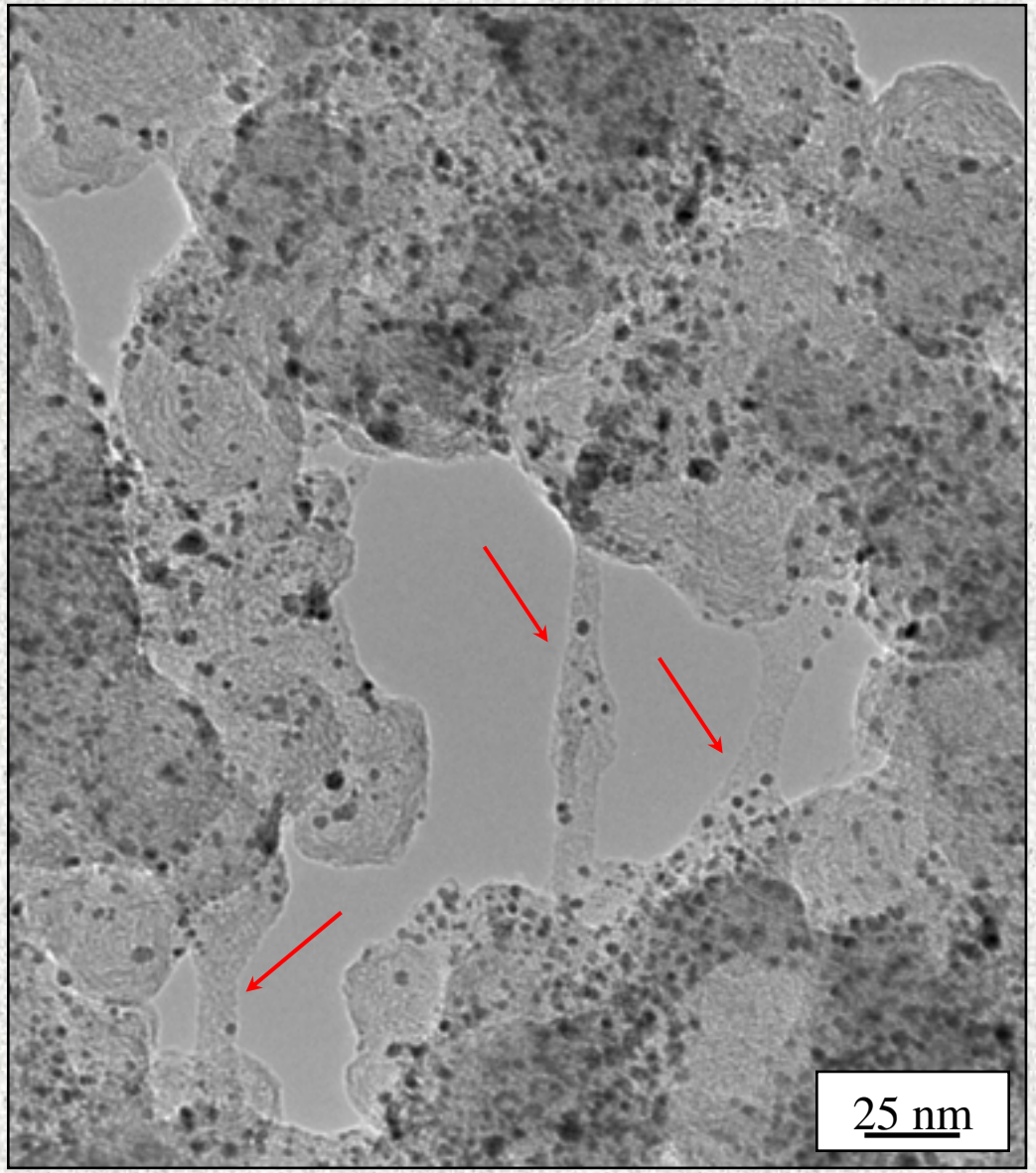
Only the top 1-5 μm of electrodes are fully embedded with epoxy during "partial" embedding - this allows for direct imaging of pore surfaces and recast ionomer regions within electrodes

TEM Image Of Partially Embedded MEA

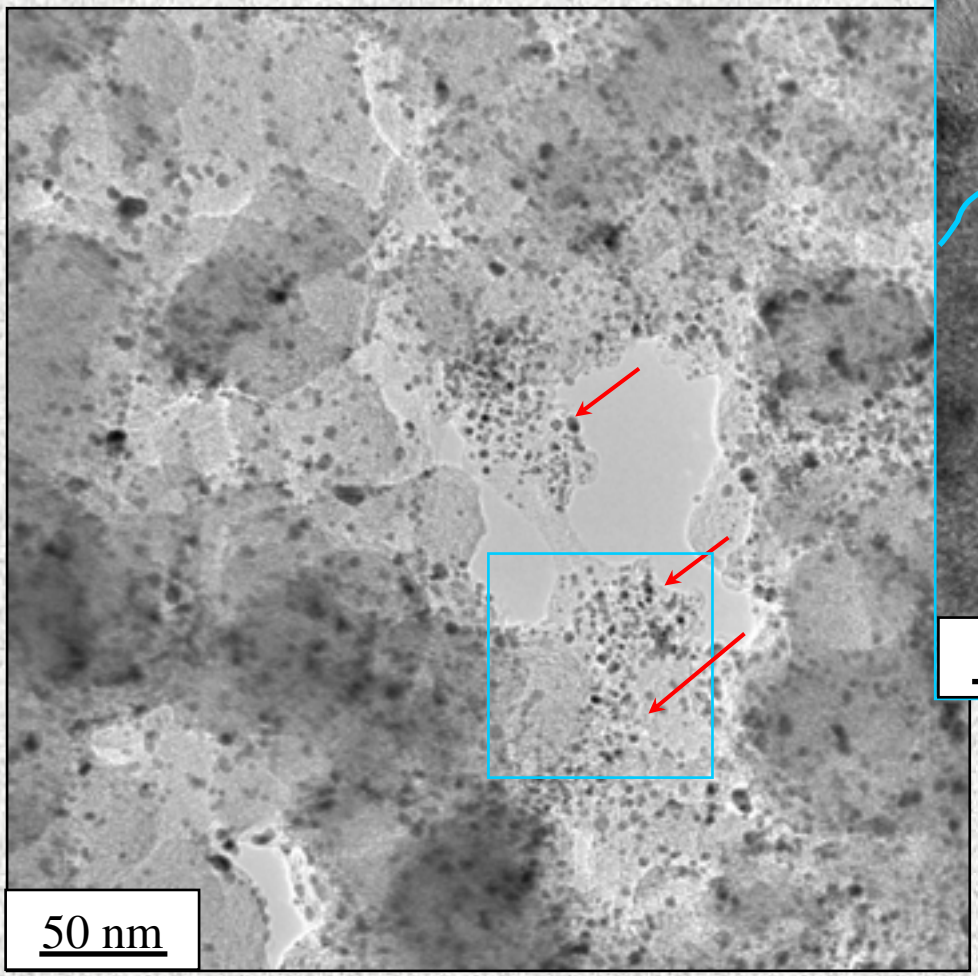


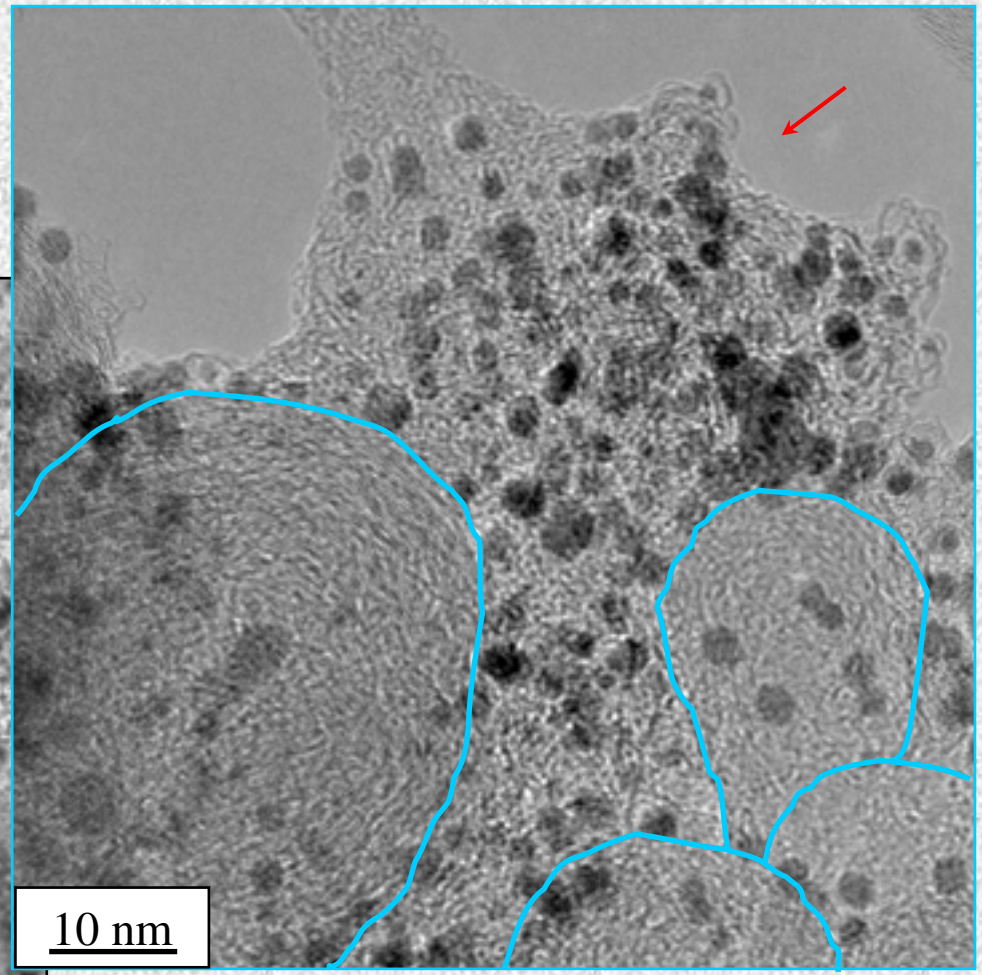
“Web-Like” Ionomer Distribution Within Porous Catalyst Layers





Non-embedded Pore Within Electrode

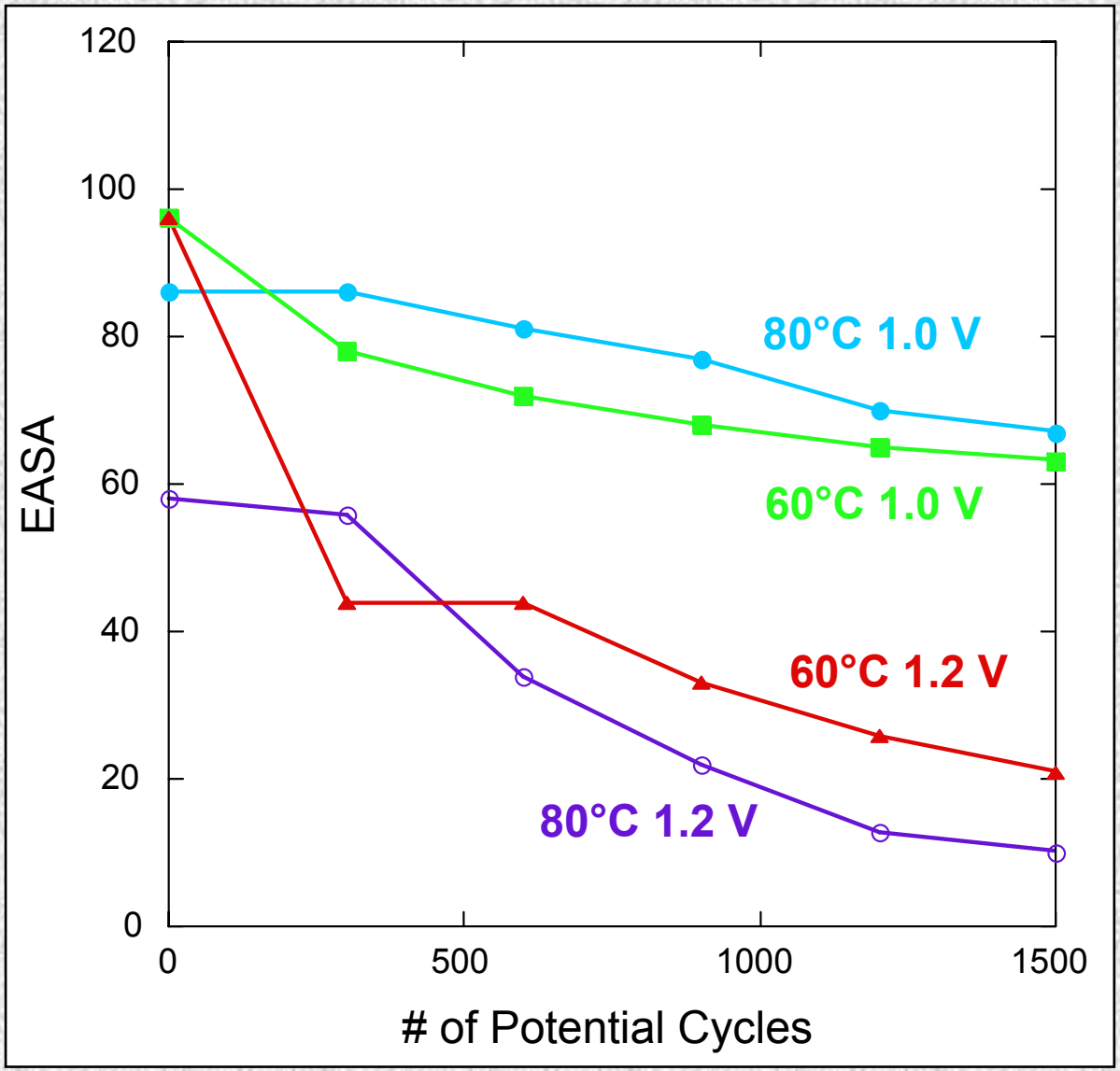




Technical Accomplishments And Progress
ORNL/LANL Collaboration

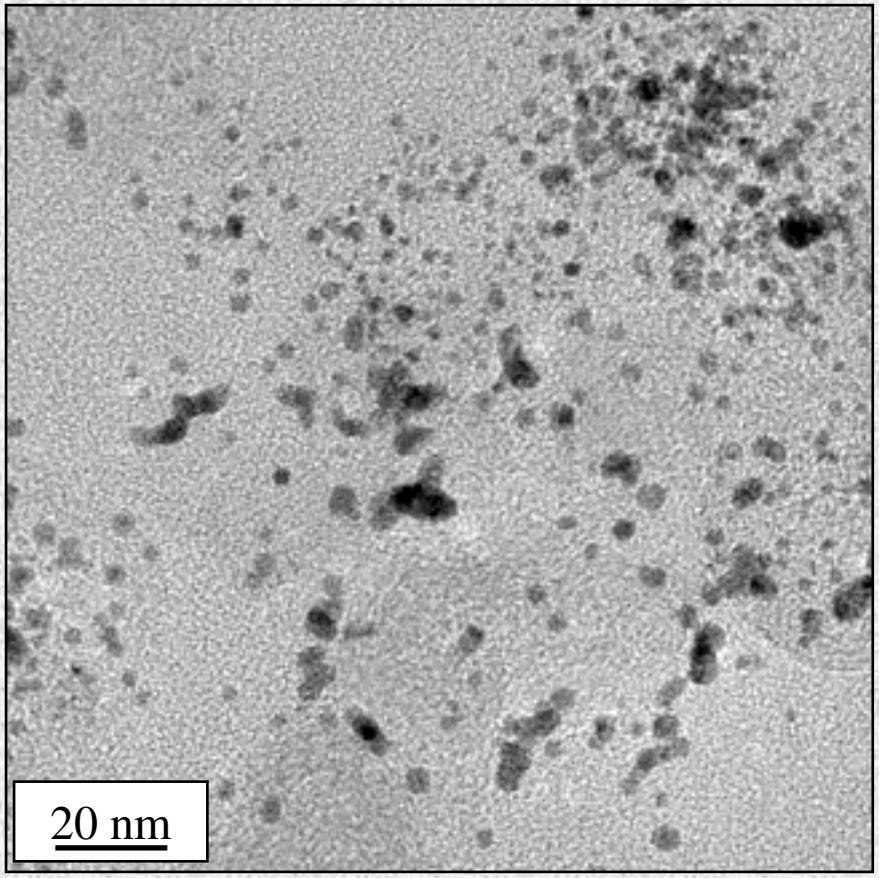
- Ionomer structure, distribution, and function
- *Effect of cycling and temperature on catalyst durability*
  - *MEAs cycled 10mV/sec, 60°C and 80°C*
    - *0.1-1.0 V, 1500 cycles*
    - *0.1-1.2 V, 1500 cycles*
    - *1200 h drive cycle*
  - *Steady-state operation 0.6 V up to 3500 h*
  - *Correlate X-ray scattering with TEM observations*
- Structural changes to MEA during electrochemical aging continues to be investigated
  - MEAs aged (500 h intervals) for times up to 1000 h
- New catalyst compositions with low loadings

Loss Of Cathode Pt Surface Area With Temperature And Cycling

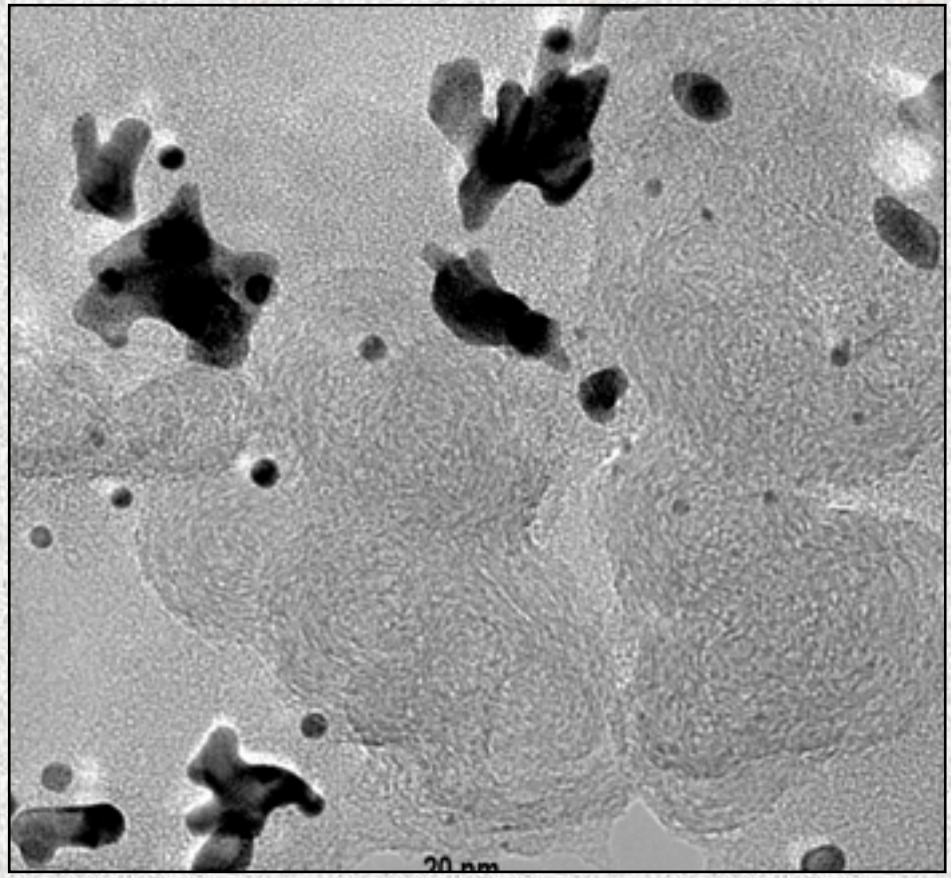


Larger degradation at 1.2 V cycling

Extensive Pt Coarsening Observed Within Cathode Following Potential Cycling

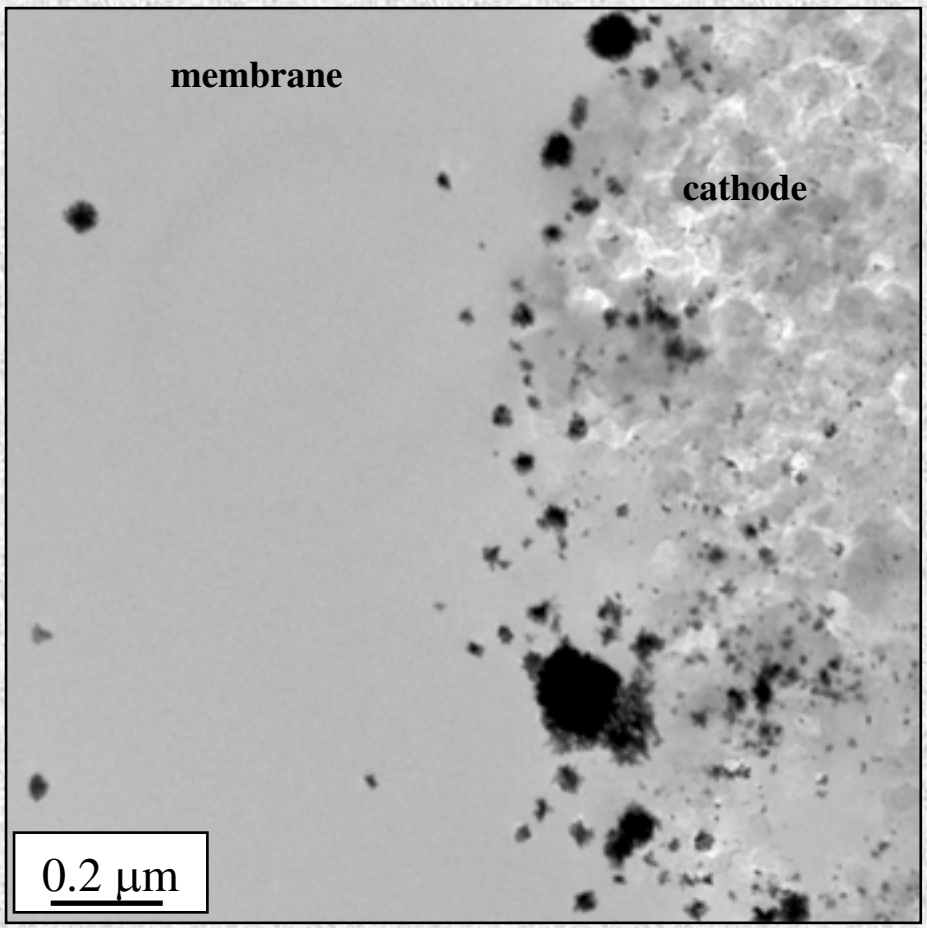


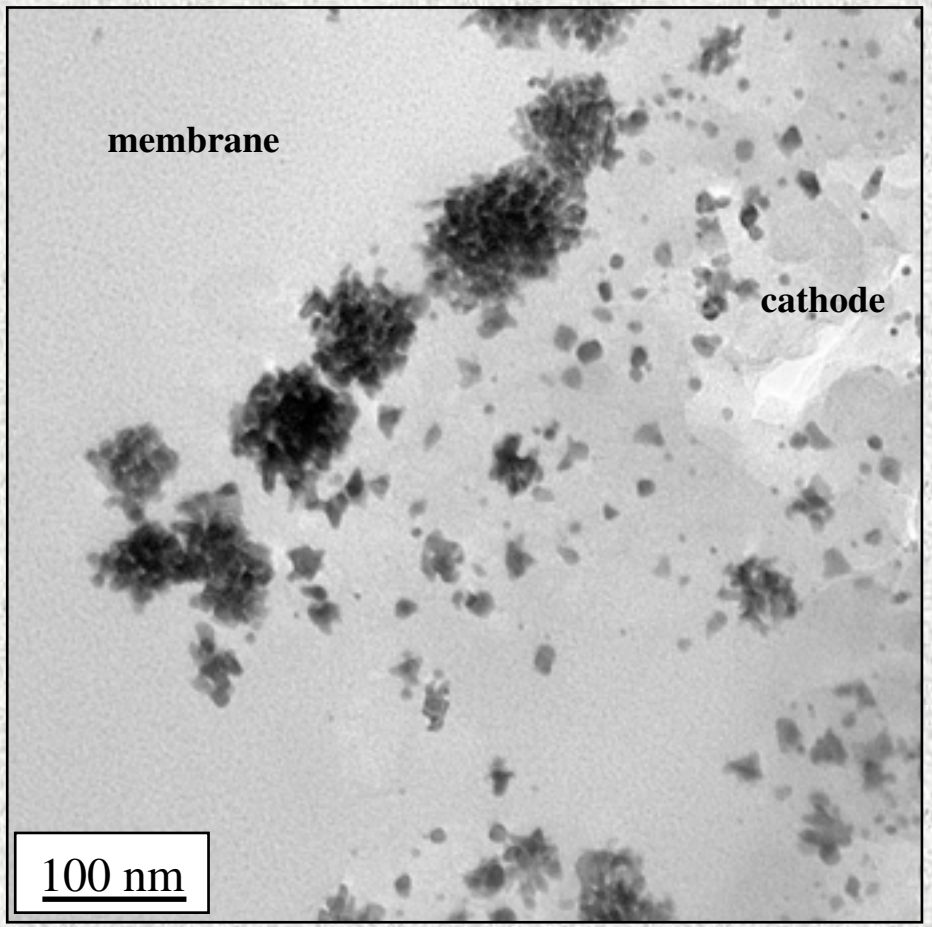
Fresh cathode Pt catalyst particles



Pt particles after 80°C cycling to 1.2 V

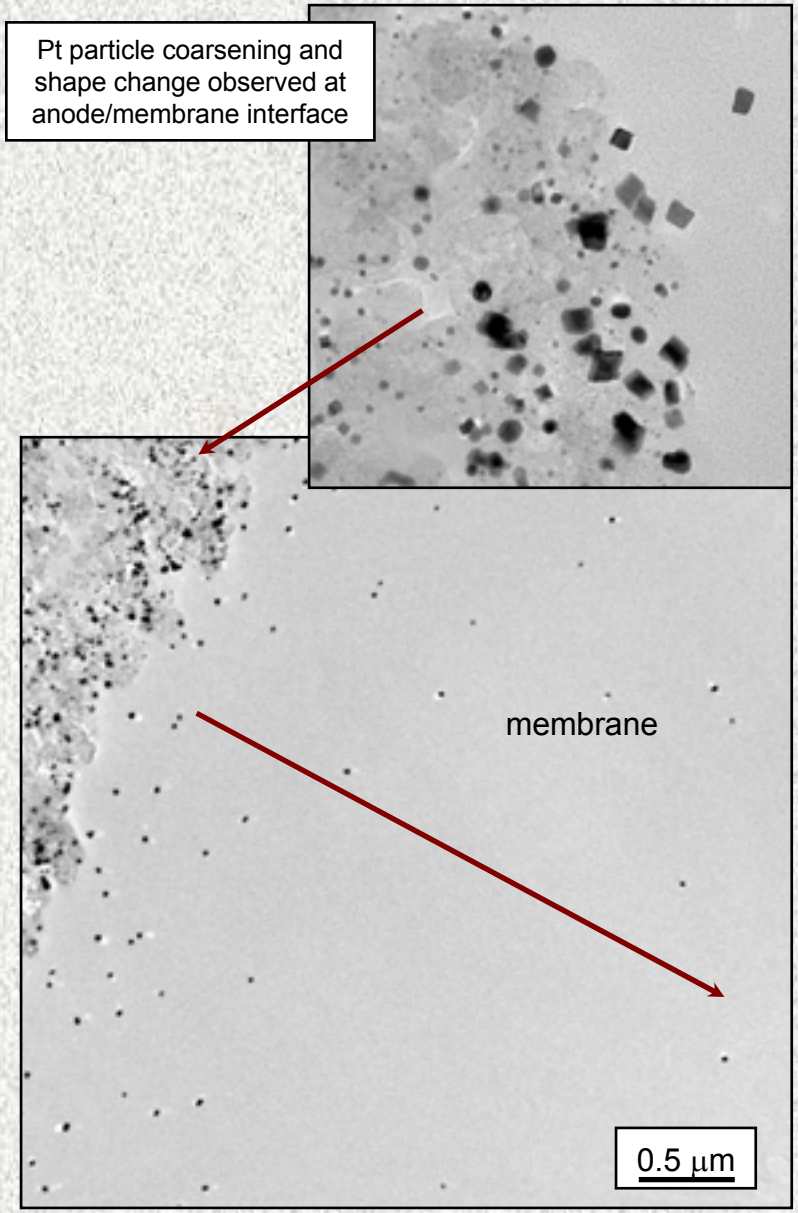
Extensive Pt Migration/Redistribution Observed At Cathode/Membrane Interface

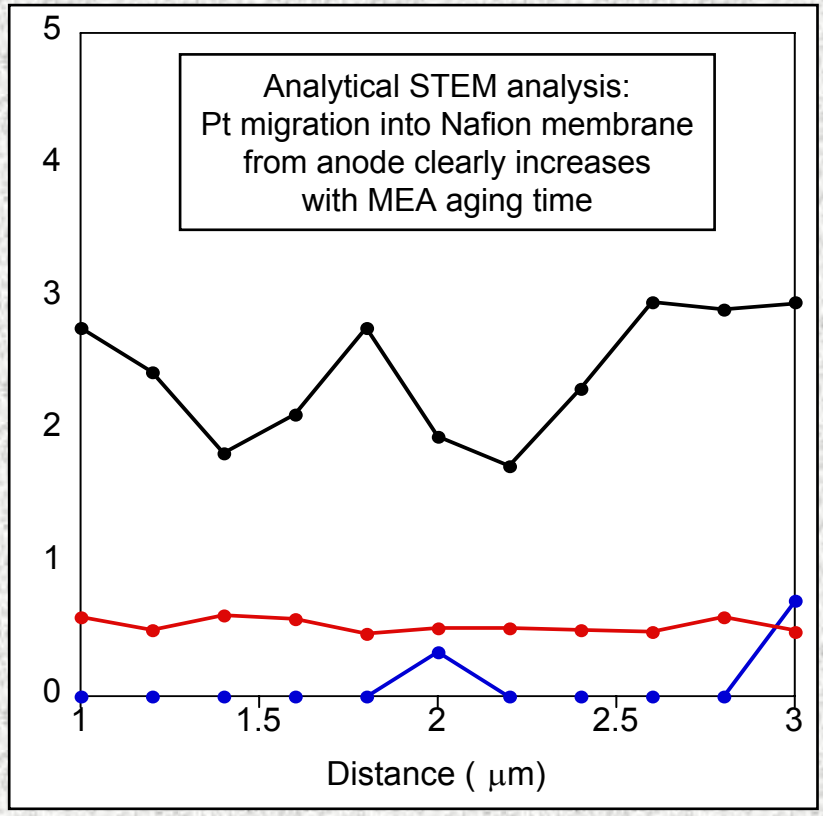




Agglomerated Pt particles ***within*** membrane at cathode interface

Extensive Pt Redistribution And Coarsening Observed In Anode After 1000 h Aging



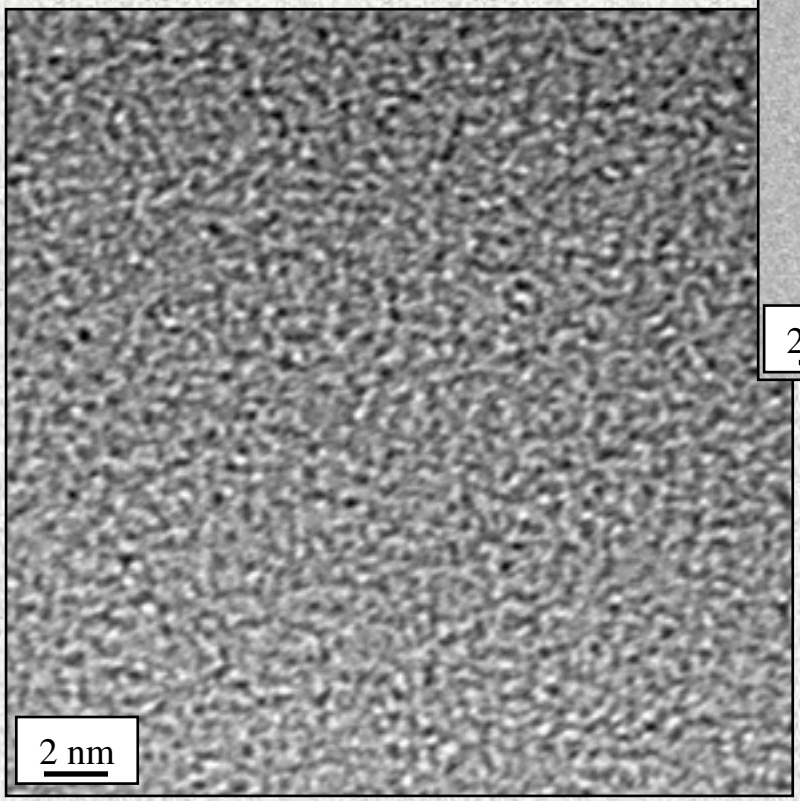


Pt-containing particles observed ~3 μm into Nafion membrane on anode side

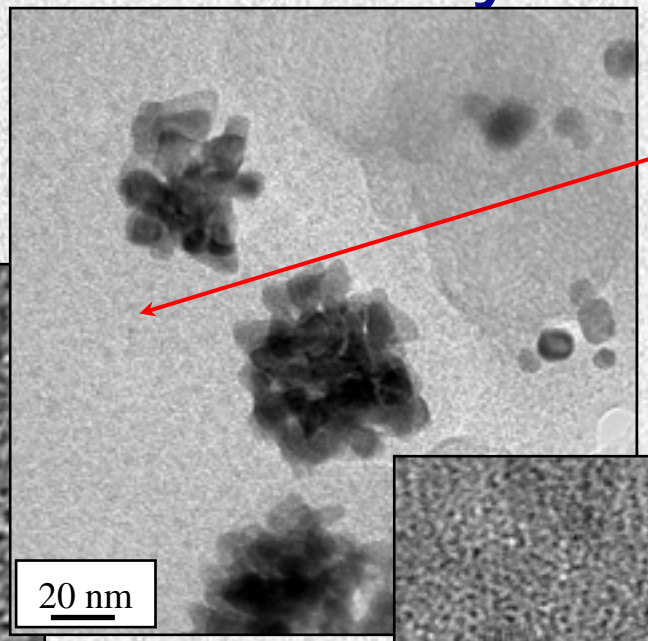
Pt particle shape change in addition to coarsening

1-12 nm in fresh → 20-40 nm 1000 h aged

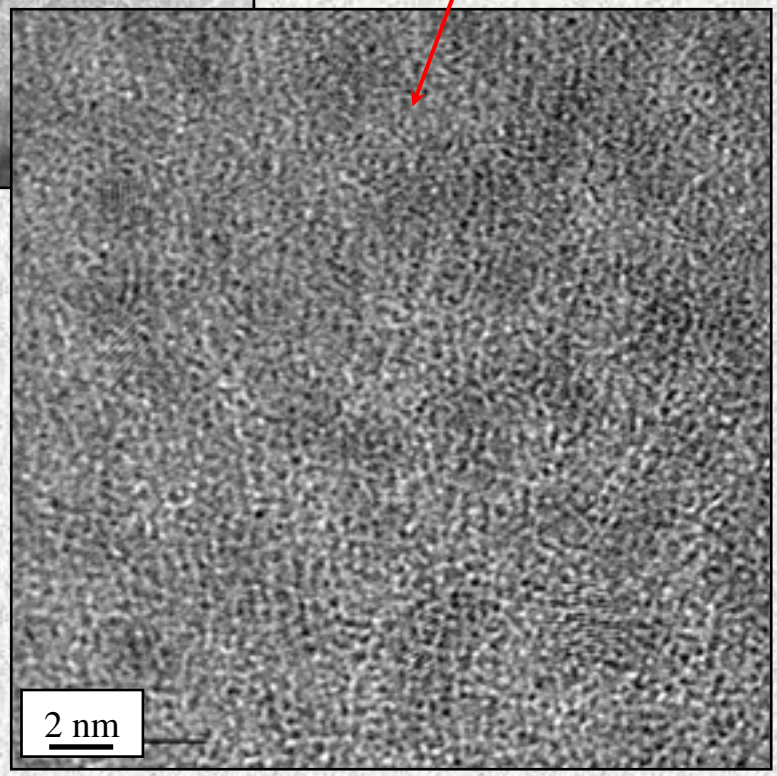
Nafion Membrane "Structure" Changes During Potential Cycling



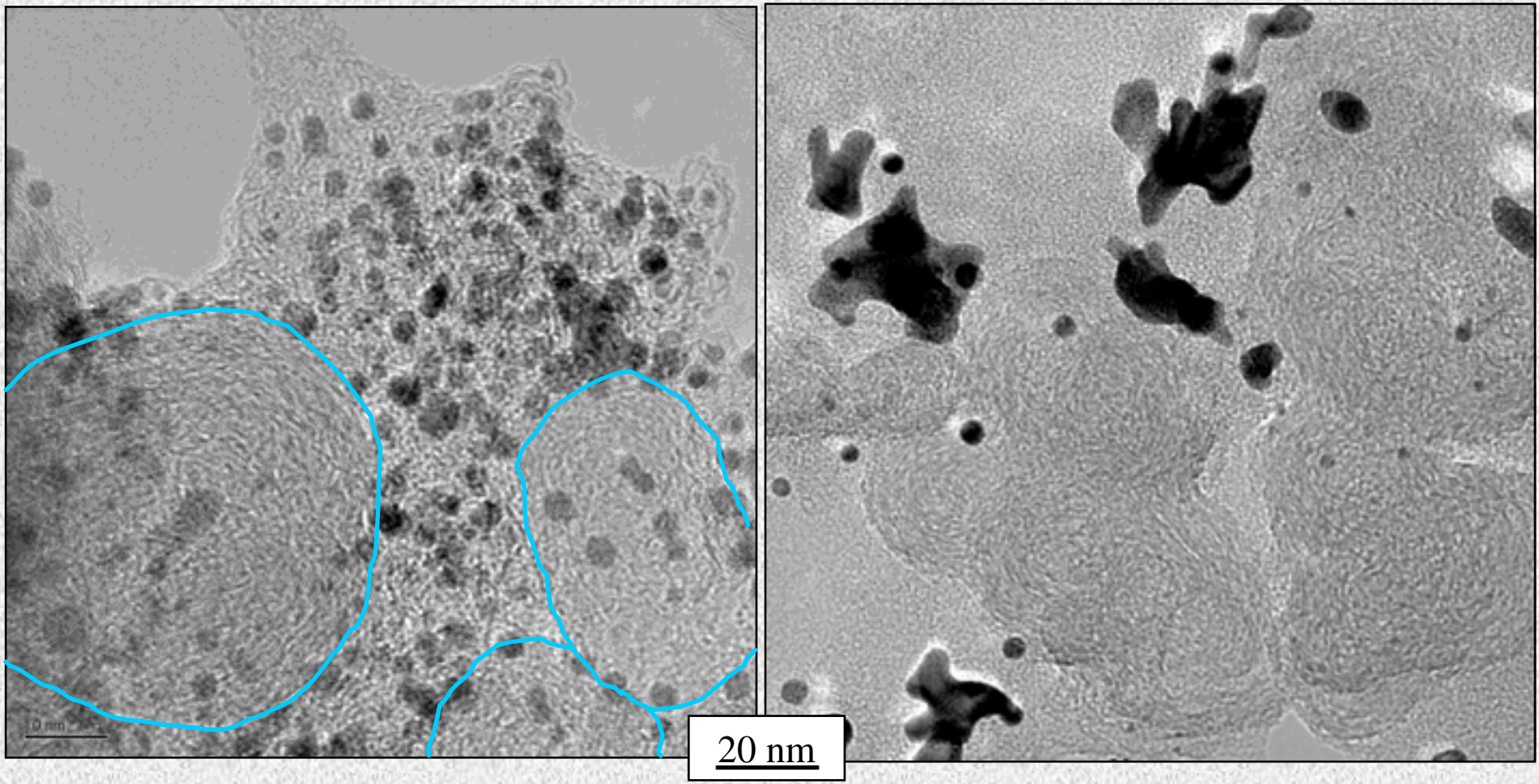
Amorphous structure of membrane
In fresh MEA



Membrane is nano-crystalline after 80°C cycling to 1.2 V



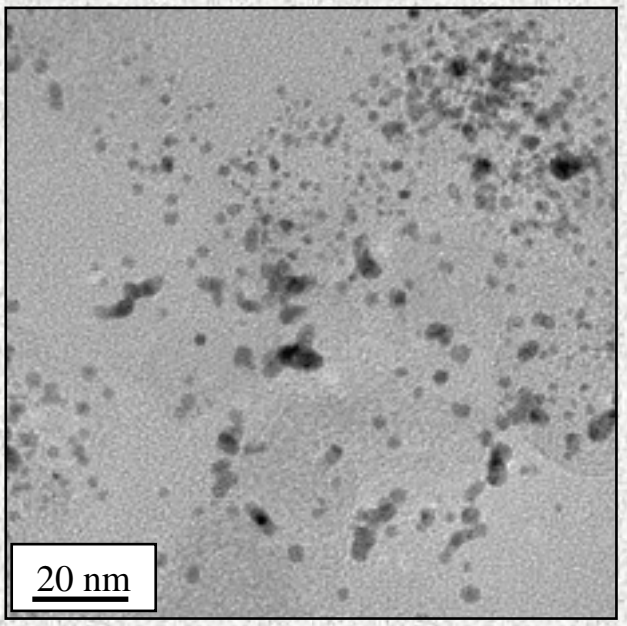
Increased Pt Coarsening Associated With Pt Concentrated Within Ionomer "Pockets"



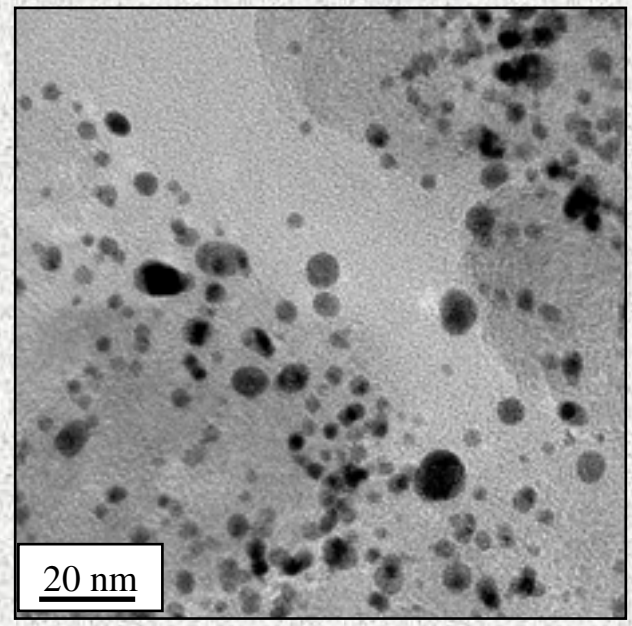
Fresh cathode Pt catalyst particles

Pt particles after 80°C cycling to 1.2 V

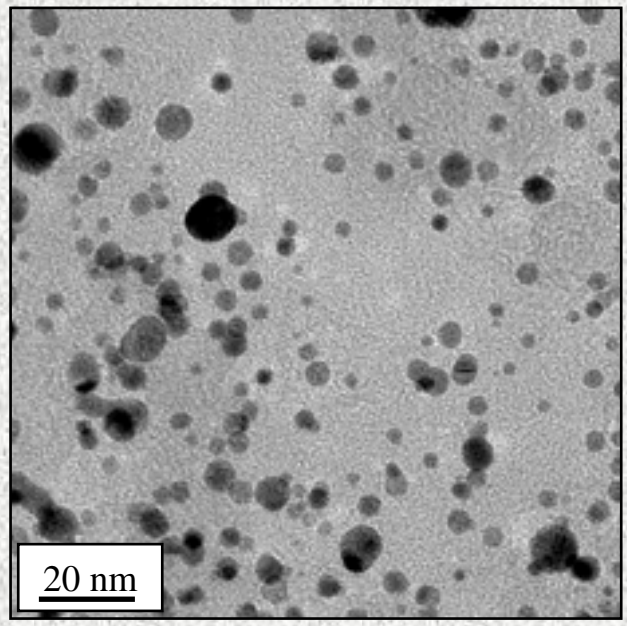
Steady-State Aging At 0.6 V - Majority Of Pt Coarsening In Early Stages Of Aging



Fresh Cathode Pt
1-3 nm



900 h SS
2.5-10 nm



3500 h SS
3-12 nm

Collaborations With PEMFC Manufacturers Are Critical To Success Of This Program

- ***Los Alamos National Laboratory***
  - Systematic study of processing effects and aging on MEA microstructure and durability

  ORNL/LANL non-proprietary collaboration is ongoing

- ***Additional Proprietary Collaborations With:***
  - Gore Fuel Cell Technologies (*as-processed & aged MEAs*)
  - PlugPower (*as-processed & aged MEAs, completed*)
  - FuelCell Energy (*as-processed & aged MEAs, completed. Currently analyzing MEA after aging with ORNL metallic bipolar plates)*
  - Battelle Memorial Institute (*MEA processing effects*)
  - Arkema Inc. *(membranes & MEAs, initiated May, 2005)*

Response To 2004 Reviewer Comments

- ***Program very important for developers to understand decay mechanisms. Analysis of degradation mechanisms is very important.***

  FY2005 work has focused on working directly with collaborators to provide quantitative imaging, composition, and degradation data to solve their durability problems and provide mechanistic understanding of relevant MEA durability issues

- ***ORNL needs to provide better services to developers and encourage dialogue. More work needed with stack developers and component suppliers (membranes and electrodes)***

  ORNL has encouraged collaborations with external developers and manufacturers! An additional three (3) collaborations were started during FY2005, all of which are considered proprietary.

- ***Pay attention to how the "network" structure changes during aging. Ionomer degradation needs to be studied.***

  FY2005 focus has been on developing the sample preparation methods for imaging and analyzing intact ionomer regions within porous electrodes. These studies, in addition to image analysis techniques developed previously, are being applied in the evaluation of aged MEAs.

Future Work

- ***Remainder of FY 2005***
  - Continue working with LANL on fundamental MEA research and initiate new studies on MEA durability.
  - Further evaluate the chemical/compositional properties of recast ionomer and membranes using advanced electron microscopy techniques such as EELS and EXELFS. Apply these techniques to electrochemically aged MEAs.
  - Continue to expand work with MEA developers and manufacturers to establish new durability studies.
- ***Goals for FY 2006***
  - Continue collaborative work with MEA developers and manufacturers to provide relevant microstructural characterization regarding MEA degradation, performance, and failure

Publications/Presentations

- K.S. Reeves, K.L. More, L.R. Walker, and J. Xie "TEM Evaluation of Aged PEMFCs" in Microscopy & Microanalysis (2004).
- K.L. More, K.S. Reeves, J. Bentley, J. Xie, "Evaluation of Processing Parameters on the Microstructure and Performance of PEMFC MEAs," presented at the 106th Annual Meeting of The American Ceramic Society, April, 2004.
- J. Xie, D.L. Wood, K.L. More, T. Zawodzinski, and W. Smith, "Influence of Cathode Ionomer Content on PEFC MEA Structure and Performance," presented at the 206th Annual Meeting of The Electrochemical Society, October, 2004. Submitted for publication to *Electrochim Acta.*
- K.L. More, K.S. Reeves, D.L. Wood, and R.L. Borup, "Microstructural Evaluation of Aged PEMFC MEAs," presented at the 107th Annual Meeting of The American Ceramic Society, April, 2005.
- 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" to be published in Microscopy & Microanalysis (2005).

Hydrogen Safety

The most significant hydrogen hazard associated with this project :

- There are NO specific hydrogen hazards associated with the MEA research conducted at ORNL (microstructural studies)
- All durability testing (stack and single cell) is conducted by project collaborators - ORNL only receives as-processed and tested MEAs

Hydrogen Safety

ORNL's approach to deal with any hydrogen hazard is:

- Project has undergone "Integrated Safety Management Pre-Planning and Work Control" (Research Hazard Analysis and Control)
- Experienced Subject Matter Experts are required for all Work Control for Hydrogen R&D including
  - Fire Protection Engineering
  - Certified Safety and Industrial Hygiene expertise
- Periodic safety reviews of installed systems
- Typical controls include:
  - Systems design to prevent air-hydrogen mixtures in the flammable-explosive range
  - Minimization of available potential energy
  - Use of robust, enclosed systems and gas cabinets, inert gas purging
  - Use of hydrogen monitors with alarms and fail-safe shutdown