2012 DOE Hydrogen Program Annual Merit Review

SPIRE

Sustained Power Intensity with Reduced Electrocatalyst

(aka: Durability of Low Pt Fuel Cells Operating at High Power Density)

Scott Blanchet (PI)

Presenter: Olga Polevaya (PM)

Nuvera Fuel Cells

5/16/2012

FC014

Overview

Timeline

- Kick-Off: December, 2009
- Nuvera and DOE agreed on extending to 4-year program ending 09/30/2013
- 70% Complete (03/30/2012)

Barriers

- Barriers addressed
  - Stack Durability with Cycling: **target: 5000hrs (2015)**
  - Stack Cost: **target: $15/kW (2015)**

Budget

- $5.642M Total Project
  - $3.875M DOE Share (Includes $0.975M for National Labs)
  - $1.767M Cost Share
- DOE FY11 Funding: $584K
- DOE Planned FY12: $411K

Partners

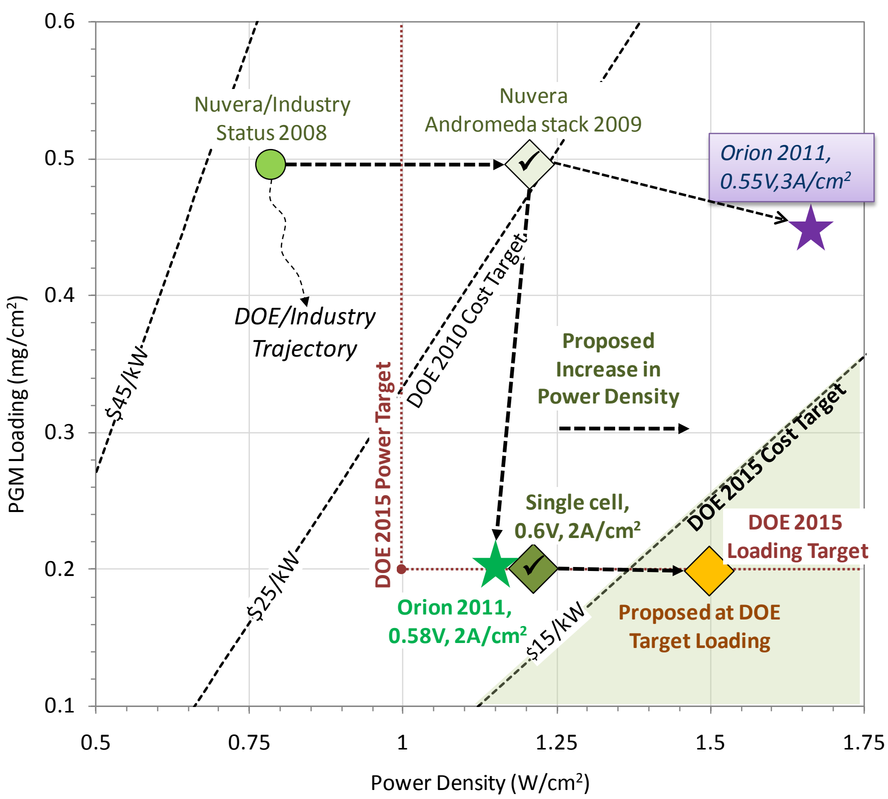
NUVERA FUEL CELLS

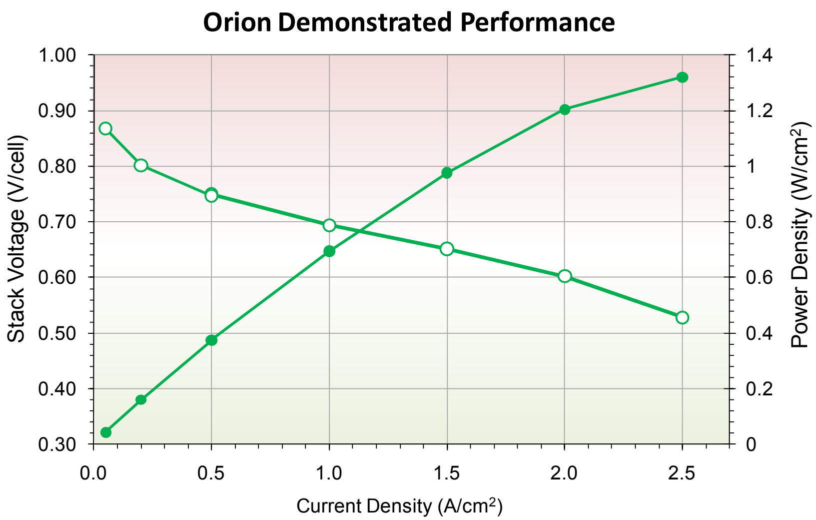
Argonne NATIONAL LABORATORY

Los Alamos NATIONAL LABORATORY

Relevance: Objective and Deliverables

The technical objective is to identify and model PEMFC durability factors associated with low-Pt MEAs operating at high(>1W/cm²) power density.





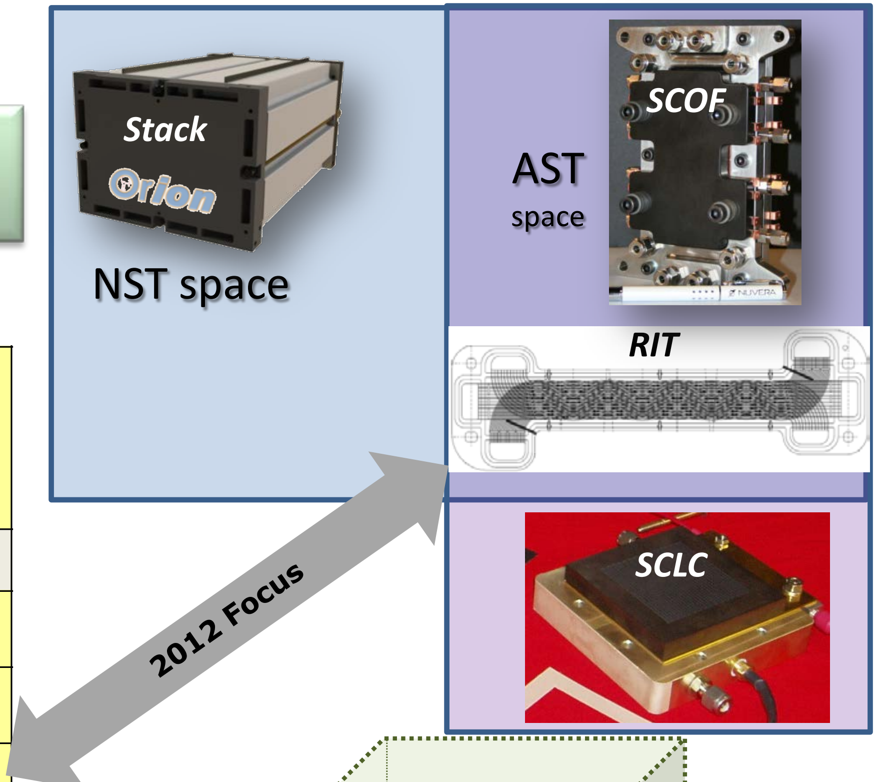
Iso-cost curves fit to 2008 DTI results for 500k vehicles per year with 2015 technology.

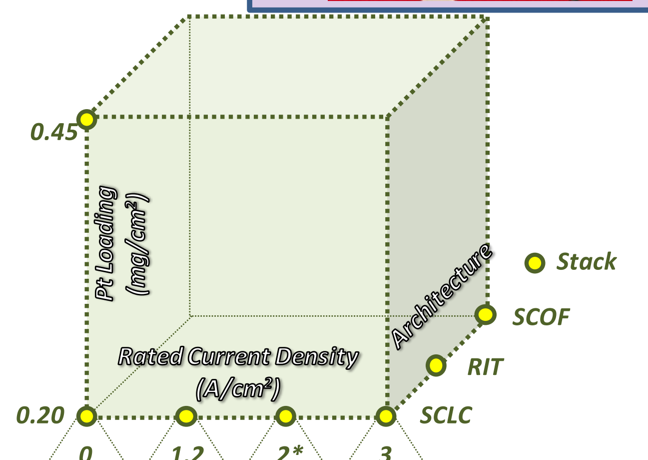
The key deliverable of this program is a durability model experimentally validated over a range of stack technologies operating at high power

Technical Approach – Experimental Design

Architectures selected to maximize applicability across industry.

Test Protocol	Cathode Pt loading $mg_{Pt}.cm^{-2}$		Description
	0.15	0.4	
Potential cycle tests			
B1 AST	√	√	Triangle wave cycle, 0.6 - 1 V, 50 $mV.s^{-1}$ scan rate
B1* AST	√		Same as B1 but the cell potential varies between 0.583 and 0.883 V
NST1A	√	√	Triangle wave cycle, 0.025 - 2 A/cm^2, ~50 $mV.s^{-1}$ scan rate, 30,000 cycles
NST3	√	√	Drive cycle N3A-2 covering 0.586 – 0.886 V (10-cell short stack, 250 cm^2/cell)
Humidity cycle tests.			
B4 AST	55 days long & inconclusive: cancelled (RIT, SCOF)		
NST1B	Equivalent to B4 with the current draw : cancelled		
NST2			FCTT recommended combined load & RH cycle





Technical Progress – Milestones and Go/no go

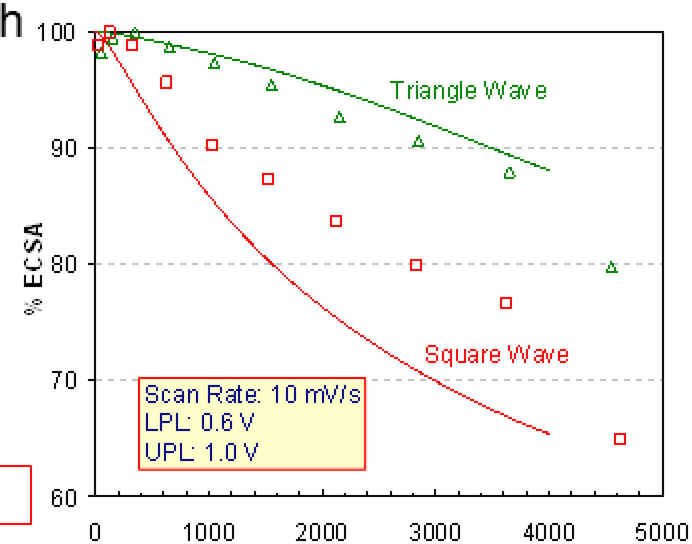
Milestone	Due date	Status
1. Model Block diagram published.	**FY2010, Q3**	**Complete**
2. Single Cell Open Flowfield (SCOF) hardware validated and delivered to LANL.	**FY2011, Q1**	**Complete**
3. Comparative data for Single Cell Land Channel (SCLC) and SCOF on AST protocol is published	**FY2012, Q1**	**Complete**
GNG decision: Demonstrate durability results (voltage decay, diagnostic and post-test measures) in SCOF are consistent with full-area short stack testing using baseline operating conditions and materials.	**FY2012, Q1**	**Passed Go at the Program Review**
4. Model correlations to full-area test results published.	FY2012, Q4	In progress
5. Validated model and data set published and available to industry	FY2013, Q4	Not started

Technical Progress – Durability Model Development

Developed Pt dissolution model for 0.15 mg-Pt(c)/cm² MEA

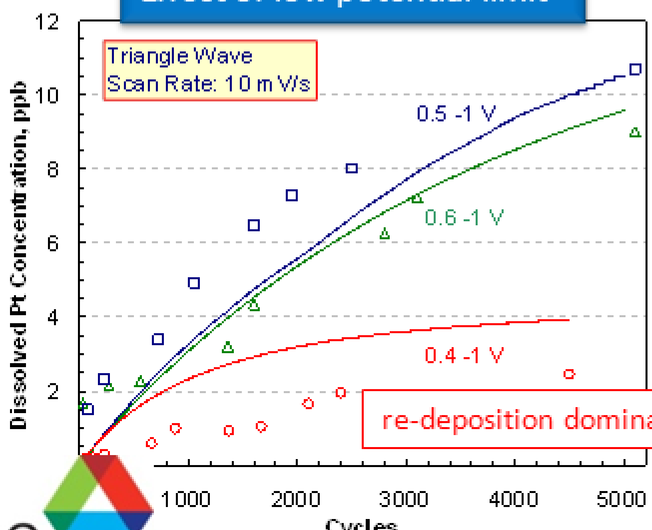
- Thermodynamics of dissolution and oxide growth are generic.
- Kinetics are MEA specific.

Model validation against cyclic data
ECSA loss and particle growth are
1) Cycle dependent,
2) Determined by coalescence mechanism

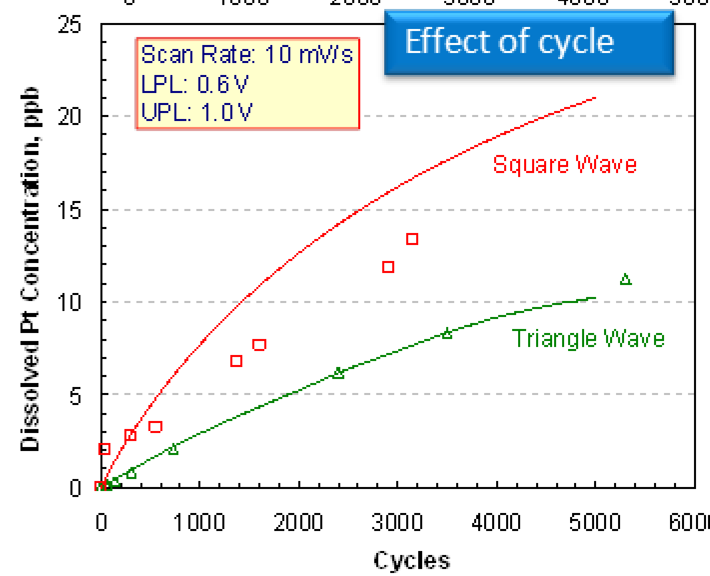


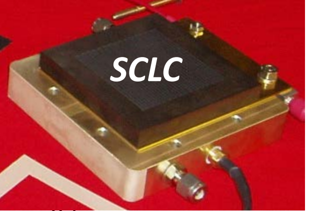
Competitive balance $PtO_x \leftrightarrow Pt \leftrightarrow Pt^2$

Effect of low potential limit



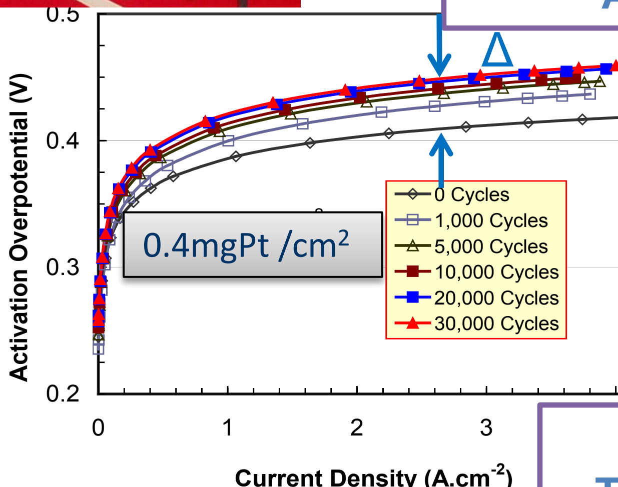
Effect of cycle

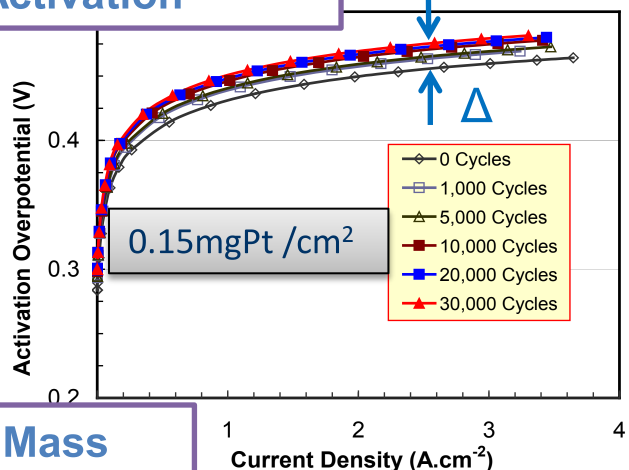




Technical Progress – AST: Effect of Pt loading

Activation

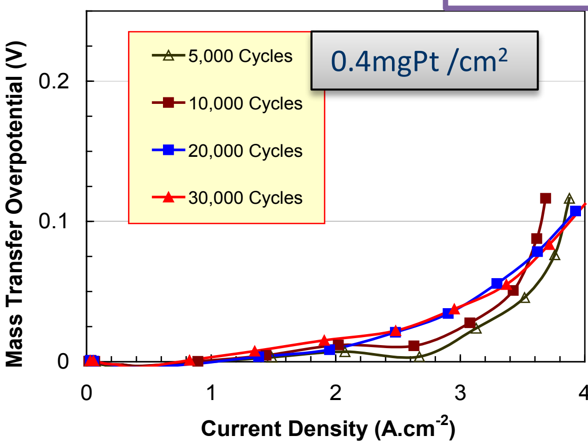


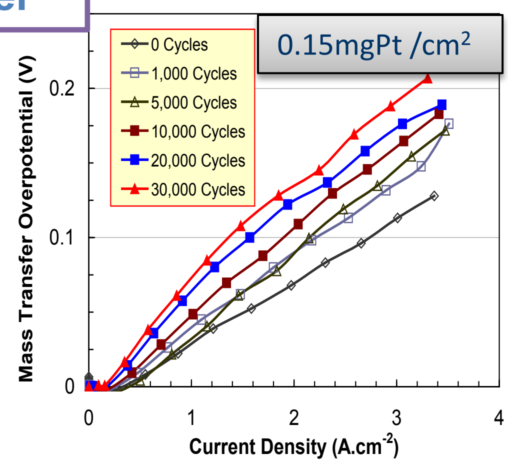


Cell decay in B1 AST , mV
(High Pressure)

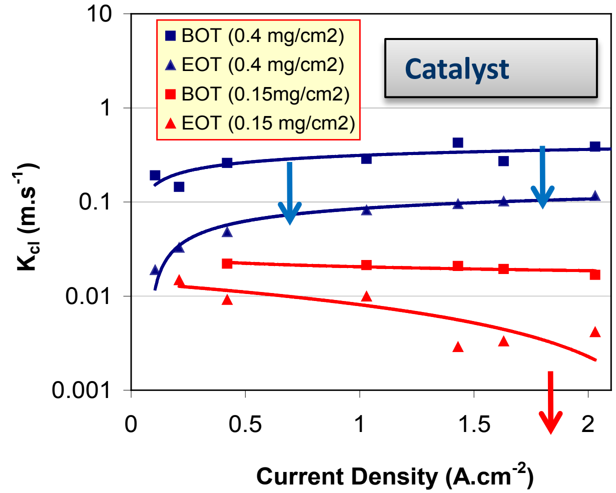
Current density, A/cm²	0.4mg Pt/cm²	0.15mg Pt/cm²
1	23	54
2	28	60
3	40	58

Mass Transfer





O_2 mass transfer

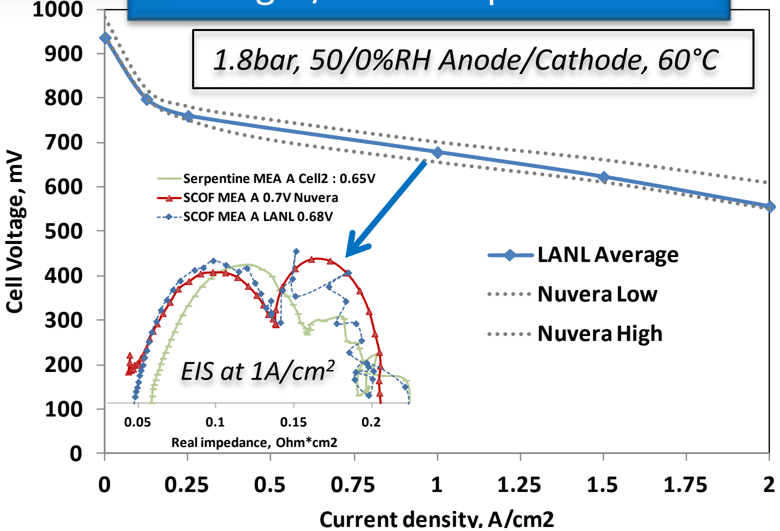


- **Activation decay Δ is greater for 0.4mg/cm² than 0.15mg/cm² cathode.**
- **Mass transfer decay is higher for 0.15mg/cm² than 0.4mg/cm² cathode.**
- **Mass transfer decay is dominated by the catalyst layer rather than GDL.**

Technical Progress- SCOF validation by LANL

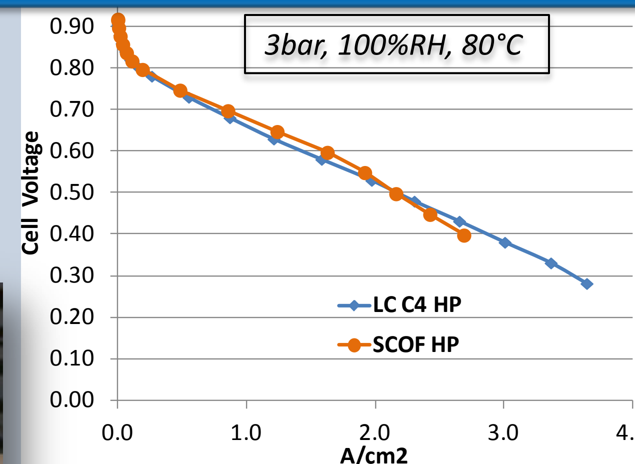
0.45mgPt/cm² BOL polarization

1.8bar, 50/0%RH Anode/Cathode, 60°C

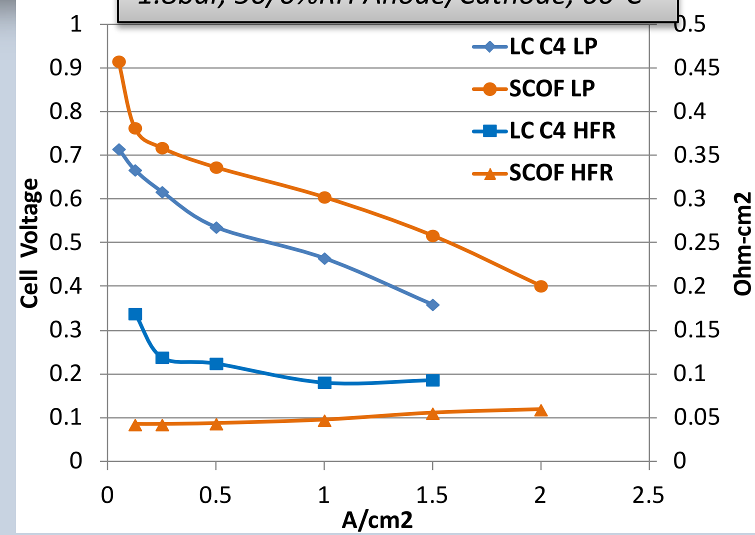


0.2mgPt/cm² MEA: SCOF vs. Serpentine

3bar, 100%RH, 80°C



1.8bar, 50/0%RH Anode/Cathode, 60°C



- **LANL performance of high Pt MEAs in SCOF matched with Nuvera data.**
- **Performance of low Pt MEAs in SCOF and SCLC are similar at high pressure conditions.**
- **Performance of Low Pt MEA in SCOF is superior to SCLC at low pressure conditions.**

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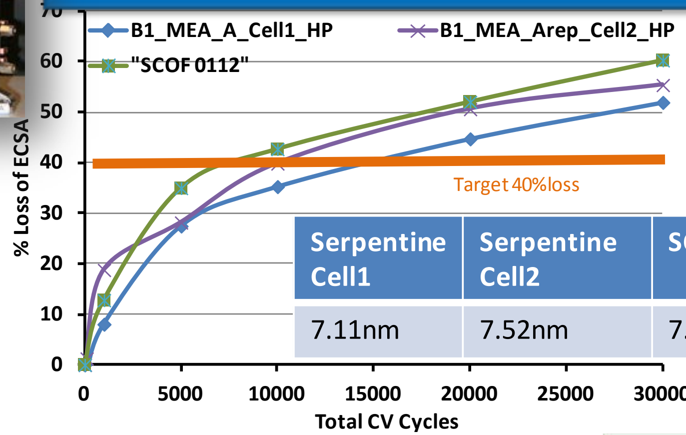
Technical Progress- Milestone 3: Benchmarking SCOF to Land-Channel cell in B1 AST

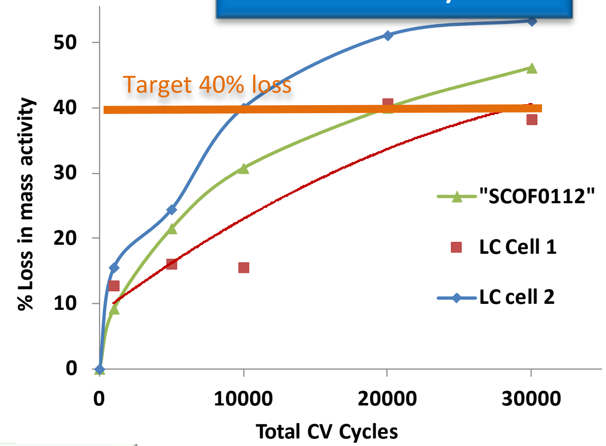
Cathode ECSA loss and Pt size by XRD

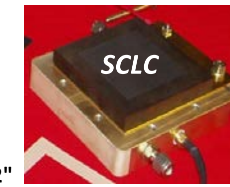


Serpentine Cell1	Serpentine Cell2	SCOF
7.11nm	7.52nm	7.6nm

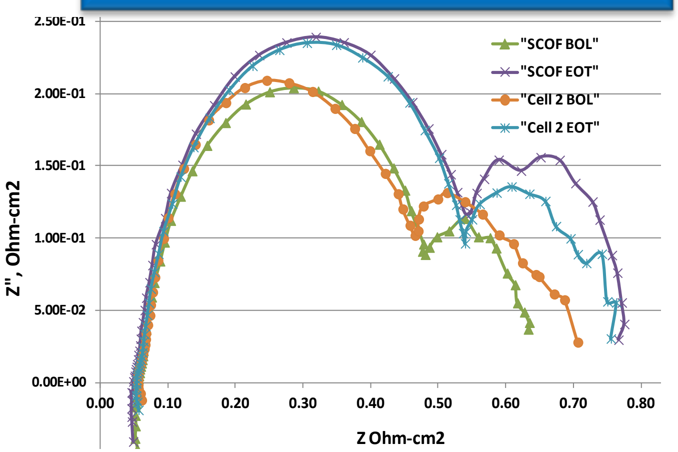
0.45 $mgPt/cm^2$ MEA

Mass activity loss



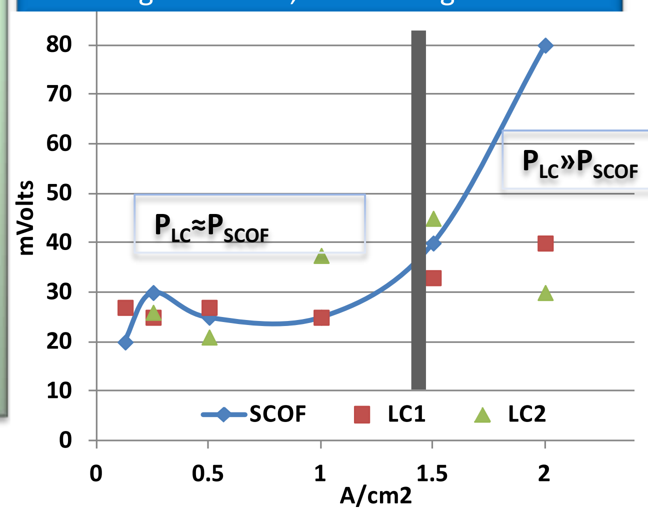


EIS at 60°C Low Pressure, 0.125A/cm2



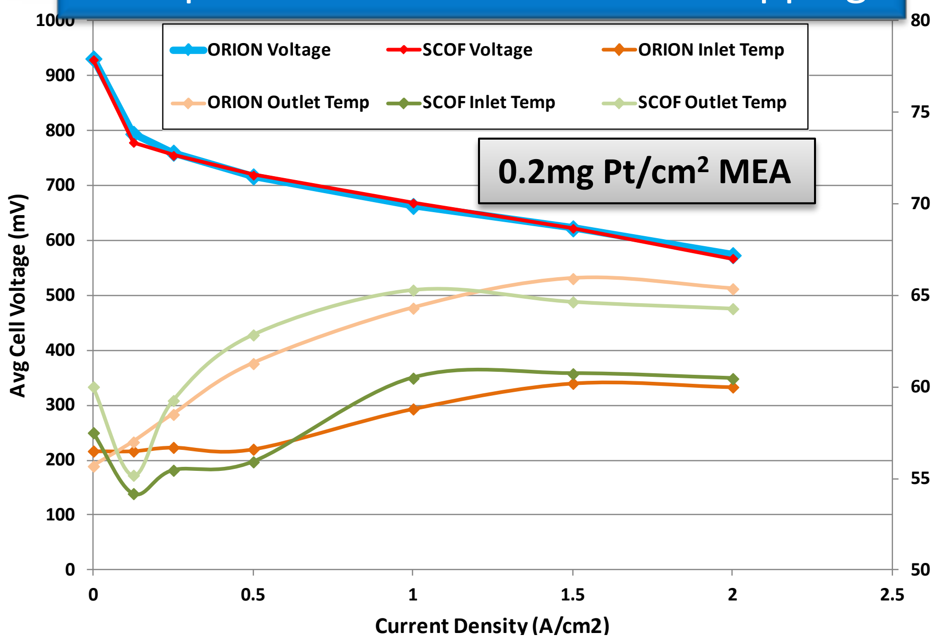
- Similar ageing in kinetic region: loss of ECSA, MA, EOT Pt size, EIS
- Anode/Membrane remain at BOL thickness.
- Valid comparison only below $1A/cm^2$ due to $\Delta P_{LC} \gg \Delta P_{SCOF}$.

High Pressure, 80°C Voltage loss



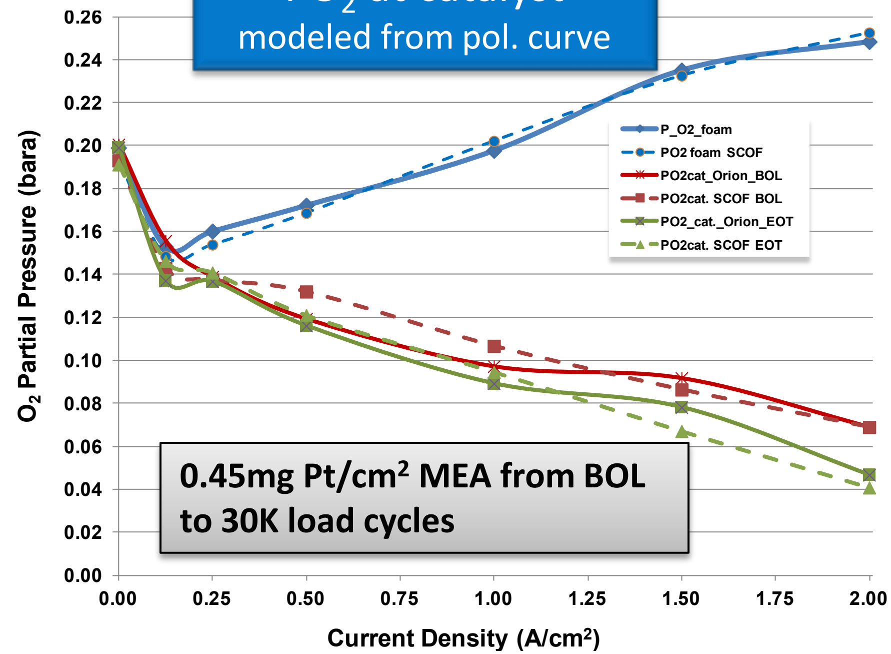
Technical Progress – Matching 50-cm² SCOF to 250-cm² stack cells.

BOL performance and thermal mapping



PO_2 at catalyst

modeled from pol. curve



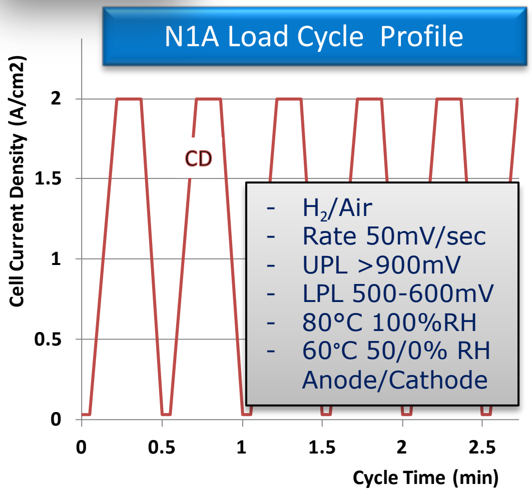
Consistency between SCOF and Orion stack in

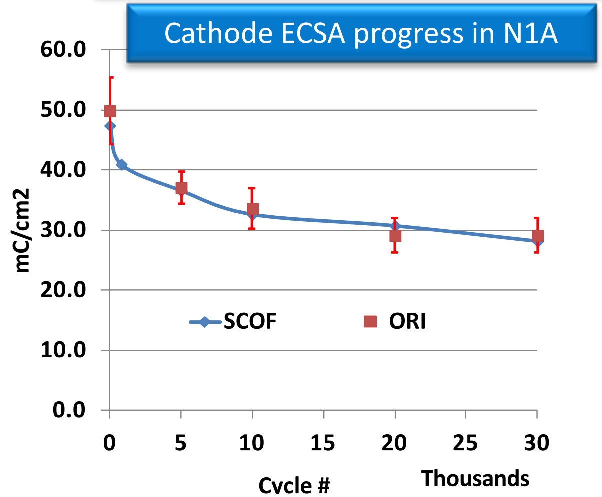
- **BOL polarization**
- **Temperature & pressure gradients along the cells**
- **Oxygen pressure at catalyst**

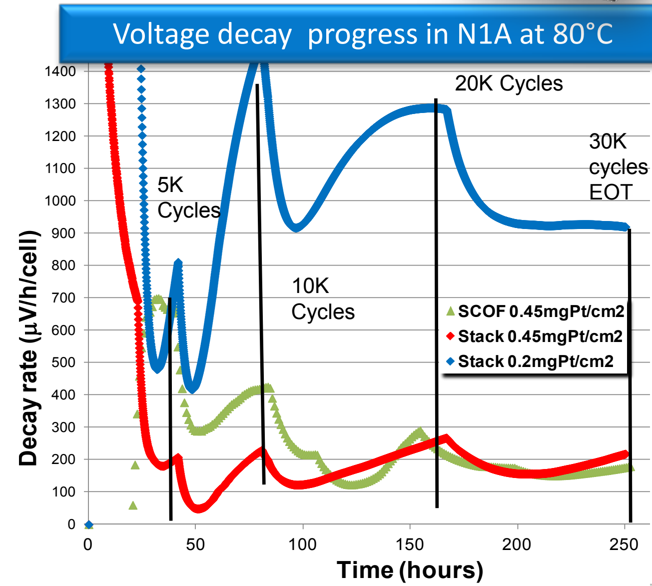
demonstrated on 0.45- and 0.2 mg Pt/cm² MEAs

Technical progress – Durability consistency between SCOF and Stack

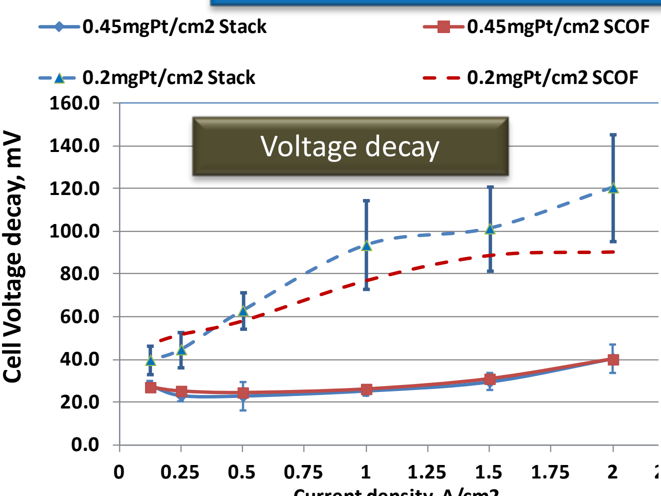
GNG Passed with GO

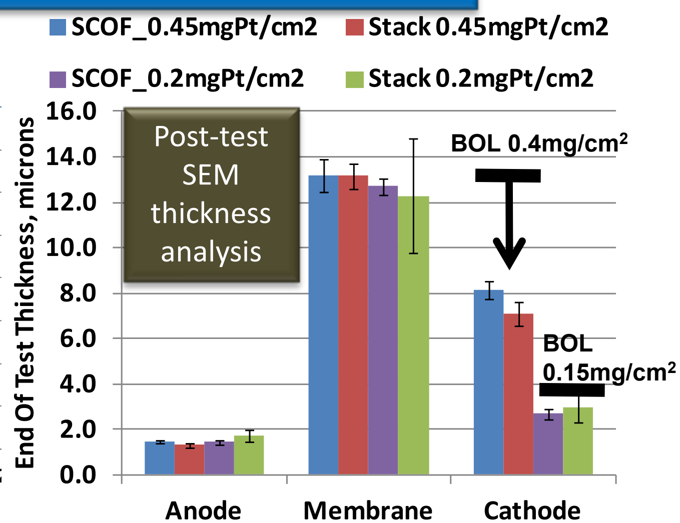






30 K cycles at 60°C End-Of-Test Evaluation





Consistency between SCOF and Orion stack:

- polarization & ECSA loss
- recovery trends
- post-test metrics

demonstrated on 0.45- and 0.2 mg Pt/cm^2 MEAs in N1A durability tests

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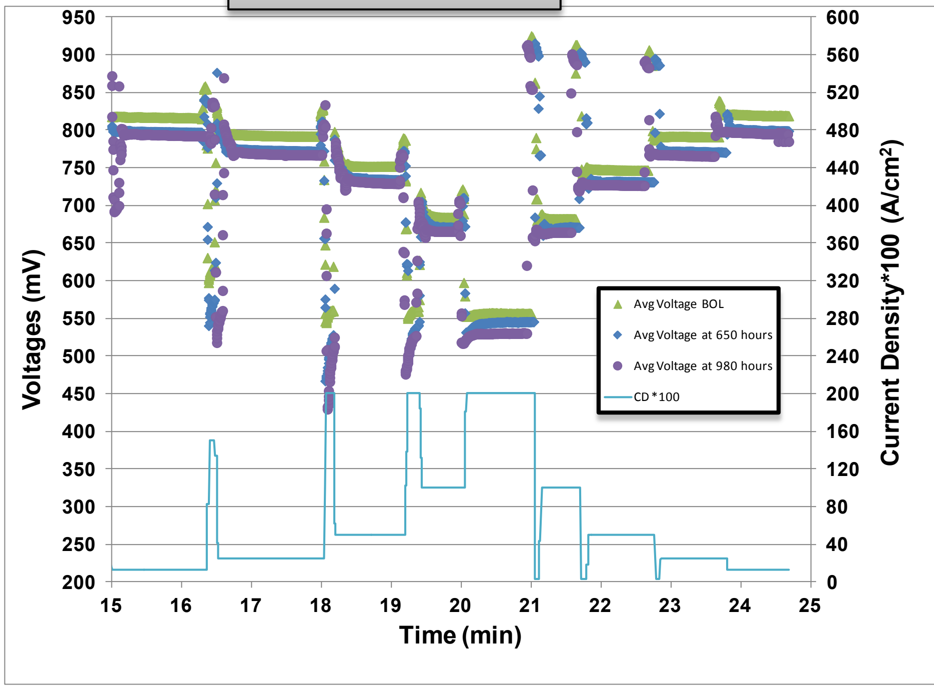
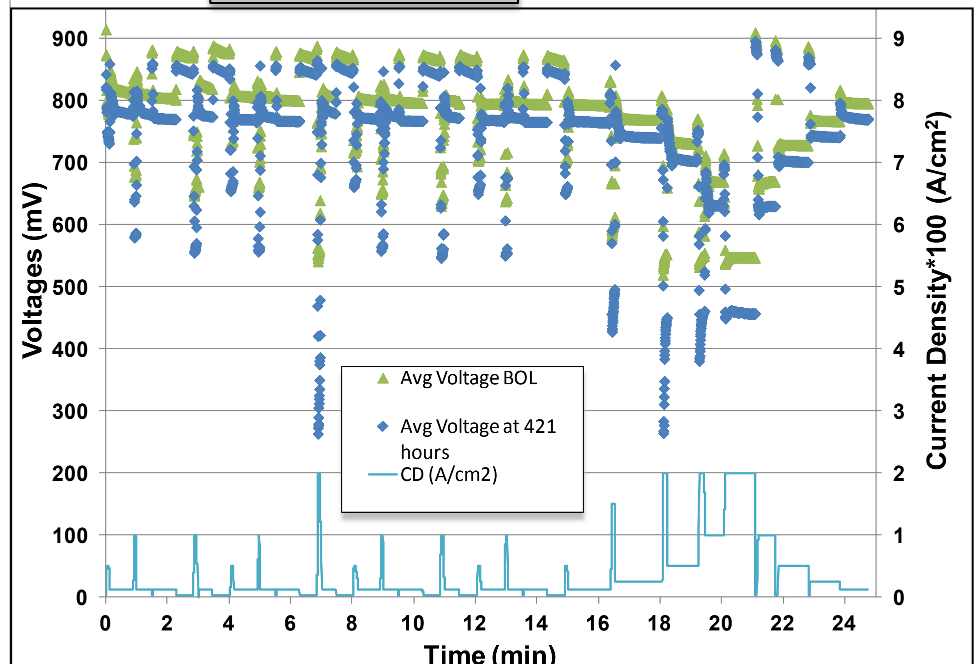
Technical Progress – Dynamic response in NST3

10-cell stacks , 250-cm^2 cell active area, 2A/cm^2 RCD

0.45mg Pt/cm^2



0.2mg Pt/cm^2



Dynamic response to the load request is slower with ageing and attributed to changes in both cathode ECSA/Pt oxide coverage and increase of diffusion resistance.

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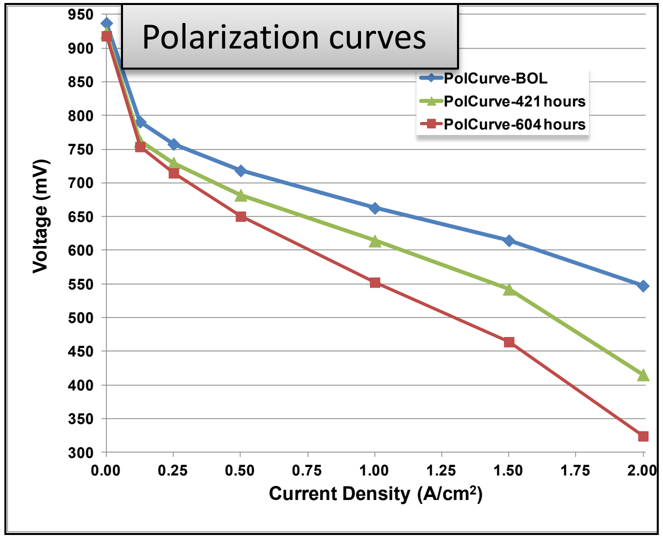
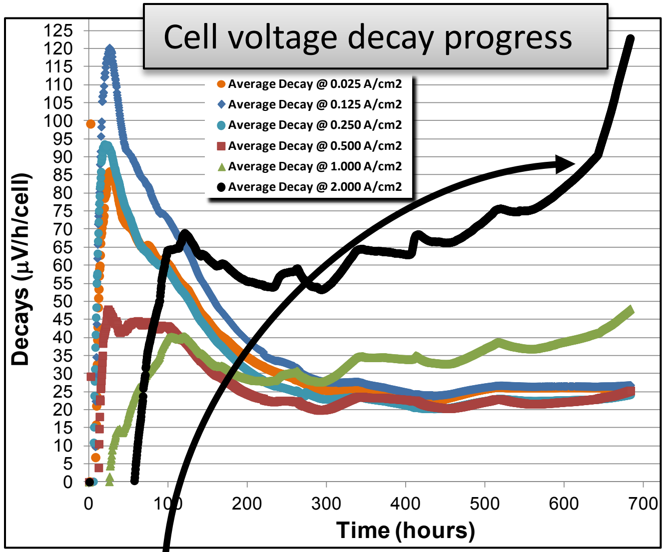
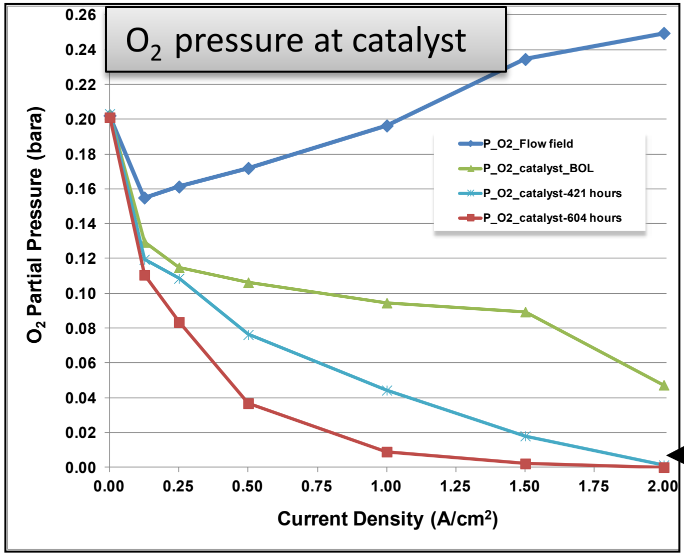
Technical Progress – NST3: Low Pt MEAs in drive cycle stress test

0.2mgPt/cm², 10-cell stacks, 2A/cm² RCD

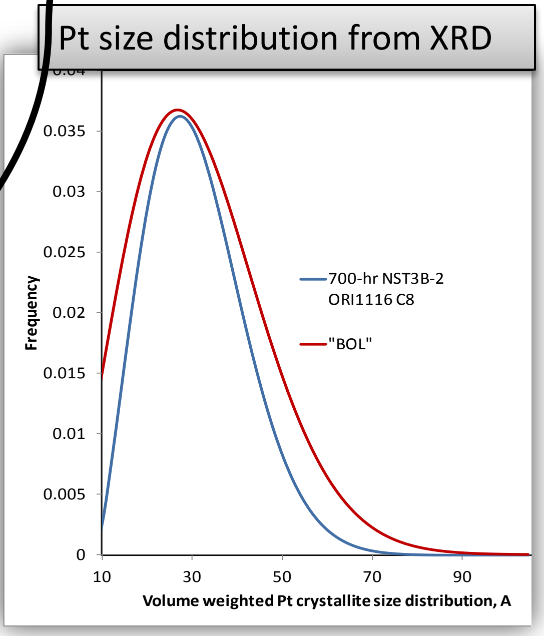




Elevated voltage loss above $1 A/cm^2$ is consistent with the loss of O_2 pressure in the thin catalyst layer as the cell ages.



$$\Delta \eta_{MT} \propto \ln \frac{P^{BOL}_{O2,cat}}{P^{EOL}_{O2,cat}}$$



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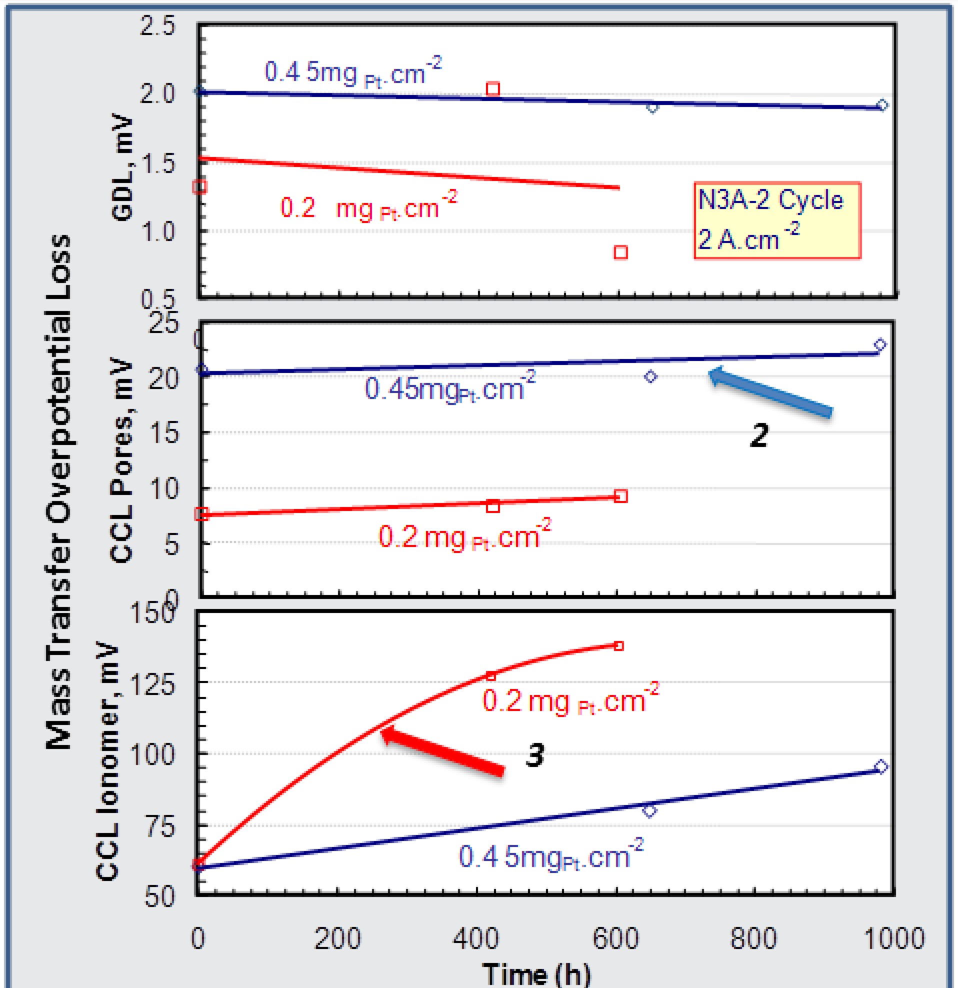
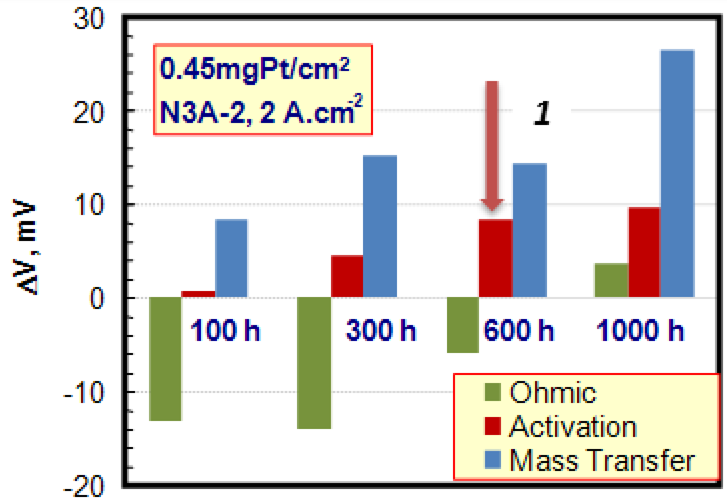
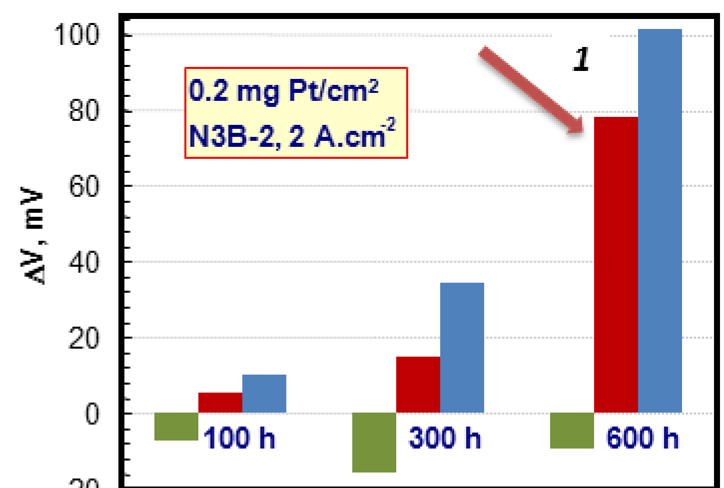
Technical Progress – Effect of Pt loading in NST3

1. Higher activation losses in $0.2 mg_{Pt}.cm^{-2}$ cell, faster increase with ageing.
2. Thicker catalyst in $0.45\ mg_{Pt}.cm^{-2}$ cell has higher CCL pore diffusion losses.
3. The CCL ionomer in $0.2\ mg_{Pt}.cm^{-2}$ cell shows faster increase of diffusion losses.



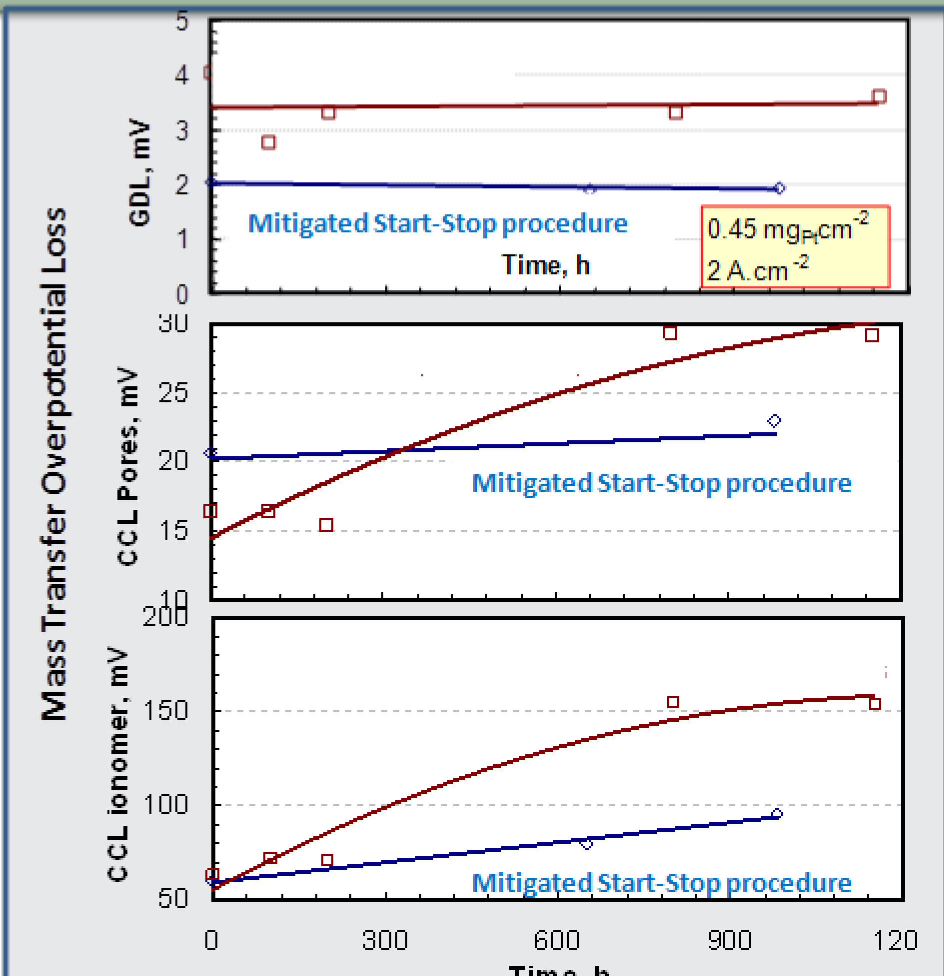


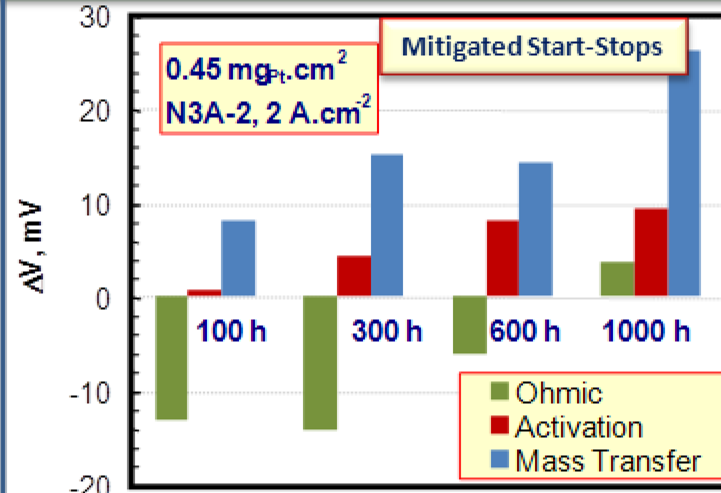


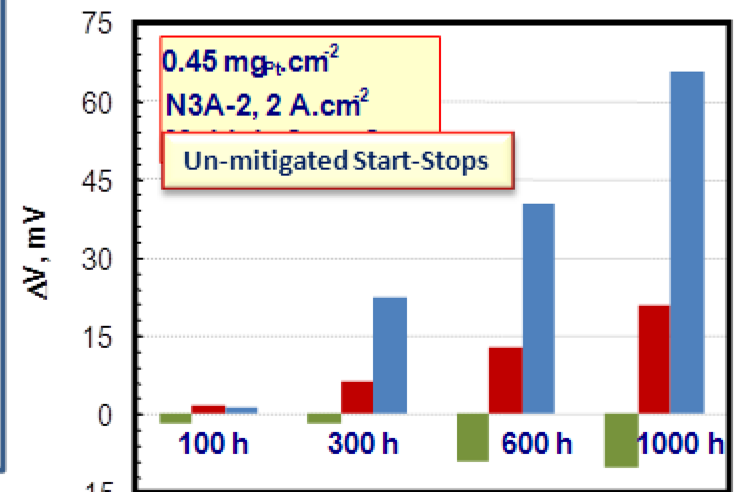
Technical Progress – Effect of Start-Stops in NST3

Significant carbon corrosion observed with un-mitigated start-stops:

- 46% loss in ECSA after 1150 h (27% after 980h mitigated start-stops).
- Increased CCL pore and ionomer diffusion losses due to carbon corrosion.







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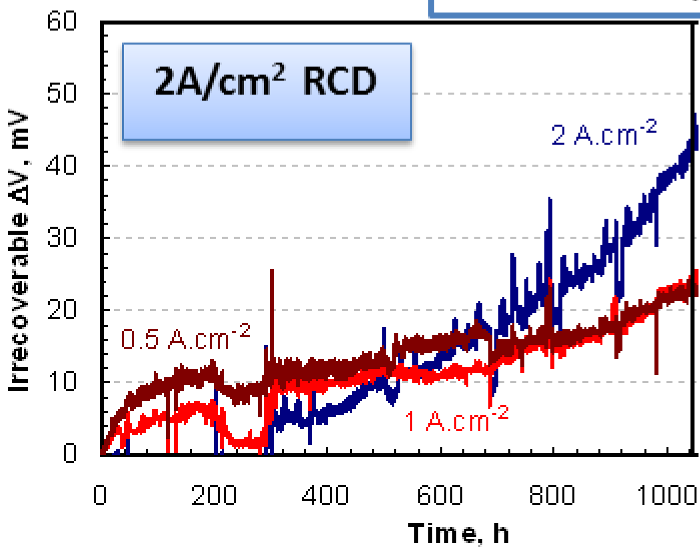
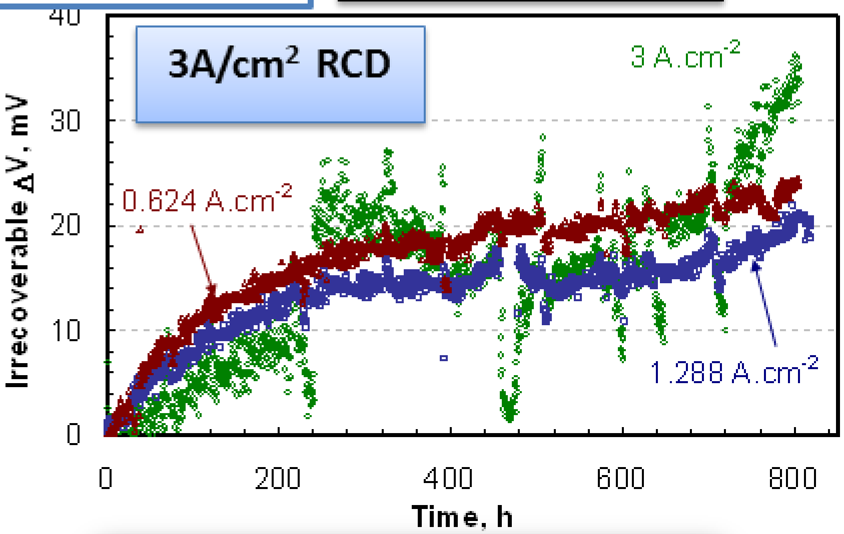
Technical Progress – Effect of Rated Current Density in NST3

Irrecoverable polarization losses

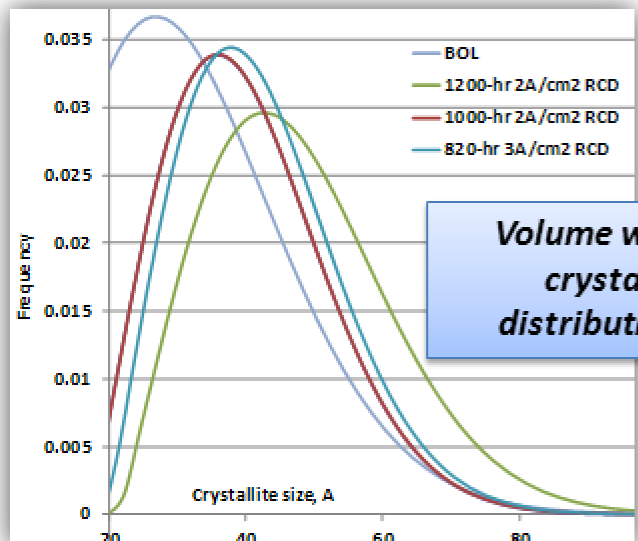
0.45mg Pt/cm²MEA





Operating the stack at higher rated current densities (N3A-3 cycle) does not accelerate degradation

- Membrane thickness at BOL
- Similar cathode thinning
- Similar Pt size distribution by XRD



Volume weighted Pt crystallite size distribution by XRD

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Technical Progress – TEM of MEAs past NST3

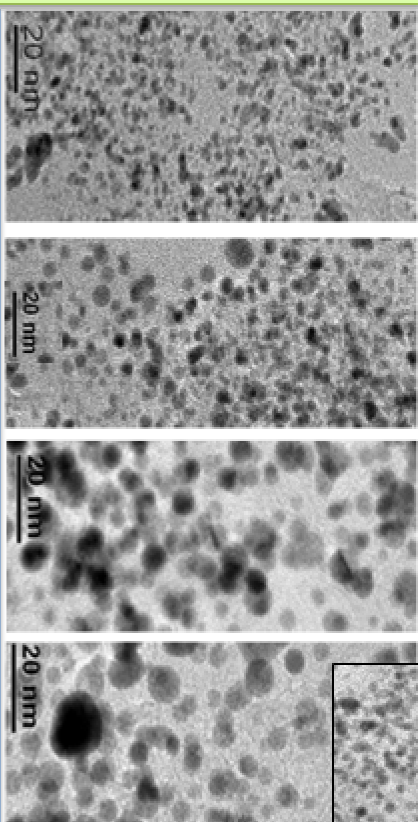
Cathode

BOL

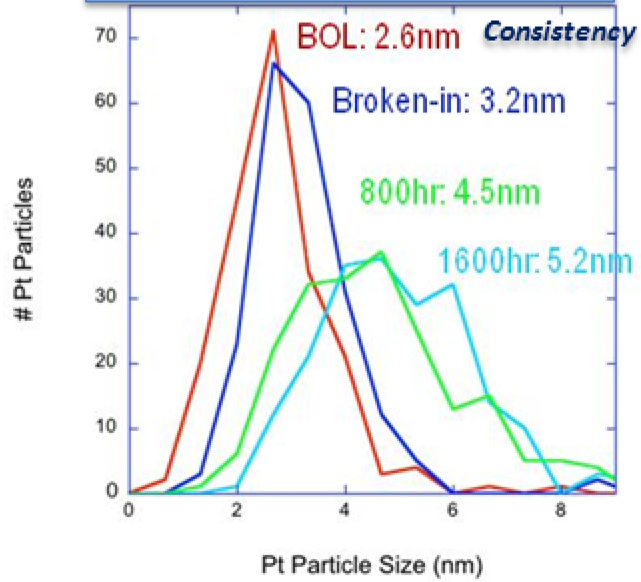
800 hrs

1000 hrs

1600 hrs

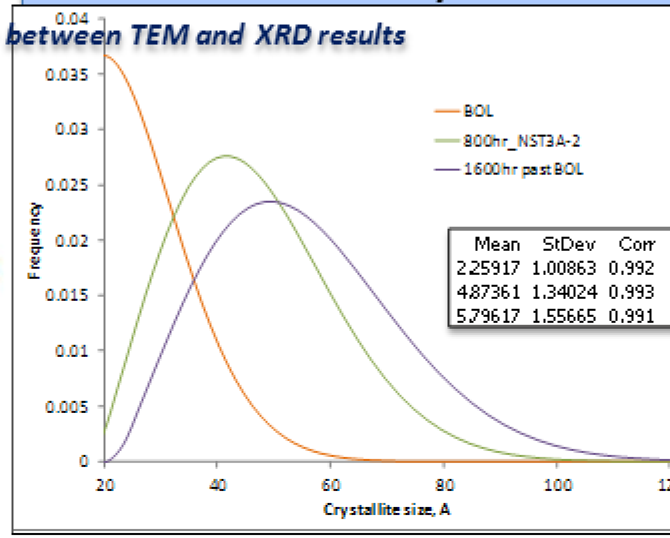


Pt particle size distribution from TEM imaging

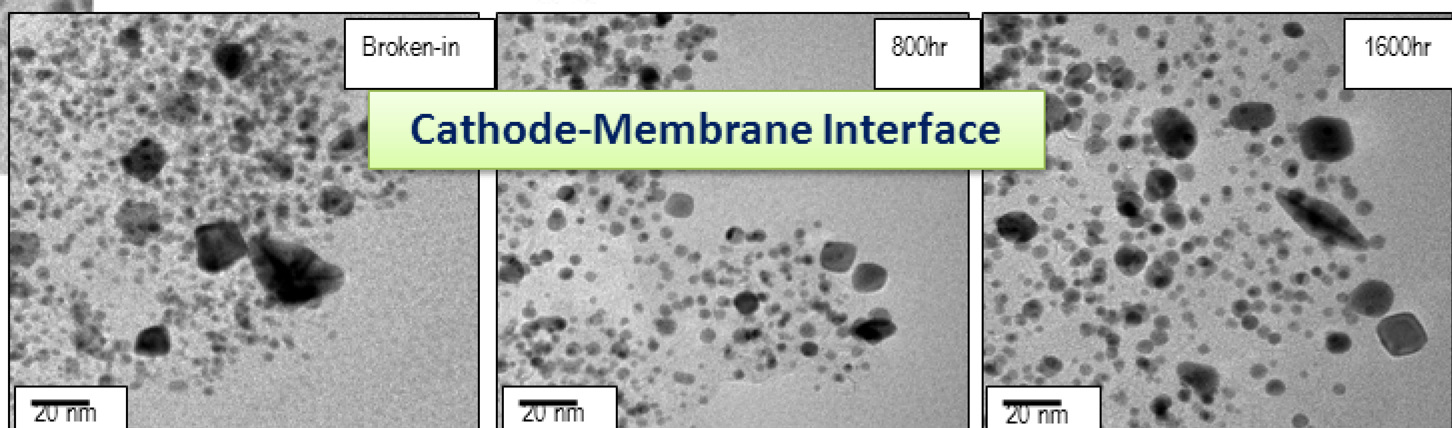


Volume weighted Pt crystallite size distribution by XRD

Consistency between TEM and XRD results



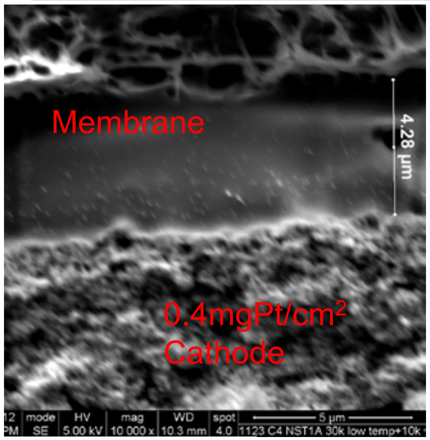
Cathode-Membrane Interface



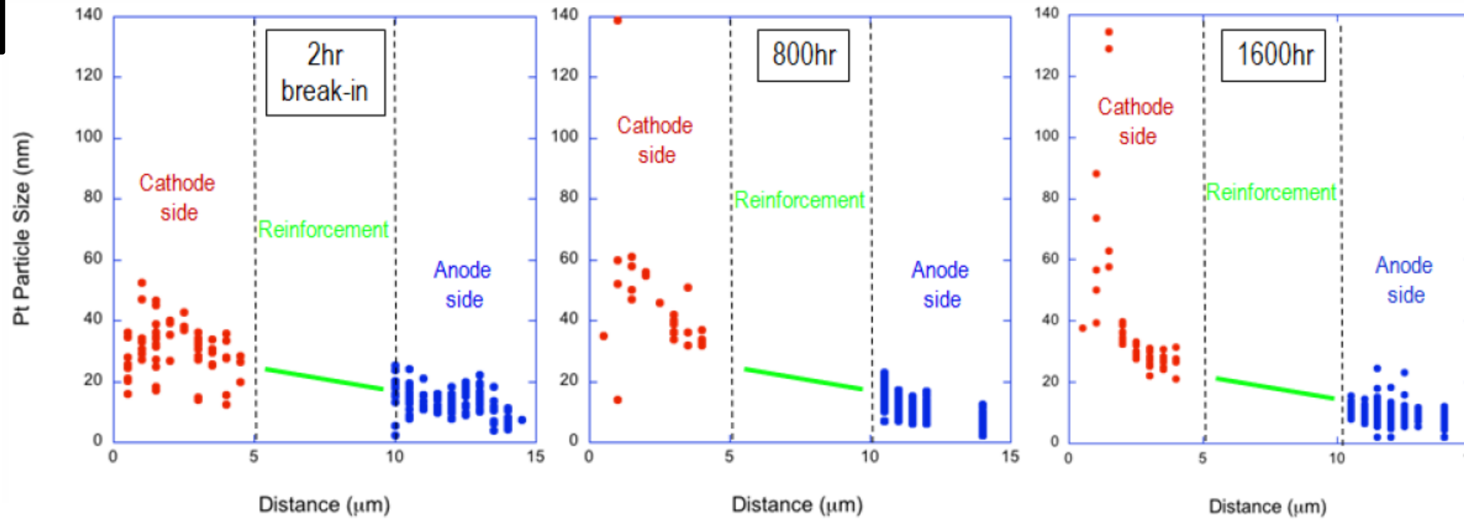
Pt particle shape/upper size at interface changed little from BOT to EOT

Technical Progress - Platinum loss to membrane

SEM of Pt band after 30K N1A load cycles

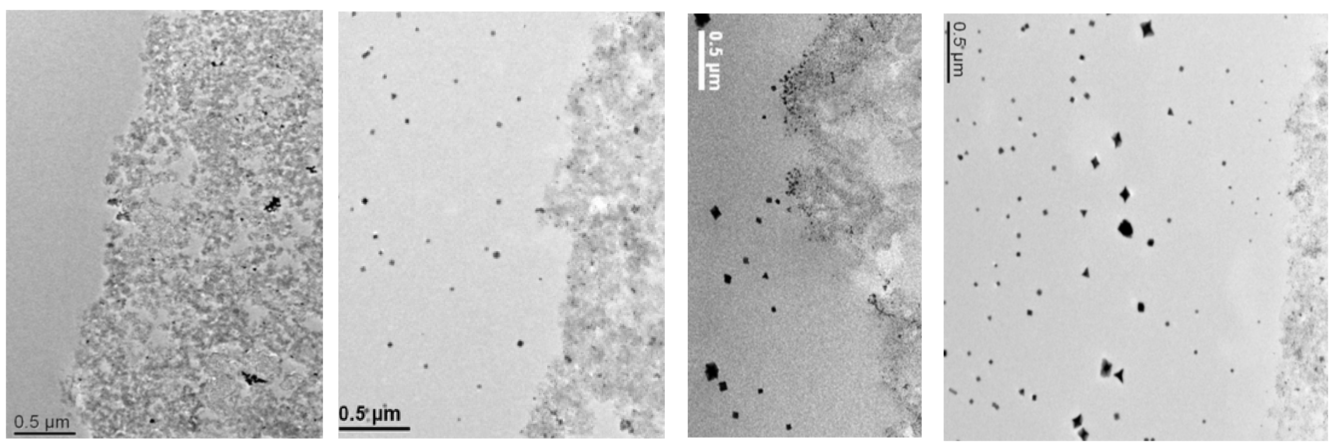


0.45mg Pt/cm² MEA from NST3 – drive cycle durability test



Quantification of the Pt loss from cathode into membrane was estimated via image analysis of the particle size distributions (total volume Pt particles) within specific areas of the membrane (base lined to Pt loading in cathode)

As manufactured	After break-in: ~4.8% Pt	800 hrs ~8.9%Pt	1600 hrs ~13.7% Pt



Collaborations

- Nuvera Fuel Cells (Industry) – prime contractor
  - Program management,
  - SCOF Development, validation and high power NSTs,
  - Stack NSTs.
- Los Alamos National Lab (Federal)– subcontractor
  - Single cell AST/NST testing,
  - Post-test characterization.
- Argonne National Lab (Federal) – subcontractor
  - Developer of Platinum stability and fuel cell durability model.
  - Lead data analysis and post-processing for LANL and Nuvera.
- Oak Ridge National Lab (Federal) – subcontractor
  - Post-test characterization.
- W.L. Gore & Associates (Industry) – lead MEA developer
- Durability Work Group – Borup/Myers lead

Proposed Future Work

FY2012-2013

- Refocus test campaign on NSTs in SCOF at Nuvera and RIT cell at LANL on low Pt MEAs.
- Develop Platinum ion transport model and integrate with the Platinum dissolution block into complete durability model.
- Validate model throughout NSTs and conduct model sensitivity study.
- Disseminate durability model to the industry.

Summary

- SCOF architecture successfully validated in ASTs and NSTs.
- MEA durability proven identical in SCOF and Orion stack under load cycle protocols.
- Benchmarking of Serpentine and Open flowfields completed.
- Degradation of Low Pt MEAs elevated with current density is attributed to mass transport within catalyst layer.
- High RCD does not accelerate the degradation of high Pt loaded MEAs.
- Good progress in durability model development.

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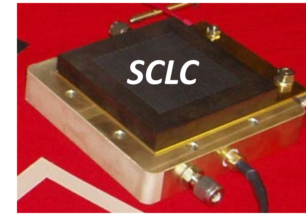
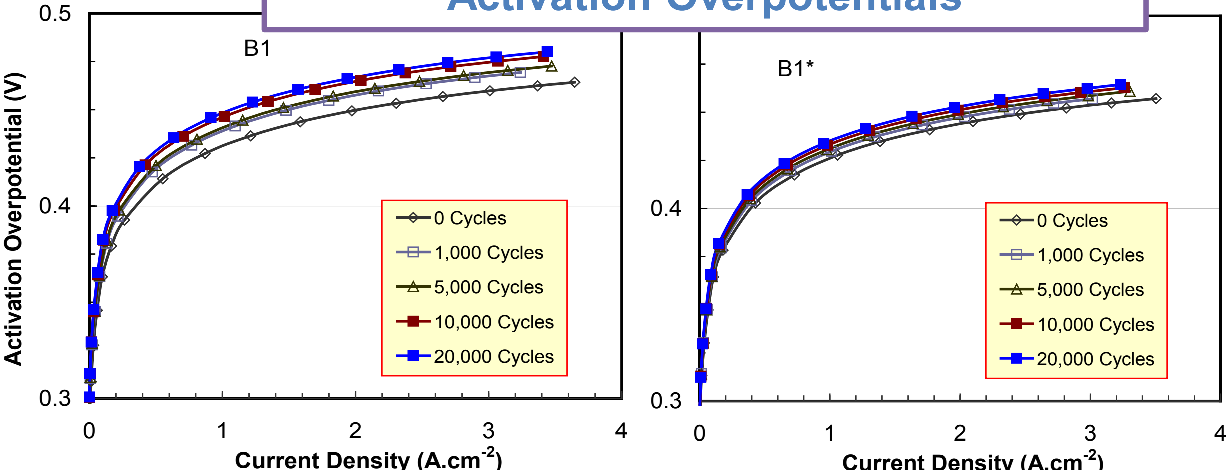
Technical Back-Up Slides

Effect of Potential Limits in AST



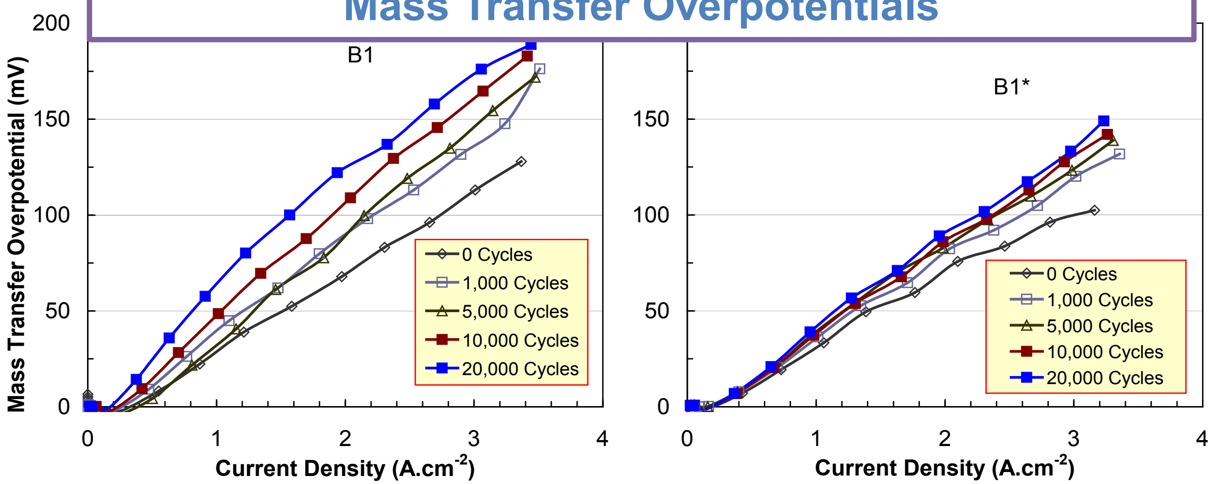
- B1 Protocol: 0.6 – 1 V triangle wave, 50 mV/s scan rate
- B1* Protocol: 0.582 – 0.886 V triangle wave, 50 mV/s scan rate

Activation Overpotentials



0.2mg/cm^2 Pt MEA

Mass Transfer Overpotentials

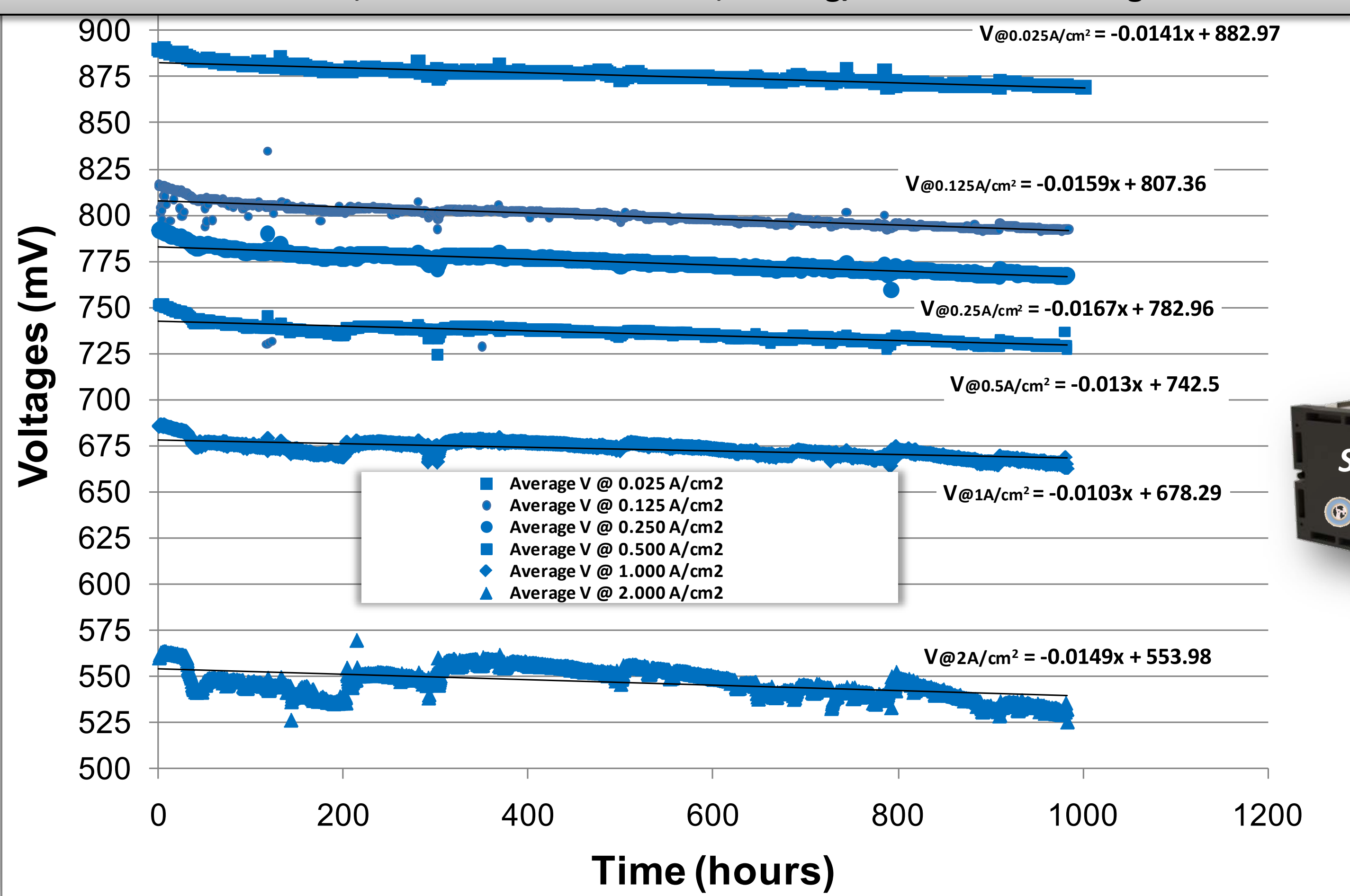


- Smaller increase in activation & mass transfer overpotentials with the B1* protocol (lower upper potential limit)
- ECSA loss and increase in overpotentials are correlated

Best-of-class Durability NST3

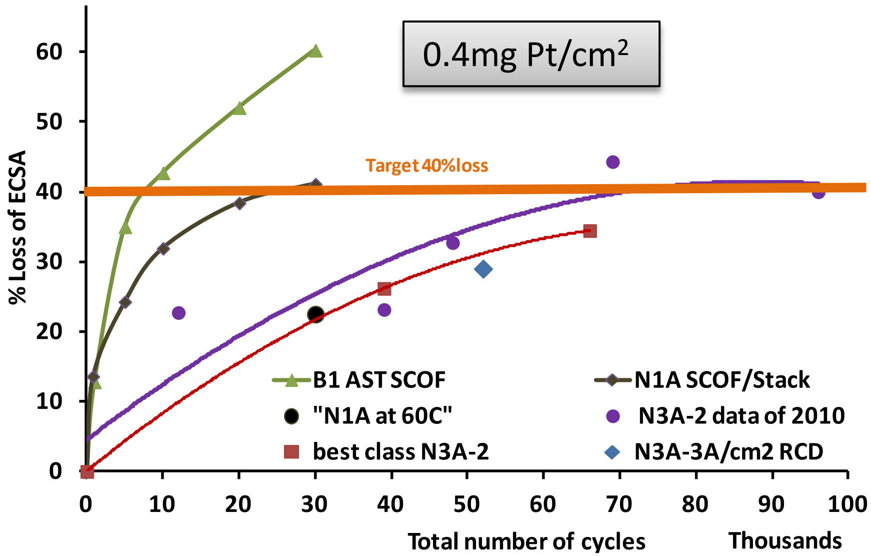
RCD 2A/cm^2

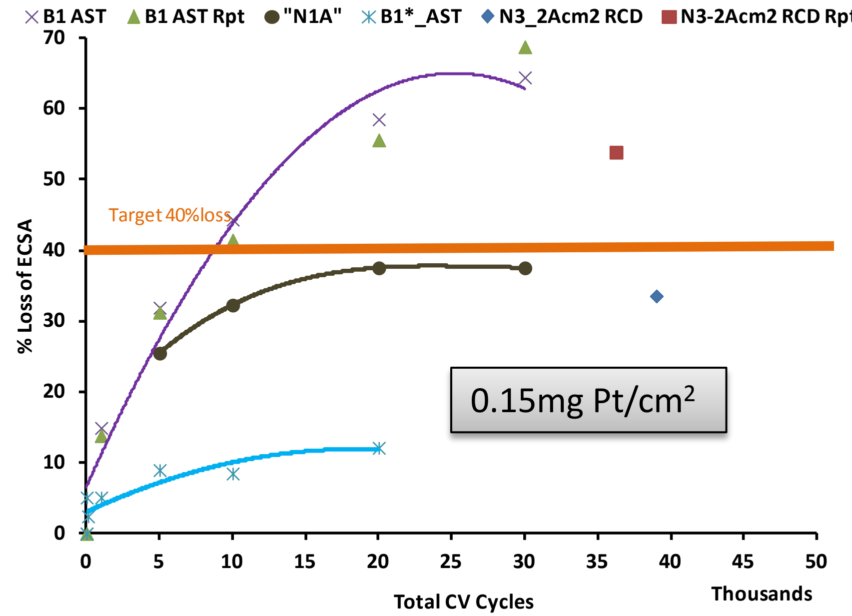
10-cell stack, 250-cm^2 cell active area, 0.45mg/cm^2 total Pt loading



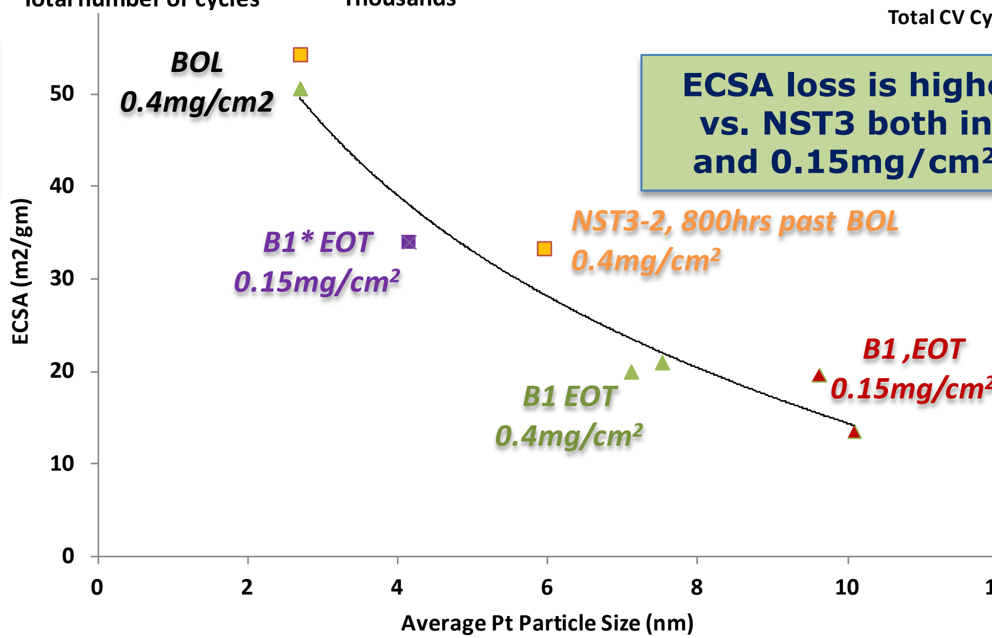
Voltage decays are in the expected range for automotive application for wide range of current densities

Technical Progress: Catalyst stability





XRD showed correlation between Pt particle size and ECSA for AST and NST



ECSA loss is higher for AST B1 vs. NST3 both in 0.4mg/cm² and 0.15mg/cm² Pt cathodes

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NUVERA FUEL CELLS

Technical Progress – Durability Model Framework

other component durability models

Model outputs: ECSA, PSD, η, V(time, A/cm²)

Inputs

- Cell Architecture
- Use cycles
- BOL data for the Electro-chemical package

Validation on NST

Pt Electrode stability Model

Pt Ion Transport Model

AST B1 inputs

Pt Aqueous Kinetics

Oxide coverage
Pt ⇔ PtOx

Dissolution-Redeposition
Pt ⇔ Pt^{2+}

Coalescence

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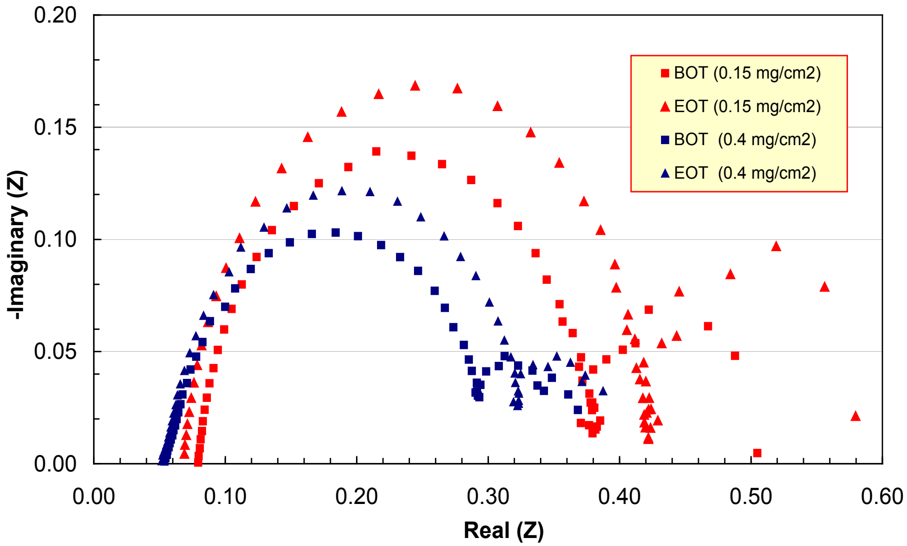
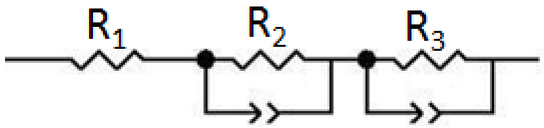
- Pt wire
- Pt/C –Etek 0.5mg/cm²
- Pt/C – Gore 0.15mg/cm²

Spire activities are synchronized with other DOE durability programs to avoid duplication of effort

Data Analysis Methodology

1. ORR kinetic constants from VIR at low current densities
2. Mass transfer overpotentials from VIR and kinetic losses
3. Analysis of EIS data for breakdown of mass transfer overpotentials





R_1: HFR

R_2: Resistance due to ORR kinetics and mass transfer in catalyst layer (CCL)

R_3: Resistance due to mass transfer in flow-field, GDL and MPL

- Multi-nodal reaction-diffusion model to determine k_g, k_c, k_i from R_2, R_3
  - k_g: O_2 diffusion across flow-field, GDL and MPL
  - k_c: O_2 diffusion in CCL micropores
  - k_i: O_2 diffusion to catalyst surface in CCL ionomer
- Supplemental helox data: k_g and k_c are higher than in air but not k_i