Analysis of Durability of MEAs in Automotive PEMFC Applications

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DuPont
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FC089

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Overview

Timeline

Start date: Sept 25, 2010

End of period 1: April 30, 2012

End of period 2: Aug 31, 2013

Currently ~20% Complete

Budget

- Total Project Funding: $5.2 M
  - DOE: $4.1 M
  - Cost Share: $1.1 M
- Total DOE Funds received: $900K
- DOE funds remaining for Budget Period 1 (ends Oct 2012): $1.06M

Barriers

Barriers addressed

- Fuel cell durability.

Technical Goals

- Cell durability model.
- MEA w/5000 hr lifetime & performance decline of <=7%

Partners

Project lead: DuPont

Subcontracts were signed on 3/26/12:

- Nissan Technical Center North America – *Kev Adjemian, Nilesh Dale*
- Illinois Institute of Technology – *Vijay Ramani*

Relevance

This project addresses several areas that intend to fill gaps in the understanding of fuel cell durability and modeling of fuel cell performance degradation.

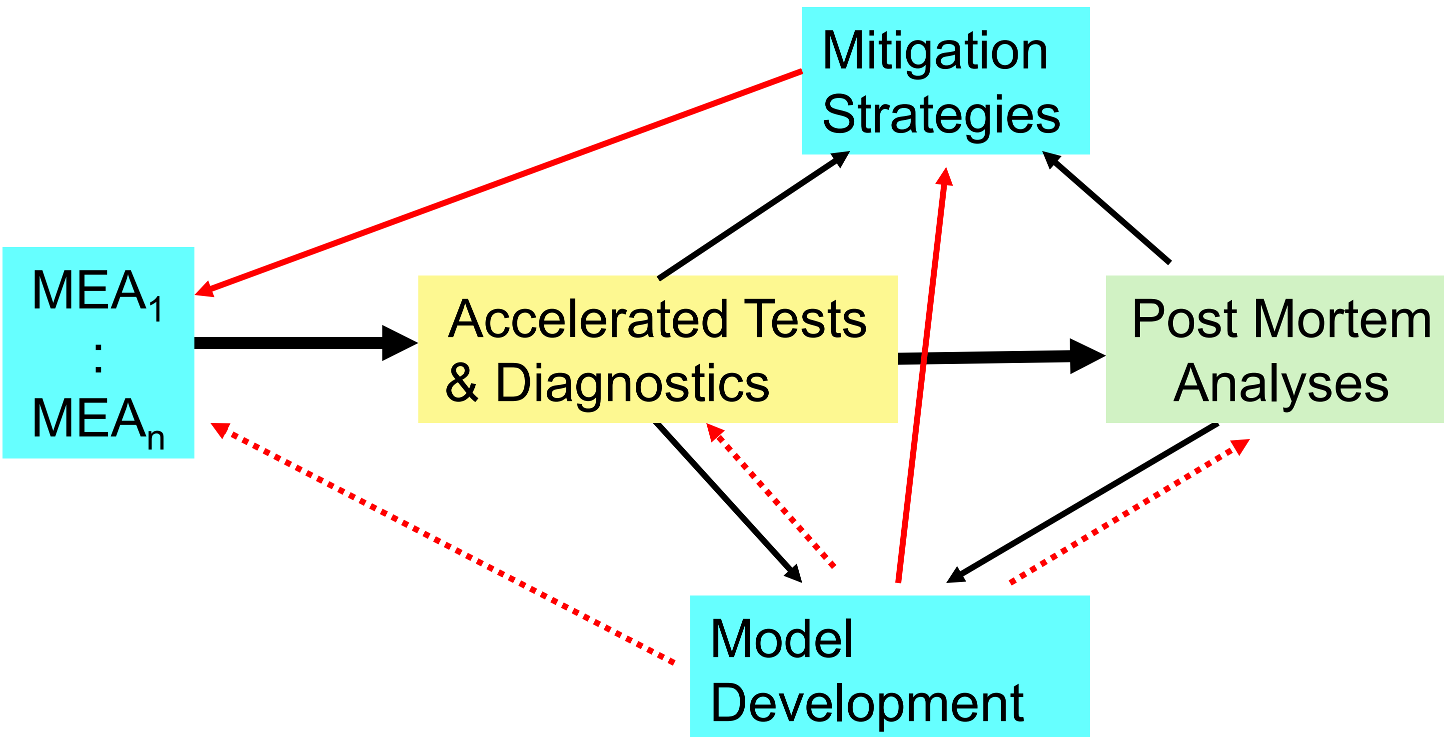
Focused on durability at low relative humidity and during automotive cycling operation, the project addresses short side-chain polymers ($-O-CF_2-CF_2-SO_3H$).

Objectives	
2011	Determine accelerated tests to be used to generate data for modeling of the individual degradation mechanisms.
2012	Develop an overall degradation model that correlates the stack operating conditions to degradation of the Membrane Electrode Assembly (MEA). (including degradation at interfaces)
2013	Develop MEAs with a design lifetime target of 5,000 hours with ≤ 7% degradation and that show a clear path towards meeting the DOE 2015 technical targets.

Approach/Milestones

Timing	Milestone/Decision Points
4/30/2012	Decide on which accelerated tests to be used in continued work. Tests will be selected based on results of post-mortem analysis. We will be evaluating: observed degradation methods vs Nissan experience, test duration, and separation of degradation mechanisms. 85% complete
9/30/2012	Selection of low-EW ionomer membrane. - Membrane design must meet accelerated durability targets. 15% complete - Results verified in repeated lab testing
10/15/2012	Define MEA design for stack test - MEA based on durable materals as determined in the lab testing. - MEA must meet minimum performance and durability goals. 15% complete
10/15/2012	**Go/No Go Decision 1 (Stack Testing)** MEA design must meet performance and accelerated durability targets with results verified in lab testing in order to proceed to fabrication and testing of a full-scale short stack. 1. Attain 5000 hr lifetime in durability in automotive cycling protocol. 2. Attain 1 kW/cm2 performance @ rated power at beginning-of-life in sub-scale testing. 3. Attain extent of performance decline over lifetime (as in #1 above) of <=7% Note: Criteria 1 and 3 above will be evaluated using projections based on accelerated testing results. (e.g., #1 will be extrapolated from 30,000 cycles).
10/31/2012	**Go/No Go Decision 2 (Completion of Model Development)** Data generated at end of the first Budget Period can discriminate among the various cell components, to allow for continued efforts on modeling. The variability determined in the initial phase of accelerated tests must be small enough to make variations in measurements as a function of time and component statistically significant to an 80% confidence level.
3/1/2013	Begin stack test. (GNG #1) 0% complete
11/1/2013	Conclude stack test. Goal = 2,000 hours. (GNG #1) 0% complete
3/31/2014	Model finalized and ready for publication. (GNG #2) 5% complete

Approach



Accelerated Tests & Diagnostics
ECSA, Crossover, …
CO_2 , F^-, SO_3^- emissions, …
RDE tests, chemical analysis of effluent, …

Post Mortem Analyses
TEM, SEM, Chemical Analyses, surface tension, cyclic voltammetry, FTIR, NMR, porosimetry, …

Accomplishments & Progress

Testing

- DuPont test stations modified for FCTT ASTs. Some modifications to procedure for safety and additional data requested by IIT.
- Nissan has added capability for helium/oxygen and increased data points in kinetic region of polarization curve.
- Tested multiple samples of baseline MEA with both sets of ASTs to compare mechanisms and generate initial data for model development.

Analysis and Modeling

- IIT completed program to automate analysis of polarization curves.

Milestone 1

- Completed most baseline ASTs, continuing post mortem analysis at DuPont.
- Preliminary decision on ASTs for remainder of model development work

Accomplishments: Accelerated Testing Comparison

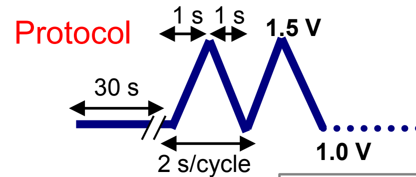
Test Protocol	Test Time	ECA Loss	IV Loss	Comments
Carbon Corrosion (Nissan Start-Stop B)	8 hrs	29-35%	30-35%	Cathode thinned ~15%
Carbon Corrosion (FCTT AST)	>400 hrs	>35%	30-35%	Cathode thinning ~25%

Test Protocol	Test Time	ECA Loss	IV Loss	Comments
Pt Dissolution (Nissan Load Cycle)	<24 hrs	35-45%	4-10%	Pt growth 5-10 nm; Pt migration (including large crystals)
Pt Dissolution (FCTT AST)	>135 hrs	>40%	14-25%	Similar to Nissan. Some larger Pt in cathode.

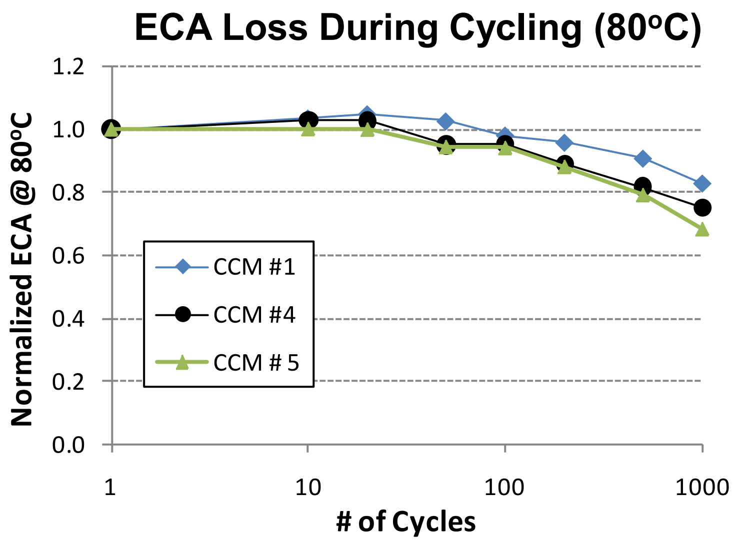
Test Protocol	Test Time	Time to fail	FER	Comments
Chemical Stability (Nissan OCV hold)	500 hrs	450-500 hrs	3-4	1 - OCV fail, 1 - no fail. Different microscopy results than FCTT AST
Chemical Stability (DOE - DuPont)	500 hrs	400 hrs	0.4-0.7	Hydrogen Crossover fail;
Chemical Stability (US Fuel Cell, DuPont)	72 hrs	N/A (72 hr)	0.05	FER is 60% of Nafion® XL; But, FER >> Nafion® XL in long-term test.

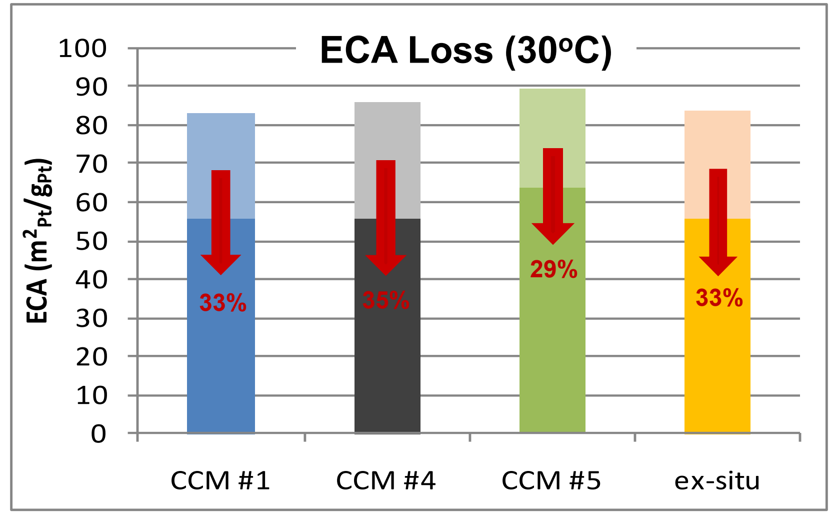
Test Protocol	Test Time	Time to fail	Cycles	Comments
Mechanical Durability (Nissan)	~1500 hrs	100 hrs	12K cycles	OCV Failure
Mechanical Durability (DOE - DuPont)	>1350 hrs	400 hrs	6000 cycles	Shorting Resistance Failure

Accomplishments:
Carbon Corrosion (Start-stop B)



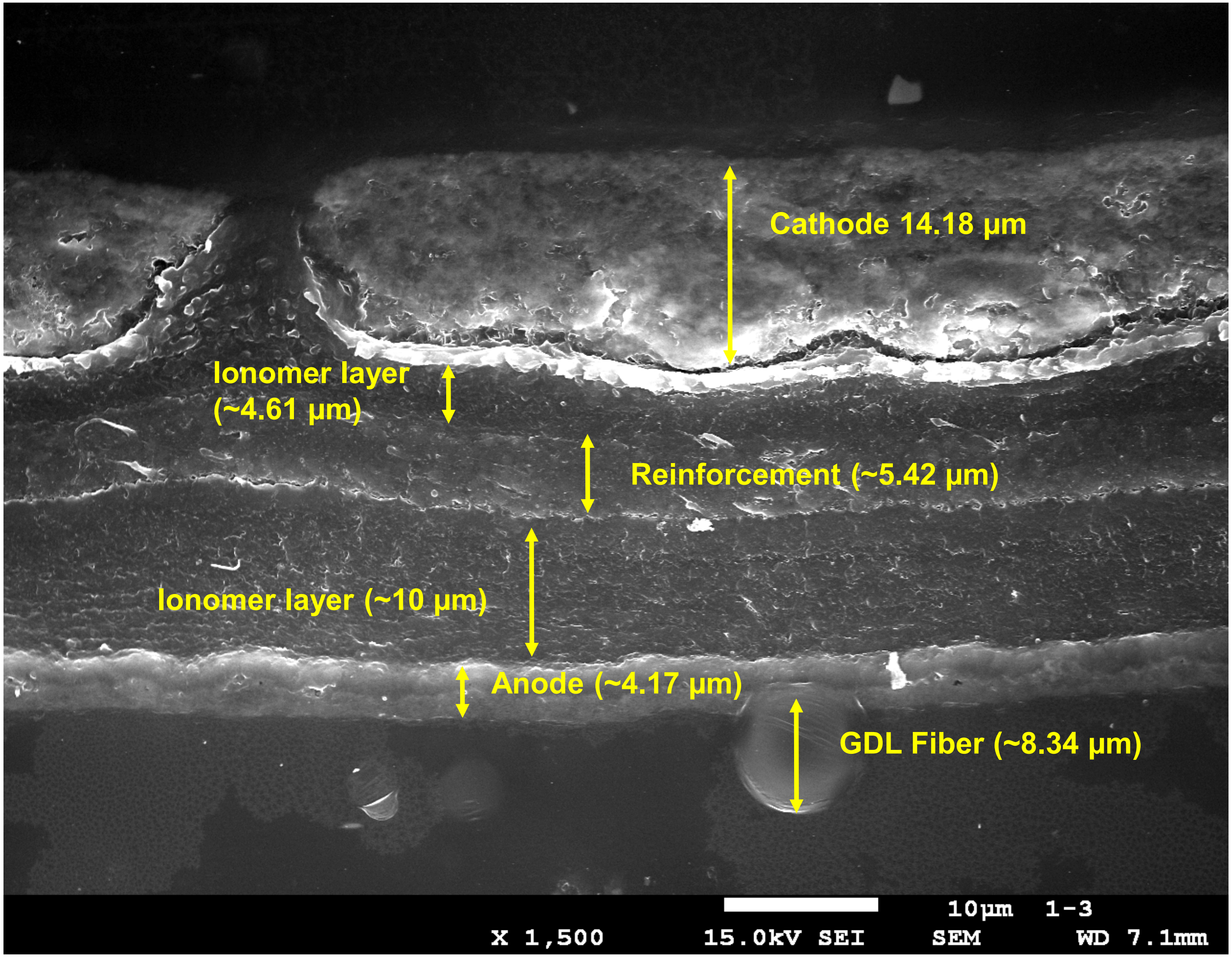
H_2/N_2 flows @ 100% RH





- Three CCMs show consistent behavior during start/stop cycling
  - Similar loss in ECA measured at 30°C
- Performance loss about 30-35% as well.
- ECA loss in the CCMs correlates very well with *ex-situ* RDE measurements of the same catalyst (TEC10F50TPM)

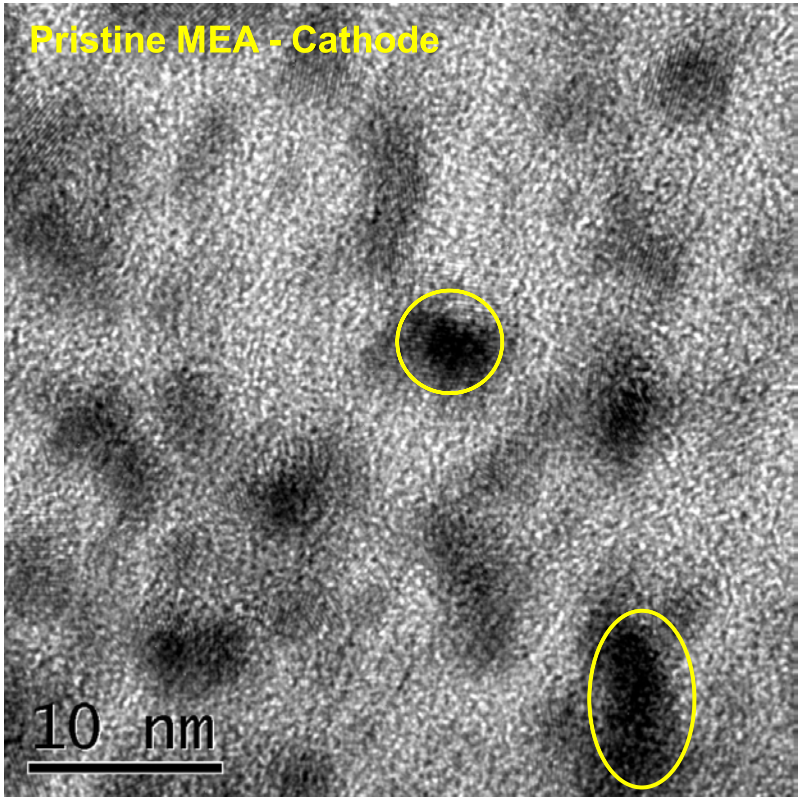
Accomplishments: Accelerated Testing
SEM: Nissan Carbon Corrosion, Thicknesses

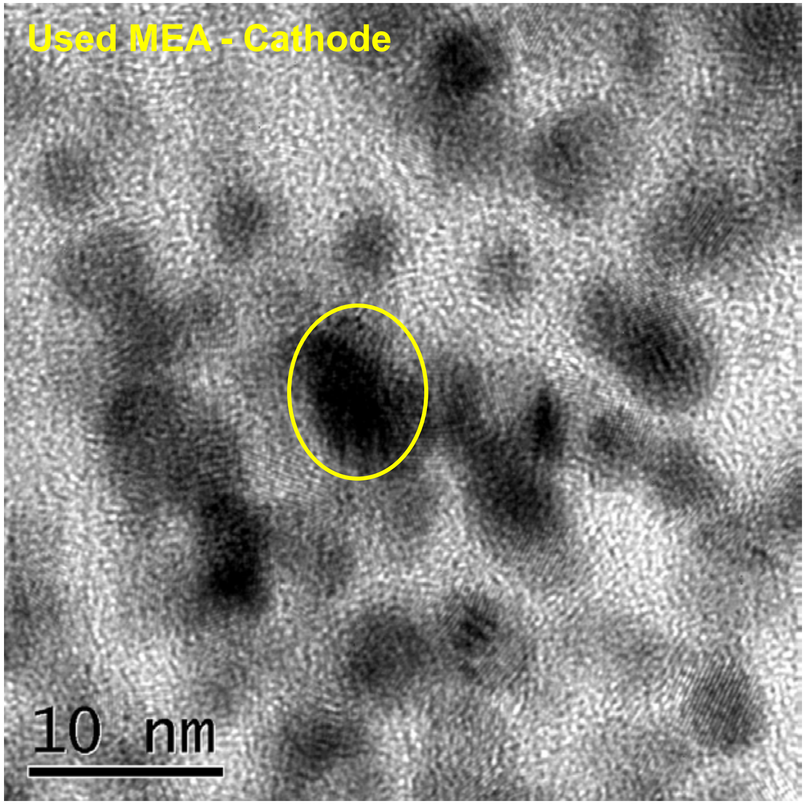


Vs 16 µm

20.0 µm
membrane

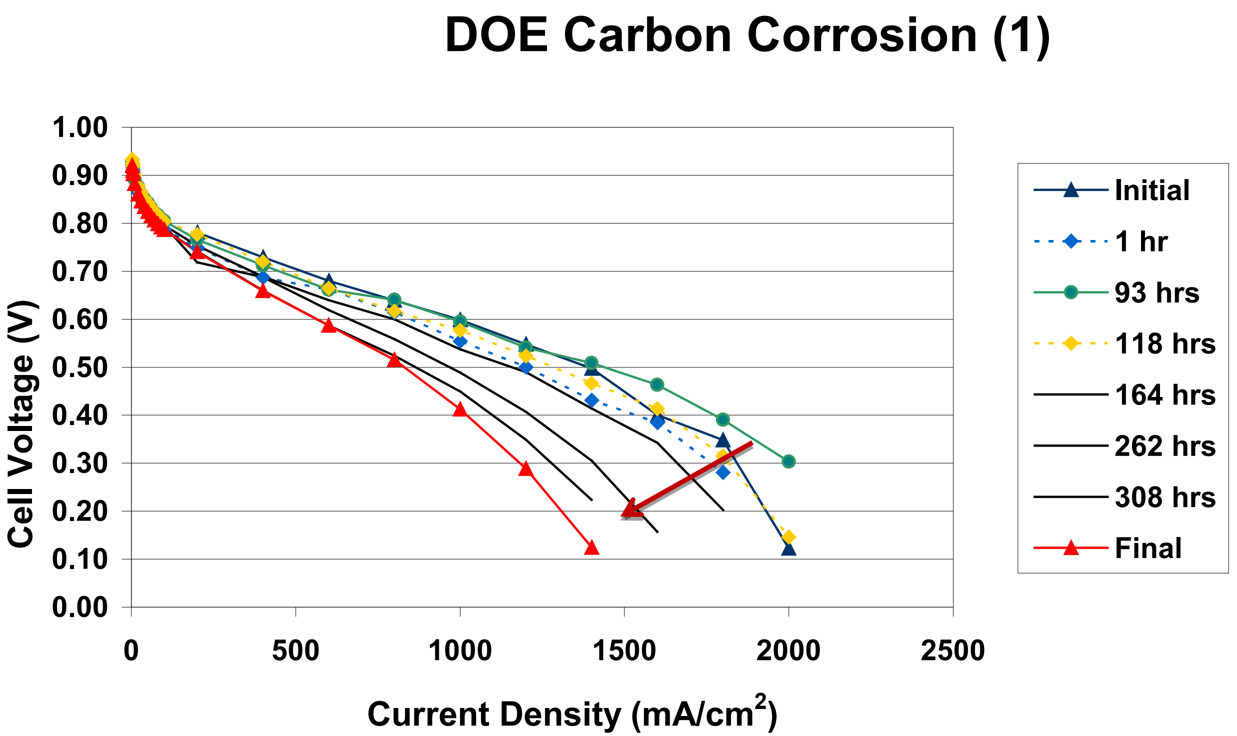
Accomplishments: Accelerated Testing
Nissan Carbon Corrosion





- In pristine cathode, ~5 nm sized platinum nanoparticles are well dispersed in the cathode layer with a small amount of agglomerated clusters.
- In the used cathode, most of the catalyst particles remained ~5 nm, demonstrating the small effect of test conditions on catalyst agglomeration in the cathode.
- Results as expected for effects of AST specific to carbon corrosion

Accomplishments: Accelerated Testing
FCTT Carbon Corrosion Test



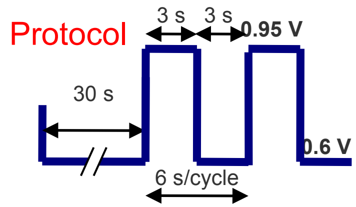
Voltage held at 1.2 V

H_2/N_2 flows @ 100% RH

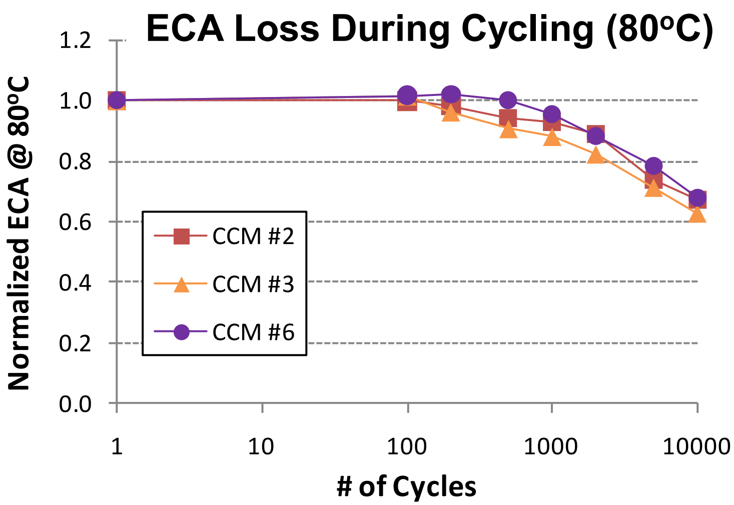
- ~30-35% loss in mass activity and in performance at 1 A/cm^2
- Similar actual losses to Nissan Start-Stop A.
- Higher ECSA loss than Nissan test

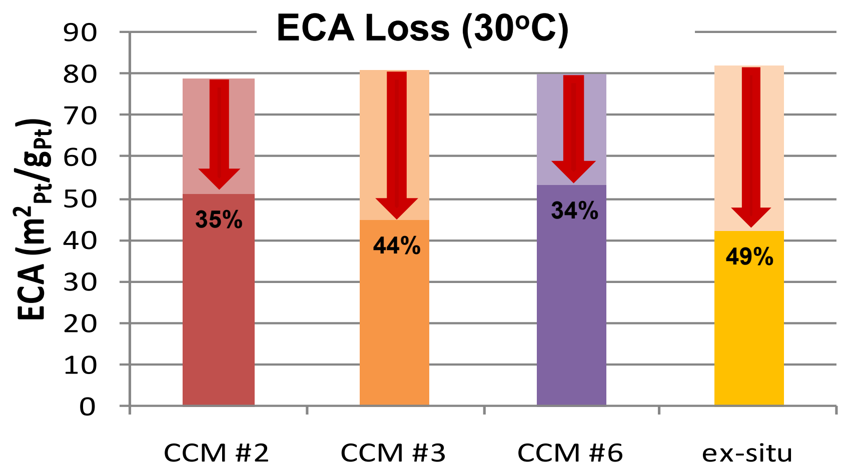
Accomplishments: Accelerated Testing
Nissan Pt Dissolution (Load Cycling)

NISSAN R&D AMERICAS



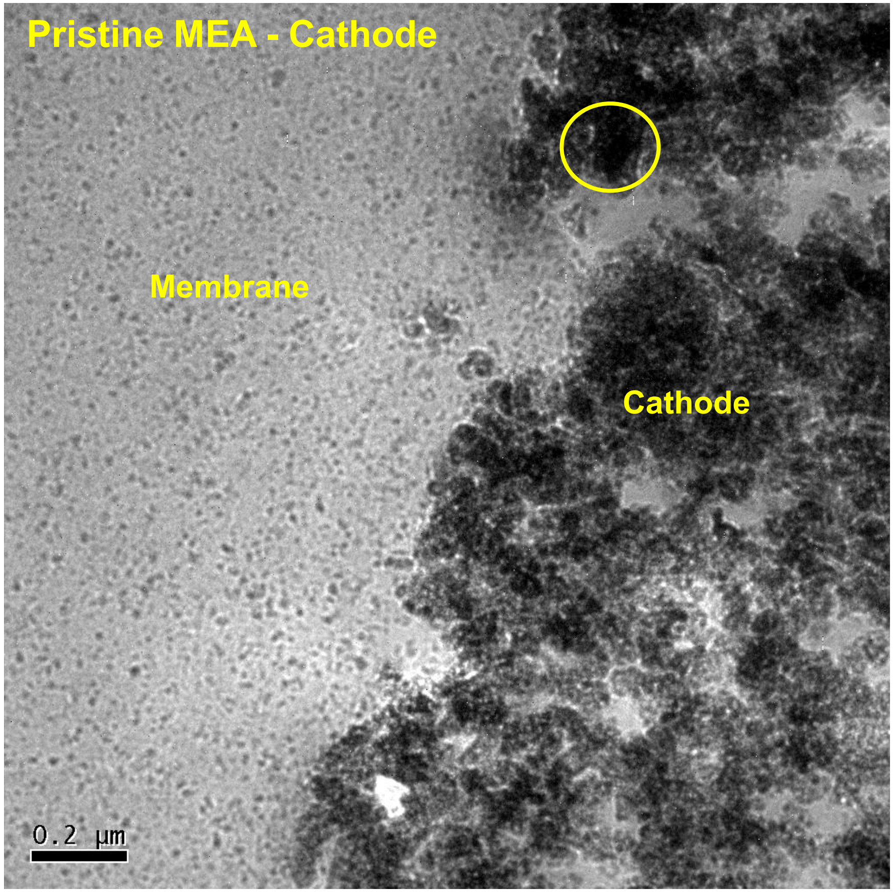
H_2/N_2 flows @ 100% RH

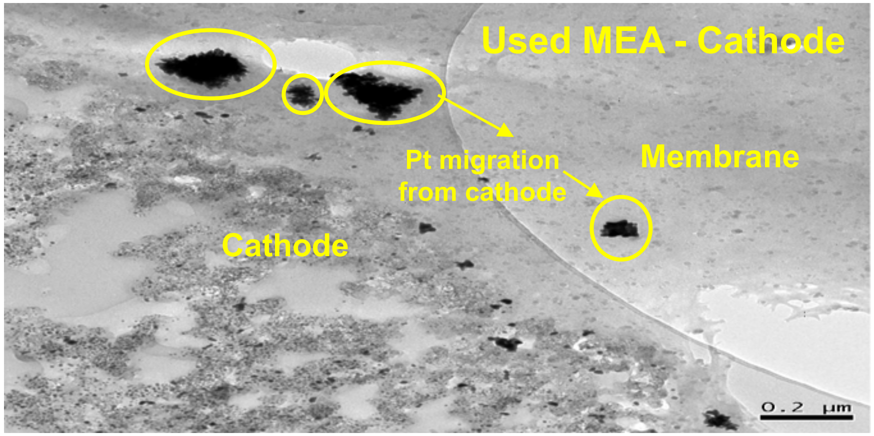


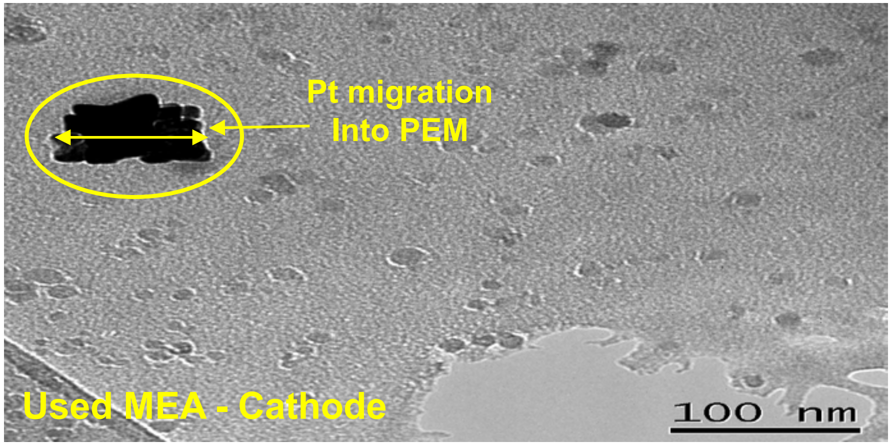


- ❑ Three CCMs show similar behavior during load cycling
  - ▪Some variation in ECA loss measured at 30°C
- ❑ Performance loss at 1 A/cm^2 is 4-10%
- ❑ <u>ECA loss of CCMs is slightly less than *ex-situ* RDE measurements of the same catalyst (TEC10F50TPM)</u>

Accomplishments: Accelerated Testing Nissan Platinum Dissolution (Load Cycling)

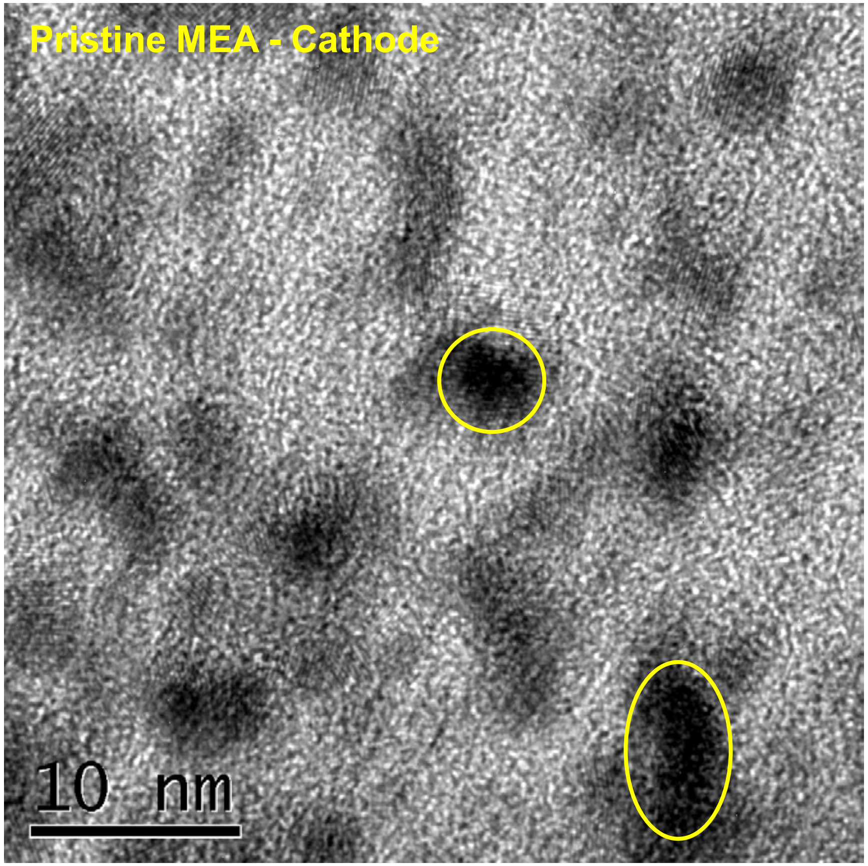


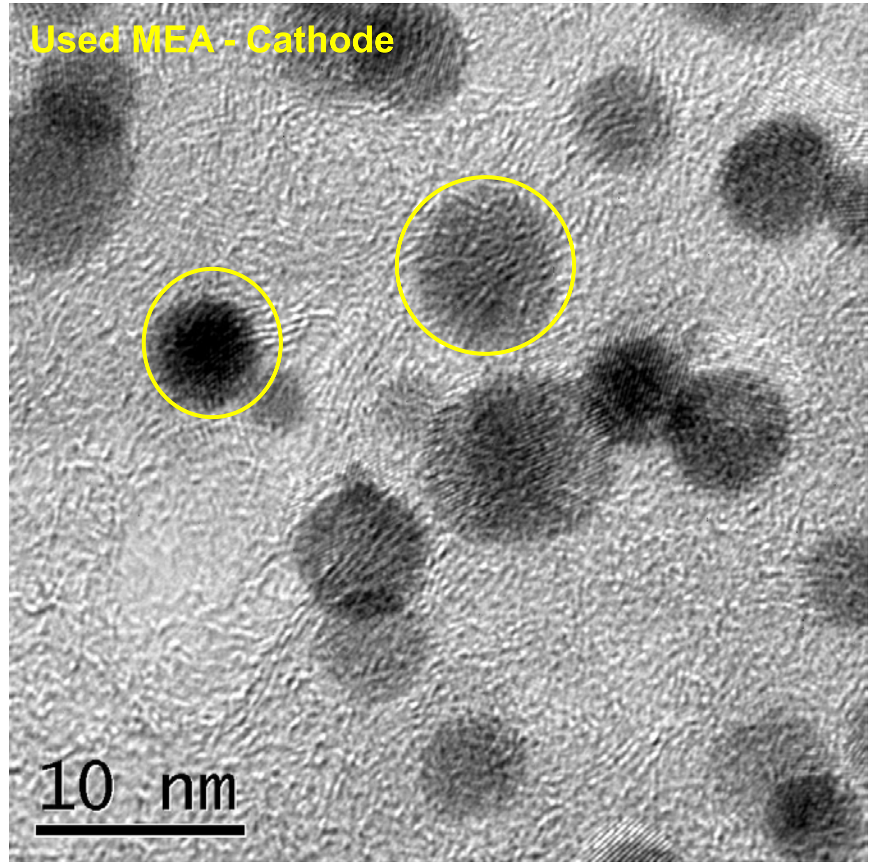




- The catalyst particles in pristine cathode are well dispersed. However, some agglomeration of catalyst particles is evident in the TEM.
- The catalyst particles in used cathode showed large Pt deposits (~80-90 nm) near membrane/catalyst interface as well as in the membrane.
- Significant amount of cathode catalyst migration from catalyst layer into the membrane was observed in cathode of the used sample.

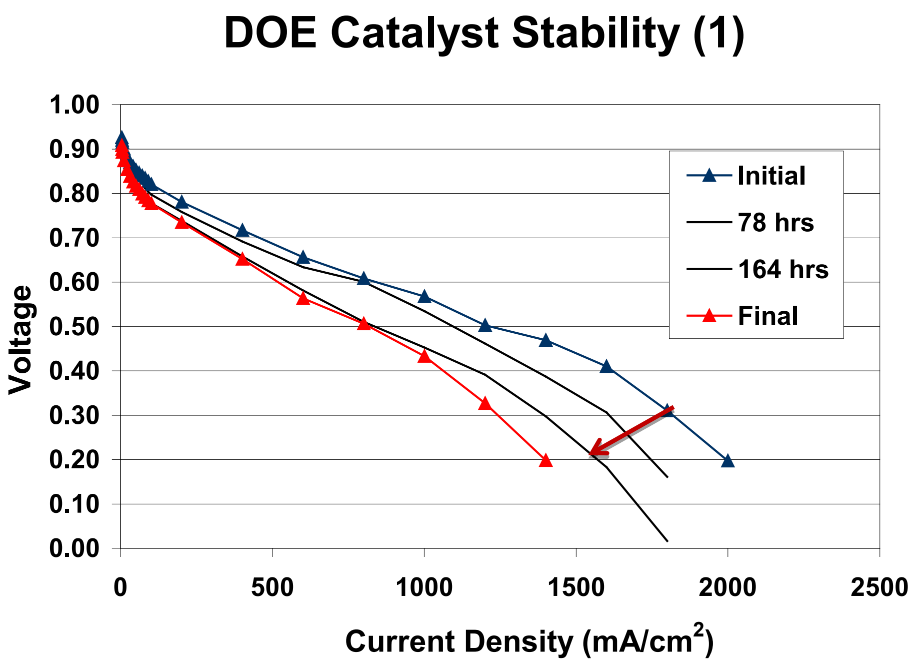
Accomplishments: Accelerated Testing
Nissan Platinum Dissolution (Load Cycling)

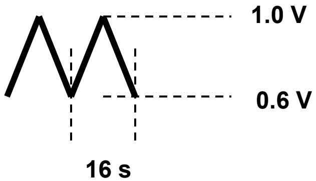




- In pristine cathode. ~5 nm sized platinum nanoparticles are well dispersed in the cathode layer.
- In pristine cathode, presence of a small amount of agglomerated clusters ~10 nm can be seen.
- In used cathode most of the catalyst particles remained ~5 nm. However, agglomerated catalyst clusters of ~80-90 nm were observed near cathode catalyst/membrane interface and in the membrane matrix.

Accomplishments: Accelerated Testing FCTT Platinum Dissolution Tests

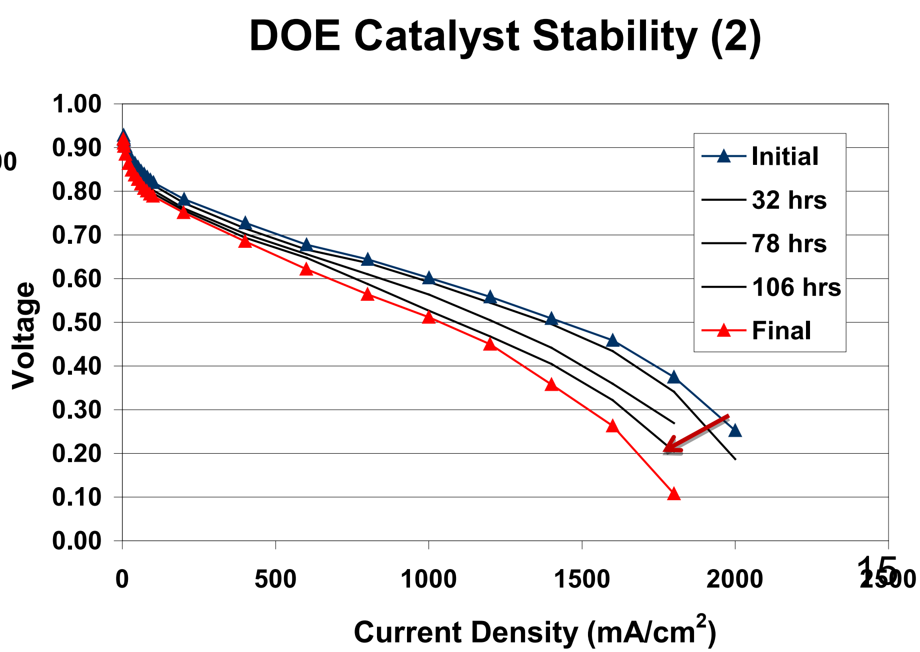




H_2/N_2 flows
@ 100% RH

These samples exhibited a performance loss of about 15-25% at 1 A/cm^2, higher than the Nissan AST.

TEMs show similar phenomena



Accomplishments: Accelerated Testing Membrane Chemical Durability (Nissan/FCTT)

OCV hold. 90C, 30% RH
Nissan - O_2; FCTT - air

SEM Results

- Definite differences between results of Nissan AST and FCTT AST.
- FCTT samples exhibited voids in the ionomer layer on both sides of the reinforcement. Nissan samples did not exhibit these voids.
- The sulfur scan in EDX for the Nissan samples showed low intensity of sulfur for the cathode ionomer layer, indicating loss of ionomer. This was not seen in the FCTT samples.
- In samples from both ASTs, the X-Ray map of Pt showed the presence of Pt in ionomer layers of the membrane

TEM Results

- Minimal evidence of sintering of Pt crystallites in anode, in the Nissan samples. No evidence was found in the FCTT samples.
- In the Nissan samples, limited numbers of small (< 10-nm) Pt crystals crossed-over to ionomer layer on anode side from cathode. There was a much more significant number in the FCTT samples.
- Large, sintered Pt crystals (~30 - 50-nm) observed in large quantities in ionomer layer (on cathode side) close to ionomer layer/reinforcement interface
- Limited numbers of sintered Pt crystals (~30 - 50-nm) observed in reinforcement layer
- FCTT samples exhibited significantly more sintering of Pt crystallites. Sintering occurred in or near the cathode, with sizes ~50 nm. For Nissan samples, Pt crystallites in cathode, if any, were minimal in extent.

Accomplishments: Accelerated Testing
Membrane Mechanical Durability (Nissan/FCTT)

Wet-dry cycles;
Nissan - 25 s; FCTT - 4 min

SEM Results (Nissan samples only).

- No voids or cracking in ionomer layer were observed
- A thin Pt layer, ~3 µm was observed into the membrane ionomer layer adjacent to the cathode, about 6 µm from the reinforcement layer.
- The presence of thin Pt layer was also confirmed by Pt line scan. The Pt peak appeared at ~ 30 µm, about center of the MEA.

TEM Results

- FCTT samples show some evidence of sintering of Pt crystallites in anode. No evidence was found in Nissan samples.
- Similarly, FCTT samples show limited numbers of Pt crystals crossed-over to ionomer layer on anode side from the cathode. Nissan samples show no evidence of any Pt crystallites from cathode crossing over to the anode side
- In FCTT samples, small (15 – 20-nm), sintered Pt crystals from cathode were found in the ionomer layer near cathode, in ionomer layer near reinforcement layer, and in the reinforcement layer, with smaller ones (~10-nm) on anode side.
- In Nissan samples, large, sintered, star-shaped Pt crystals (~50-nm) were observed about 4 - 5 µm into ionomer layer from cathode-membrane interface.
- Sintered Pt crystal size decreases from membrane interior (cathode side) to ionomer/reinforcement interface on cathode side
- In FCTT samples, there was evidence of limited numbers Pt crystals having crossed-over from the cathode to ionomer layer on anode side. Nissan samples showed no evidence of any Pt crystallites in reinforcement layer or beyond reinforcement layer into ionomer layer on anode side

Collaborations

DuPont NAFION®

- Program management
- Membranes, ionomers, & MEAs
- Materials characterization & analysis.
- Membrane/ionomer degradation mechanisms
- Durability testing using internal and FCTT accelerated tests.

Nissan Technical Center North America—Dr. K. Adjemian

- Accelerated durability testing
- Fundamental Electrochemical Analyses
- Model development
- Stack testing

Illinois Institute of Technology—Dr. V. Ramani

- Post mortem characterization of component materials.
- Fundamental understanding guidance for testing necessary to complete model development.
- Develop model of degradation mechanisms.

Summary

Milestone 1 (Decide on ASTs to utilize for modeling work)

- Baseline material set and test protocols show reasonable consistency and behave (in most ways) as expected.
- Nissan ASTs for catalyst degradation appear to demonstrate the same degradation mechanisms as the FCTT ASTs.
- Suggests that Nissan catalyst ASTs are advantageous for data generation due to much shorter test duration. Some supplemental FCTT tests will be run to generate data more representative of end-of-life.
- Differences in the post mortem results of the FCTT and Nissan membrane durability tests were surprising. We will continue some of both tests until the reasons for the differences are understood.

Model and Degradation Mechanisms

- Protocols and equipment upgraded to generate additional data.
- Computer program developed for rapid data organization and analysis.
- Membrane degradation data generated that continue to suggest an interaction between mechanical & chemical degradation.
- An RDE method was developed that mimics much of the ASTs, and can be used as a screening tool for come CCM designs.

Future Work

Short term:

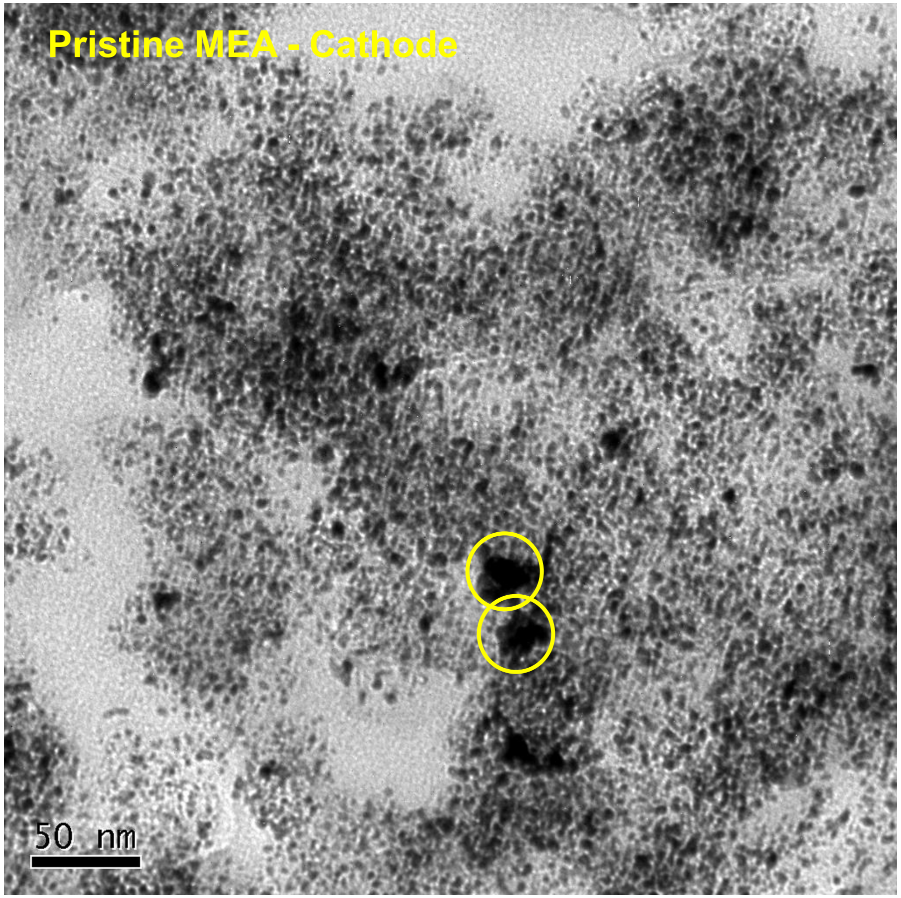
- Complete durability testing replications & post mortem analyses to finalize test plan decisions (Milestone 1).
- Begin tests with high surface area catalyst.
- Test effect of polymer morphology on durability.
- Fully implement analytical recommendations made at FCTT February review.

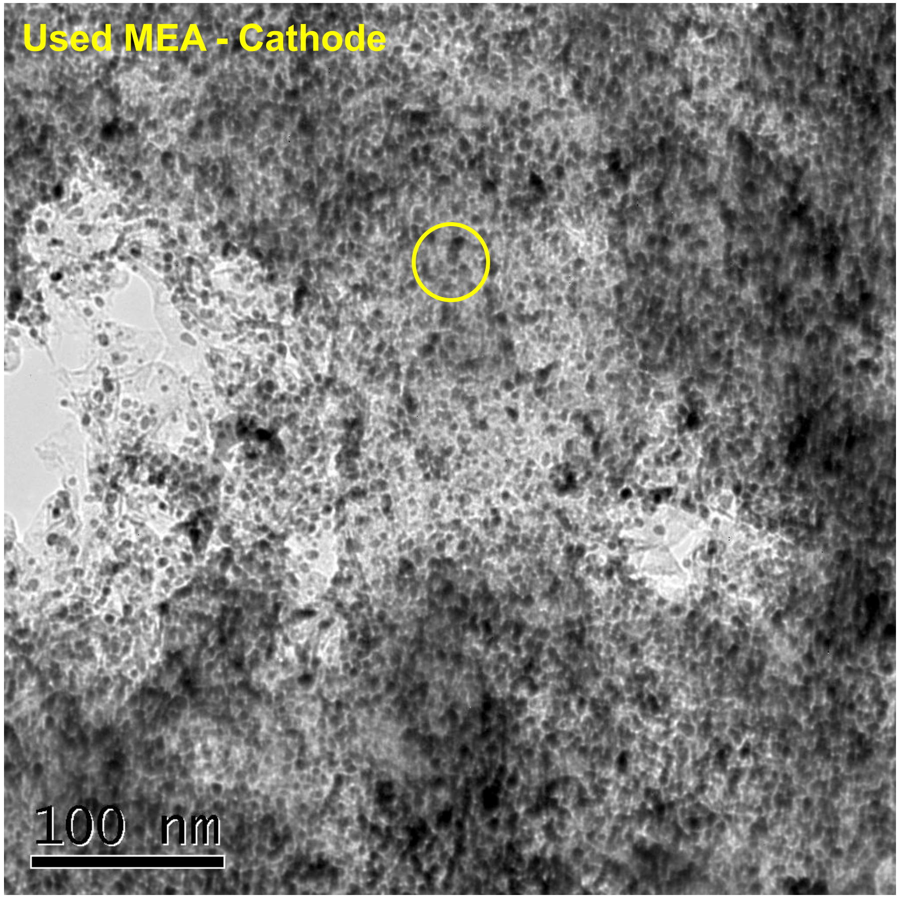
2-4 Q 2012

- Begin post mortem testing of GDL and plates.
- Continue generating data for modeling, using variants of baseline MEA & GDL.
- Include new ionomers and alternative reinforcements into durability testing.
- Preliminary design and initial testing of MEAs for Go/No-go decision.

Technical Back-Up Slides

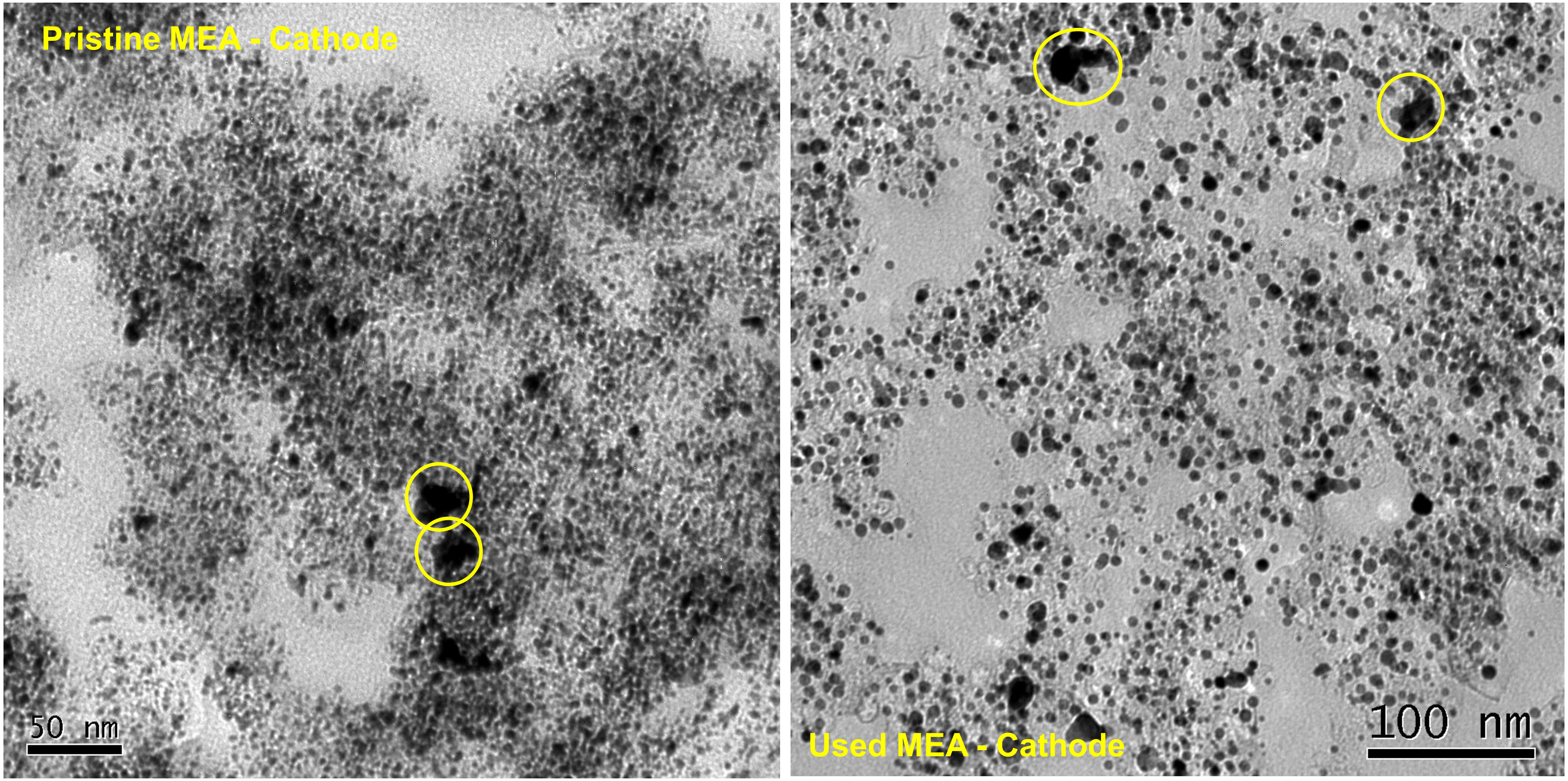
Accomplishments: Nissan Carbon Corrosion (Start-Stop B)





- No extra catalyst agglomeration in bulk of the used cathode was observed after carbon corrosion cycle.
- The dispersion of cathode particles in used sample 5-1 remained unchanged after cycling in the cell.
- Some catalyst agglomeration was present in pristine cathode. After cycling they didn't grow much in bulk electrode. This indicates that the carbon corrosion cycle had very little effect on catalyst agglomeration in the bulk cathode, but has significant effect near the membrane cathode catalyst interface.

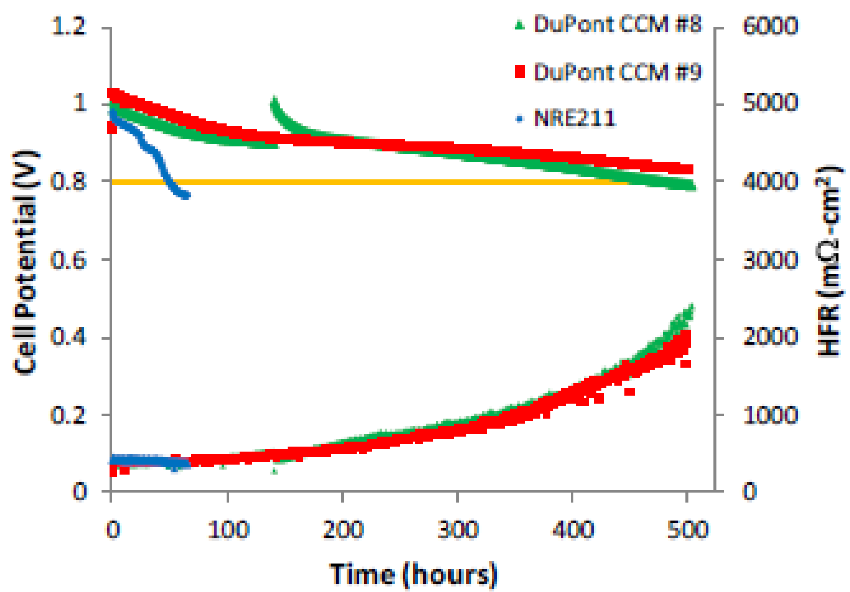
Accomplishments: Nissan Platinum Dissolution (Load Cycling)



- Some catalyst agglomeration was present in pristine cathode. After cycling there was little change in the bulk catalyst layer. However, a significant amount of catalyst agglomeration occurred near cathode/ membrane interface and in the membrane of the used cathode sample.
- In used cathode, large amount of catalyst migration into the membrane was also observed. The migrated catalysts were not distributed into the membrane matrix, rather they formed aggregated clusters in the membrane.

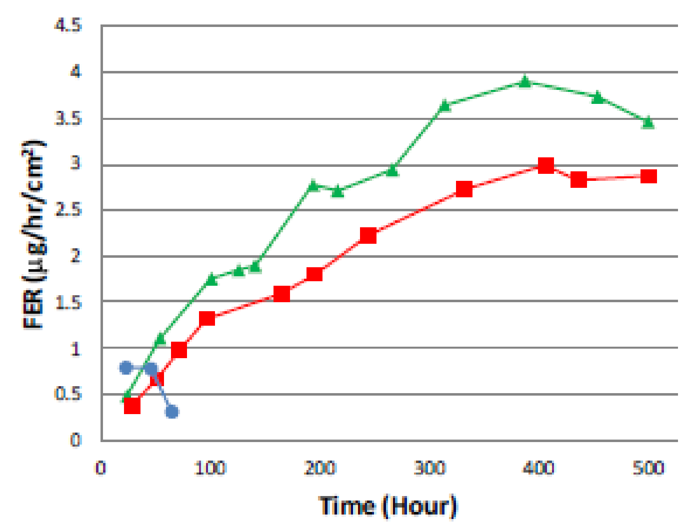
Accomplishments: Membrane Chemical Durability OCV Hold

OCV Hold: H_2/O_2, 30% RH, 90°C, 0.5 / 0.5 NLPM



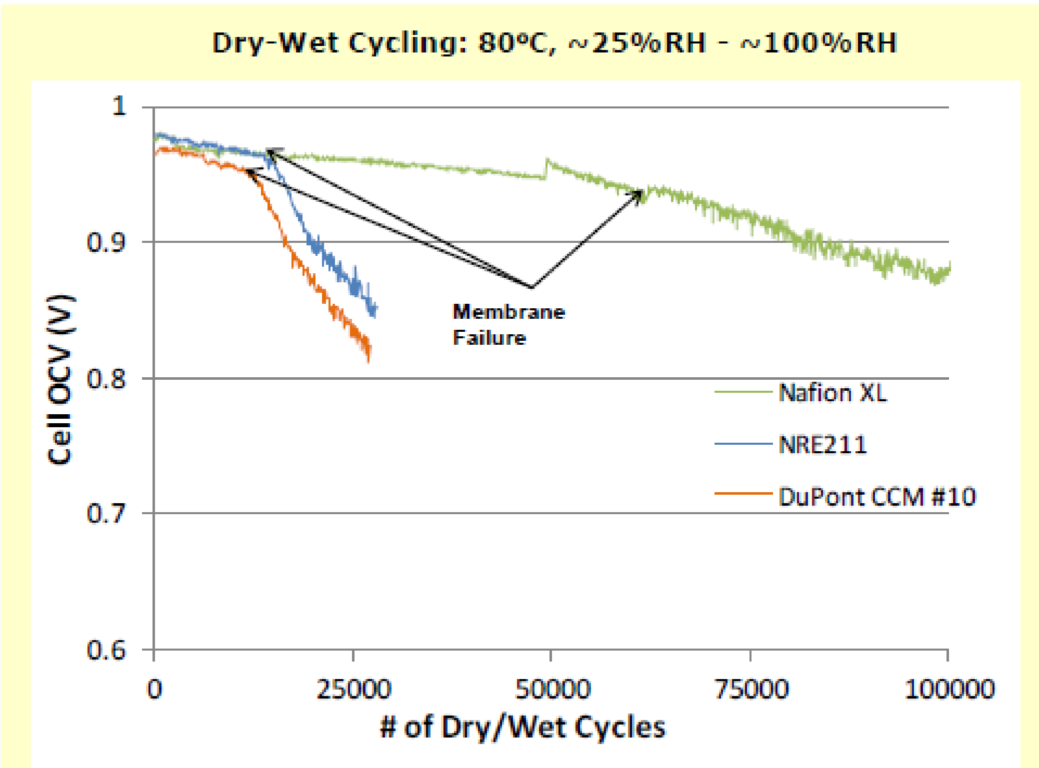
- CCMs #8 & #9 showed consistent potential loss in the OCV Hold test
- Outperformed NRE211CS
- Both DuPont CCMs show the same trend of an increasing FER through the OCV Hold test

Fluoride Ion Emission Rate



- CCM #8 showed consistently higher FER than CCM #9. This may be seen in the higher OCV loss in CCM #8 as well.

Accomplishments: Membrane Mechanical Durability (Nissan)



- CCM #10 showed very poor mechanical durability in Dry-Wet Cycling test
- Exhibited membrane failure after ~12k cycles (Target = 190k cycles)
- Failure of 25μ reinforced membrane was earlier than 25μ unreinforced NR211

Future Work: Diagnostics and Modeling (IIT) - Overview

- Objective: For an initial starting set of materials, determine cell performance as a function of time using a simple and tractable model.
- First: Identify which key measurable properties/parameters (P_i) are sensitive to accelerated tests and can be clearly discriminated through experiment
- Second: Identify time rate of change of these parameters for a given starting set of materials and establish kinetic models [$P_i = f(t)$].
- Third: Relate P_i to parameters that fit into tractable cell performance model (i.e. exchange current density, Tafel Slope, ionic resistance within membrane, Ionic resistance within electrode, limiting current etc.)
- Fourth: Describe tractable model. Combine steps 2 and 3 into step 4 to yield a model that can predict cell performance (drop) as a function of time.
- Fifth: In collaboration with industry, identify acceleration factors that account for time-temperature and time-potential superpositions. Incorporate into kinetic models in step 2.