Microstructural Characterization Of PEMFC MEAs

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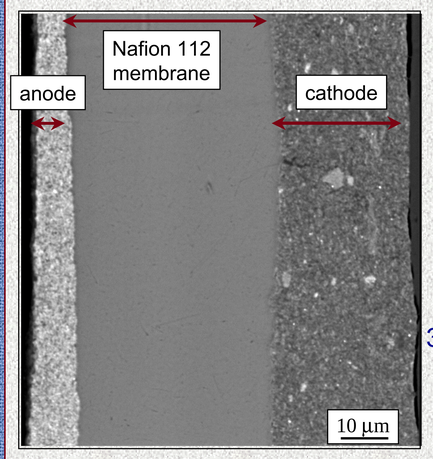
Program Objectives

- ***Collaborate*** with PEMFC developers/manufacturers to evaluate MEAs using advanced microstructural characterization techniques
- ***Elucidate*** MEA degradation mechanisms
  - Structural and compositional changes as a function of MEA processing
  - Morphological changes occurring during MEA aging/use
- ***Optimize*** MEA performance by utilizing the microstructural information

Collaboration with industry, academia, and national labs is welcome!

For This Study, MEAs Were Produced At Los Alamos National Laboratory (LANL)



Typical LANL MEA cross-section

MEAs were fabricated at LANL using the "decal process":

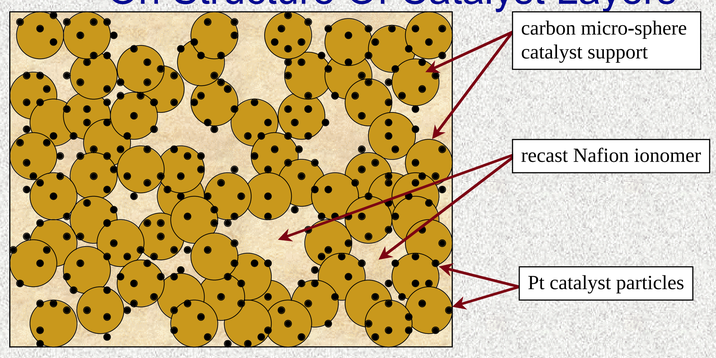
1. catalyst inks painted onto Teflon-coated fiberglass substrate (decal) and heat-treated
2. decals hot-pressed onto both sides of Nafion 112 membrane (5min @ 205°C)
3. decals peeled off leaving MEA
4. MEA boiled in 0.5M H_2SO_4 for 2h, boiled in DI H_2O For 2h, then dried @60°C for 30min

MEA Processing And Aging Effects Are The Focus Of ORNL/LANL Collaboration

- The full study was designed to evaluate several aspects of MEA *processing*, including effects of:
  - recast Nafion content in catalyst layers
  - different catalysts (Pt, PtRu, Pt_3Cr, PtCoCr) on the distribution of recast Nafion in electrocatalysts
  - catalyst painting process (hand vs. mechanical)
  - effect of H_2SO_4 boiling step on MEA structure
- Structural changes to MEA due to *aging* were also investigated:
  - Performance was measured using LANL single cell testing system (see Springer et al, *J. Electrochemical Soc.* **140** (1993))
  - MEAs aged for times up to 4000h

Effect of Processing Parameters on MEA Structure

Effect Of Recast Nafion Ionomer Content On Structure Of Catalyst Layers

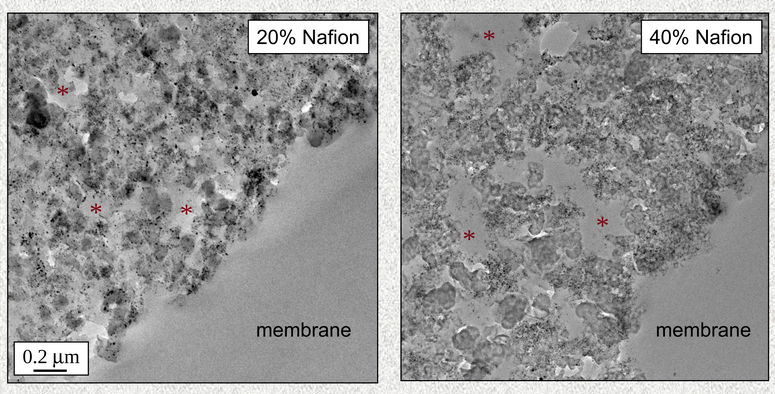


*The amount of recast Nafion polymer **within** catalyst layer is important to overall performance:*

- Binds catalyst/carbon together (structural integrity)
- Serves as proton conductor (as well as oxygen barrier)

Thus, recast Nafion content must be optimized in electrodes.

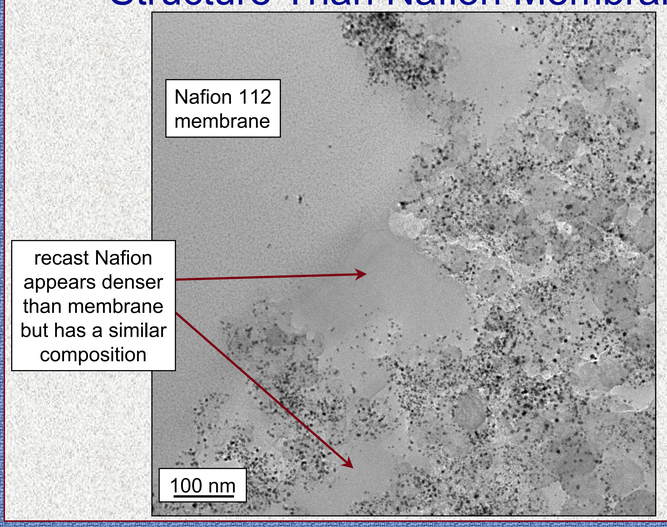
LANL MEA Electrode Recast Nafion Content Was Varied From 20%-40%



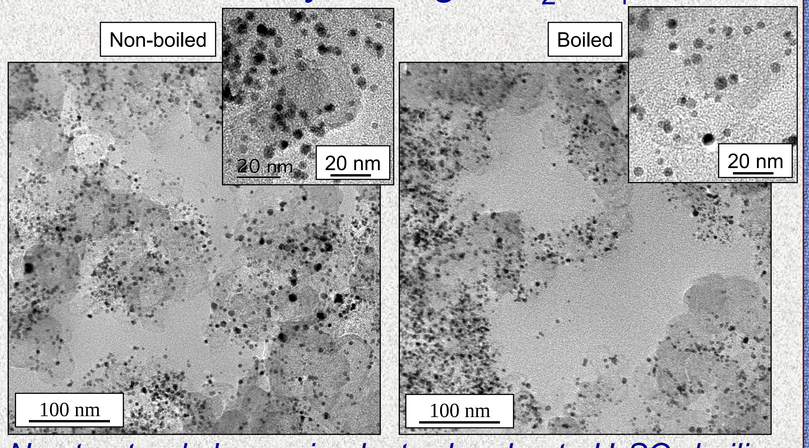
*Higher recast Nafion polymer content **within** catalyst layer (marked by *)results in a more open structure with greater separation between aggregated carbon micro-spheres.*

Pt particles are not present within recast Nafion areas of electrode structure.

Recast Nafion Polymer Has A Different Structure Than Nafion Membrane

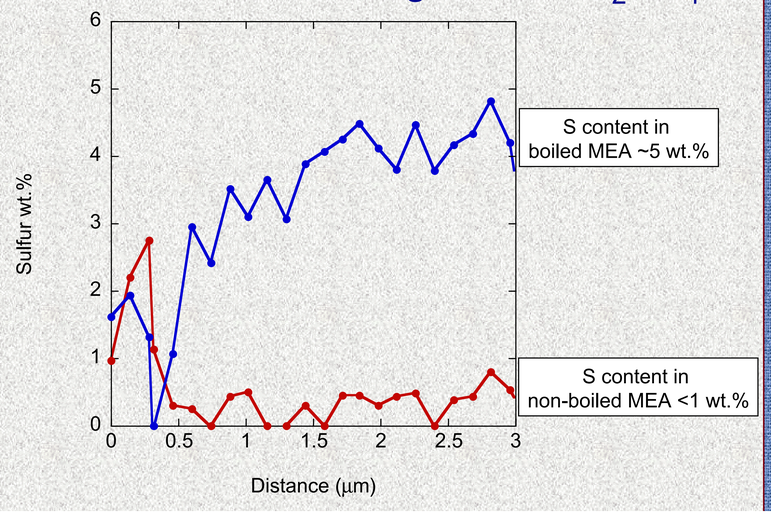


LANL MEAs Are Converted To The Proton Form By Boiling In H_2SO_4



No structural change in electrodes due to H_2SO_4 boiling. There is a compositional change in Nafion membrane.

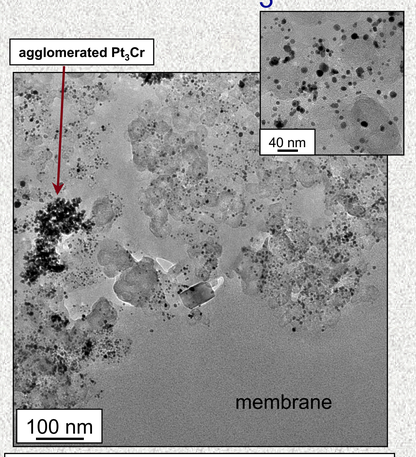
The Sulfur Content In Nafion Membrane Is Increased After Boiling MEA In H_2SO_4

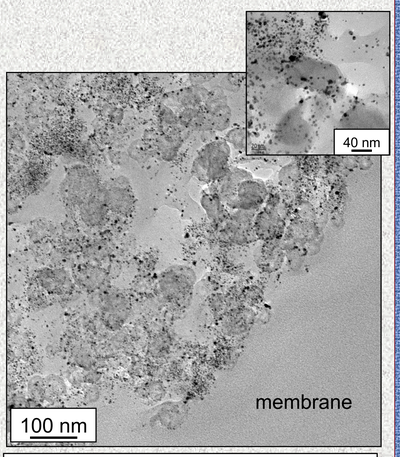


Effects of Aging on MEA Structure

Microstructure Of Fresh LANL MEA

Cathode Pt_3Cr/C Anode Pt/C

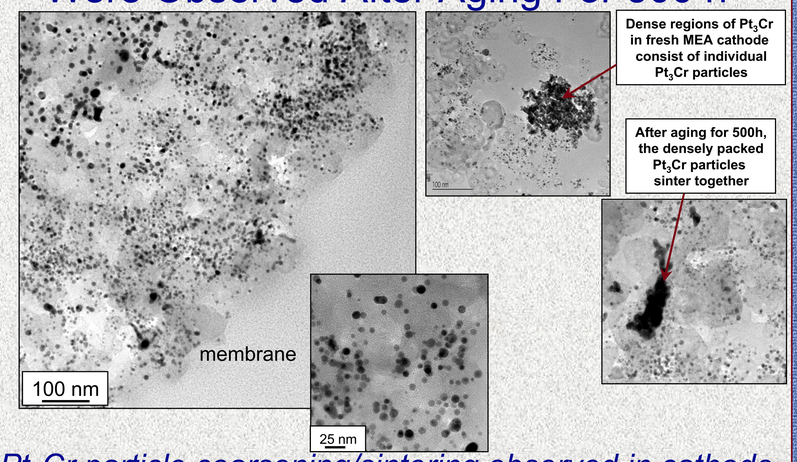




Cathode **- Pt_3Cr particle size ~ 4-12 nm**
Inhomogeneous dispersion of catalyst

Anode **- Pt particle size ~ 1- 6 nm**
Homogeneous dispersion of catalyst

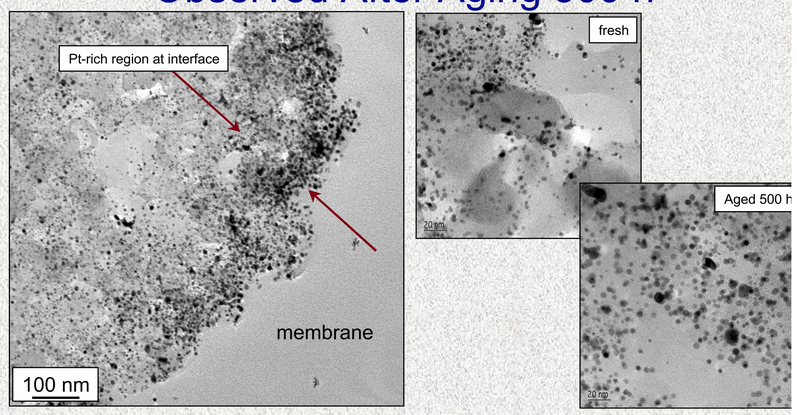
Microstructural Changes In MEA Cathode Were Observed After Aging For 500 h



Pt_3Cr particle coarsening/sintering observed in cathode

4 - 12 nm in fresh ⟶ 6 - >>20 nm 500 h aged

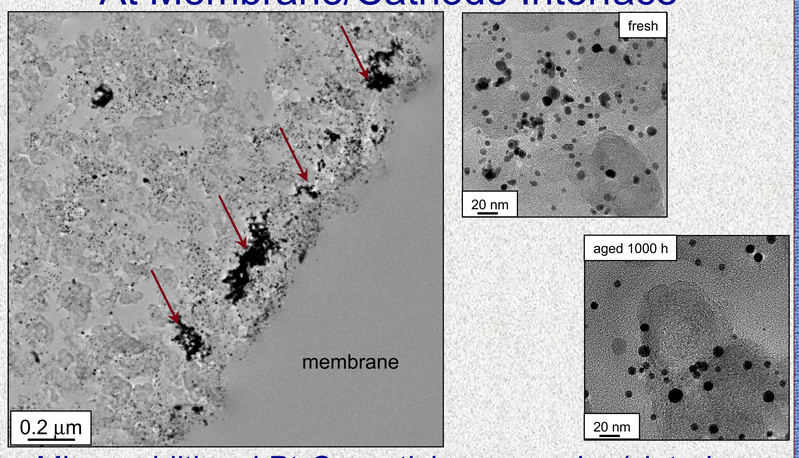
Redistribution/Migration Of Pt In Anode Observed After Aging 500 h



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

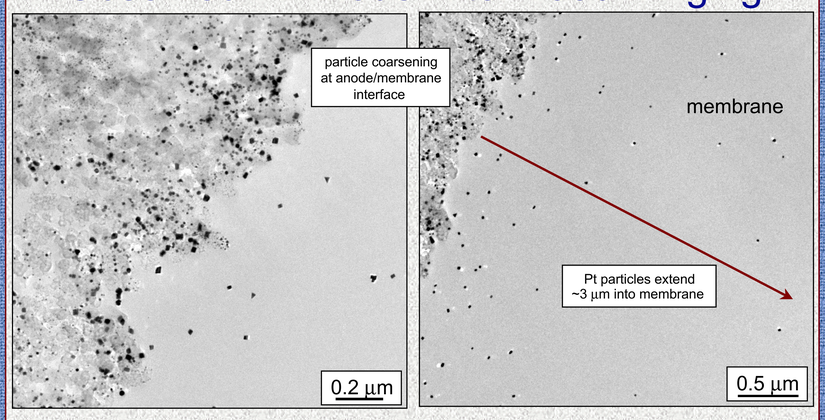
1-6 nm in fresh ⟶ 3-15 nm 500 h aged

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



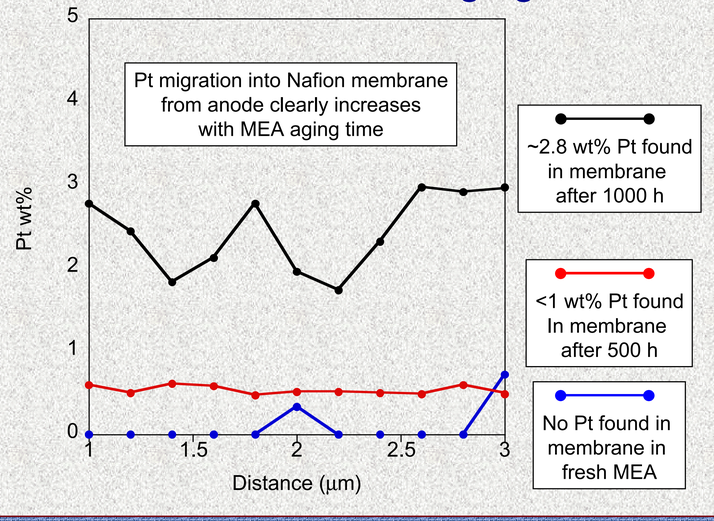
Minor additional Pt_3Cr particle coarsening/sintering observed in cathode from 500 h to 1000 h age

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

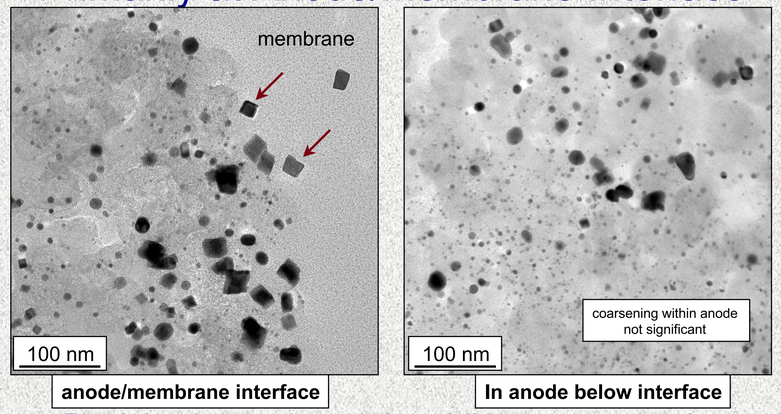


Pt-containing particles observed well into Nafion membrane near anode

Increased Pt Diffusion Into Membrane From Anode Observed With Aging Time



Coarsening of Pt Catalyst Observed Primarily at Anode/Membrane Interface



anode/membrane interface **In anode below interface**

Particle shape change in addition to coarsening

1-6 nm in fresh ⟶ 20-40 nm 1000 h aged

Due to possible Pt oxidation at interface?

A combination of microstructural characterization techniques has been utilized in this study to evaluate MEAs before and after aging. These, and future results, will be used to interpret MEA performance data and to understand MEA degradation mechanisms. Additional work in progress.

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