Microstructural Characterization Of PEM Fuel Cells

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Program Objectives

Elucidate MEA degradation mechanisms

- Structural and compositional changes as a function of MEA processing; correlate microstructure with performance
- Morphological changes occurring during MEA aging/use

Collaborate with PEMFC developers/manufacturers to evaluate MEAs using advanced microstructural characterization techniques and provide feedback for MEA optimization

Program Budget

Fiscal Year	2000	2001	2002	2003	2004
Allocated Budget (k$)	$150	$200	$200	$200	$200

Technical Barriers And Targets

- DOE Technical Barriers For Fuel Cell Components
  - O. Stack Materials and Manufacturing Cost
  - P. Durability
  - Q. Electrode Performance

- DOE Technical Barriers For Fuel Cell System For 2010 (Transportation Propulsion Systems)
  - Cost $30/kW
  - Durability - 5000 h lifespan

Approach: Focus On MEA *Processing* And *Aging* Effects On Performance

- Studies are typically designed to evaluate several aspects of MEA *processing* on performance using high-resolution electron microscopy techniques:
  - effect of recast Nafion content in catalyst layers
  - effect of different electrocatalysts (Pt, PtRu, Pt_3Cr, PtCoCr)
  - effect of catalyst application technique (hand vs. mechanical)
  - effect of H_2SO_4 boiling step
- Structural changes to MEA during *aging* and understanding failure/degradation mechanisms

  MEAs received have been aged for times up to ~5000 h

Project Safety

- 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

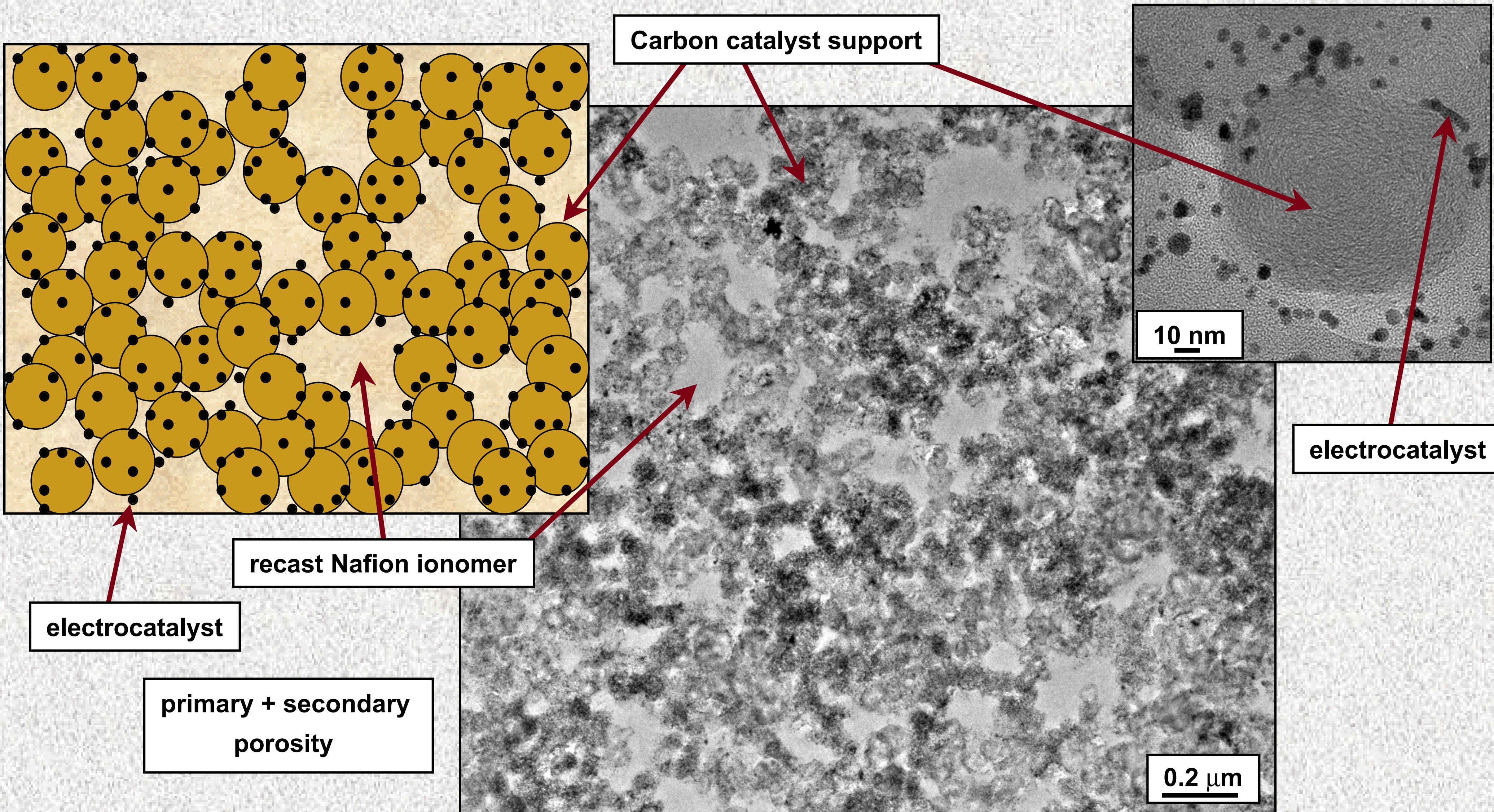
MEA Characterization Project Timeline

1999-2003	2004-2007
Technique Development (Ultramicrotomy For TEM) → Verification of Preparation & Microscopy Techniques	Technique Applied to Problem Solving → Aged MEAs → MEA Processing Effects → Working with PEMFC Manufacturers on Relevant FC Issues

Technical Accomplishments And Progress

- FY 1999-2003, techniques were developed to produce uniformly thin (<100 nm) MEAs using ultramicrotomy for TEM/STEM analysis
- In FY 2004, program has been redirected to focus on using the state-of-the-art microscopy facilities at ORNL *to solve problems and work directly with customers*
- FY 2004, techniques were improved to provide rapid specimen preparation of MEAs already at ORNL and to initiate new collaborations for MEA characterization
  - Significant progress made on characterization of LANL-produced MEAs (processing and aging effects)
  - Initial stage of an existing collaboration Gore Fuel Cell Technologies was completed
  - 4 new proprietary collaborations were initiated

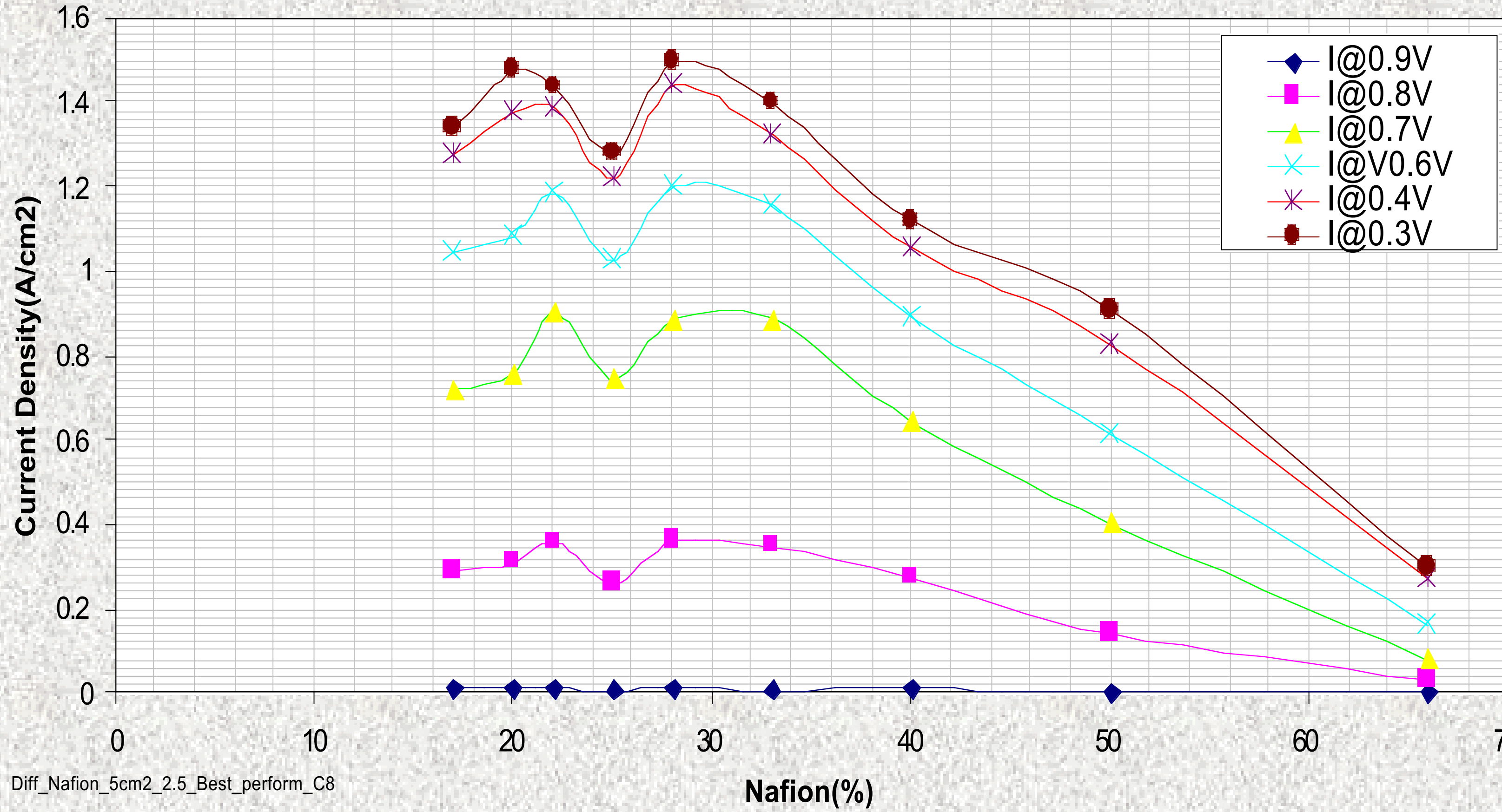
TEM Is The Primary Characterization Tool Used To Evaluate MEA Microstructure



High-performance MEA incorporates recast Nafion ionomer
gas, electrons, protons to active catalyst sites → increasing "triple access"

Completed Study With LANL Evaluating Nafion Content On Cathode Performance

- Performance measurements were conducted at LANL in single cell test
- 6 MEAs (prepared using the “thin film decal” method) were provided by LANL for microstructural evaluation
  (17%, 20%, 25%, 28.8%, 40%, and 66.7% recast Nafion)
- Distinct microstructural differences were observed which were correlated with performance

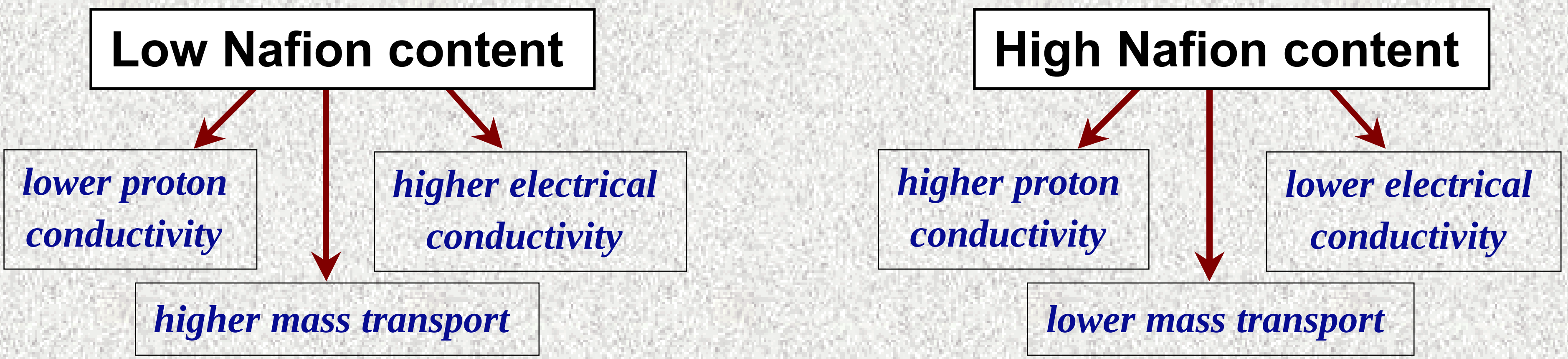


A Microstructural "Compromise" Must Be Established To Optimize Performance

Catalyst layer performance is affected by:

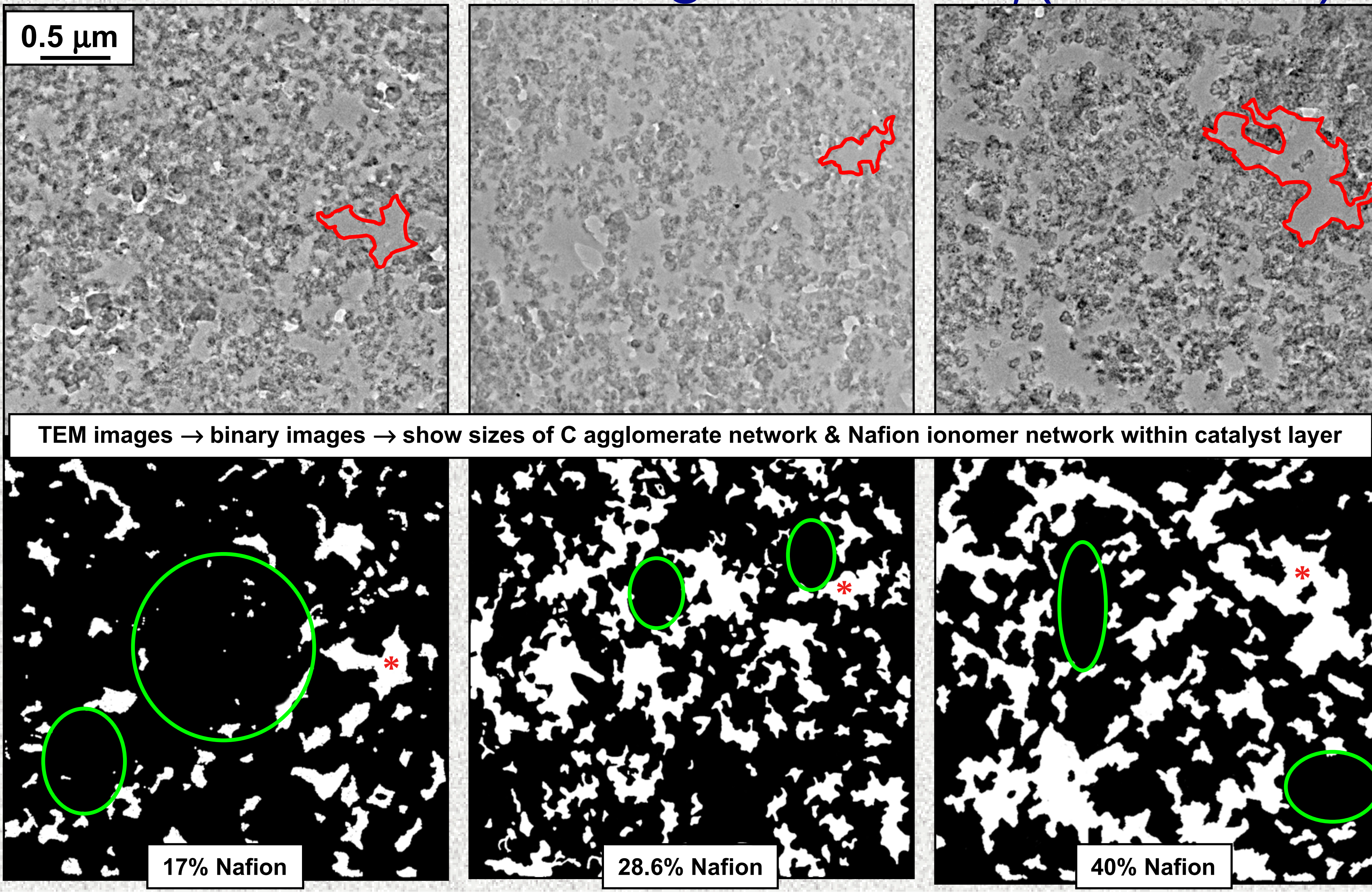
- **Proton conductivity (Nafion)**
- **Electronic conductivity (Pt/C)**
- **Mass transport of gases (porosity)**

Interpenetrating percolating networks for conduction and cathodic ORR



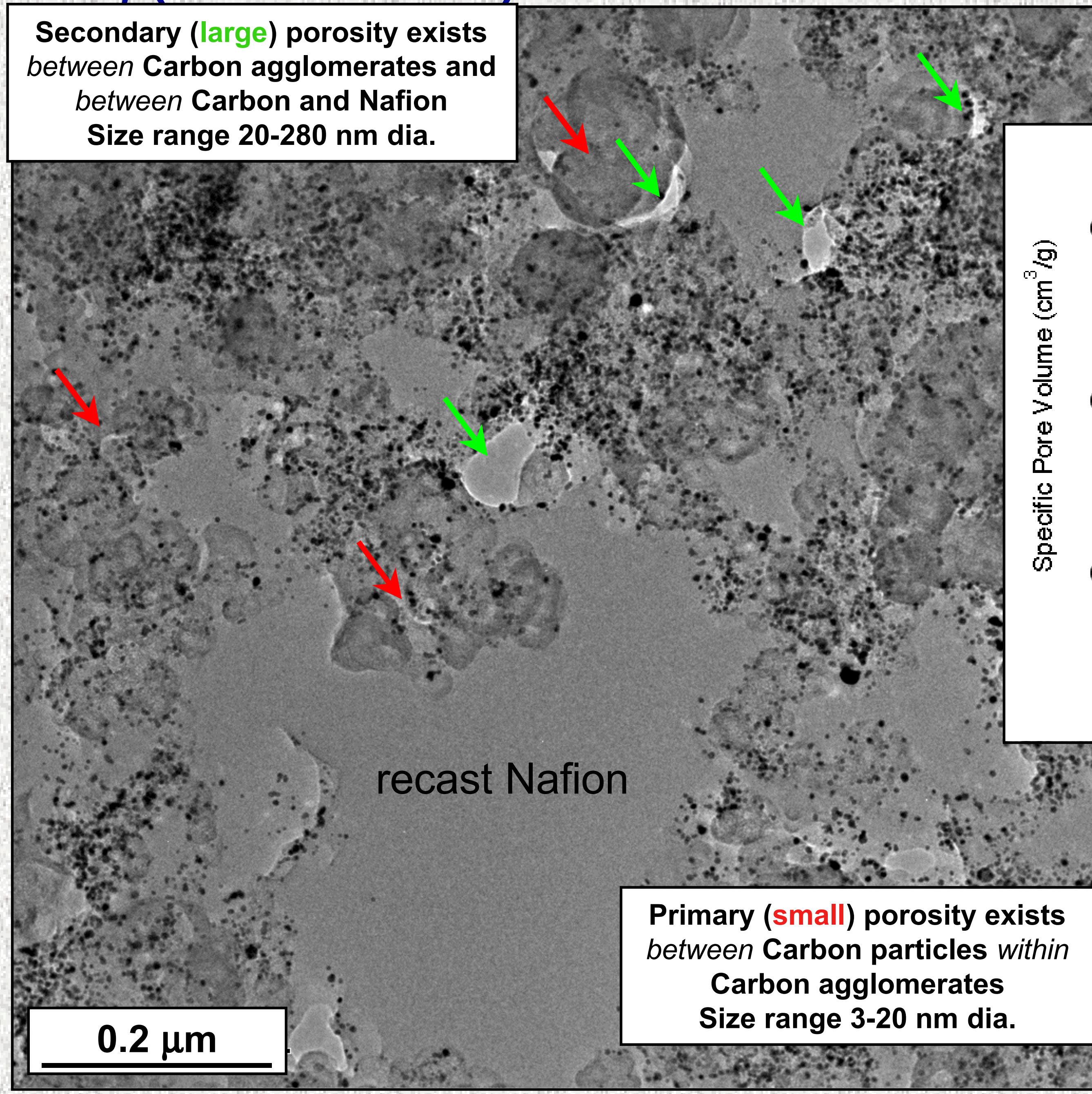
How does the Nafion content affect the distribution of (1) carbon agglomerates and (2) porosity and what is the effect on performance?

TEM Of Cathode Showed Differences In Carbon & Nafion Region Sizes f(%Nafion)

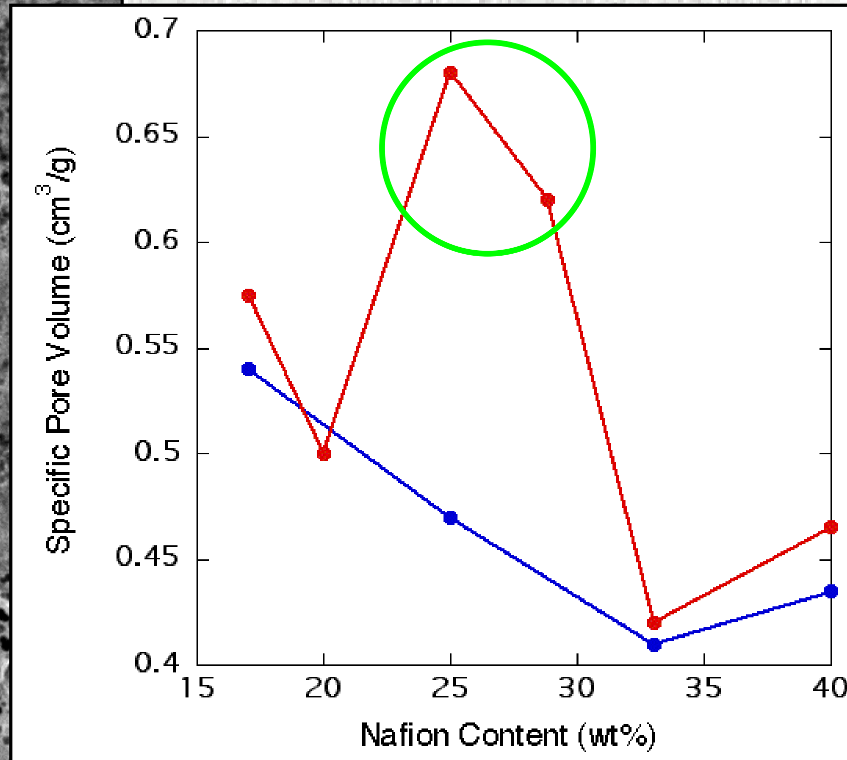


Pore *Size Ranges* Do Not Change *f*(%Nafion) But *Vol%* Of Porosity Does

Secondary (large) porosity exists *between* Carbon agglomerates and *between* Carbon and Nafion
Size range 20-280 nm dia.



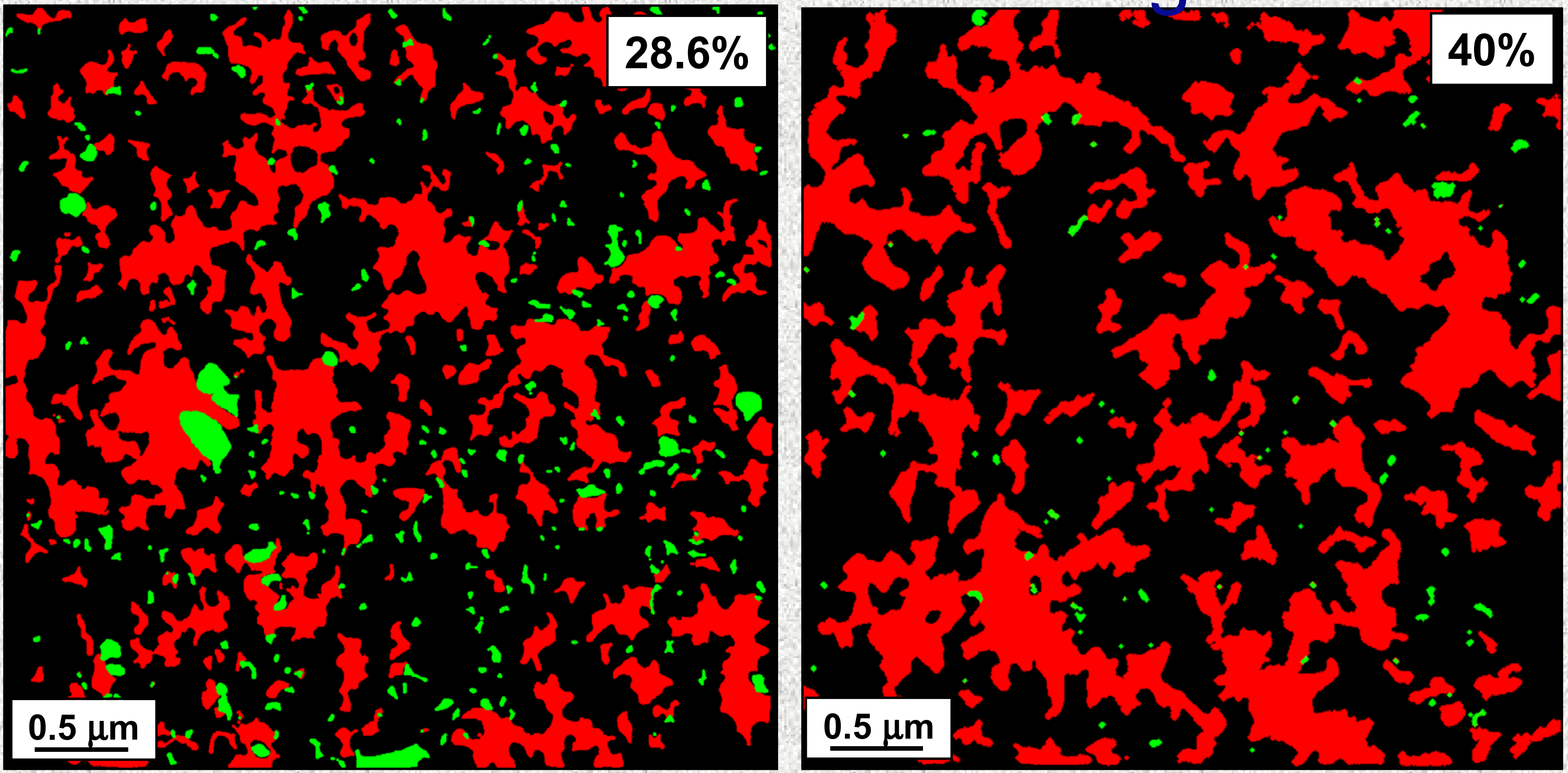
Primary (small) porosity exists *between* Carbon particles *within* Carbon agglomerates
Size range 3-20 nm dia.



Secondary porosity plays critical role in mass transport and exhibits major change as a function of Nafion content in cathode.

Primary porosity decreases with Nafion content in cathode.

Increased Pore Vol% And Improved C And Nafion Distribution → Percolating Networks



Overlapping binary images show relationship between Nafion ionomer - C agglomerate - pore networks

• Amount of secondary porosity is consistently much greater in 28.6% Nafion •

• Improved (more homogeneous) Carbon and Nafion distribution in 28.6% Nafion •

• Reduced Carbon agglomerate and isolated Nafion region size in 28.6% Nafion •

Increased "triple access" to active catalyst sites!

Completed Study With LANL Evaluating Effects Of Aging On MEA Performance

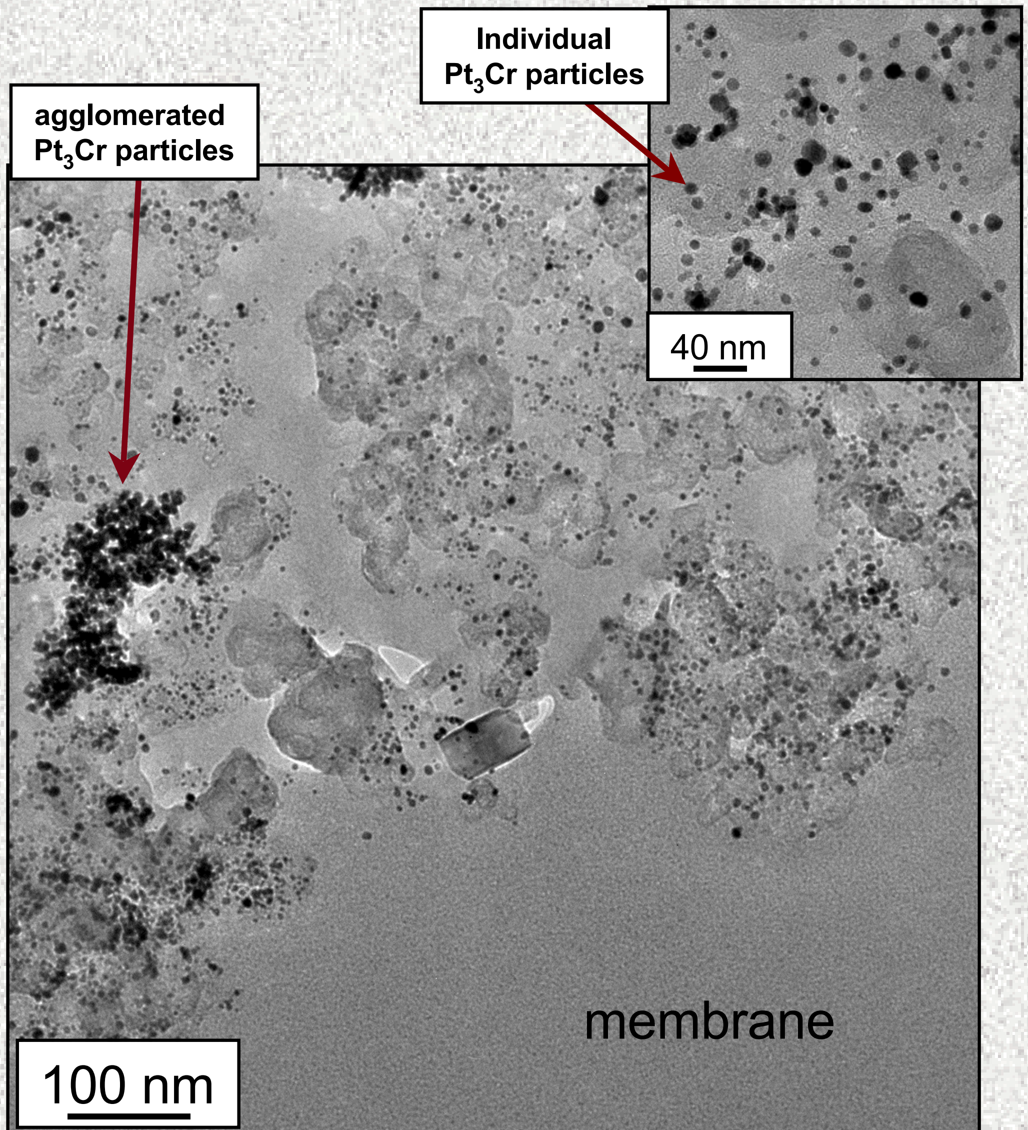
- Performance measurements were conducted at LANL
- 2 sets of fresh & aged MEAs provided for microstructural evaluation to elucidate MEA degradation/failure mechanisms

  (1) C:PtCoCr at 0.4mg PM/cm^2, A:PtRu at 0.27mg PM/cm^2

  (2) C:Pt_3Cr at 0.2mg PM/cm^2 , A:Pt at 0.2mg PM/cm^2
- MEA (1) was aged until failure ~2200 h
- MEA (2) aged in 500 h increments for total aging time of 1000 h

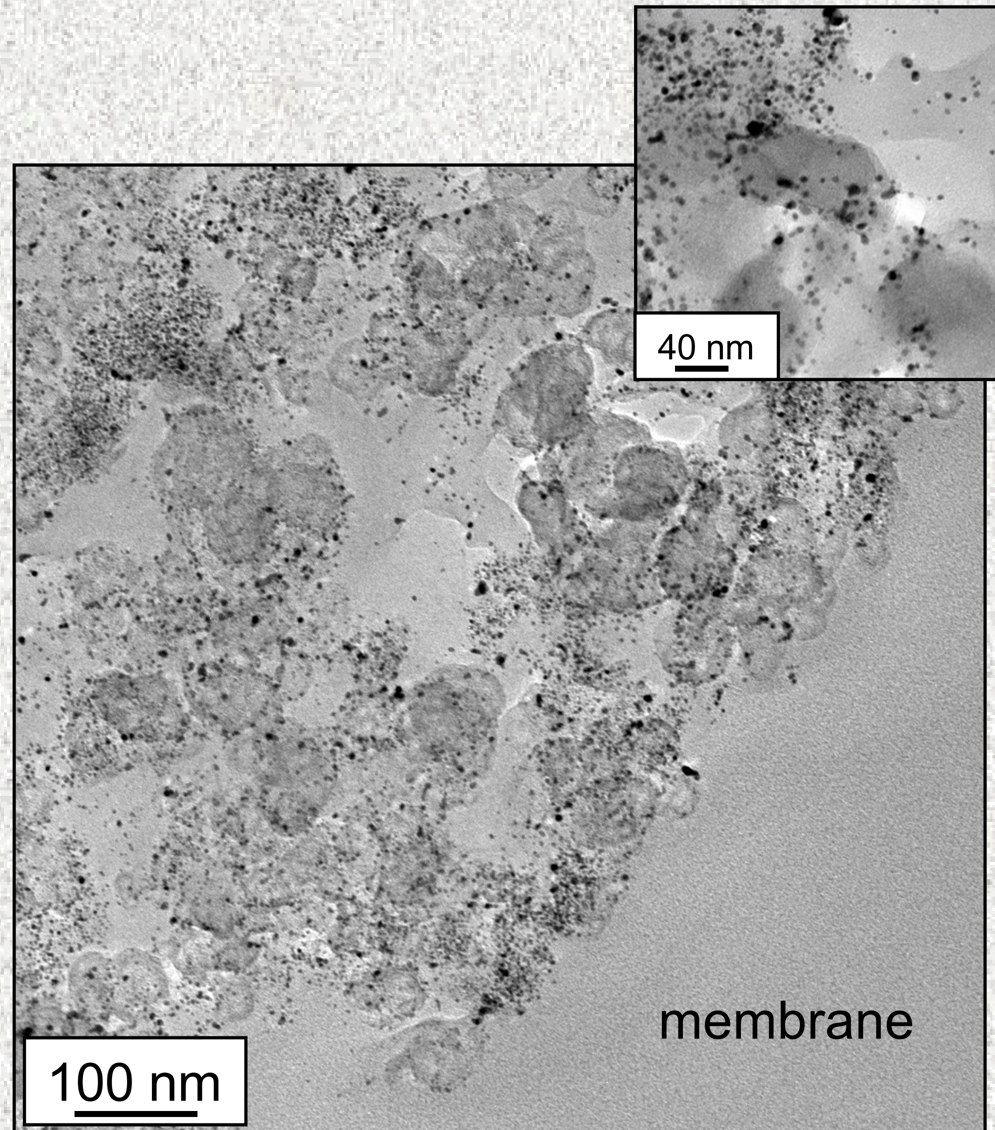
Microstructure Of Fresh LANL MEA

Cathode Pt_3Cr/C



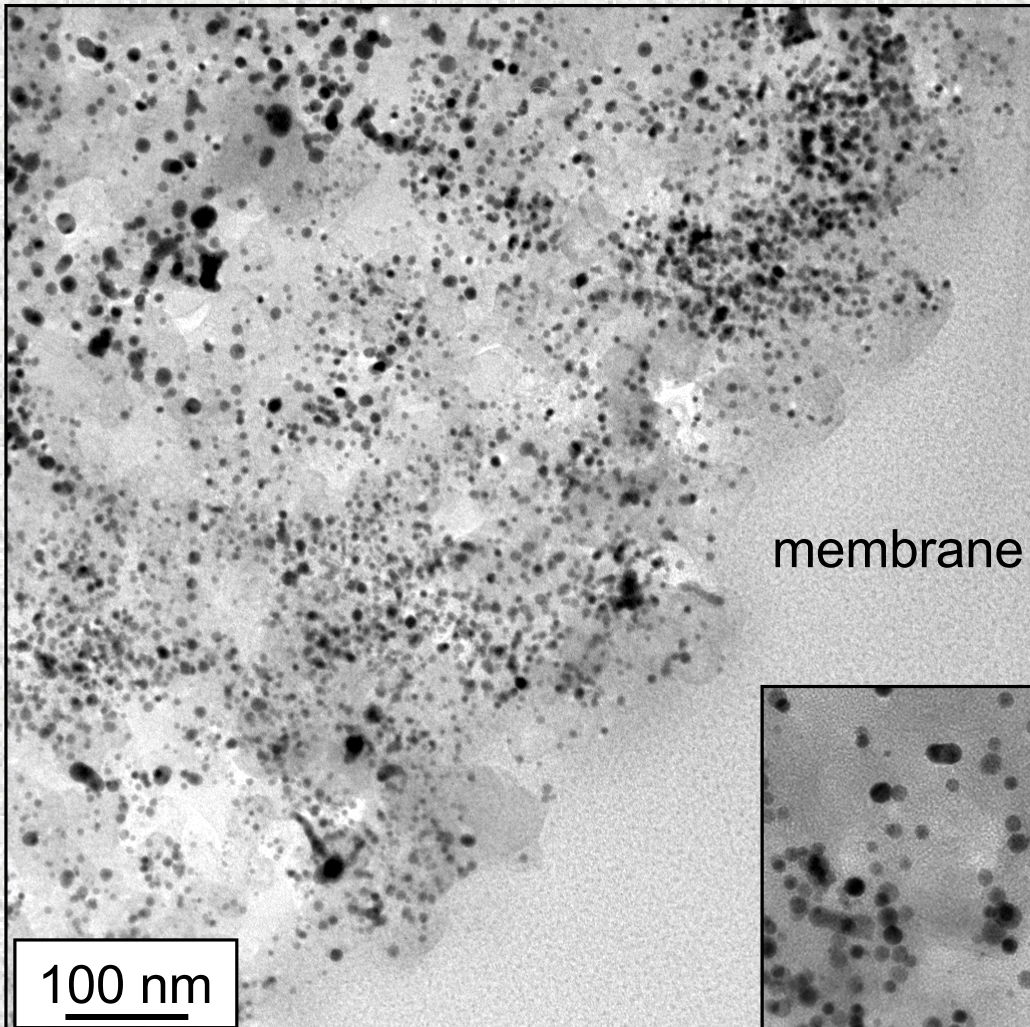
Cathode **- Pt_3Cr particle size ~ 3-10 nm**
Inhomogeneous dispersion of catalyst

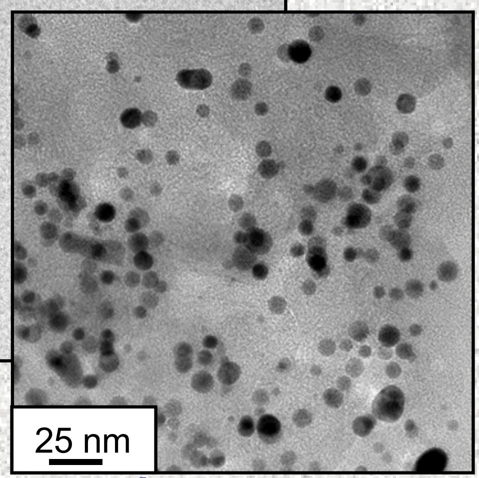
Anode Pt/C

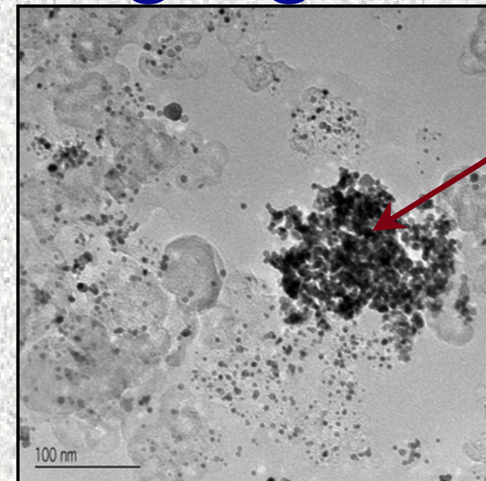


Anode **- Pt particle size ~ 1- 12 nm**
Homogeneous dispersion of catalyst

Microstructural Changes In MEA Cathode Were Observed After Aging For 500 h

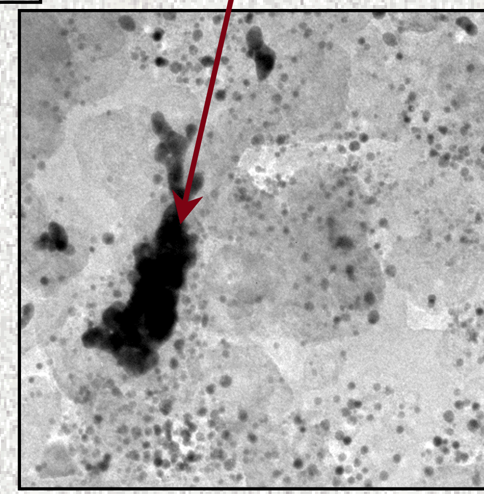






Dense regions of Pt_3Cr in fresh MEA cathode consist of individual Pt_3Cr particles

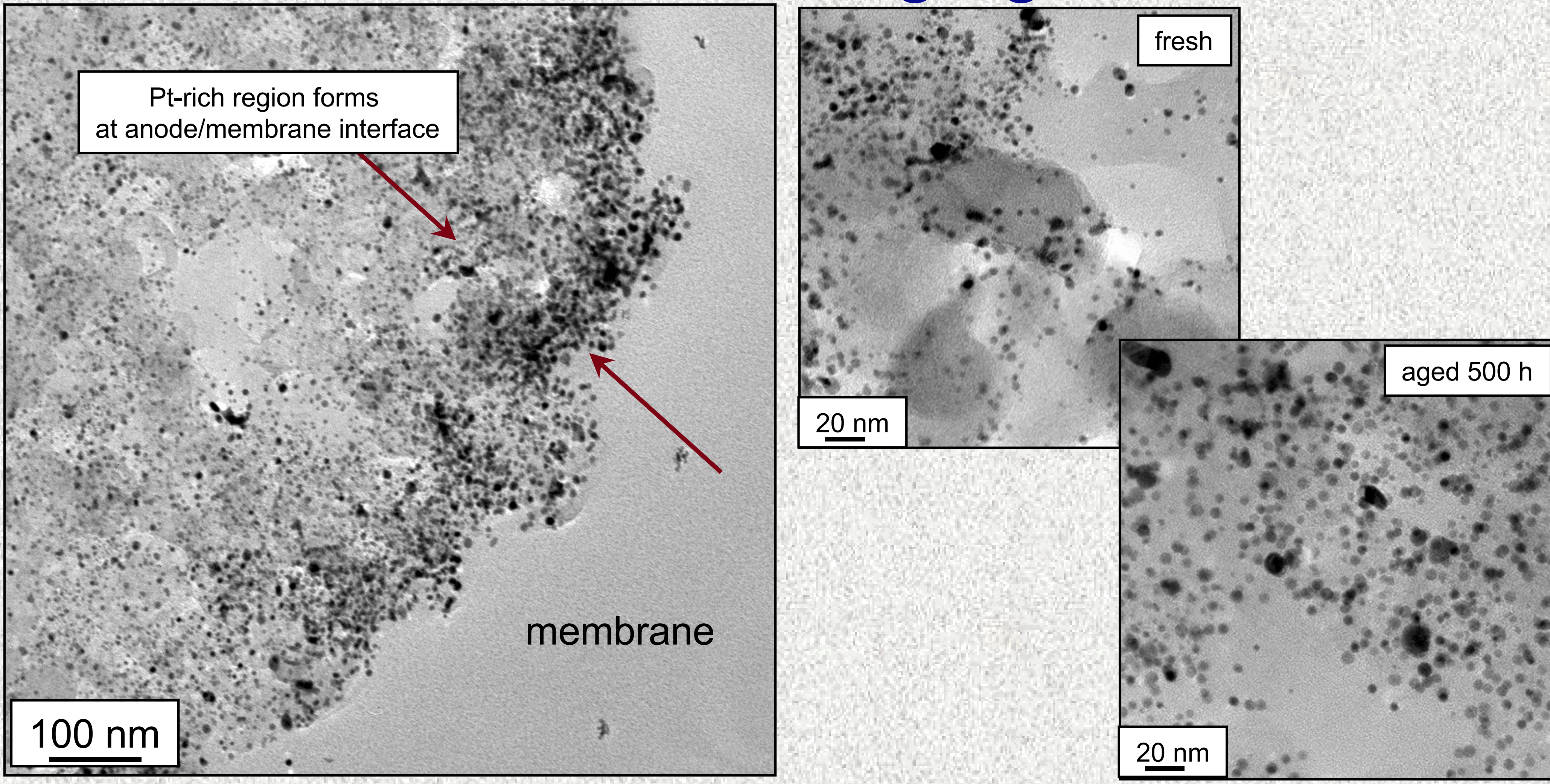
After aging for 500h, the densely packed Pt_3Cr particles sinter together



Pt_3Cr particle coarsening/sintering observed in cathode

3 - 10 nm in fresh ⟶ 6 - >>20 nm 500 h aged

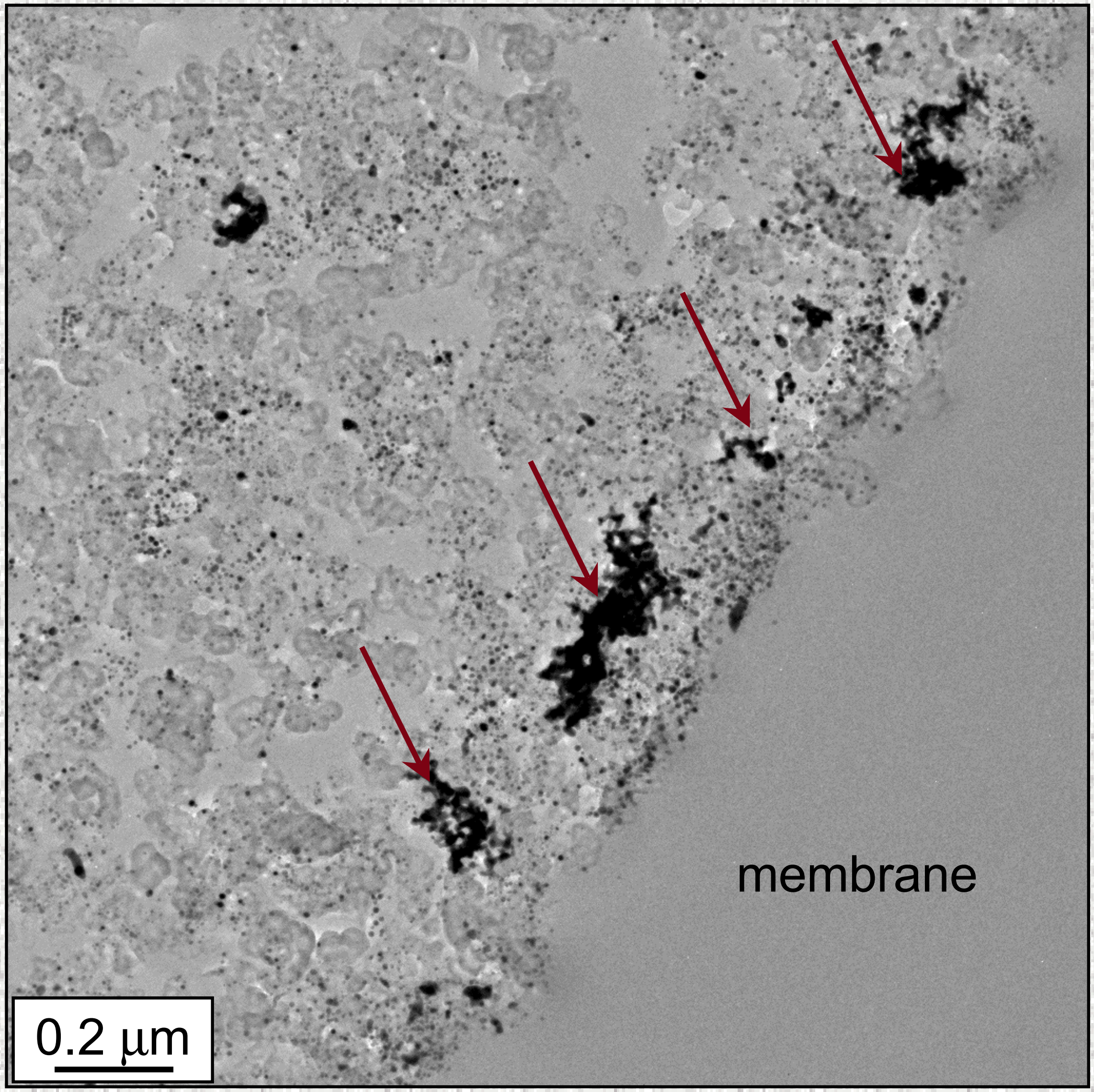
Redistribution/Migration Of Pt In Anode Observed After Aging 500 h

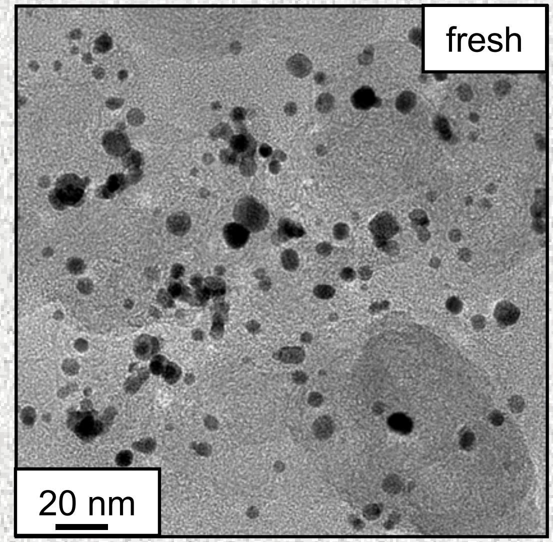


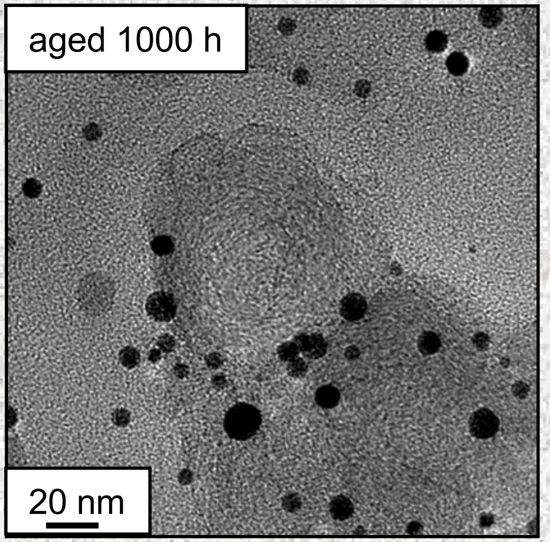
Membrane/Anode interface Pt-enriched after 500 h accompanied by Pt coarsening (~2.5X)

1-12 nm in fresh ⟶ 5-15 nm 500 h aged

Aging MEA For 1000 h Results In Pt_3Cr-Enrichment At Membrane/Cathode Interface

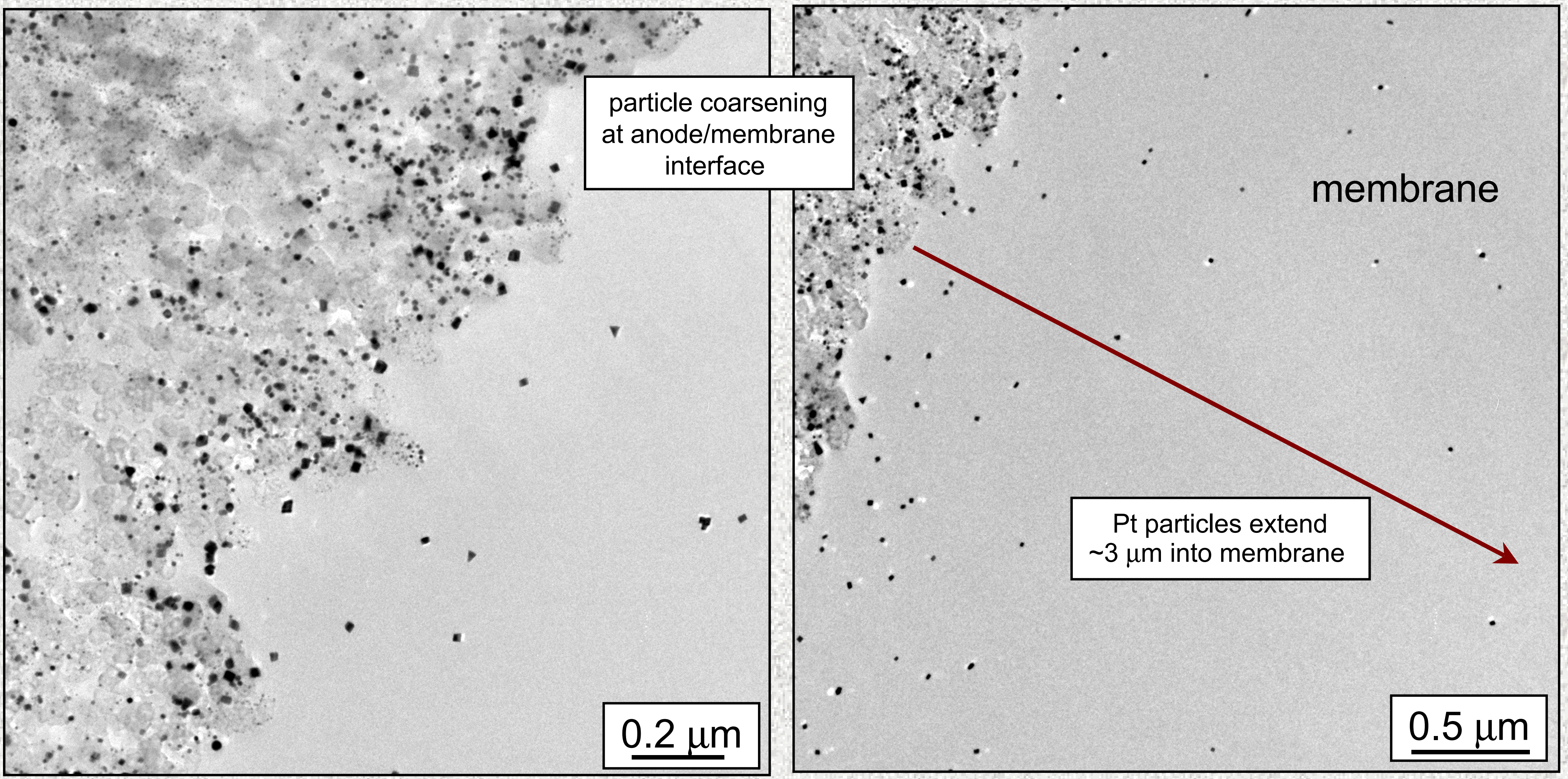






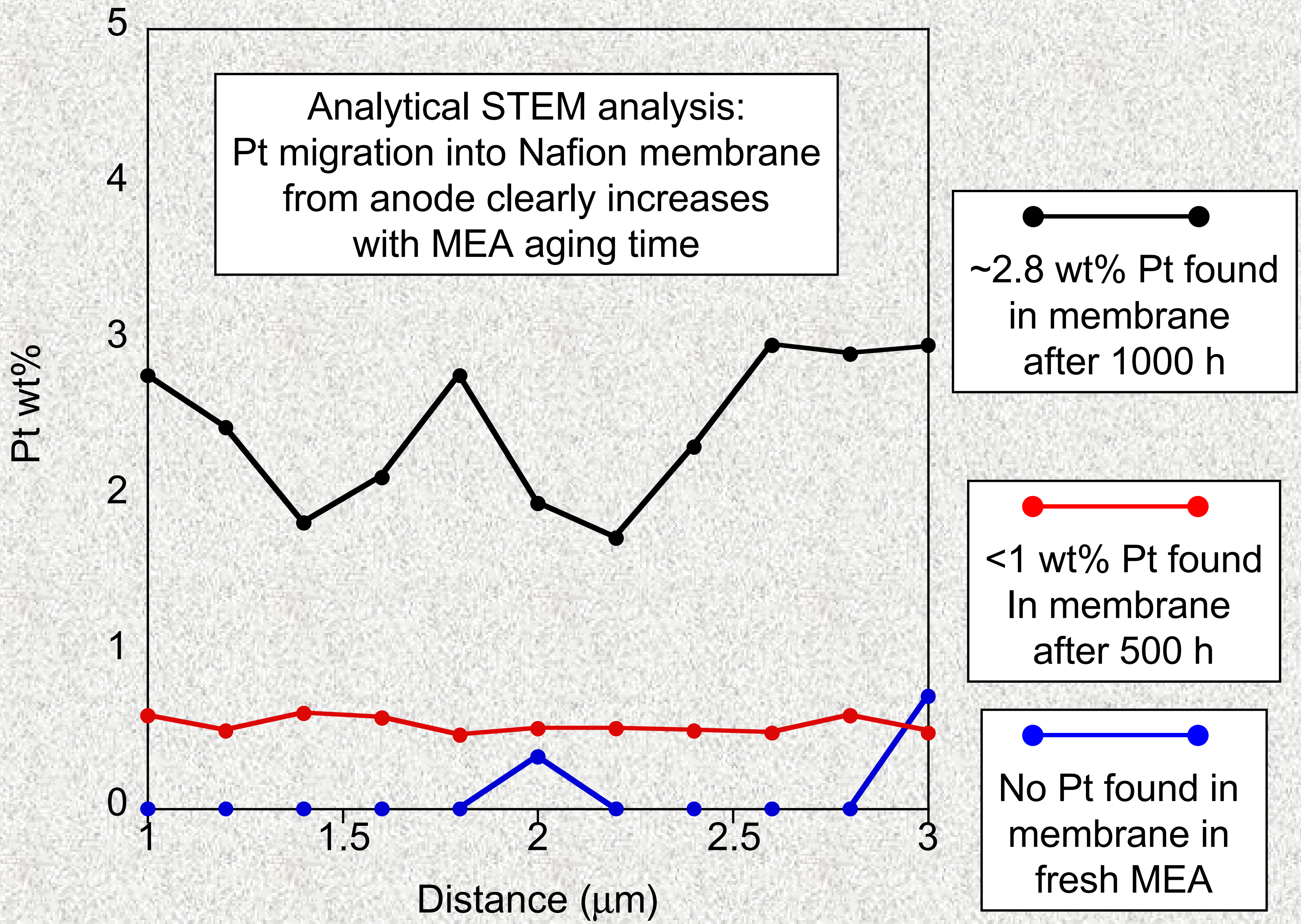
Minor additional Pt_3Cr particle coarsening/sintering observed in cathode from 500 h to 1000 h age

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

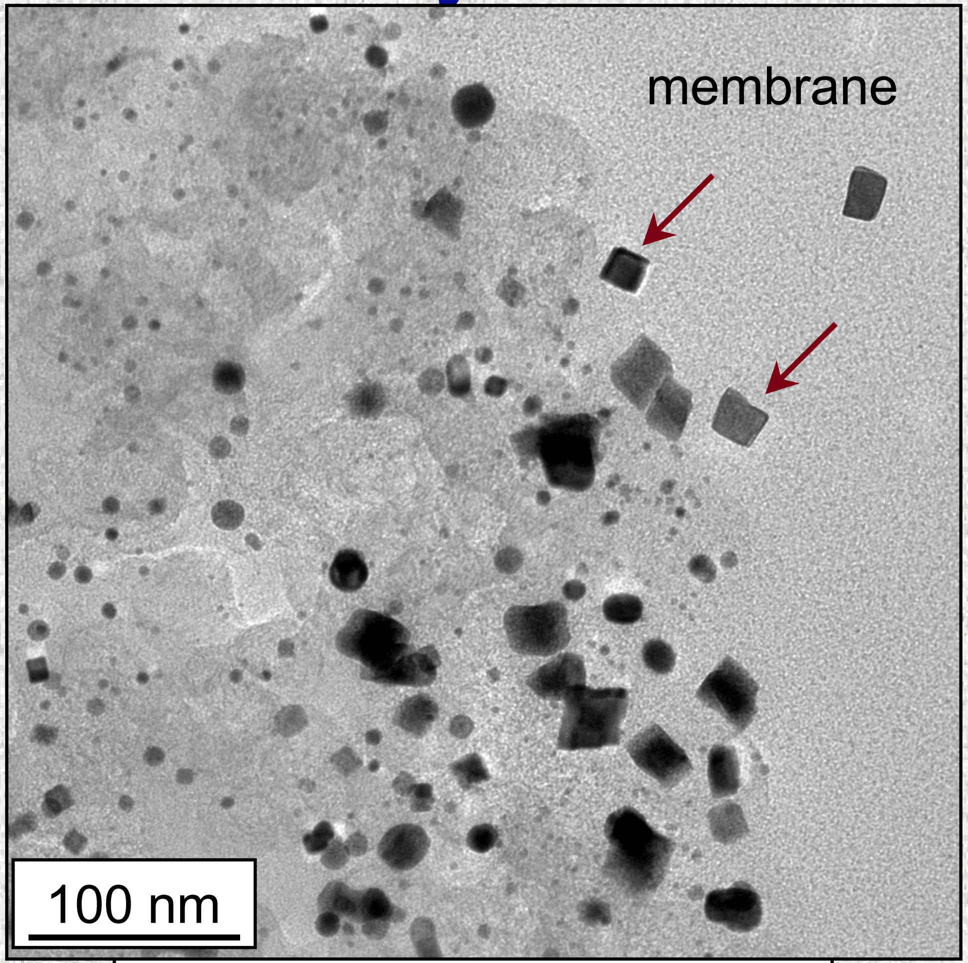


Pt-containing particles observed ~3 µm into Nafion membrane

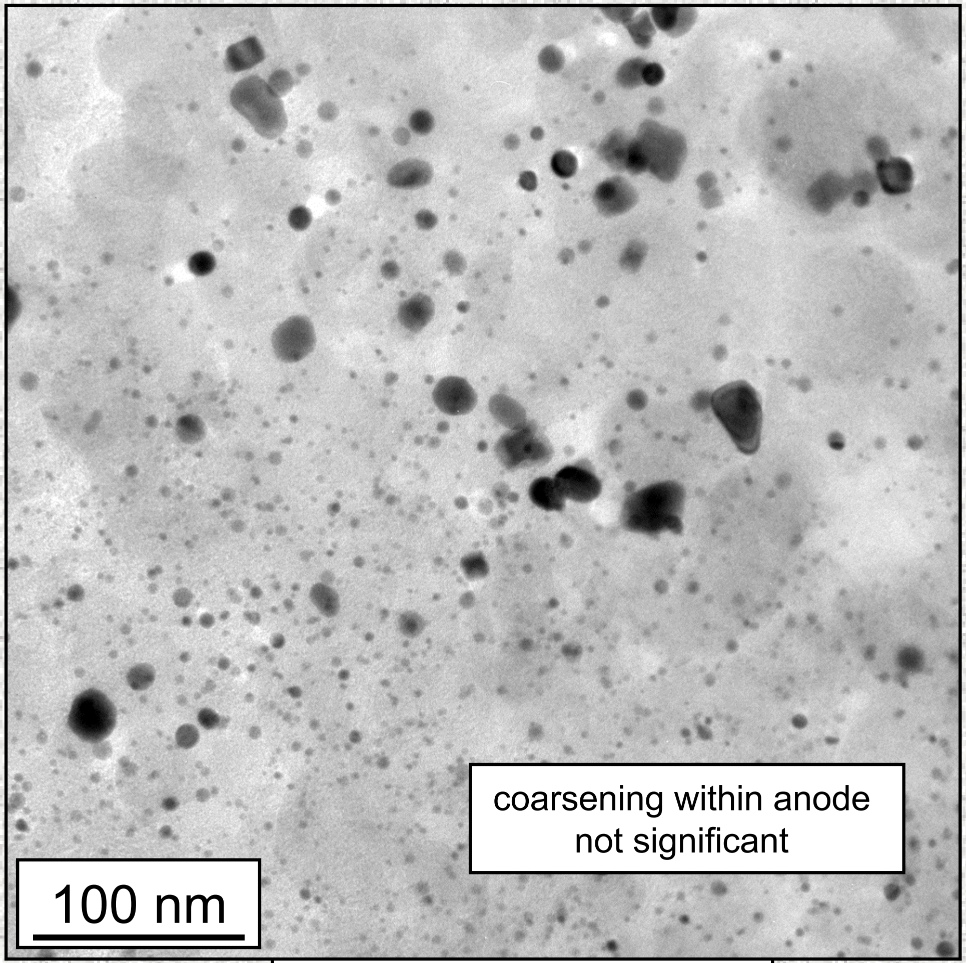
Increased Pt Diffusion From Anode Side Into Membrane Observed With Aging Time



Coarsening of Pt Catalyst Observed Primarily at Anode/Membrane Interface



anode/membrane interface



In center of anode

Pt particle shape change in addition to coarsening

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

Collaboration With PEMFC Manufacturers Is Critical To Success Of This Program

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

ORNL/LANL collaboration is ongoing and is the primary topic of this presentation

- ***Additional Proprietary Collaborations With:***
  - Gore Fuel Cell Technologies (*as-processed, aged MEAs, 1st stage completed*)
  - Plug Power (*as-processed & aged MEAs, in progress*)
  - Fuel Cell Energy (*as-processed & aged MEAs, completed*)
  - Battelle Memorial Institute (*under development*)
  - Nuvera Fuel Cells (*co-investigators on proposal*)

Response To 2003 Reviewer Comments

- ***Not enough focus in activity, ORNL has great tools but is not being challenged, more direct link to problem solving:***

  FY2004 work has focused on working directly with collaborators to provide quantitative imaging, composition, and degradation data to solve their problems and provide mechanistic understanding

- ***More correlation with single-cell testing and additional characterization techniques:***

  TEM/AEM data is being correlated with other characterization techniques, such as porosimetry, as well as aging/performance data

- ***Stronger teaming with PEMFC manufacturers is necessary, too few industrial collaborations, show relevance to FC community:***

  FY2004 focus has been on initiating collaborations with other laboratories and industry and making rapid progress on existing LANL collaboration. To date, three new collaborations have been initiated and two more are being processed

  A strong emphasis has been placed on using the advanced microscopy techniques available at ORNL to provide ***relevant*** microstructural information for the optimization of MEA processing, not just as a demonstration of high-resolution characterization technique. Problem solving is a primary goal.

Future Work

- ***Remainder of FY 2004***
  - Complete work currently underway with LANL and initiate new studies on aging effects
  - Improve TEM preparation technique for preparing GDLs
  - Further evaluate the chemical/compositional properties of recast Nafion ionomer and Nafion membrane using advanced electron microscopy techniques such as EELS
  - Complete characterization effort with current collaborators and work with these manufacturers to establish new studies
- ***Goals for FY 2005***
  - Continue collaborative work with PEMFC laboratories/manufacturers to provide the relevant microstructural data regarding MEA degradation, performance, and failure