2013 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)

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Nuvera Fuel Cells

5/14/2013

FC014

Overview

Timeline

- Kick-Off: December, 2009
- 4-year program ending 09/30/2013
- 90% Complete

Barriers

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

Budget

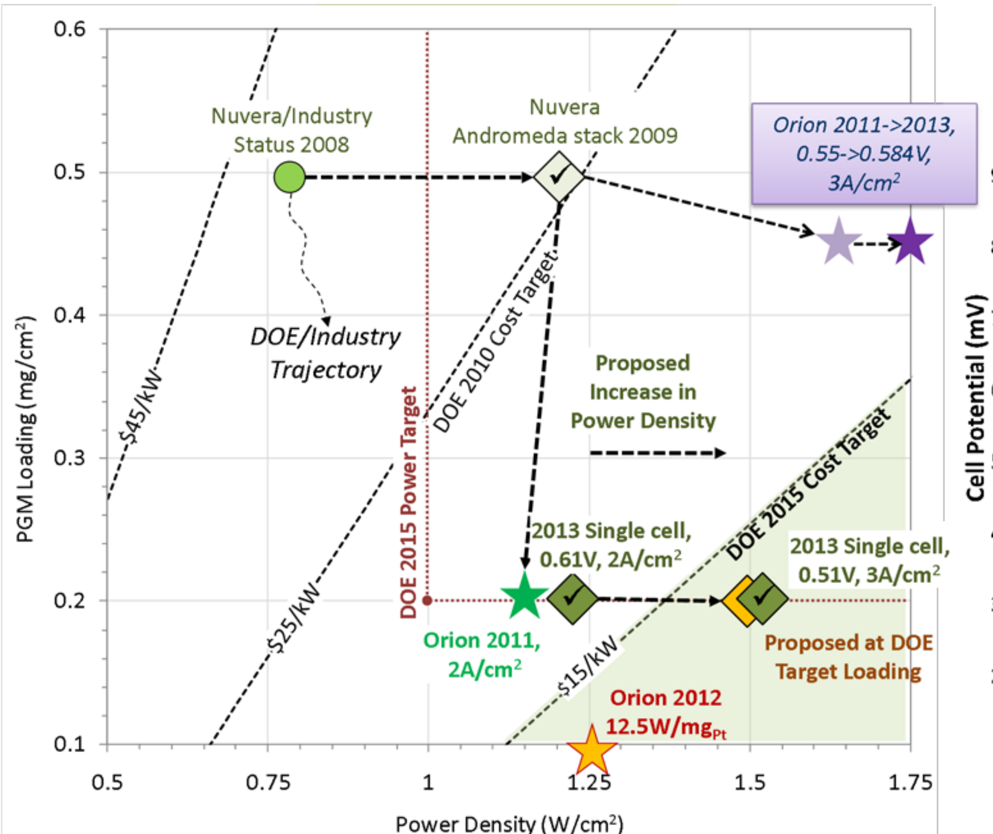
- $5.642M Total Project
  - $3.875M DOE Share (Includes $0.975M for National Labs)
  - $1.767M Cost Share
- DOE FY12 Funding: $386.5K
- DOE Planned FY13: $708.4K

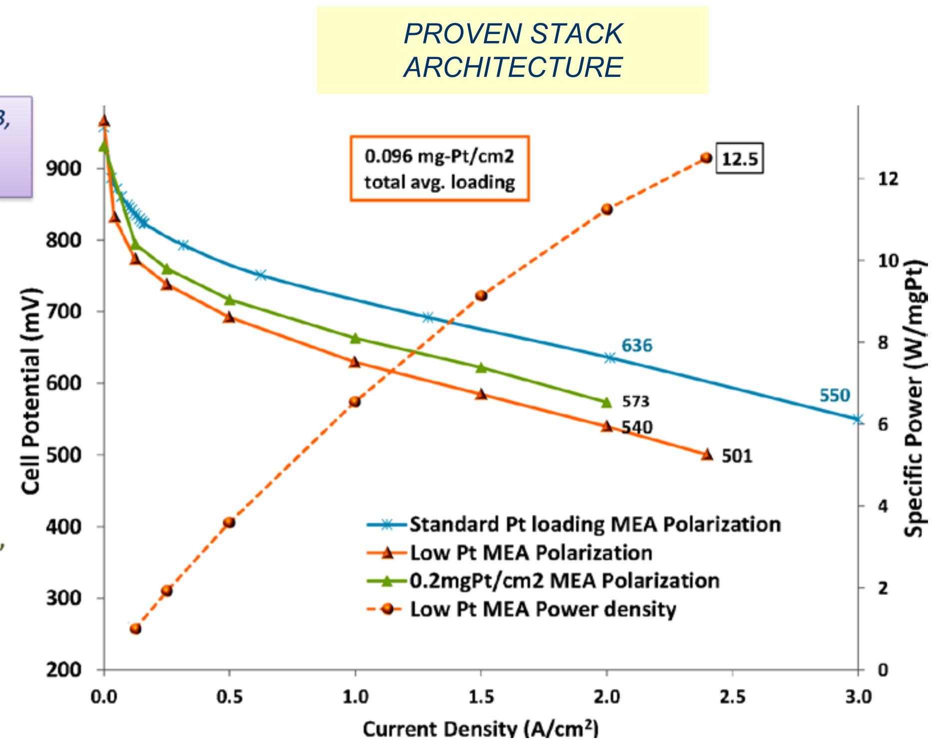
Partners

- Los Alamos National Laboratory
- Argonne National Laboratory
- Nuvera Fuel Cells (lead)

Relevance: Objectives and Deliverables

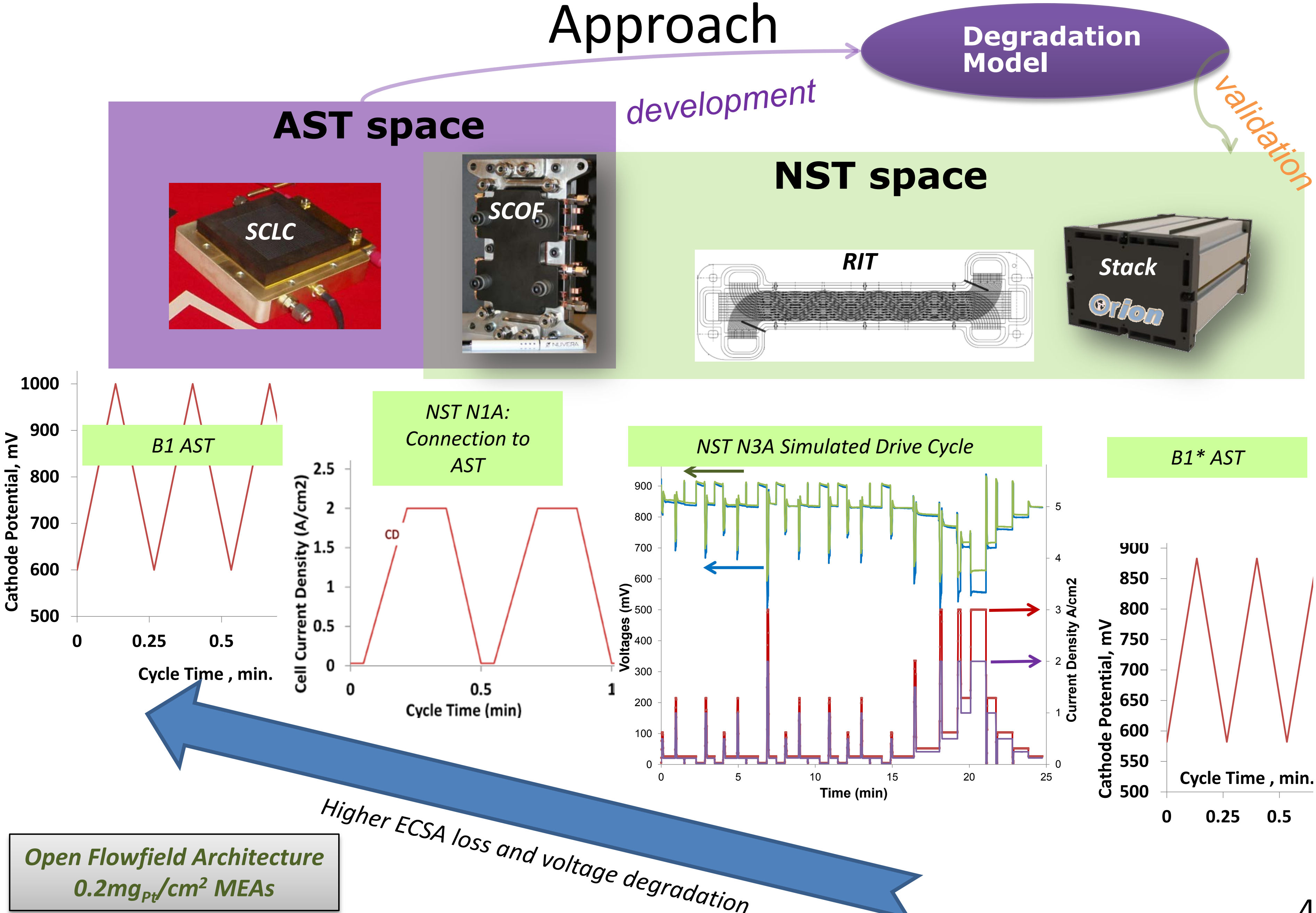
The technical objective is to identify and model PEMFC durability factors associated with low-Pt MEAs operating at high(>1W/cm²) power density.





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

Approach



Degradation Model
development
validation
AST space
SCLC
SCOF
NST space
RIT
Stack
Orion
B1 AST
Cathode Potential, mV
1000
900
800
700
600
500
0
0.25
0.5
Cycle Time , min.
NST N1A: Connection to AST
Cell Current Density (A/cm2)
2.5
2
1.5
1
0.5
0
CD
0
0.5
1
Cycle Time (min)
NST N3A Simulated Drive Cycle
Voltages (mV)
900
800
700
600
500
400
300
200
100
0
Current Density A/cm2
5
4
3
2
1
0
0
5
10
15
20
25
Time (min)
B1* AST
Cathode Potential, mV
900
850
800
750
700
650
600
550
500
Cycle Time , min.
0
0.25
0.5
Higher ECSA loss and voltage degradation
Open Flowfield Architecture
0.2mgPt/cm2 MEAs

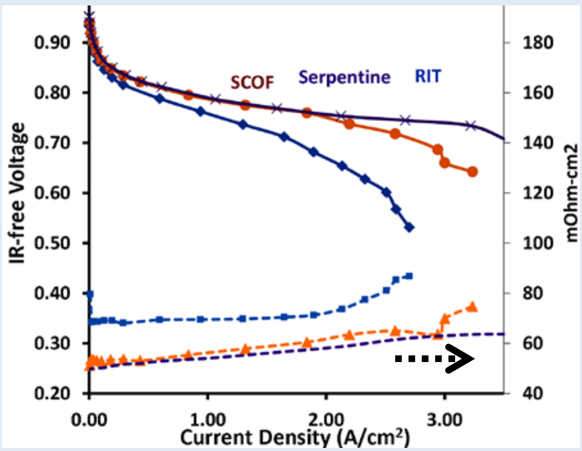
Approach – Milestones and Go/No GO

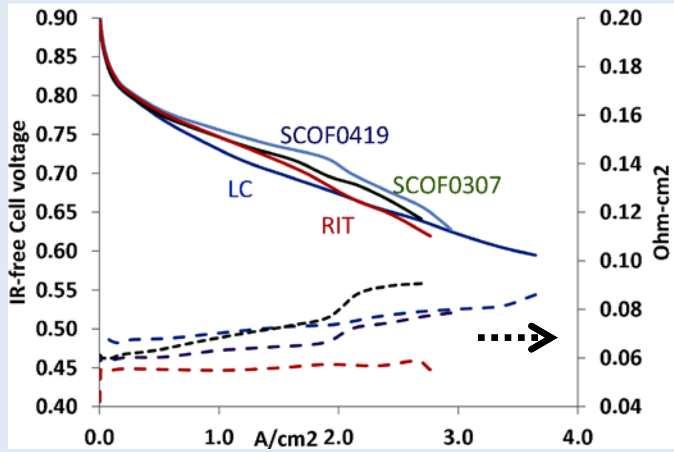
Milestone	Due date	Status
1. Model Block diagram published.	FY2010, Q3	Complete
2. Single Cell Open Flowfield (SCOF) hardware validated and delivered to LANL.	FY2011, Q1	Complete
3. Comparative data for Single Cell Land Channel (SCLC) and SCOF on AST protocol is published	FY2012, Q1	Complete
GNG decision: 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	Complete
5. Validated model and data set published and available to industry	FY2013, Q4	In Progress

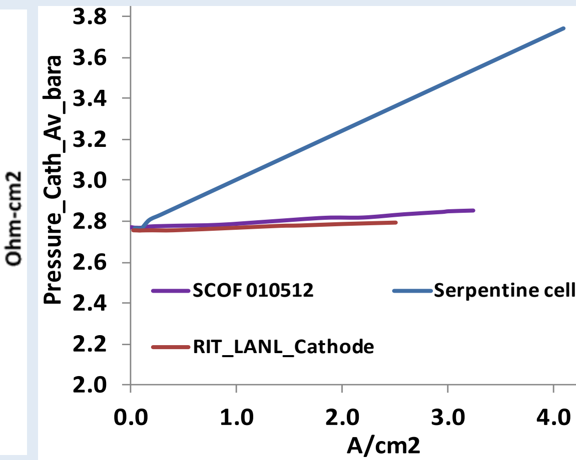
Technical Accomplishments: BOL Performance Serpentine - SCOF – RIT Architecture

$0.45 mg_{Pt}/cm^2$ | $0.2 mg_{Pt}/cm^2$ | Average. Cathode Pressure in flowfield

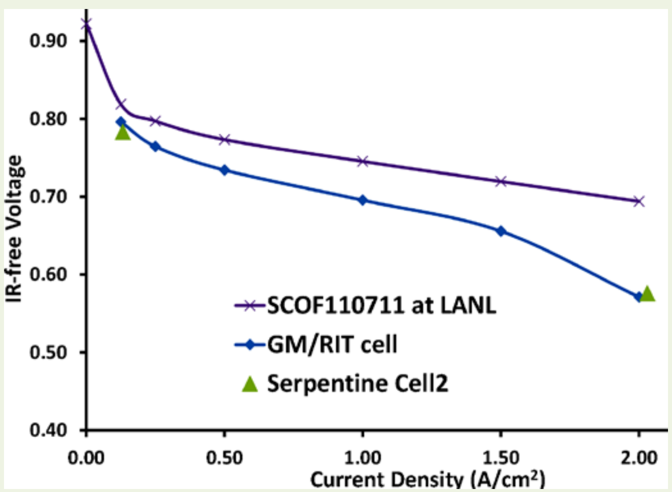
High Pressure LANL Conditions



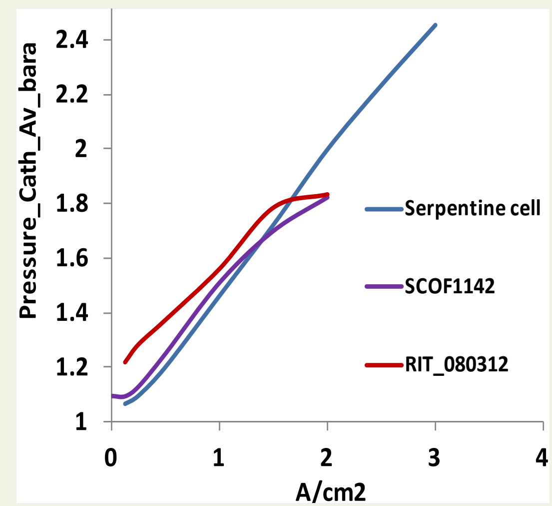




Low Pressure Nuvera conditions



- **At high pressure conditions SCOF showed mass transport performance benefits over RIT with 0.45- and 0.2- mg_{Pt}/cm^2 MEAs.**
- **At low pressure condition SCOF showed mass transport benefits over RIT and Land-channel cells with 0.45 mg_{Pt}/cm^2 MEAs.**



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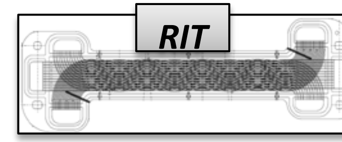
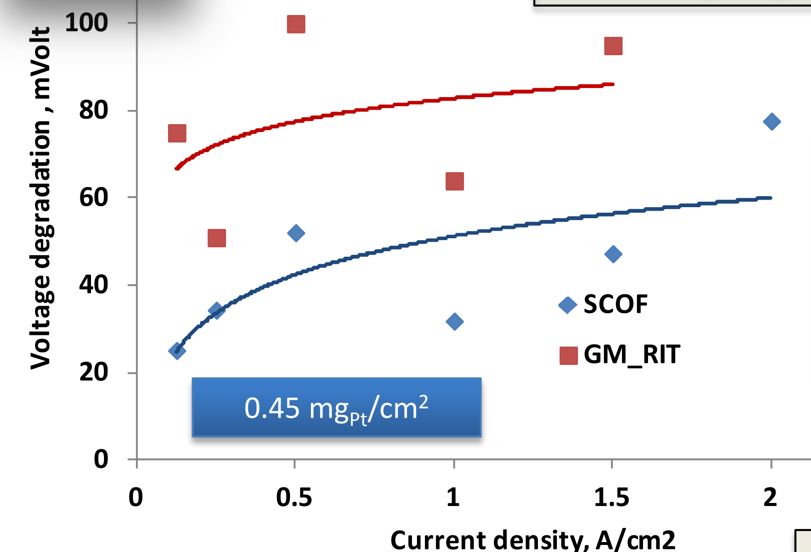
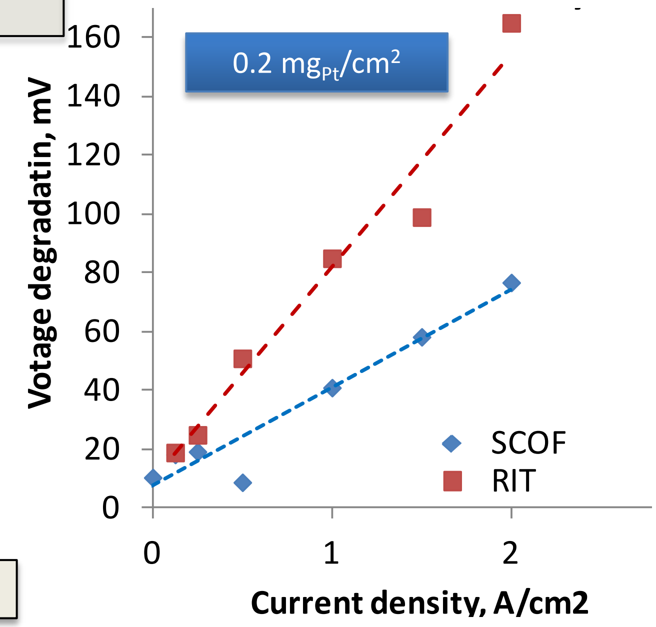
Technical Accomplishments
Durability with current draw.



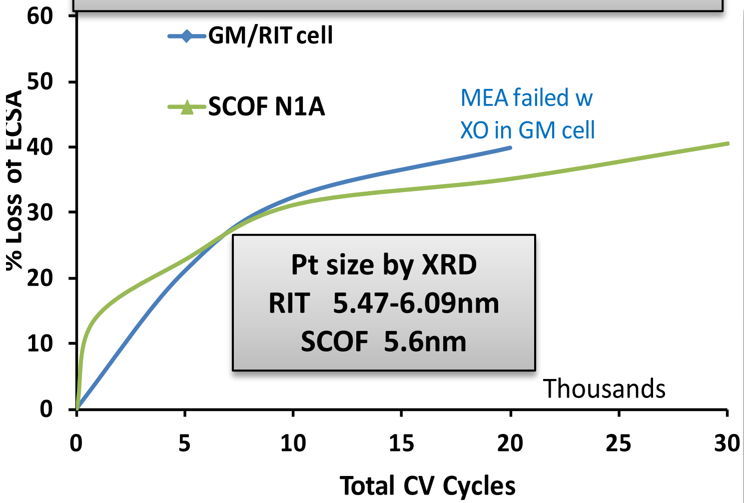
Voltage degradation by Polarization Curve



N1A-2 load cycle test (0.025-2A/cm²,
constant A/C flows at 2A/cm², 80°C, 100% RH).

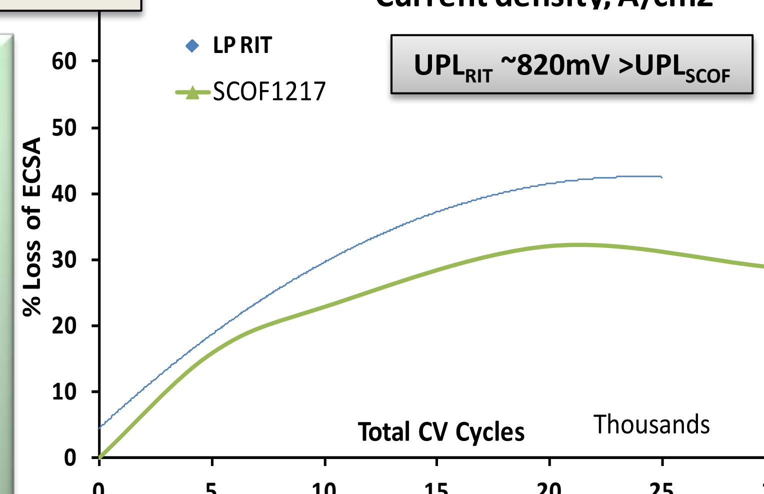


UPL in SCOF and RIT is ~890mV



Loss of ECSA in N1A test

Pt loss is independent of cell architecture, but voltage decay is higher for RIT regardless of Pt loading.



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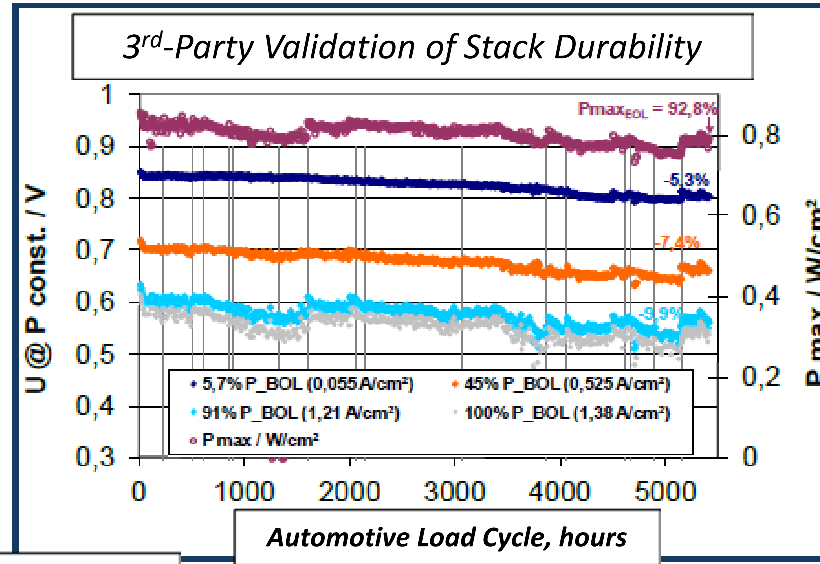
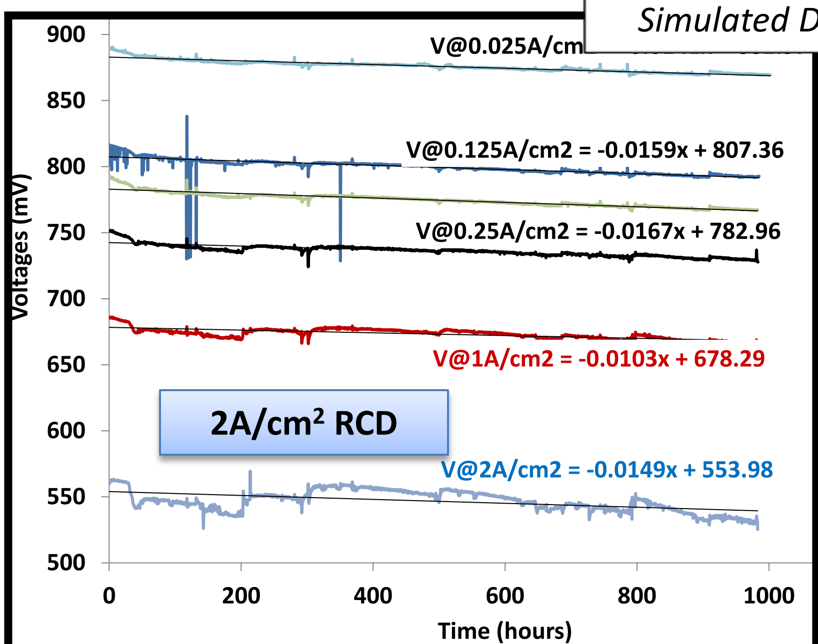
Technical Accomplishments: Short Stack Durability

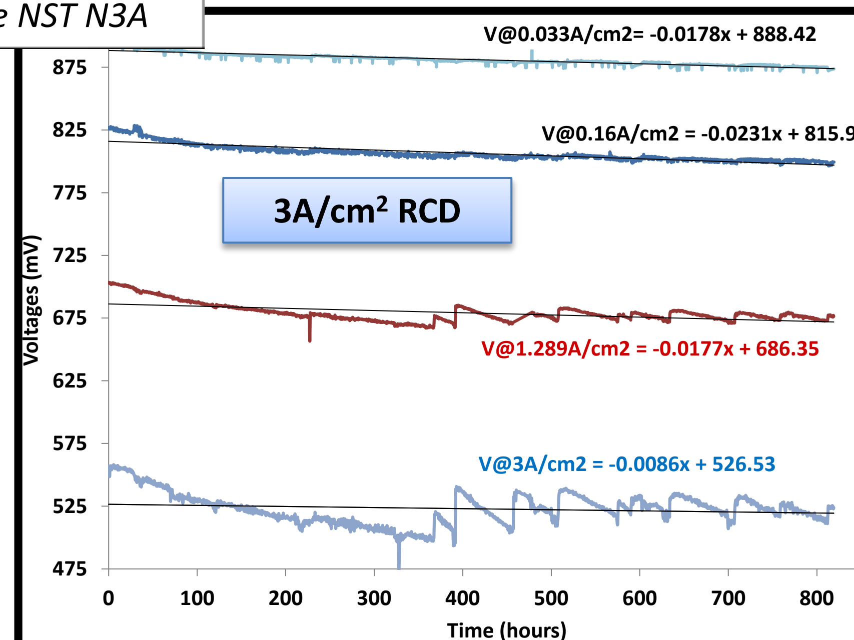
8-10-cell stacks , 250 and 360-cm² cell active area, 0.45mg/cm² total Pt loading

Operating the stack at higher rated current densities does not accelerate degradation
- Membrane thickness does not change at any RCD.
- Pt size distribution increases the same at all RCD.



Simulated Drive-Cycle NST N3A

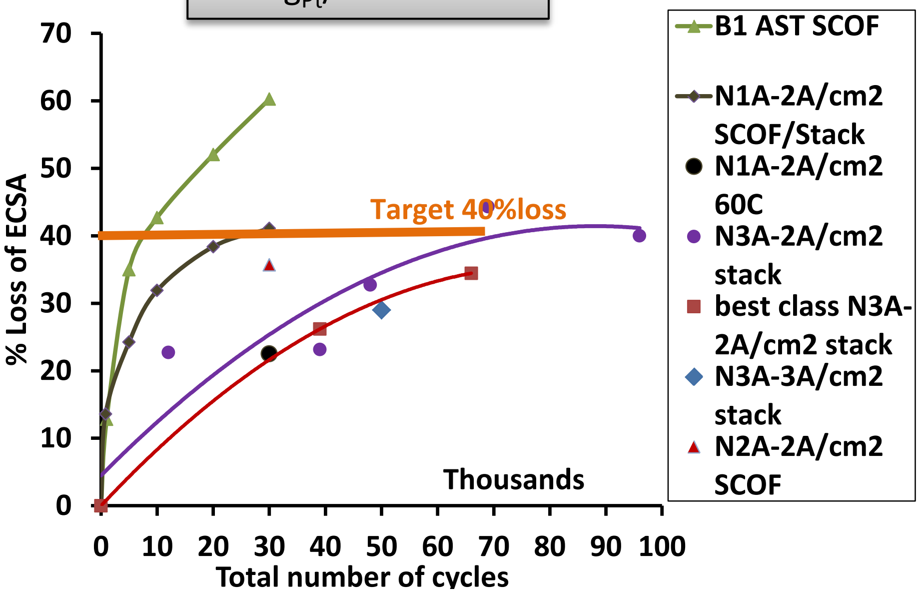




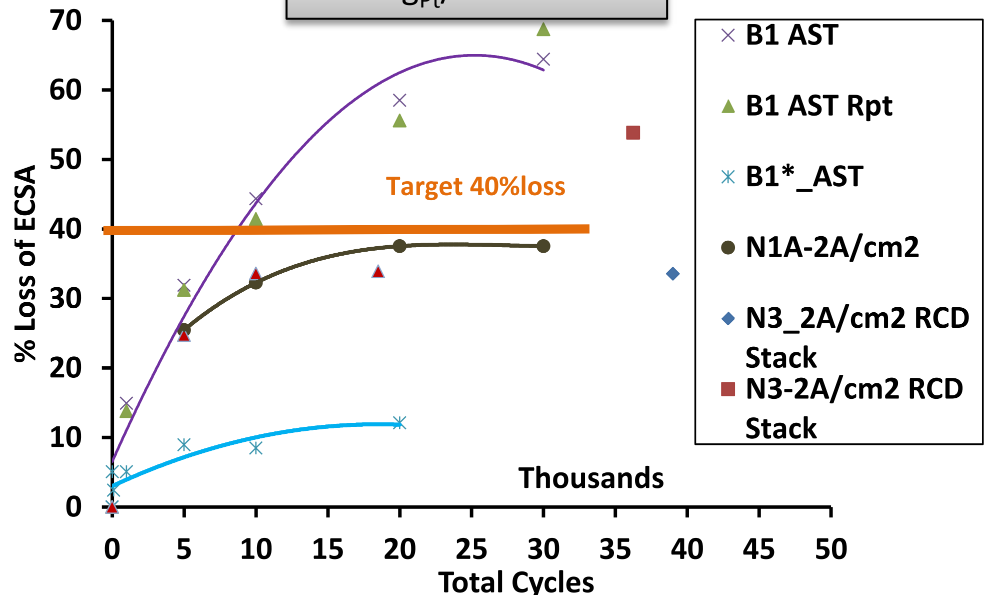
Technical Accomplishments: Effect of Cycle

Cathode ECSA loss in cycle tests

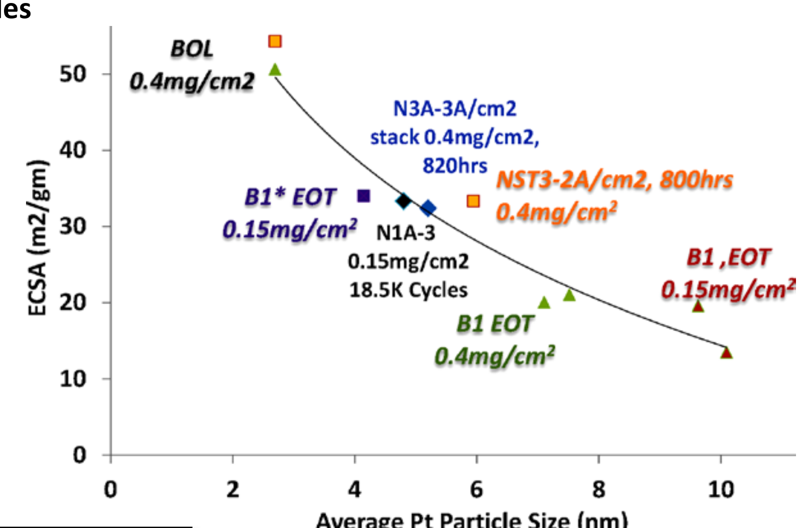
0.4mg$_{Pt}$/cm^2 cathode



0.15mg$_{Pt}$/cm^2 cathode



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



ECSA loss:

- **in ASTs B1>N1A>N3A>B1***
- **is similar in 2- and 3-A/cm2 RCD NSTs**
- **in N1A is similar at both loadings**

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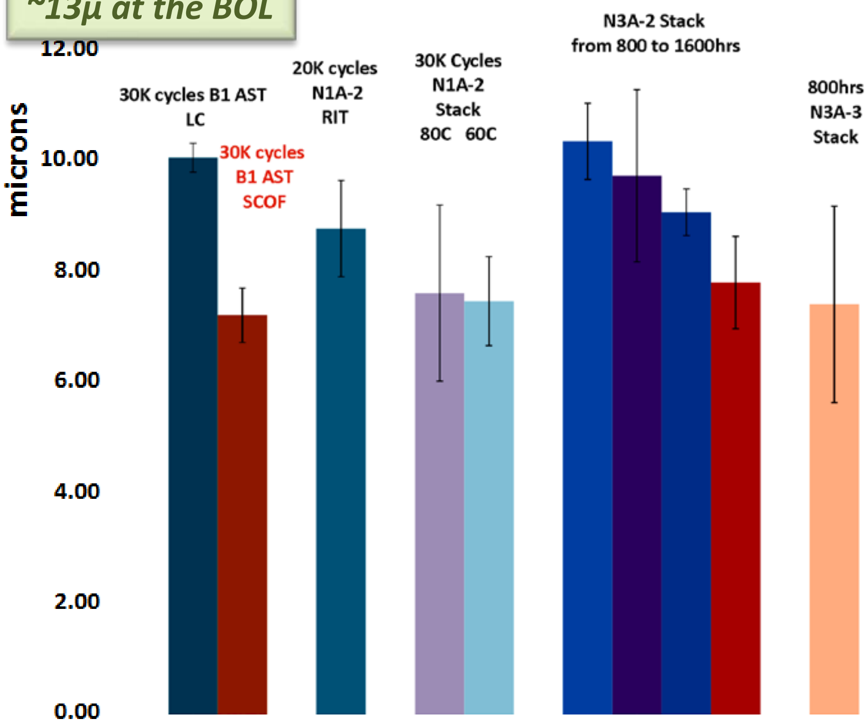
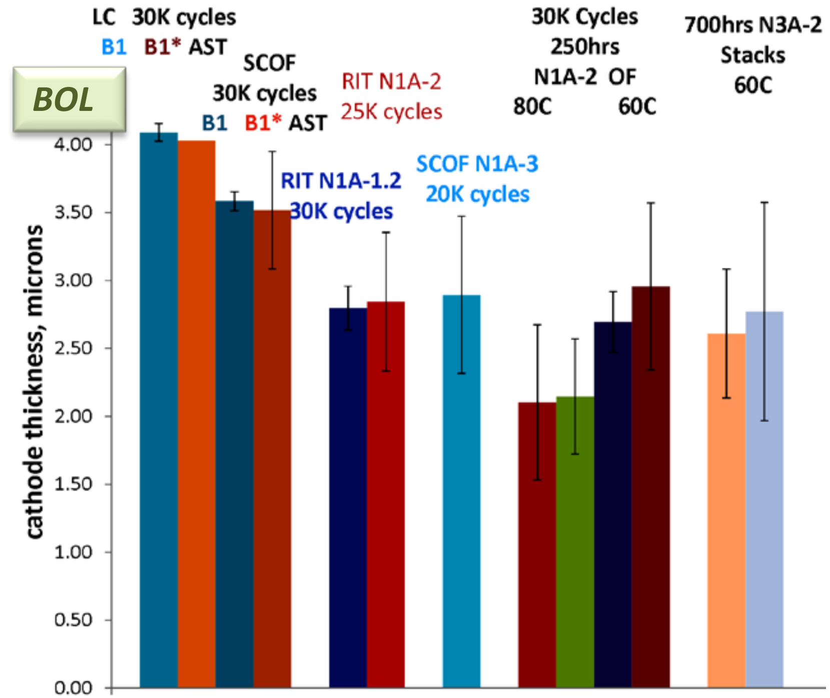
Technical Accomplishments
Post Test Analysis of Cathodes by SEM

Normal Platinum Cathode

~13μ at the BOL

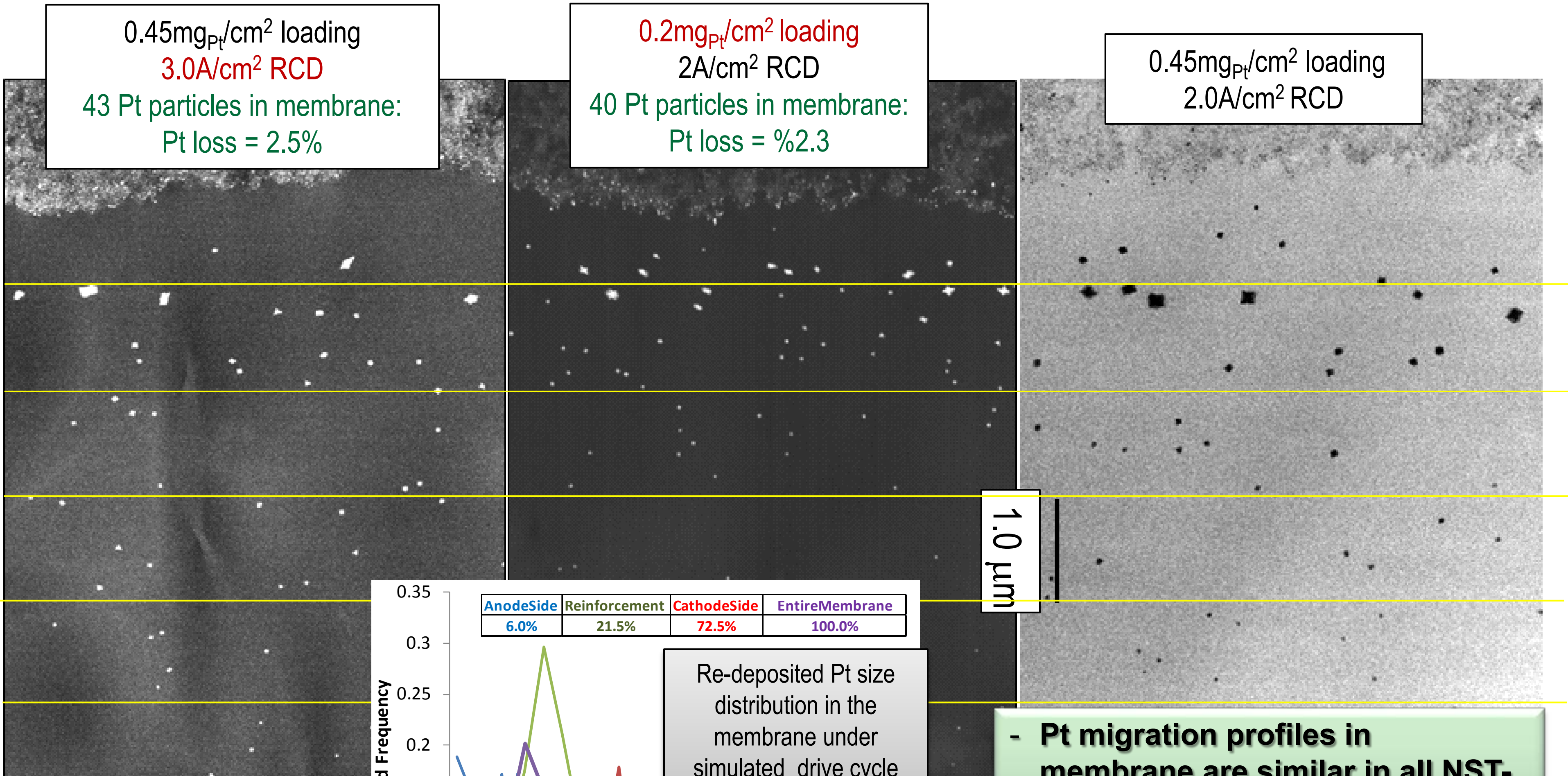


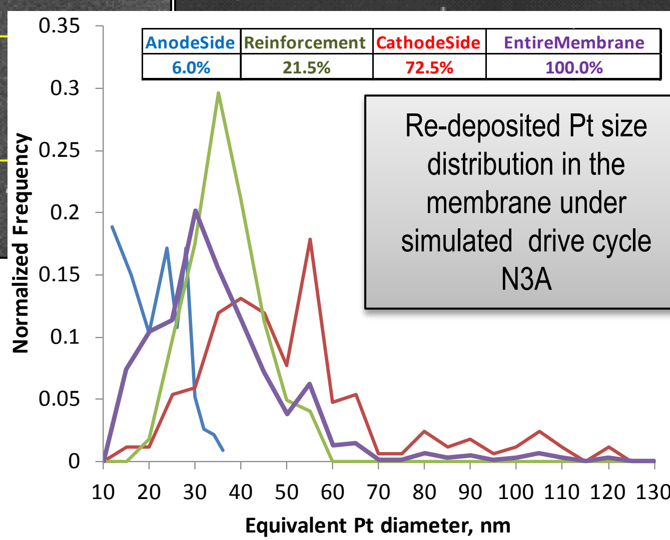
Low Platinum Cathode



- Thinning of normal Pt cathodes start at conditioning and is progressing with cycle time.
- Thinning of low Pt cathodes
  - did not correlate with voltage degradation in B1 and B1* ASTs ;
  - higher in 80°C than 60°C N1A-2;
  - similar at different RCDs.
- Thinning is often local, possibly higher in OF>RIT>Serpentine – more data needed.

Technical Accomplishments
Platinum in the Membrane by TEM





- **Pt migration profiles in membrane are similar in all NST-N3 tests at 800hrs since BOL.**
- **Pt mass is dominant at cathode side of the membrane.**

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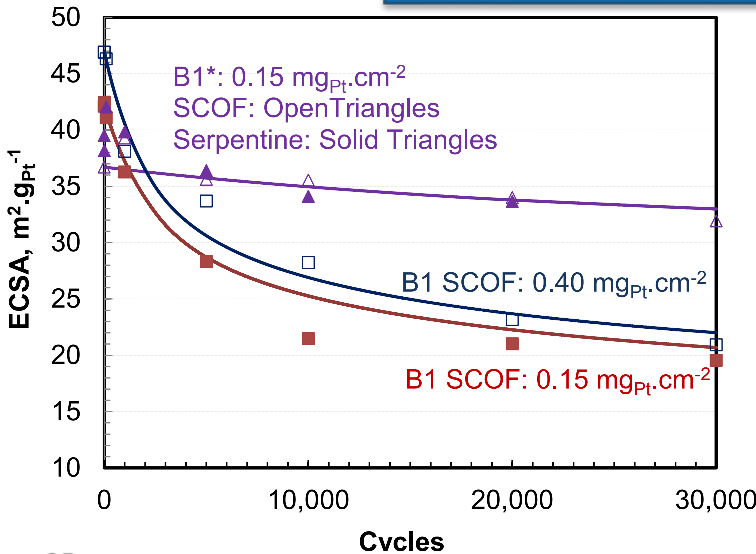
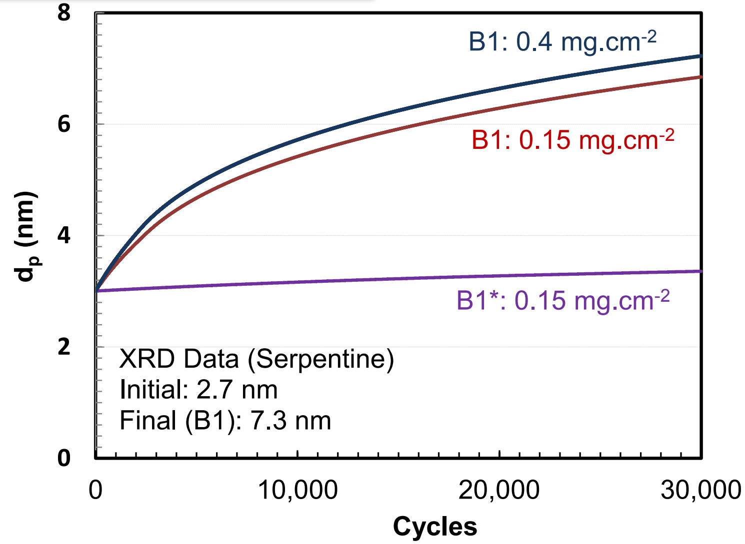
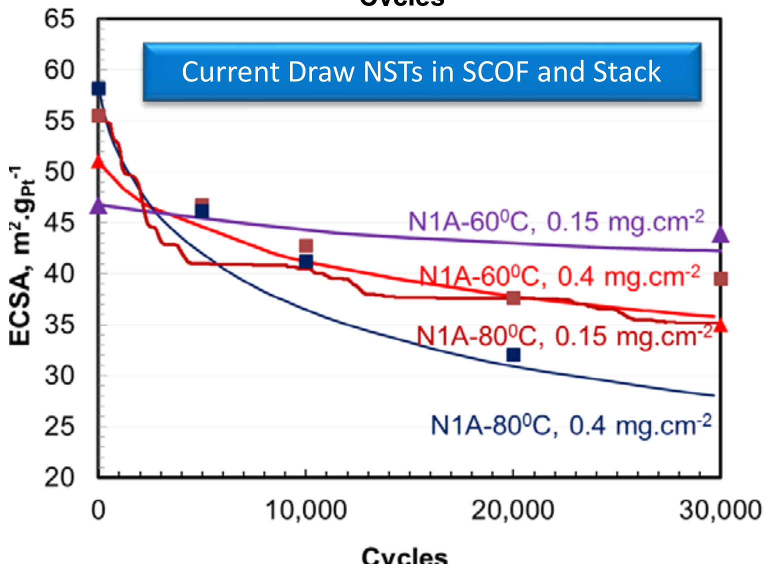
Technical Accomplishments
Platinum Dissolution - Model Validation

ASTs in SCOF and Serpentine Single Cells







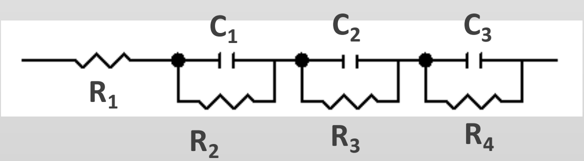
N1A-60°C: Model is consistent with SCOF data
N1A-80°C: SCOF and stack data used.
Faster dissolution rate constant at 80°C

Measured ECSA loss in ASTs and N1A NSTs is consistent with the thermodynamic and kinetic constants derived from the aqueous data

Technical Accomplishments
Catalyst Performance Degradation Model

EIS based GDL and CCL Degradation Model

1. ORR kinetic constants from VIR at low current densities.
2. Total mass transfer overpotentials from VIR and kinetic losses.
3. Analysis of EIS data for breakdown of mass transfer overpotentials.
4. ZVIEW equivalent circuit, R_i and C_i determined to fit EIS data.



R_1: HFR including contact resistances

R_2: Resistance due to:

ORR kinetics +

proton conduction in cathode catalyst layer (CCL) +

O_2 diffusion across ionomer to TPB*

R_3: Resistance due to O_2 diffusion in CCL pores (and GDL + flow field)

R_4: Resistance due to O_2 diffusion across GDL (and flow field)

Reaction-Diffusion model parameters are calibrated with the impedance data

Multi-nodal reaction-diffusion model of GDL and CCL

$$k_g = \frac{D^g_{O_2}}{\delta_g}$$

$$k_c = \frac{D^c_{O_2}}{\delta_c}$$

$$k_i = \frac{D^i_{O_2}}{t_f}$$

$$t_f = d_p\left[\left(\frac{V_i}{V_c}\right)^{\frac{1}{3}} - 1\right]$$

$$A_{Pt}L_{Pt}\left(\frac{k_i}{\delta_c}\right)H_{O_2}\left(P^c_{O_2} - P^s_{O_2}\right) = \frac{j}{4F}$$

Symbols

A_{Pt}: ECSA, $m^2.g^{-1}$

D: Diffusivity, $m^2.s^{-1}$

d_p: Pt particle diameter

δ: Thickness

H: Henry's law constant, $mole.m^{-3}.atm^{-1}$

j: ORR rate, $A.m^{-3}$

k: Mass transfer coefficient, $m.s^{-1}$

L_{Pt}: Pt loading, $mg.cm^{-2}$

t_f: Ionomer film thickness

V: Volume

Subscripts and Superscripts

c: CCL

g: GDL

i: Ionomer

s: Catalyst surface

- Transport coefficients k_g, k_c, k_i determined such that the cell voltage E from multi-nodal diffusion model satisfies the following conditions

$$R_\Omega + R_2 + R_3 = -\frac{dE(k_g=\infty, k_c, k_i, I)}{di}$$

$$R_2 + R_\Omega = -\frac{dE(k_g=\infty, k_c=\infty, k_i, I)}{di}$$

$$E(k_g, k_c, k_i, I) = E(measured)$$

*TPB: Three-phase boundary

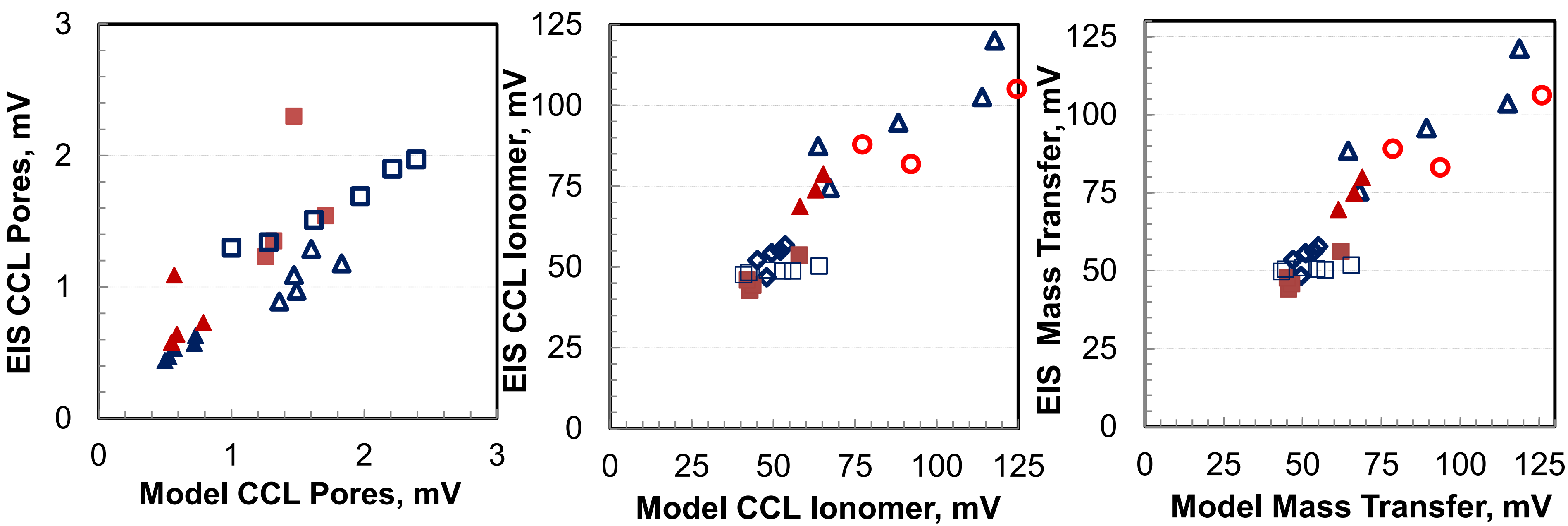
Accomplishments: Transport Model Calibration

Nuvera Open Flowfield

Model transport parameters are in agreement with coefficients derived from EIS experiments

Transport Model Accuracy	
Overpotential	R^2
GDL	
CCL Pores	0.904
CCL Ionomer	0.982
Mass Transfer	0.985

- ■ 0.4 mg.cm-2, 1 A.cm-2, N1A80C
- △ 0.4 mg.cm-2, 2 A.cm-2, N1A80C
- ■ 0.15 mg.cm-2, 1 A.cm-2, N1A80C
- ▲ 0.15 mg.cm-2, 2 A.cm-2, N1A80C
- □ 0.4 mg.cm-2, 1 A.cm-2, B1
- ○ 0.4 mg.cm-2, 2 A.cm-2, B1

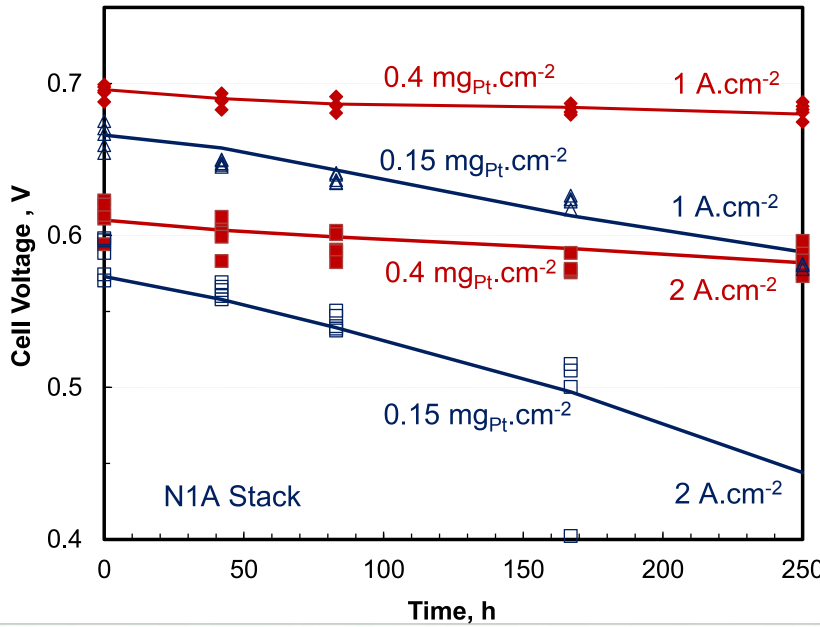


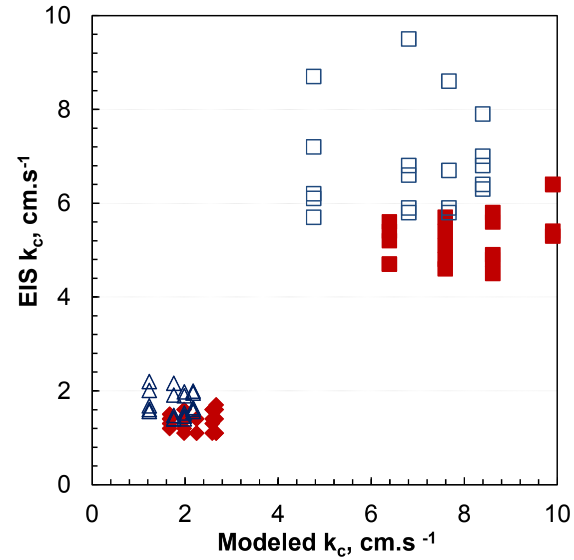
Technical Progress: Degradation Model Validation N1 Stack Data

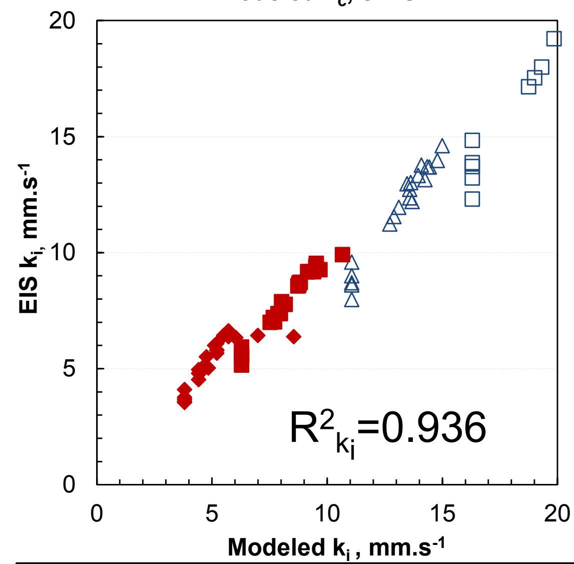
Model Inputs

- Pt particle size estimated from ECSA measured for each cell at 0, 40, 75, 160 and 250 h.
- BOT and EOT catalyst layer thicknesses for one cell.
- Compared to SCOF data, i_0 increased by 20% to match the BOT stack voltages.

Voltage degradation at 65°C: pol-data (solid lines) and model (symbols)







Modeled voltage degradation is in good agreement with the experimental performance of MEAs in the accelerated load cycle test N1.

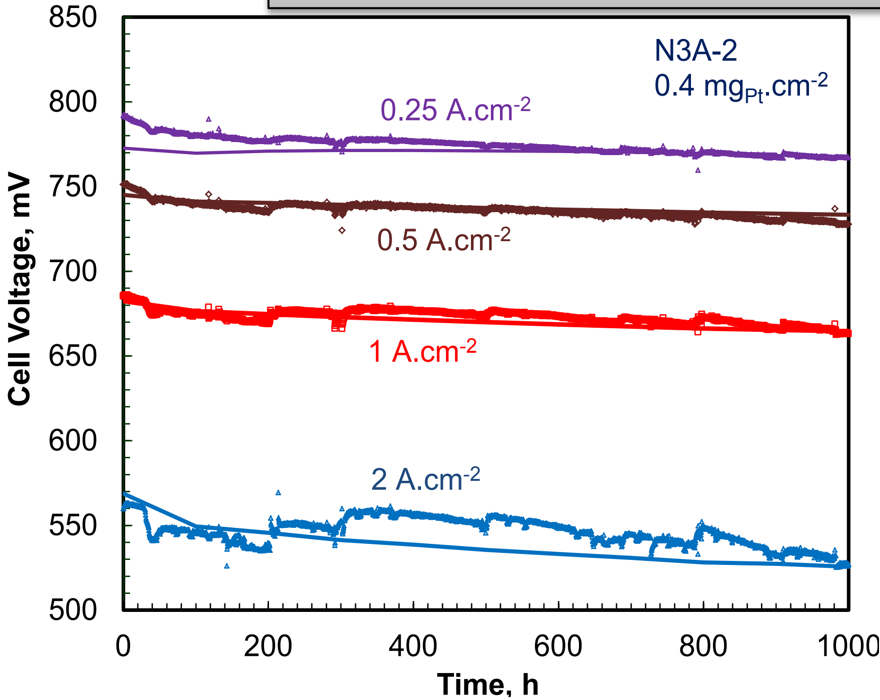
Transport coefficients from N1A EIS data and SCOF model correlations

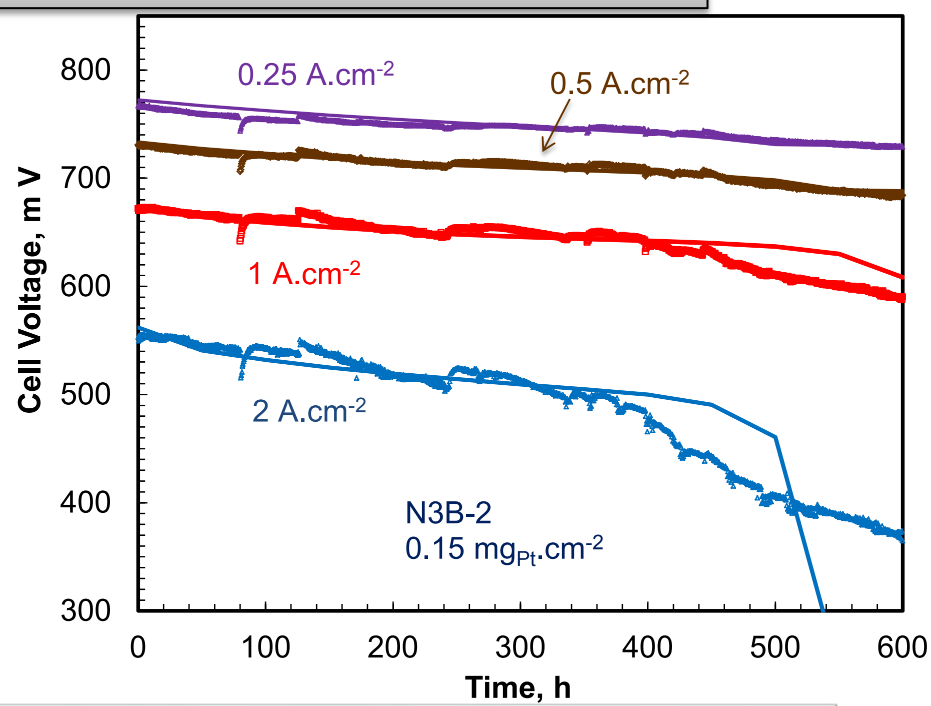
Technical Progress: Performance Degradation Model Validation –N3 Stack Data

Model Inputs

- Pt particle size estimated from ECSA at 0, 650 and 1100 h in N3A-2 and 700 h in N3B-2 tests.
- Cathode catalyst layer thicknesses interpolated from measured values at BOT and EOT.
- Compared to SCOF data, exchange current density increased by 75-80% to match the BOT stack polarization data.

Voltage degradation at 60-66°C: data (symbols) and model results (solid lines)





Voltage degradation model predicted performance of studied MEAs throughout wide range of current densities in the simulated drive cycle test.

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

FY2013

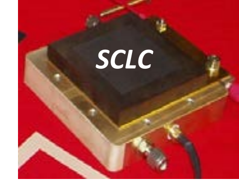
- Complete test campaign on NSTs in SCOF at Nuvera and LANL on low Pt MEAs.
- Verify model correlations using additional EIS diagnostics in H2/air/Helox during NSTs.
- Disseminate durability model to the industry – Final program milestone.

Summary

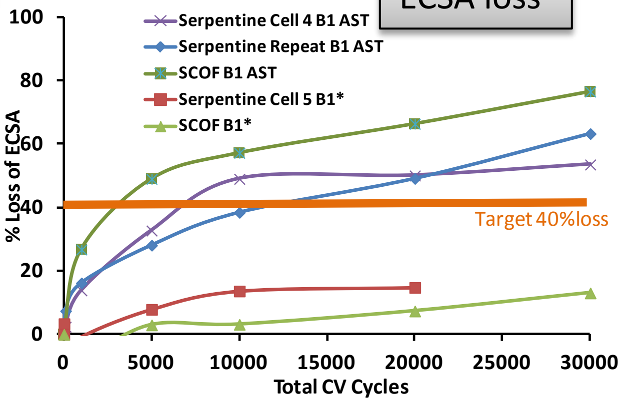
- Normal platinum loading MEAs meet automotive targets for lifetime over a wide range of power densities.
  - High power density does not accelerate the degradation of $0.4 mg_{Pt}/cm^2$ cathode loading MEAs.
- Reducing the cathode thickness results in a 5X increase in decay rate at high power density due to degradation of transport properties of the cathode electrode.
  - Ionomer factors dominate the degradation of transport functionality.
- ECSA loss is independent of flow field design (serpentine, SCOF or RIT).
- ECSA loss and performance degradation is lower in power cycling (N1A) than potential cycling (AST-B1) and lower at 60^oC than 80^oC .
- ECSA loss is higher for normal platinum loading while performance degradation is higher for low-Pt loading in power cycling (N1A).
- Pt in the membrane is significant upon conditioning, but is inconsequential to the ECSA.
- Both Pt dissolution/re-deposition and coalescence mechanisms are required to accurately model ECSA degradation in cathodes.
- Open flowfield architecture proved to benefit low diffusion resistance over the land-channel flowfield at the BOL at RCDs above $1A/cm^2$.
- Subscale single cell adequately represents full-area stack for performance and durability under automotive load protocols.

Technical Back-Up Slides

Benchmarking SCOF and Serpentine cells under catalyst cycling ASTs



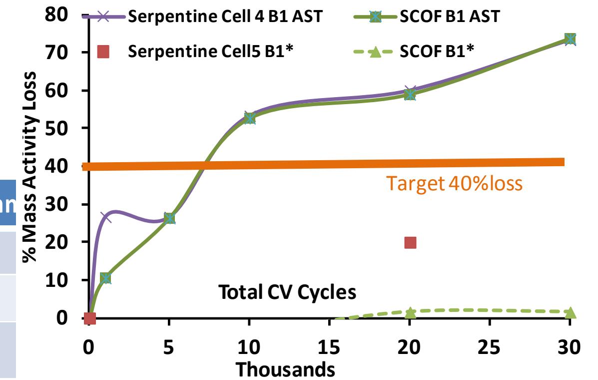
ECSA loss



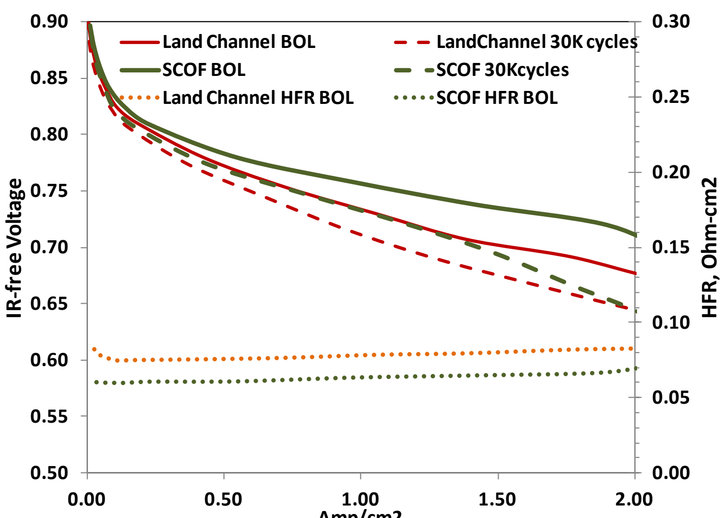
0.2mgPt/cm²
MEA ASTs:
B1 – 0.6-1V
B1* – 0.582-0.883V

	Cathode thickness, EOT,µ		Pt size by XRD, nm
AST cycle	B1	B1*	
SCOF	3.58+/-0.07	3.52+/-0.43	4.33
Serpentine	4.09+/-0.07	4.03	4.15

Mass activity loss

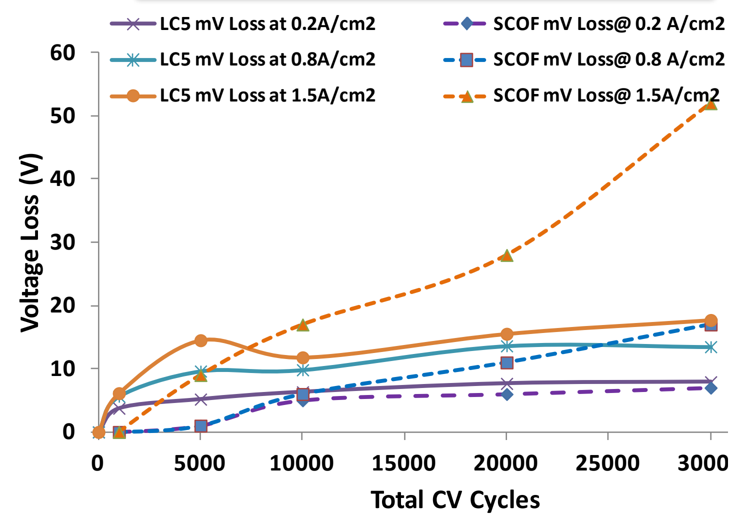


High Pressure polarization in B1* test



- Similar Pt growth,
-Kinetic region in Serpentine is wider due to higher P_{O2} in the flowfield
➔Higher degradation in SCOF over Serpentine

IR-free voltage loss in B1*cycle test, High pressure data



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Technical Progress – Durability Model Framework

other component durability models

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Pt wire

Pt/C –Etek 0.5mg/cm²

Pt/C – Gore 0.15mg/cm²

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

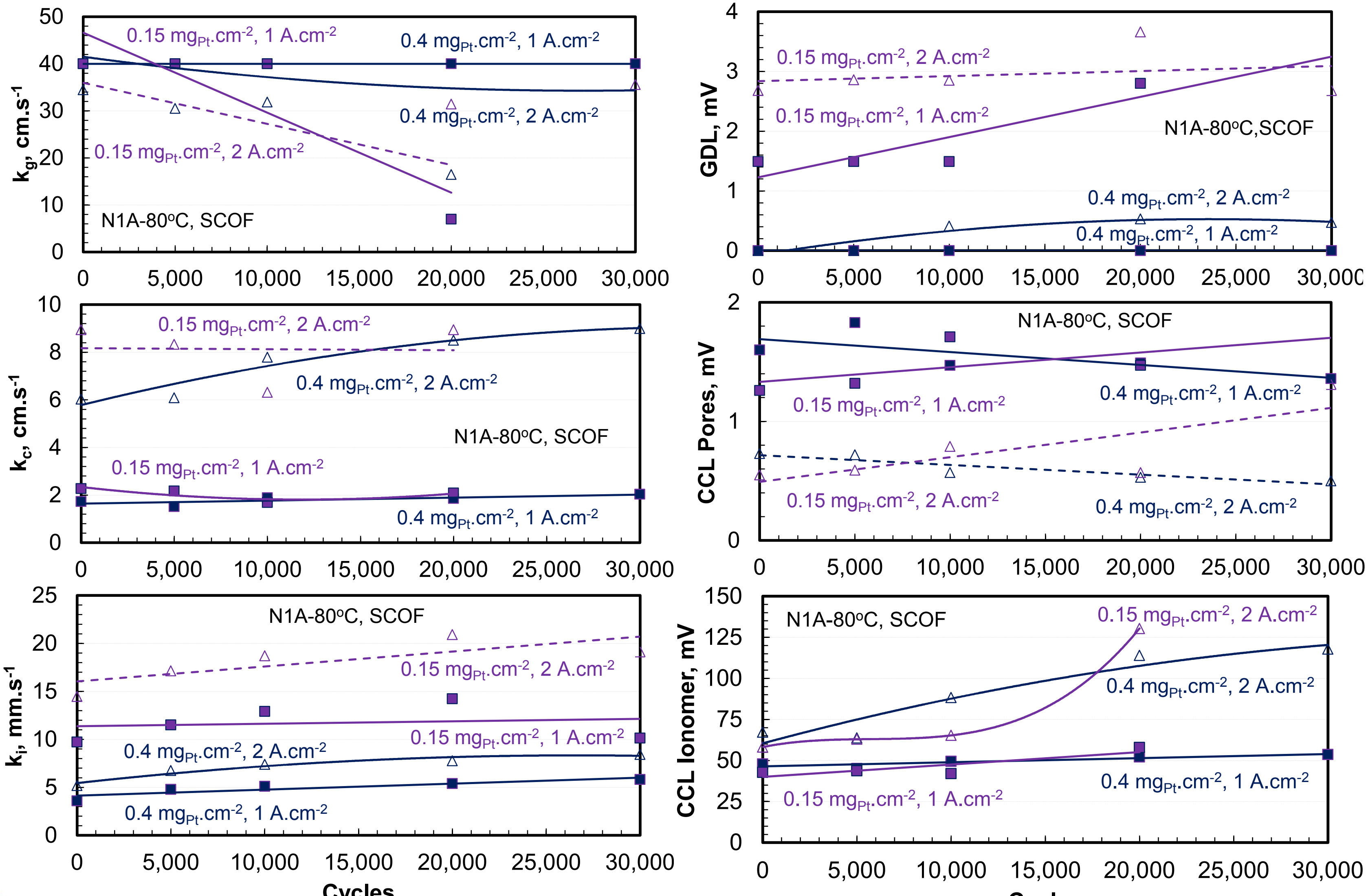
Pt ⇔ Pt^{2+}

Coalescence

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

Effect of Pt Loading on O_2 Mass Transfer (EIS Data)

- Overpotentials in CCL ionomer >> in CCL pores and GDL
- Consistent with pol data, η_m increases with current density and ageing



EIS data at 65ºC with pressure varying with current density

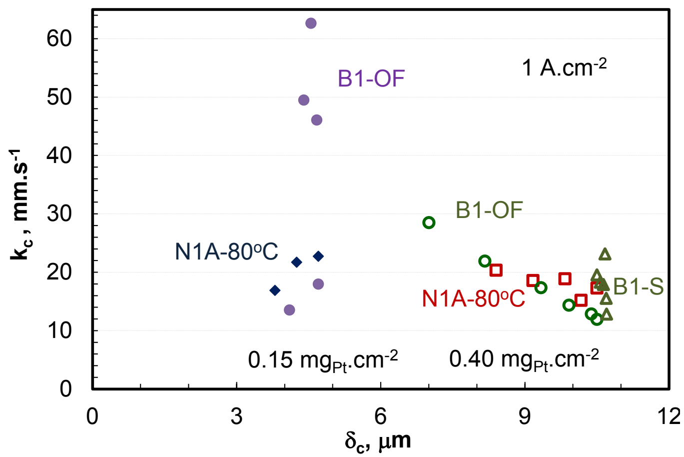
Transport Coefficient Correlations - k_c

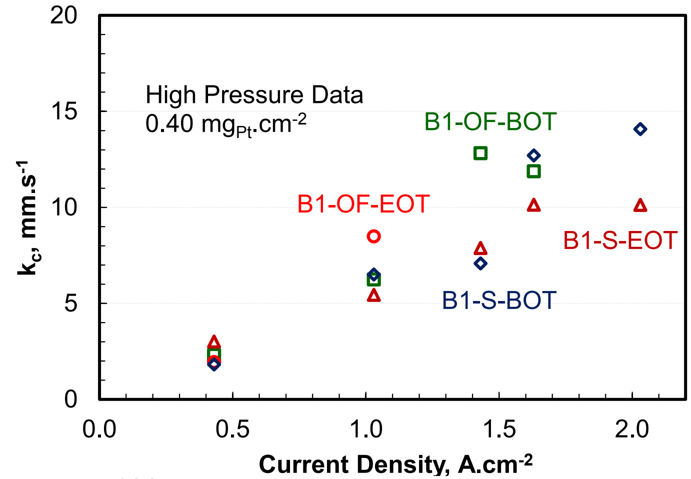
- Correlations derived using data from AST and NST for 0.15 and 0.4 $mg_{Pt}.cm^{-2}$ cathode loadings, 0–2 $A.cm^{-2}$, serpentine and open flow fields
  - $k_c = k_c(P, T, I, u, \delta_c)$, δ_c: CCL thickness, u: gas velocity in flow field

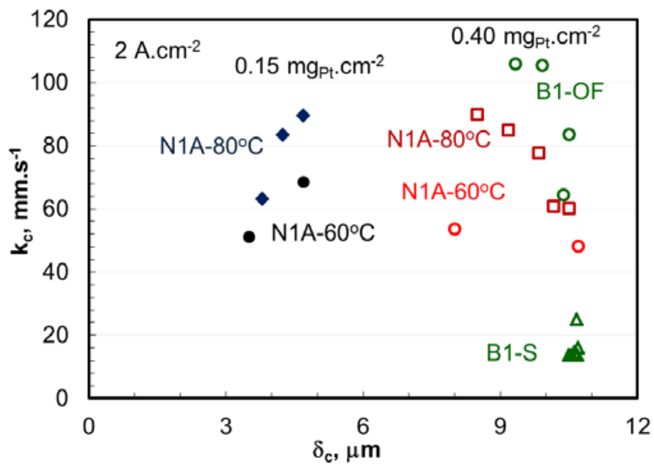
Theoretically, k_c should be inversely proportional to δ_c, but data indicates second-order dependence.

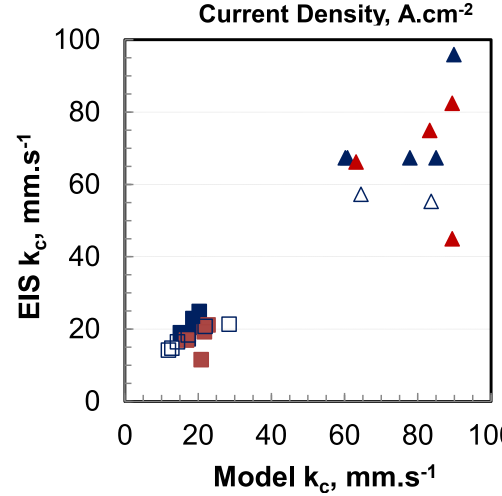
k_c increases if u is increased or current density is reduced (more data needed).

k_c increases if P is reduced or T is raised.









Transport Coefficient Correlations - k_i

- Correlations derived using data from AST and NST for 0.15 and 0.4 $mg_{Pt}.cm^{-2}$ cathode loadings, 0–2 $A.cm^{-2}$, serpentine and open flow fields
  - $k_i = k_i(P, T, I, L_{Pt}, d_p)$, L_{Pt}: Pt loading, d_p: particle diameter

Theoretically, k_i is inversely proportional to d_p, but data indicates that k_i increases as particles grow in size.

k_i decreases if Pt loading is increased.

k_i increases at higher current densities.

k_i increases if P is reduced or T is raised.