2014 Annual Merit Review
DOE Hydrogen and Fuel Cells and
Vehicle Technologies Programs

High Performance, Durable, Low Cost Membrane Electrode Assemblies for Transportation Applications

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3M Company
June 18th, 2014

Project ID: FC104

This presentation does not contain any proprietary, confidential, or otherwise restricted information

Project Overview

Timeline

- Project start: 9/1/12
- Project end: 8/30/14

Budget

- Total DOE Project Value: $4.606MM*
- Total Funding Spent: $2.556MM*
- Cost Share Percentage: 20%

* Includes DOE, contractor cost-share, and FFRDC funds, as of 3/31/14.

Partners

- Johns Hopkins Univ. (J. Erlebacher)
- Oak Ridge Nat'l Lab. (D. Cullen)
- Lawrence Berkeley Nat'l Lab.(A. Weber)
- Michigan Technological Univ. (J. Allen)
- Freudenberg FCCT (C. Quick)
- Argonne Nat'l Lab. (R. Ahluwalia)
- Los Alamos Nat'l Lab. (R. Mukundan, R. Borup)
- General Motors (B. Lakshmanan)

Barriers

A. MEA Durability

B. Stack Material & Mfg Cost

C. MEA Performance

DOE Technical Targets

Electrocatalyst (2017)

- Mass Activity: 0.44A/mg
- Inv. Spec. Power: 0.125g/kW(rated)
- PGM Total Loading: 0.125mg/cm^2
- Electrocatalyst, Support Durability: < 40% Activity, ECSA Loss

MEA *(2017)*

- Q/ΔT: 1.45 kW/ºC
- Cost: $9 / kW
- Durability w/cycling: 5000 hrs
- Performance @ 0.8V: 0.300 A/cm^2
- Perf. @ Rated Power: 1 W/cm^2

Objective and Relevance

Overall Project Objective: Development of a durable, low-cost, robust, and high performance membrane electrode assembly (MEA) for transportation applications, able to meet or exceed the 2017 DOE MEA targets.

Primary Objectives and Approaches This Year	Barriers Addressed
1. Improve MEA Robustness for Cold Startup and Load Transient via Materials Optimization, Characterization and Modeling.	B. Cost C. Performance
2. Evaluate Candidate MEA and Component Durability to Identify Gaps; Improve Durability Through Material Optimization and Diagnostic Studies.	A. Durability
3. Improve Activity, Durability, and Rated Power of MEAs based on Pt_3Ni_7/NSTF Cathodes via Post-Processing Optimization and Characterization.	A. Durability B. Cost C. Performance
4. Integrate MEAs with High Activity, Rated Power, and Durability with Reduced Cost.	A. Durability B. Cost C. Performance

MEA, Catalyst Targets Addressed		
2017 Targets	**Target Values**	**Obj.**
Q/ΔT	1.45kW / °C	3,4
Cost	$9 / kW	3,4
Durability with cycling	5000 hours w/ < 10% V loss	2,3,4
Performance @ 0.8V	0.300A/cm^2	3,4
Performance @ rated power	1W/cm^2	3,4
PGM Content (both electrodes)	0.125g/kW$_{RATED}$ 0.125mg$_{PGM}$/cm^2	3,4

Approach, Milestones, and Status v. Targets

Approach: Optimize integration of advanced anode and cathode catalysts, based on 3M's nanostructured thin film (NSTF) catalyst technology platform, with next generation PFSA PEMs, gas diffusion media, cathode interfacial layers, and flow fields for best overall MEA performance, durability, robustness, and cost.

1. Place appropriate emphasis on key commercialization and DOE barriers.
2. Through advanced diagnostics, identify mechanisms of unanticipated component interactions resulting from integration of low surface area, low PGM, high specific activity electrodes into MEAs.

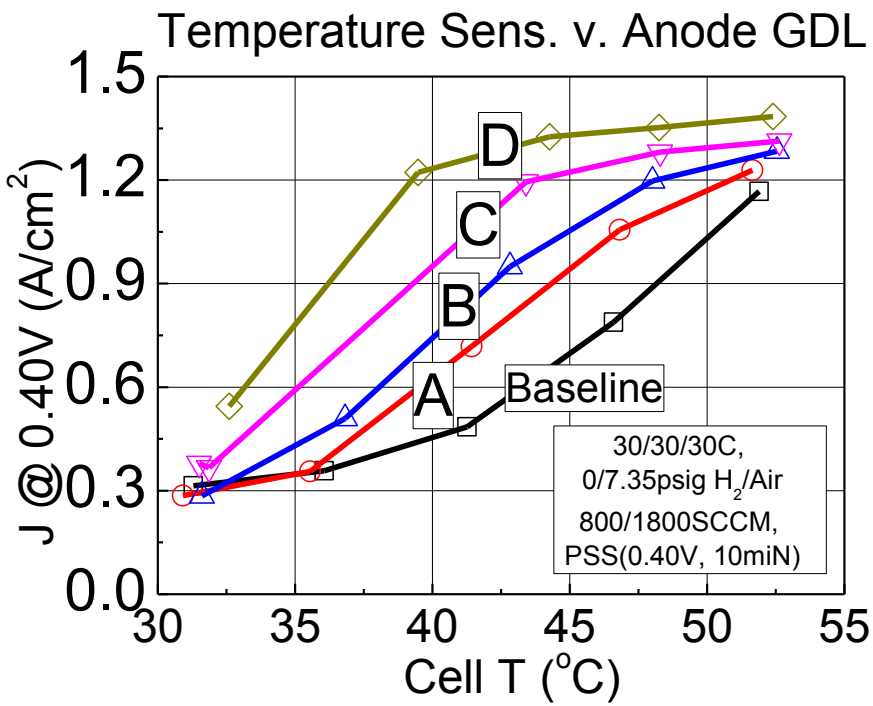
MS ID	QTR	Project Milestone MS 1.1, 2.1, 5.1 based on 4-5 Project Goals (See Backup Slides)	% Complete (Apr. '14)
BUDGET PERIOD 1 (Sept. '12-May '14)			
6.1	2	**Baseline MEA: Short Stack Eval. Complete.**	**CANCELLED**
1.1	7	**Comp. Cand. Meet Interim Perf./Cost Goals.**	**75% (3 of 4)**
2.1	7	**Comp. Cand. Meet Interim Cold-Start Goals.**	**75% (3 of 4)**
5.1	7	**Comp. Cand. Meet Interim Durability Goals.**	**66% (8 of 12)**
3.1	7	**GDL Pore Network Model Validation With ≥ 2 3M Anode GDLs.**	**50% (1 of 2)**
6.2	7	**Interim BOC MEA: Short Stack Eval. Complete.**	**10% (1 of 3)**
4.1 Go/ No-Go	**7**	**2014(Mar.) Best of Class MEA Meets G/NG** **1) ≤ 0.135mg$_{PGM}$/cm^2 (Total)** **2) Rated Power, Q/ΔT:** **≥0.659V@ 1.41A/cm^2, 90°C, 1.5atm H_2/Air**	**100%** **0.129mg/cm^2** **0.668V**

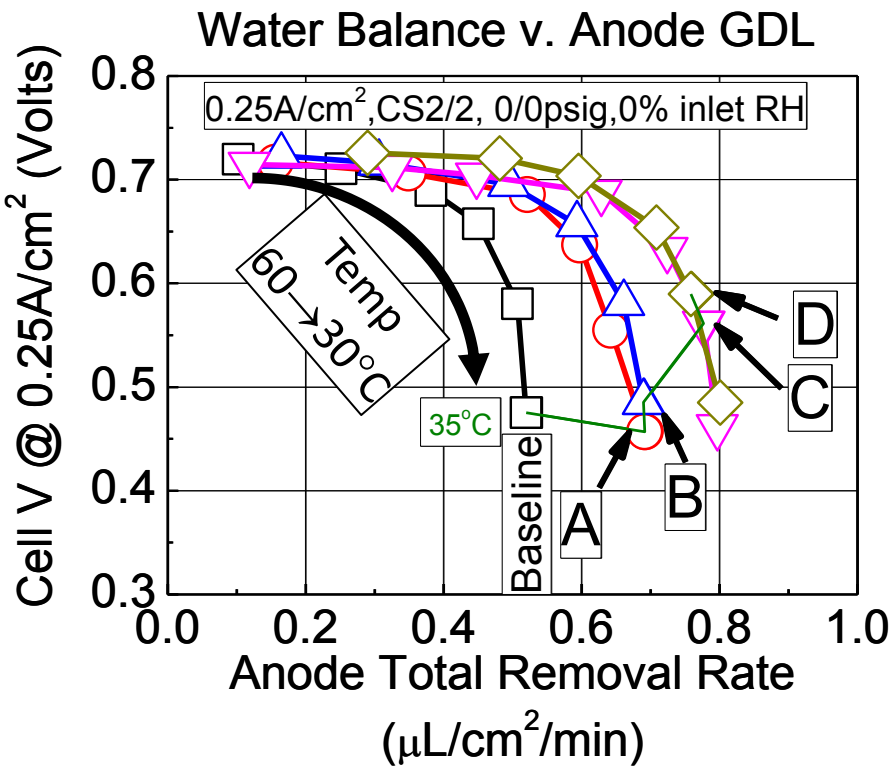
Status Against DOE 2017 Targets		
Characteristic	**2017 Targets**	**Status, '13/'14**
Q/ΔT (kW / °C)	1.45	1.56/1.56 (0.670V)
Cost ($ / kW)	9	6 / 5 (PGM only @ $35/g$_{Pt}$)
Durability with cycling (hours)	5000	NA
Performance @ 0.8V (mA/cm^2)	300	203/125
Performance @ rated power (mW/cm^2)	1000	871/932 (0.670V)
PGM total content (g/kW (rated))	0.125	0.157/0.138 (0.670V)
PGM total loading (mg PGM / cm^2 electrode area)	0.125	0.137/0.129

Accomplishments and Progress

Improved Robustness for Cold Startup, Load Transient (Task 2):

New Anode GDLs Improve Startup Capability - *Higher H_2O Removal Out Anode*



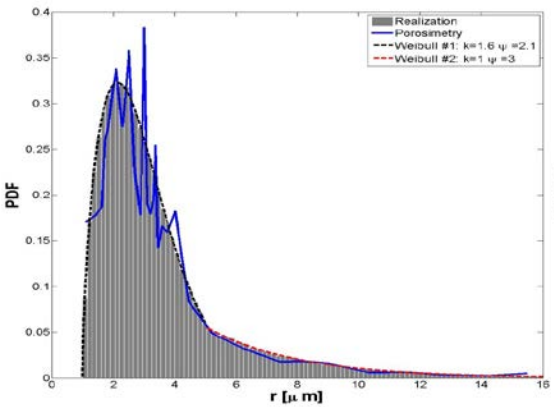


- New anode GDL candidates show good promise for improving cold-start capability.
- Improvements in low T performance as the anode GDL is varied correlate with higher anode water removal rates @ 0.25A/cm².
- As T decreases, performance loss occurs as anode water removal rate limit occurs.

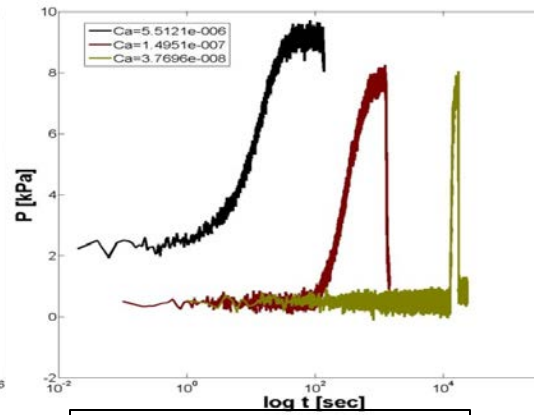
Accomplishments and Progress

Cold Startup Modeling (Task 3): MTU Pore Network Model results validated against experimental liquid water transport in 3M GDL (Milestone)

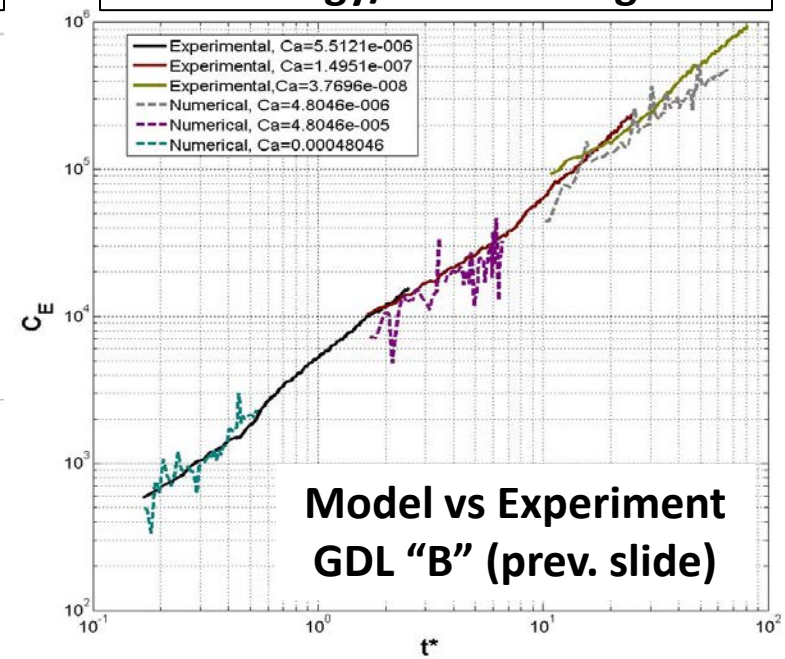
Pore Size Distribution



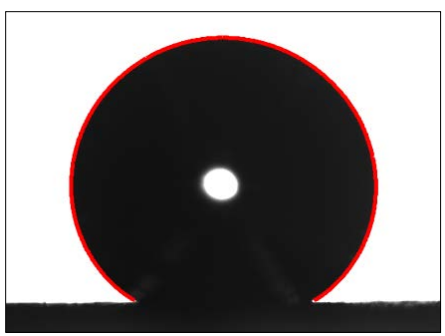
Injection Pressure



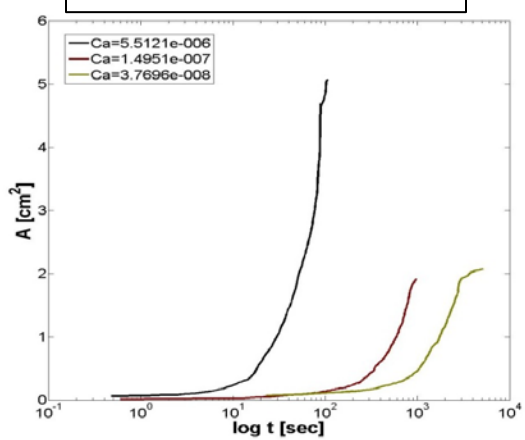
Energy/Time Scaling



Contact Angle



Wetted Area



MTU Model Inputs:

- PSD, thickness, and contact angle
- Operating conditions

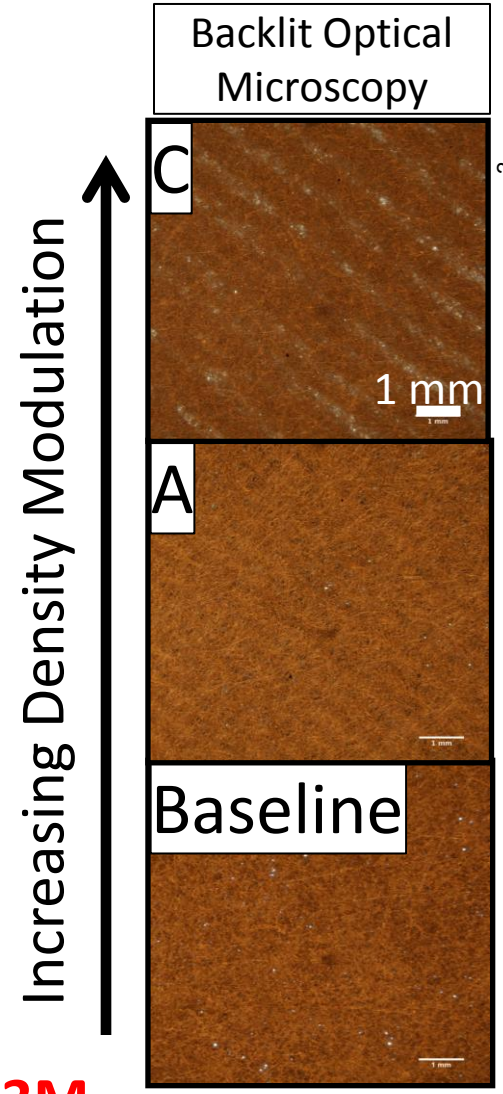
MTU Model Results:

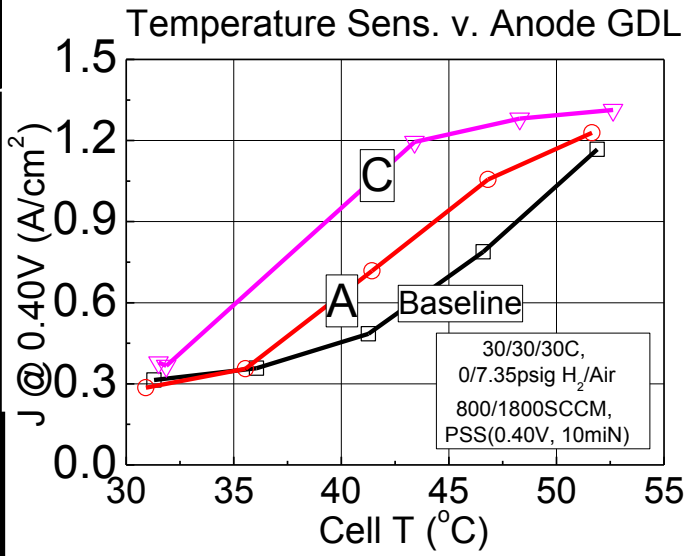
- Transient water distribution
- Transient effective permeability, conductivity, and diffusivity

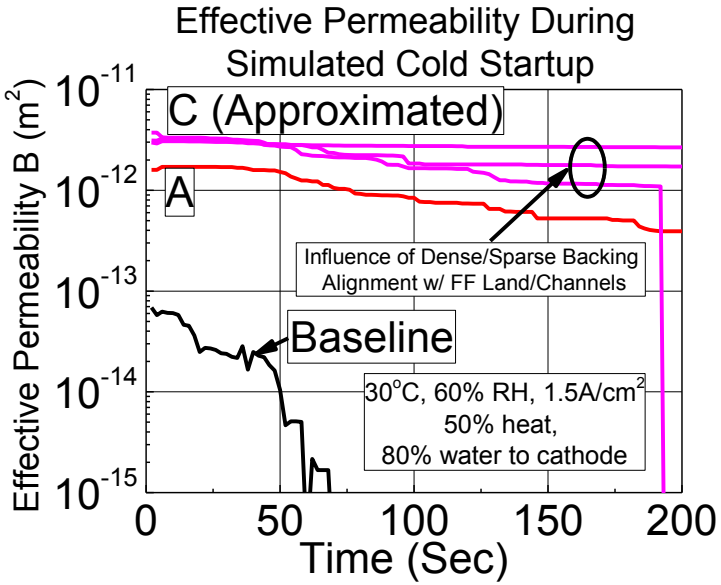
E. F. Médici and J. S. Allen, *Phy. Fluids* 23 (2011): 122107.
E. F. Médici and J. S. Allen, *Int. J. Heat Mass Trans.*, 65 (2013): 779-788.

Accomplishments and Progress

Cold Startup Modeling (Task 3): Possible Backing Structural Factor Identified Which Correlates with Improved Low T Response; MTU Modeling Provides Insight





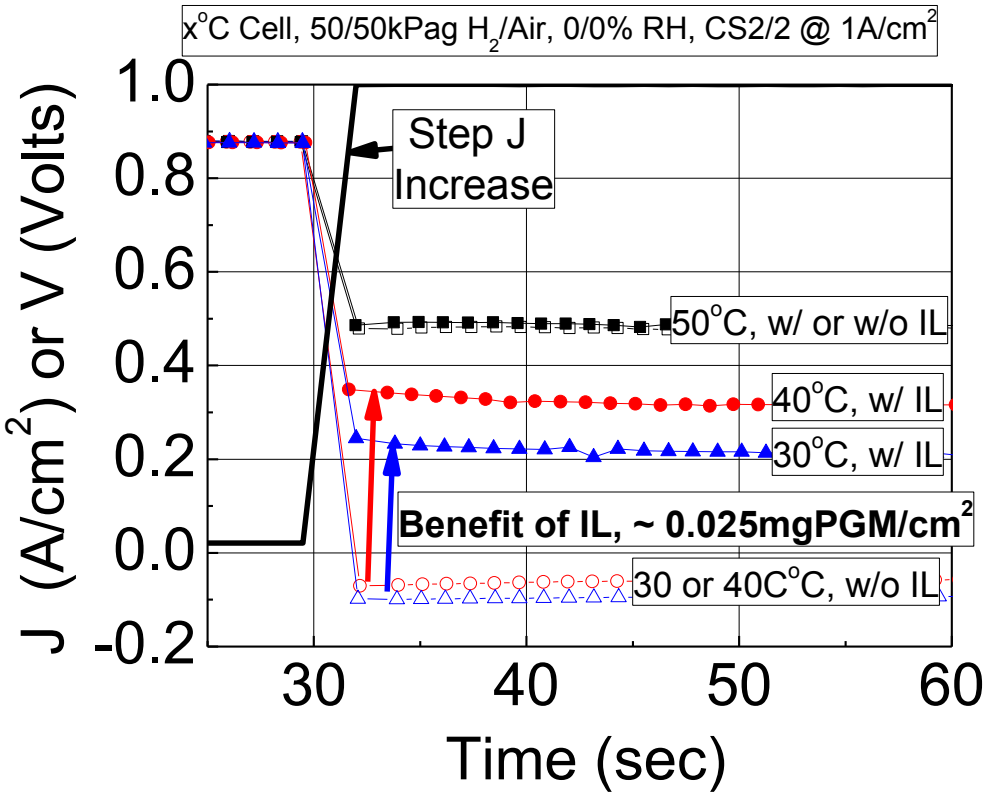


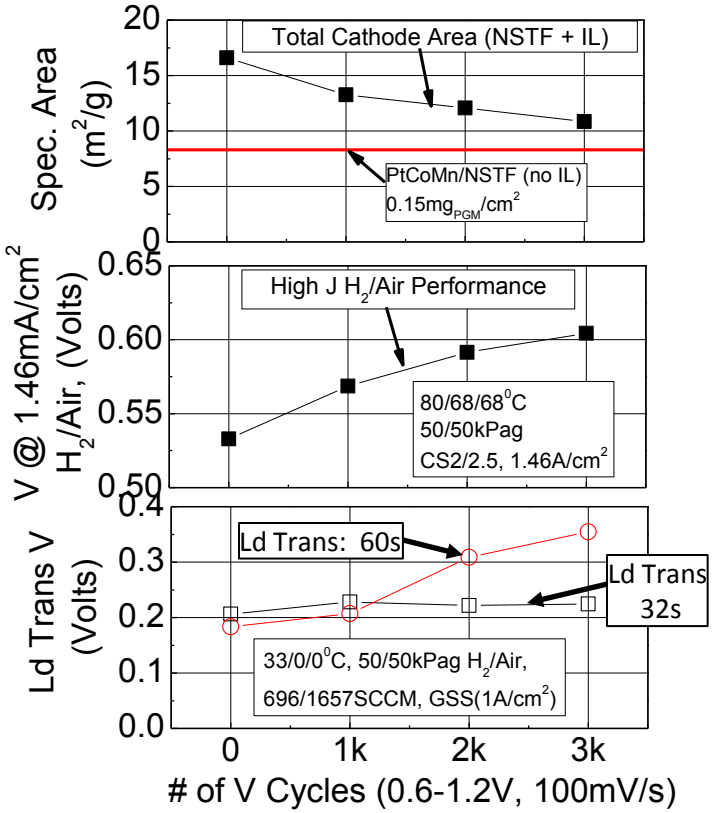
- Some backings show apparent physical "banding" (dense/sparse regions) on ca. 1mm scale.
- Qualitative extent of banding correlates with improved low temperature performance.
- MTU model shows that banding can help retain higher gas permeability during simulated cold start and influences local catalyst temperature distribution.

Accomplishments and Progress

Improved Robustness for Cold Startup, Load Transient (Task 2):

Cathode Interlayer Developed: 20°C Improvement in Operating Window, and Is Durable



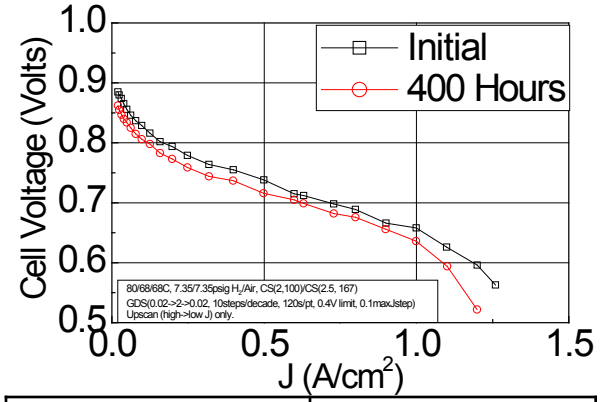


- Low loaded Pt/C interlayer (between NSTF cathode and cathode GDL) improves minimum "passing" load transient temperature: 50°C (no IL) to 30°C (w/ IL).
- *Durability* - Degradation of IL surface area w/ CV cycling results in *improved* MEA performance at rated power, and load transient is similar or improved.

Accomplishments and Progress

Component Durability Evaluation (Task 5): Component Candidates Generally Show Acceptable Durability; Cathode Cyclic Durability Insufficient

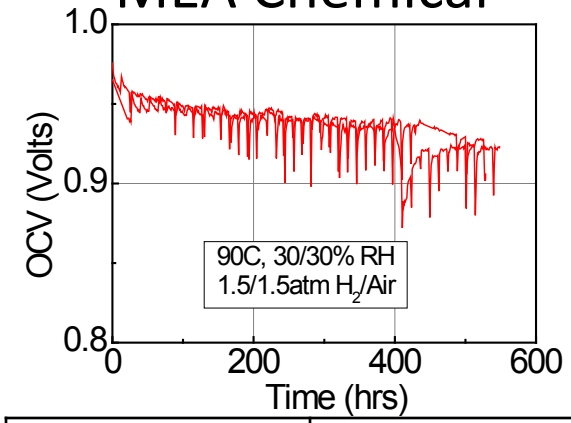
Support Cycle



Metric	Change/Tgt
Mass Activity (A/mg)	-40±7 % / -40%
V @ 0.8A/cm²	-11±3 mV / -30mV
Surf. Area (m²/g)	-19±3% / -40%

- Pt_3Ni_7 cathode passes support cycle (previous 400hr 1.2V hold test).

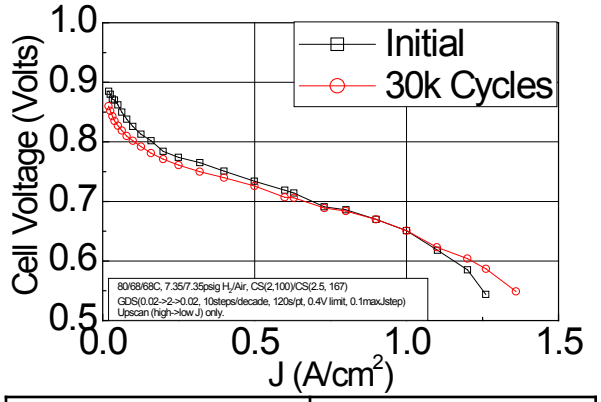
MEA Chemical



Metric	EOT / Target
H_2 Xover (mA/cm²)	3.7±0.3 / 2
OCV Loss (%)	-6 ± 2 / -20
Short Res. (ohm-cm²)	1300±90 / 1000

- 2013 (March) BOC MEA passes (little change after 500 hours).
- 8 Candidates Evaluated (An., PEM, Cath.); *All Pass if PEM Additive Present at Low Level.*

Electrocatalyst Cycle



Metric	Change/Tgt
Mass Activity (A/mg)	-66±4% / -40%
V @ 0.8A/cm²	-13±15mV/-30mV
Surf. Area (m²/g)	-28±4% / -40%

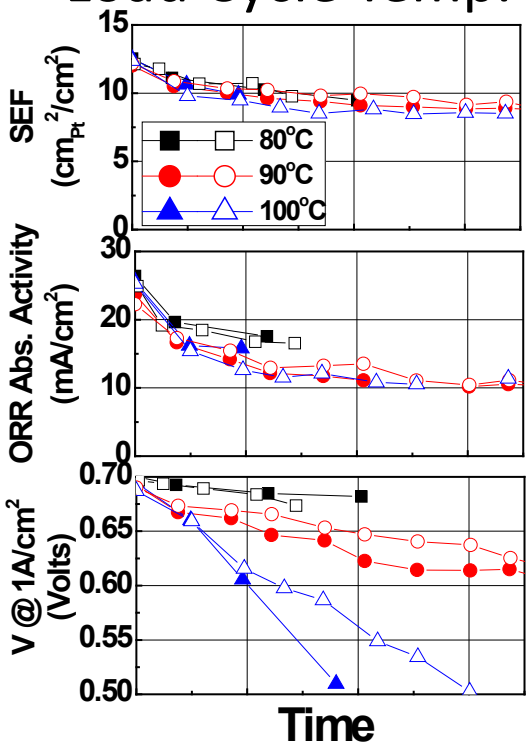
- Pt_3Ni_7 cyclic durability insufficient to achieve mass activity target; passes others.
  - *Mostly Spec. Act. loss.*
  - TEM, EDS (ORNL): Modest coarsening *and severe Ni loss.*

Accomplishments and Progress

MEA Rated Power Durability (Task 5): 3 Primary Factors To Date

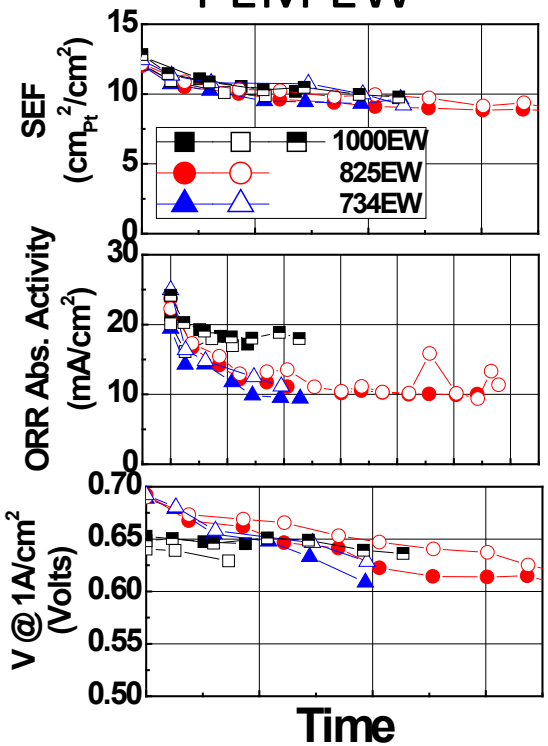
Method: Mod. Tech Team Load Cycle. Baseline: 0.05/0.15PtCoMn/NSTF, 825EW 20µ PEM, 90°C

Load Cycle Temp.



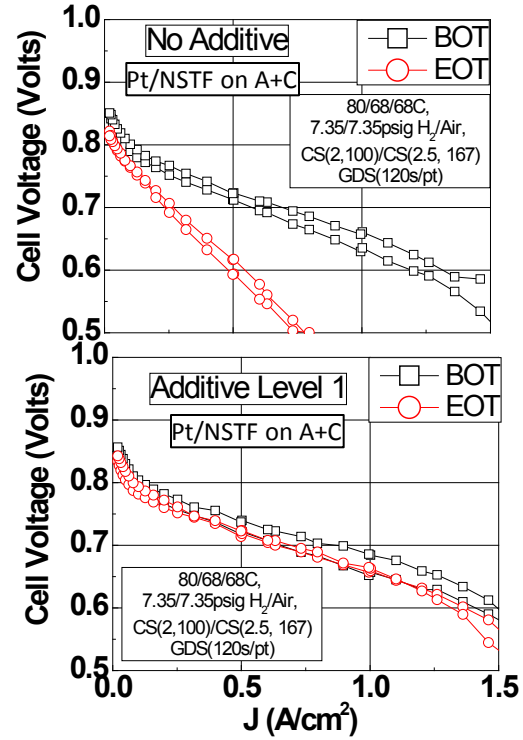
Cell Temp (°C)	V @ 1A/cm² Accel. Factor
80°C	**0.6**
90°C	**1**
100°C	**4**

PEM EW



PFSA EW (g/mol)	V @ 1A/cm² Accel. Factor
1000	**0.5**
825	**1**
734	**1.9**

PEM Additive

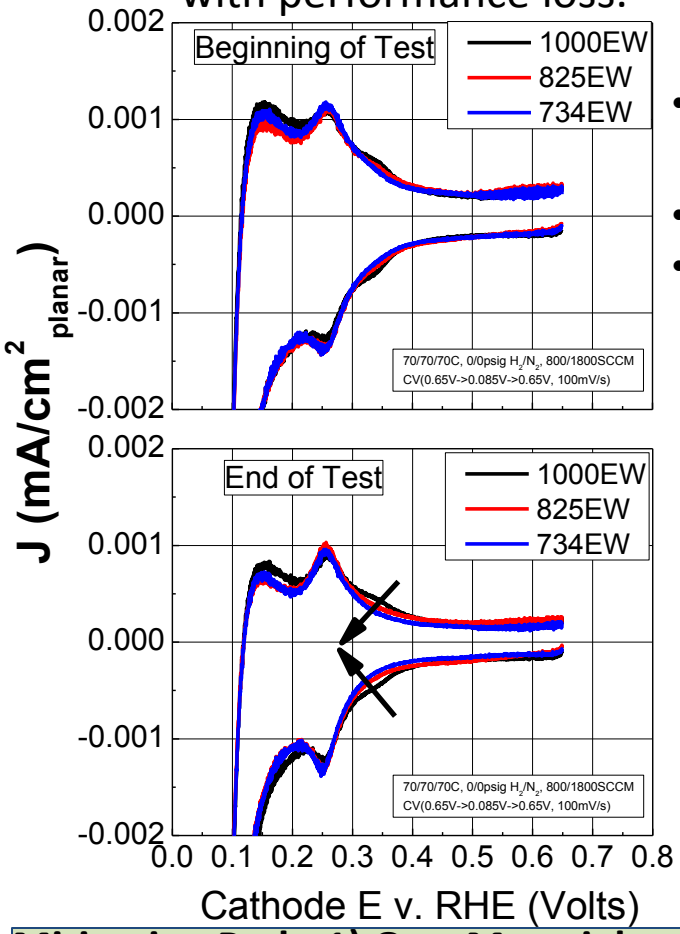


Add. Level (Arb.)	V @ 1A/cm² Accel. Factor
1	**1**
0	**10**

Accomplishments and Progress

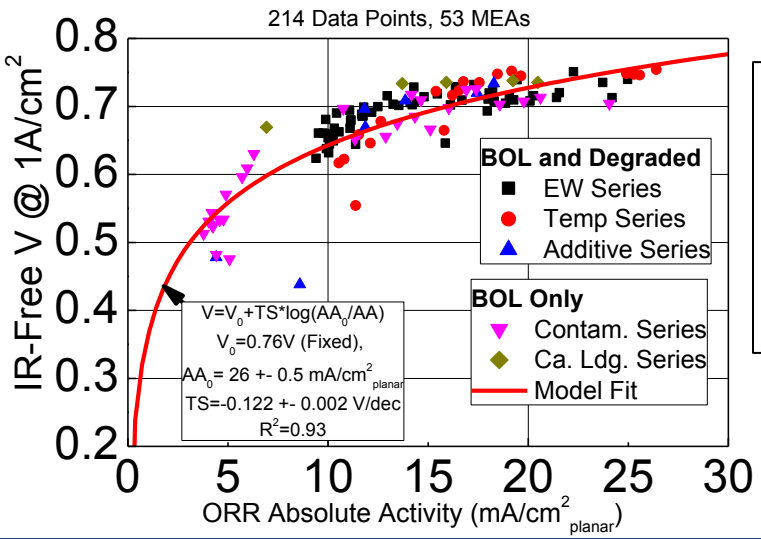
MEA Rated Power Durability (Task 5): Voltammetry Suggests Accumulation of Anionic Contaminant; Rated Power Loss Due to ORR Kinetic Loss

H_{UPD} E shift at EOT trends with performance loss.



- **PEM EW, additive, and temp. factors, ORR Act. loss, and H_{UPD} shift consistent: <u>PEM decomp. → cathode deact. → rated power loss, due to "irreversibly" adsorbed PEM decomp. product(s).</u>**
- *Species?* $CF_3(CF_2)_nCOOH$ (small n), SO_4^{2-} known *<u>reversible</u> contaminants for NSTF, Pt/C cathodes; <u>why "irreversible" here?</u>*
- *Can 20-30mV kinetic loss be related with 200mV loss at 1A/cm²?*
- Loss at 1A/cm² (air) becomes exceptionally large as cathode ORR activity (O_2) decreases below ~10mA/cm²$_{planar}$.

"Rated Power" Loss Due to ORR Kinetic Loss

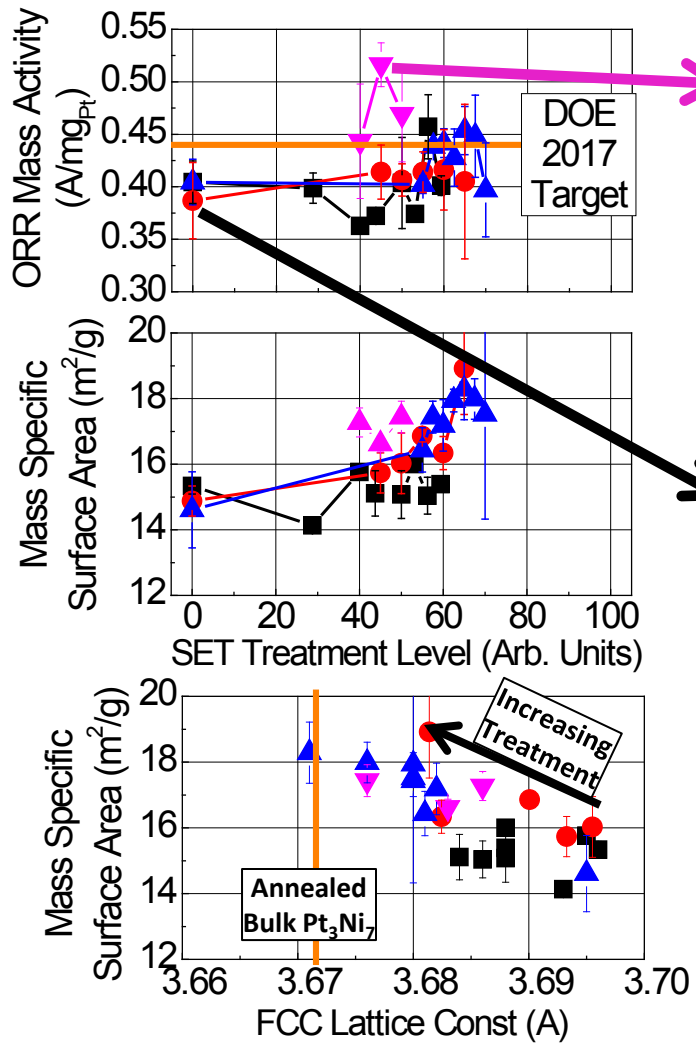


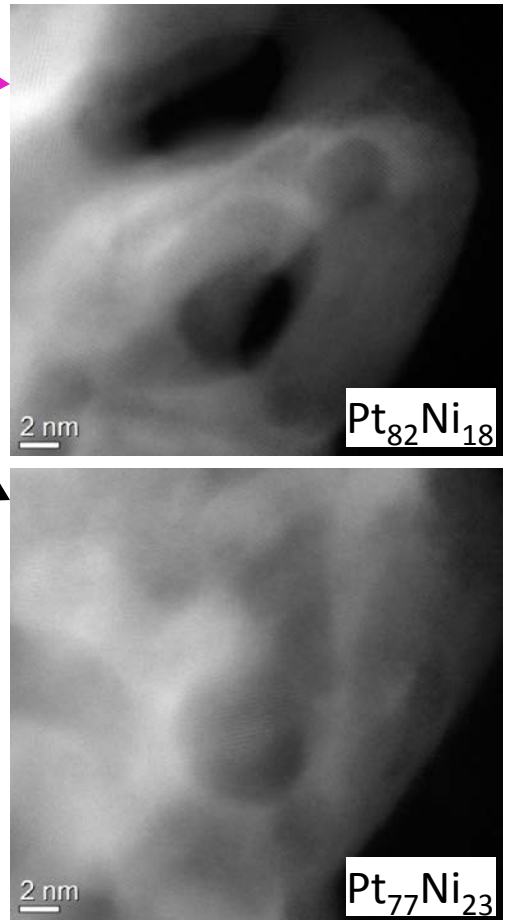
Correlation with both degraded and BOL MEAs with various BOL ORR activities.
53 MEAs

<u>Mitigation Path:</u> 1) Opt. Materials to Min. Contam. Generation 2) Recovery Method Development

Accomplishments and Progress

Improved Activity, Rated-Power Capable ORR Catalysts (Task 1.1):
SET (Annealing) Improves Activity, Area of Pt_3Ni_7/NSTF Cathodes



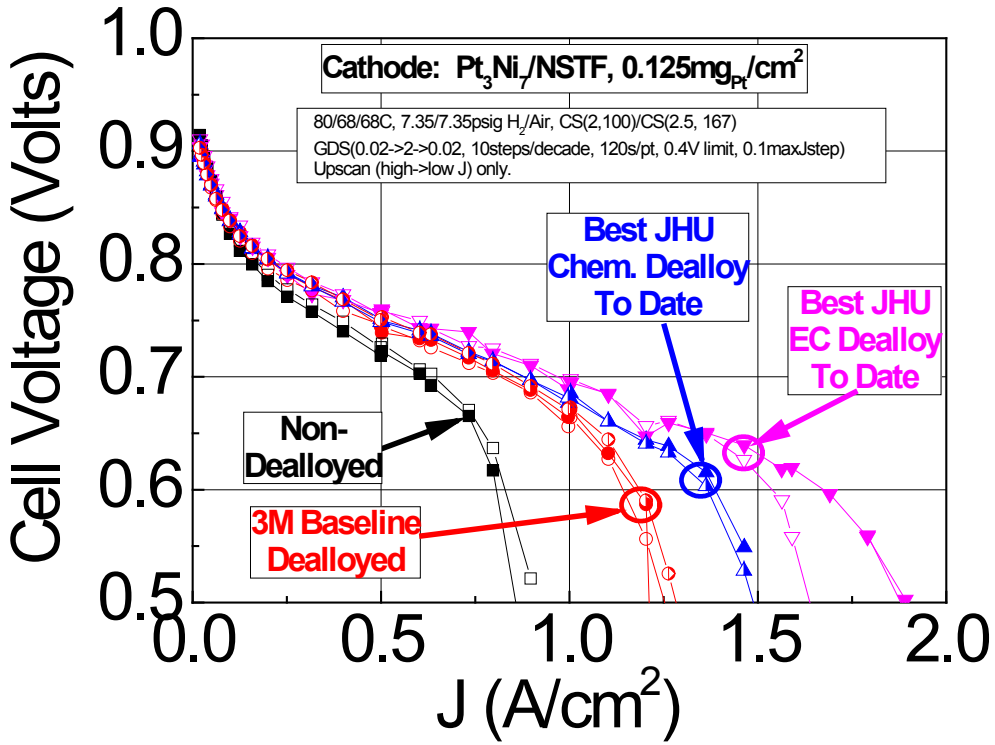


D. Cullen, ORNL

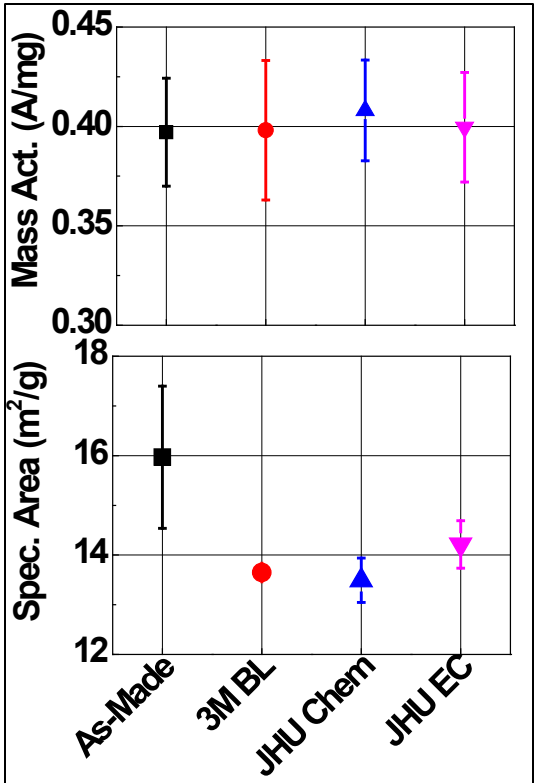
- Annealing optimization:
  - +30% mass activity, in MEA.
  - +20% specific area.
- *DOE Mass Activity target exceeded.*
- Increasing grain size, decreasing lattice constant (XRD) correlates with specific area gains.
  - Alloy homogenization, defect reduction.
- ORNL TEM: annealing improves in-situ nanoporosity and increases Ni dissolution.

Accomplishments and Progress

Improved Activity, Rated-Power Capable ORR Catalysts (Task 1.1):
Substantially Increased Rated Power; Mass Activity Retained.



- JHU dealloying development has substantially increased rated power capability with Pt_3Ni_7 cathodes.
  - Best Chem/EC: +20/+40%% J @ 0.60V
- Optimization for volume production needed.



Mass activity is retained after dealloying; small area loss.

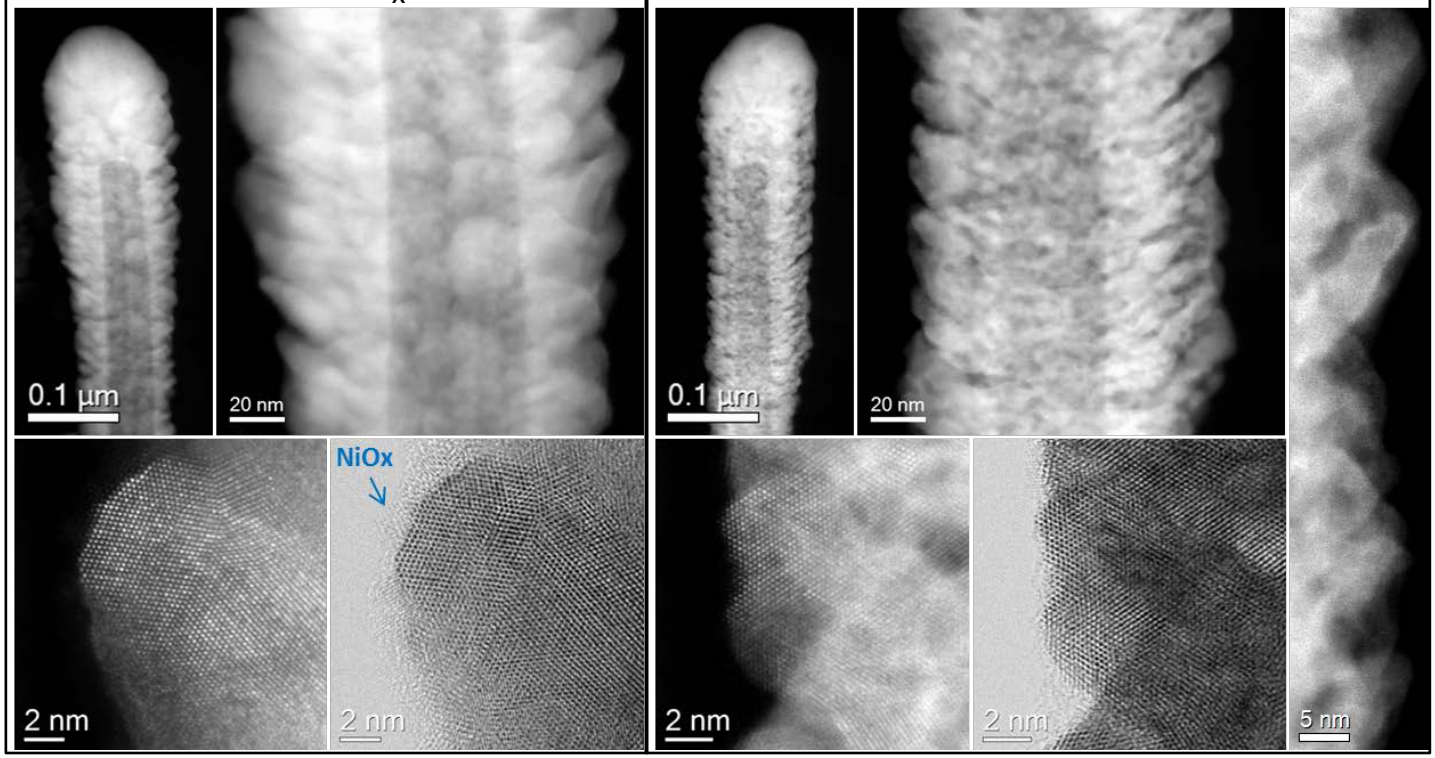
Accomplishments and Progress

Improved Activity, Rated-Power Capable ORR Catalysts (Task 1.1):

Dealloying Transforms Pt_3Ni_7/NSTF Surface from NiO_x to Pt Rich; Forms Nanoporosity

No Dealloy – Nonporous Pt_3Ni_7 with thin NiO_x layer.

JHU Chem. Dealloy – Porous $Pt_{42}Ni_{58}$ with Pt enriched surface layer.



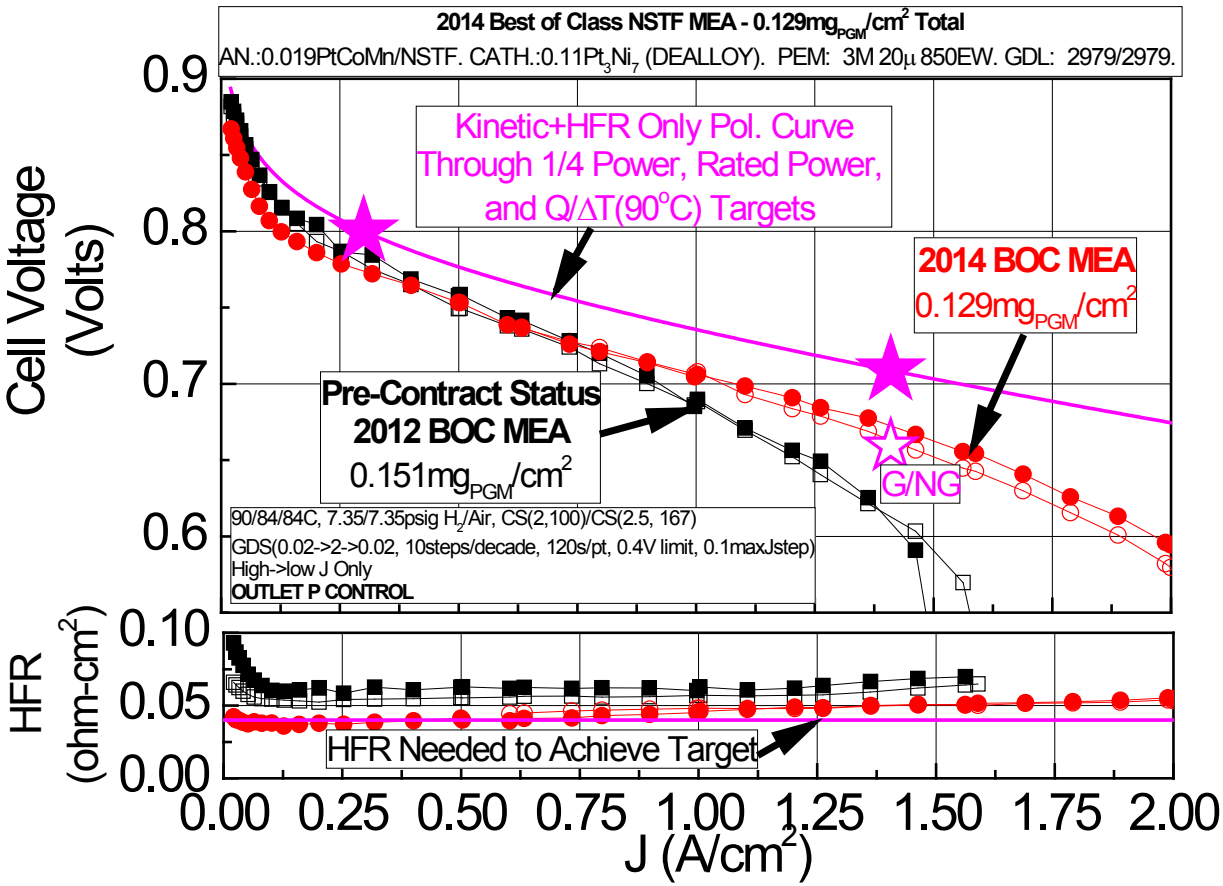
Bulk vs. surface Pt (at.%) in Pt_3Ni_7/NSTF

	Bulk$_{(STEM)}$	*Surface*$_{(XPS)}$	*Surface Layer*
No Dealloy	30	20	Ni Oxide
JHU Chem.	42	53	Pt-rich

Scanning transmission electron microscopy (STEM) and X-ray photoelectron spectroscopy (XPS) – **ORNL**, D. Cullen, H. Meyer

Accomplishments and Progress

Best of Class Component Integration (Task 4.1): 2014 3M NSTF Best of Class MEA - High Rated Power and Mass Activity; G/NG Achieved



Go/No Go Metrics Achieved

Go/No Go Metrics	Pre-Proj. Mar. '12	2014 BOC Mar. '14
≤0.135 mg$_{PGM}$ /cm^2	0.151	0.129
≥0.659V @1.41A/cm^2	0.609	0.668

Key Improvements

1. Anode optimization to min. PGM.
2. Best practice cathode dealloying – **high J *and* 0.38A/mg mass activity.**
3. Improved flow field w/ modestly narrower lands, channels than FC Tech. Quad Serp. – in line with current trends.
4. 15% thinner PEM.

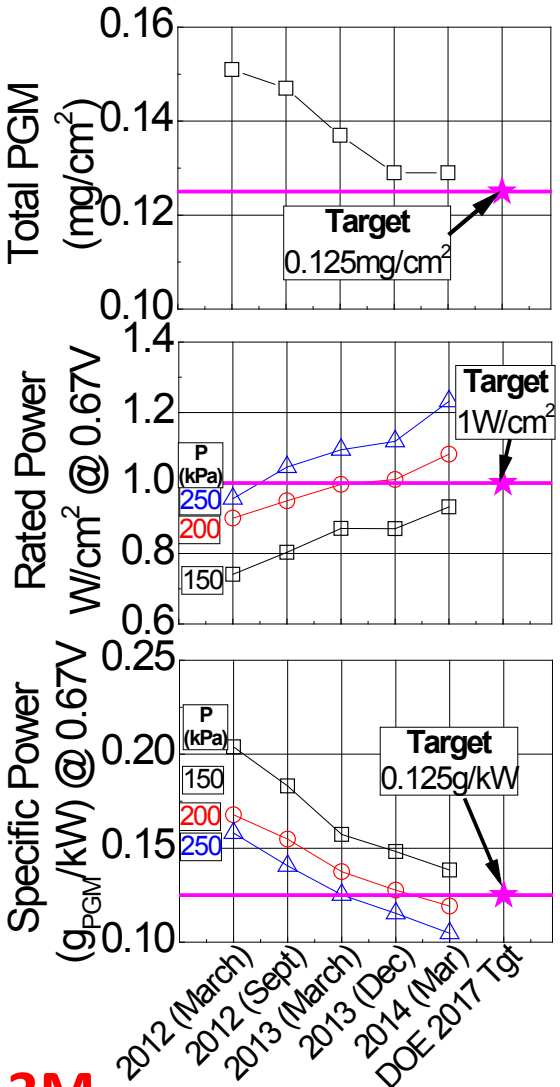
Path to 2017 MEA Performance, Loading Targets:

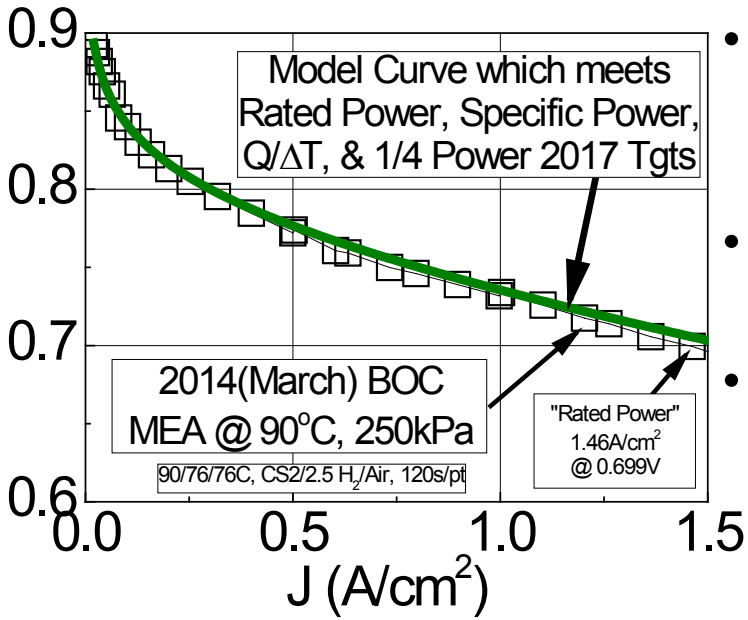
1) Increase 0.80V H_2/Air Activity (Min. Transport Loss; Increase Mass Activity > 0.5A/mg (anneal+dealloy))

2) Reduce HFR (Thinner, Low EW Supported PEM; GDLs; Interfacial R. Minimization).

Accomplishments and Progress

Best of Class Component Integration (Task 4.1): PGM, Rated and Specific Power Targets Approached @ 150kPa, 0.67V ; All 2017 MEA Perf. Targets @ 250kPa





- Steady improvement in total PGM, rated power, and specific power.
- At 150kPa, within 10% of 4 DOE 2017 targets @ 0.67V.
- At 250kPa, all 2017 performance targets approached or achieved.

Characteristic	Unit	Target	Value @ 150kPa	Value @ 250kPa
Performance @ 0.80V	mA/cm²	≥300	125 (~190 w/ low RH)	285
Q/ΔT	kW/°C	≤ 1.45	1.56 (0.67V,90°C) (+20mV @ 90°C) or (+4°C @ 0.67V)	1.42 (0.70V,90°C)
Performance @ rated power	mW/cm²	≥ 1000	932 (0.67V)	1020 (0.70V)
Specific Power	g/kW	≤ 0.125	0.138 (0.67V)	0.127 (0.70V)
PGM Content	mg/cm²	≤ 0.125	0.129	0.129

Response To Reviewers' Comments

Addressing NSTF MEA Operating Condition and Impurity Sensitivities

- "…project is limited to "optimization of existing components and processes" and … "NO COMPONENT DEVELOPMENT." … unfortunate, since **what is required … is … a new catalyst layer architecture**."
- "**major barrier** to commercialization of NSTF is the **high sensitivity to operating conditions**, yet … **progress** on these tasks **is delayed** or not even started."
- "…**NSTF MEAs** … extremely **sensitive to both temperature and impurities** relative to conventional MEAs."

•***Component development not allowed*** *in Topic 4 of* ***2011 FOA****. New catalyst layer architecture could require its own project.* ***We believe current Task 2+3 approach will be sufficient****.*

•*Work to address* ***operating temp. sensitivity*** *was in progress prior to AMR, but was too early in development for reporting. We agree, this* ***is a key issue and is actively being addressed****.*

•*To our understanding,* ***impurity sensitivity is proportional to surface area****.* ***Pt_3Ni_7/NSTF surface areas are increasing*** *under Task 1, and added area from* ***Task 2 interlayers should help****.*

OEM Participation; Validation in Stacks

- "…3M has a history of showing **great lab results that do not translate well to practical stacks**…"
- "… good … to see what **stack formats and operating conditions** will be used for…integration activities."
- "For a ... (MEA) project, it is extremely **surprising** to see that the list of collaborators **does not include a stack developer** (either automotive or otherwise)."
- ***General Motors is the project partner responsible for stack testing****, but wasn't finalized until after last year's AMR.*
- ***We agree that integration into stacks is important****. Cold-startup is much less challenging with low heat capacity stacks than estimates from single cells.* ***Stack optimization to enable demonstrated NSTF MEA rated power capability is necessary, but not in project scope.***

Collaborations

Johns Hopkins University (Jonah Erlebacher) – *Subcontractor*

•Task 1 - Pt_3Ni_7/NSTF dealloying optimization.

Oak Ridge National Laboratory (David Cullen) – *Subcontractor*

•Task 1 - Characterization of dealloy/SET post-processed Pt_3Ni_7/NSTF cathodes.

Freudenberg FCCT (Christian Quick) – *Vendor*

•Task 2 – Experimental anode GDL backings.

Michigan Technological University (Jeffrey Allen) – *Subcontractor*

•Task 3 -GDL char.; Integration of 3M anode GDLs into MTU pore network model.

Lawrence Berkeley National Laboratory (Adam Weber)–*Subcontractor*

•Task 3 - GDL char.; Integ. MTU PNM into LBNL MEA model; Cold startup modeling.

Argonne National Laboratory (Rajesh Ahluwalia) – *Collaborator*

•Task 4 - NSTF BOC MEA HOR/ORR kinetic char. studies; FC systems modeling.

Los Alamos National Laboratory (Mukundan, Borup) – *Subcontractor*

•Task 5 – Load cycle durability evaluation

General Motors (Balsu Lakshmanan) – *Subcontractor*

•Task 6 – Short stack evaluation.

Key Future Work – FY14, FY15

Task 1 – Integration Activities Toward ¼ Power, Performance @ rated power…

•Demonstrate Scale-up Feasibility of Downselected Dealloying, Annealing Methods

•Integration of Next Generation Supported, Low EW PEMs

Task 2 - Integration …. Transient Response, Cold Start Up …

•Continued Anode GDL and Cathode Interlayer Optimization; Diagnostic Studies.

Task 3 - Water Management Modeling for Cold Start

• Finalize GDL Modeling @ MTU, Integrate MTU-LBNL Models→ Identify Key A. GDL Factors.

Task 4 - Best of Class MEA Integration Activities

•Best of Class Component Integration Towards Project Goals:

(≤ 0.125mg$_{PGM}$/cm^2; Rated Power, Q/ΔT: 0.709V @ 1.41A/cm^2 @ 90°C).

•Improvement in Cathode Activity, Durability Critical

Task 5 - Durability Evaluation and Performance Degradation Mitigation

•Evaluation of New Cathodes (as available) to Achieve Electrocatalyst Durability Targets.

•Irreversible Peak Power Loss Mitigation (Material Optimization; Recovery Methods)

Task 6 - Short Stack Performance, Power Transient, and Cold Start Evaluation

• Achieve Required Robustness Metrics Through Incorporation of Improved Anode GDLs, Cathode Interlayers, and Next Generation PEMs.

•Implement Short Stack Testing of Interim and Final Project Best of Class MEAs.

Summary

Operational Robustness (Cold Start; Load Transient)

- Experimentally confirmed operational mechanism of cold-startup variation with anode GDL backings. MTU GDL model experimentally validated w/ one project GDL to date. Benefits of sparse/dense GDL structures becoming evident.
- Cathode interlayer developed which improves load transient operating window by 20°C and has good durability and low PGM prospects.

Durability (MEA Load Cycling; MEA Chemical; Cathode)

- Key mechanism of rated power loss identified – development direction for improvement is forming. LANL onboarding into task has occurred smoothly.
- MEA chemical durability of all components appears sufficient.
- Cathode mass activity durability insufficient; being addressed outside project.

Power, Cost (Cathode Post Processing; Best of Class MEA Integration)

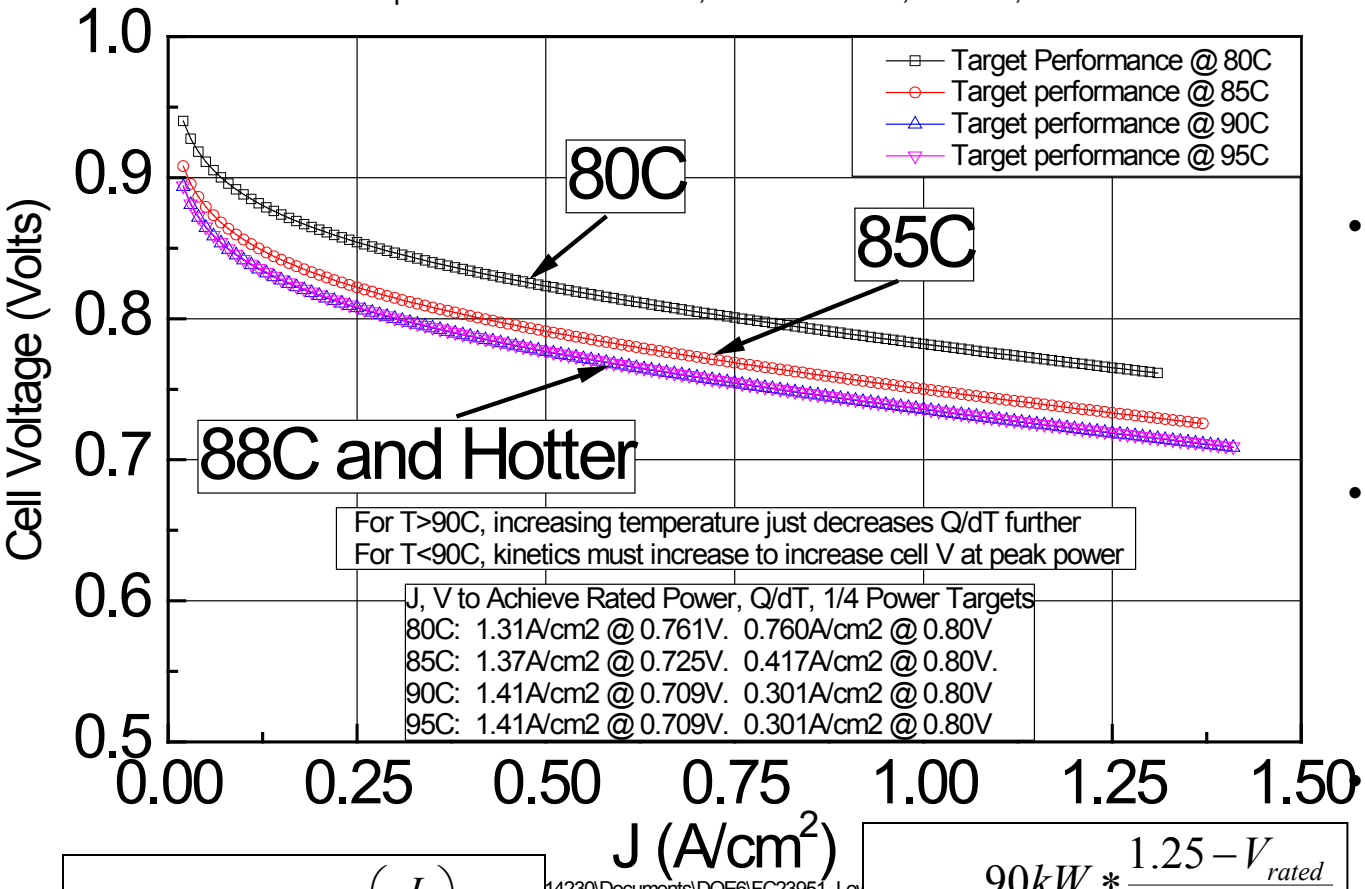
- Annealing: 30% mass activity gain, via method development and improved structural understanding. Dealloying: +20-40% lim. J over baseline method. Annealing & Dealloying integration, process feasibility are key next steps.
- MEA integration - substantial gains in specific power (+47% kW/g v. pre-proj.) due to improved absolute performance and PGM reduction towards target. Path to 2017 targets identified. Go/No Go Performance and Loading Metrics Achieved.

Technical Back-Up Slides

Target Polarization Curve Calculation

Performance Needed To Simultaneously Achieve DOE2017 MEA Targets At Various Cell Temperatures

Targets Addressed: J @ 1/4 Power (0.8V, 0.30A/cm^2), Rated Power (1W/cm^2), and Q/ΔT (1.45kW/degC)
Model Assumptions: HFR: 0.04ohm-cm^2, Tafel: 70mV/dec, No MTO, 90kW Stack



$$V = V_0 - 0.07 LOG\left(\frac{J}{J_0}\right) - JR$$

$$\frac{Q}{\Delta T} = \frac{90kW * \frac{1.25 - V_{rated}}{V_{rated}}}{T_{rated} - 40C}$$

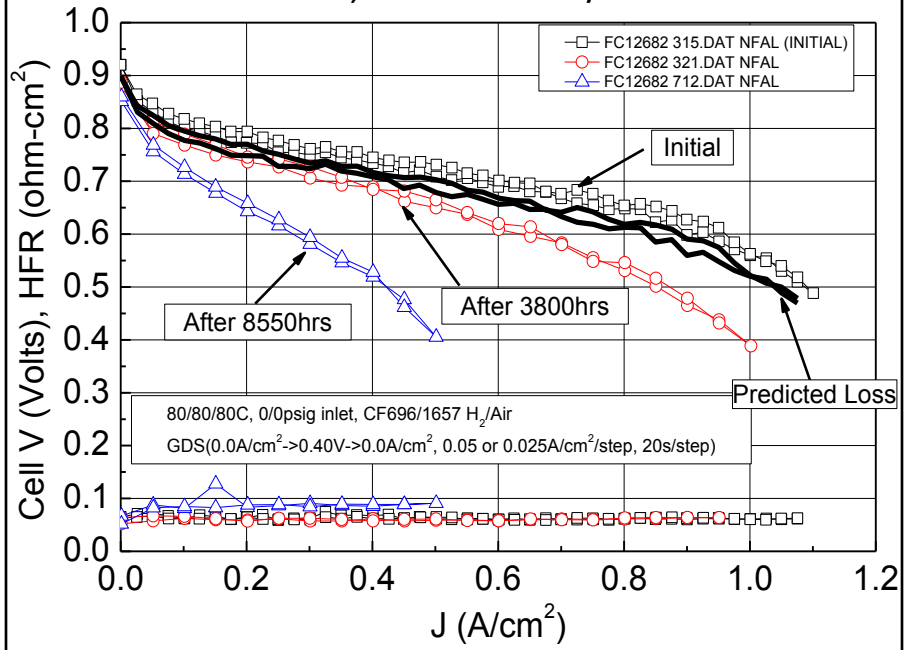
- Polarization curves calculated which simultaneously meet ¼ power, Q/ΔT, and rated power targets.
- Required performance *decreases* as cell temperature *increases* to 88°C (Q/**ΔT**)
- Q/ΔT target puts strict requirements on:
  - Cell T (≥88°C)
  - HFR (≤0.04ohm-cm^2)

Peak power (1W/cm^2) occurs at < 1.5A/cm^2 and >0.70V.

MEA Rated Power Durability – Background

Historical H_2/Air Performance w/ 80°C Load and RH Cycling, 8500 hours

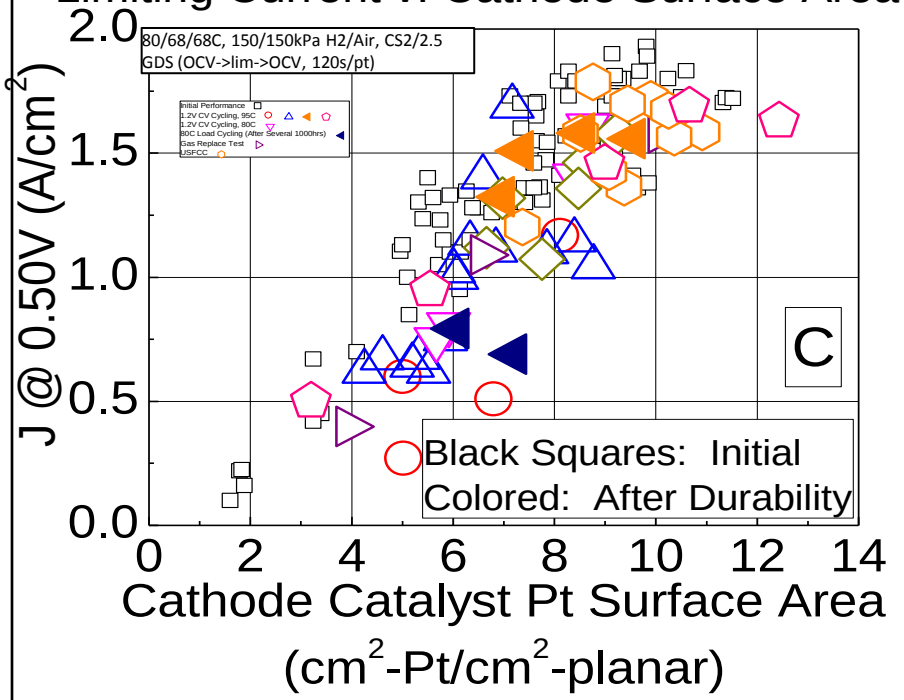
1000EW PEM, 0.20PtCoMn/NSTF on A+C



- While PtCoMn/NSTF surface area is relatively stable, MEA performance degradation under H_2/Air load cycling can be substantial.
  - Much larger than kinetic (70mV/dec) and ohmic losses predict.
  - *Appears irreversible – thermal cycling, high E scans, … ineffective to date towards fully recovering performance.*

BOL and Durability Aged

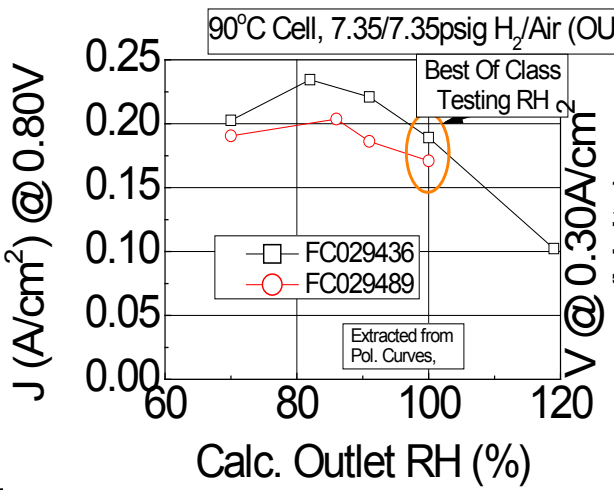
Limiting Current v. Cathode Surface Area

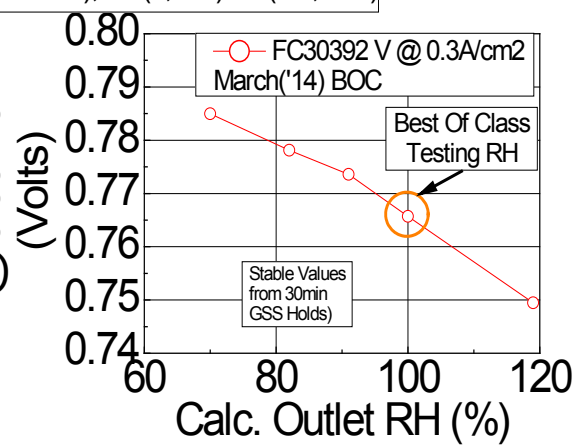


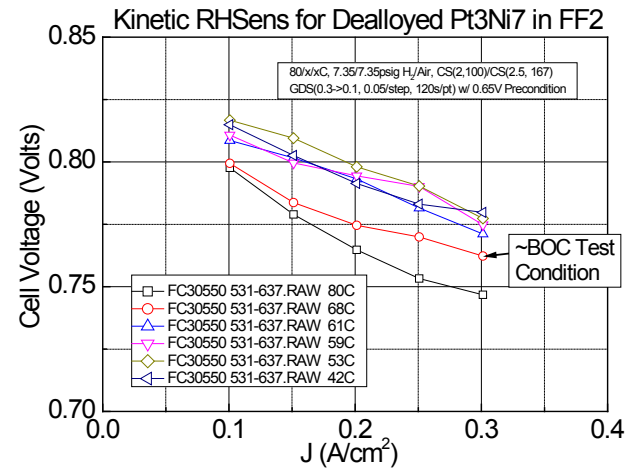
Factors

1. H_2/Air performance sensitivity to cathode surface area (< 9cm²/cm²)
2. Previous work by collaborator suggested 2nd possible mode, related to PEM degradation → catalyst contamination.

2014 (March) Best of Class MEA – Kinetic Analysis





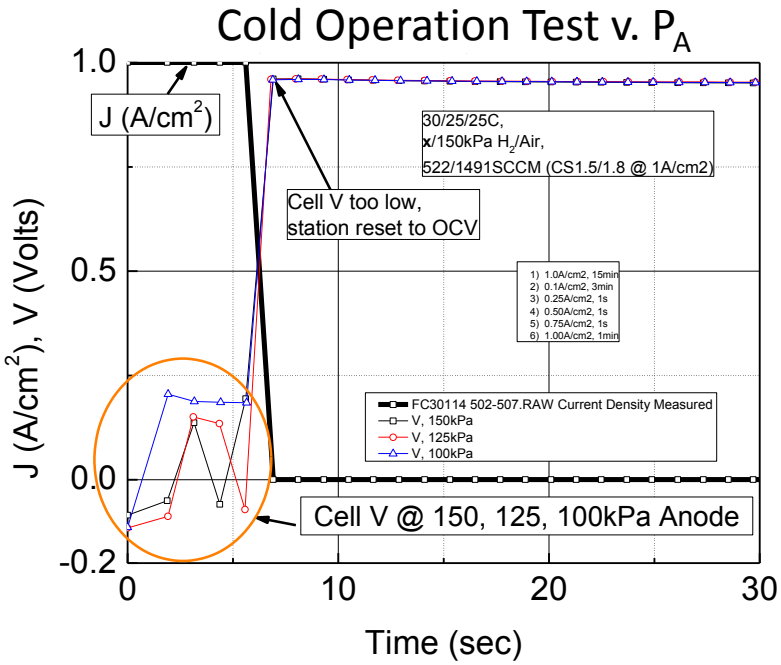


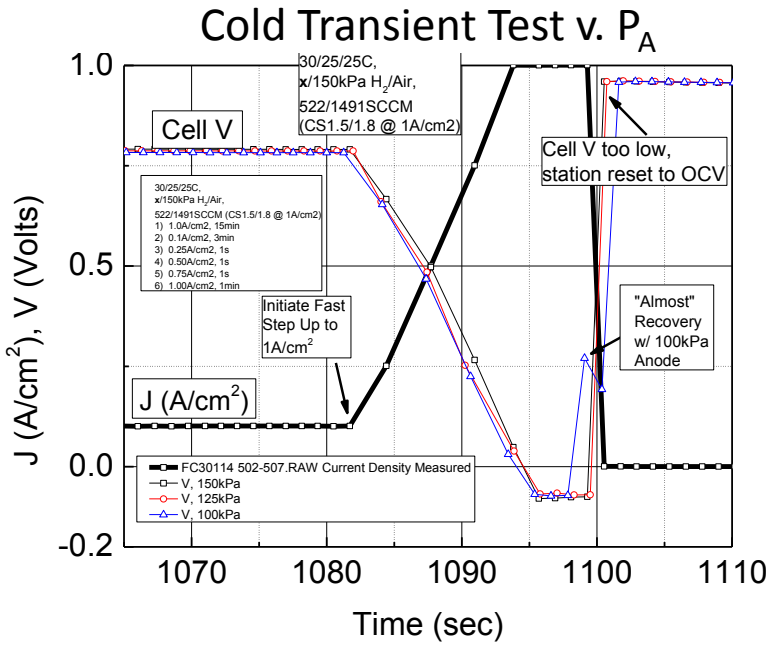
Best of Class MEA H_2/Air Kinetics, Mass Activities			
MEA	H_2/Air J @ 0.80V (A/cm²	H_2/O_2 ORR Mass Activity (A/mg)	Ca. PGM (mg/cm²)
2012 (March)	0.19	0.37 ± 0.01	0.121
2014 (March)	0.125	0.38 ± 0.02	0.110

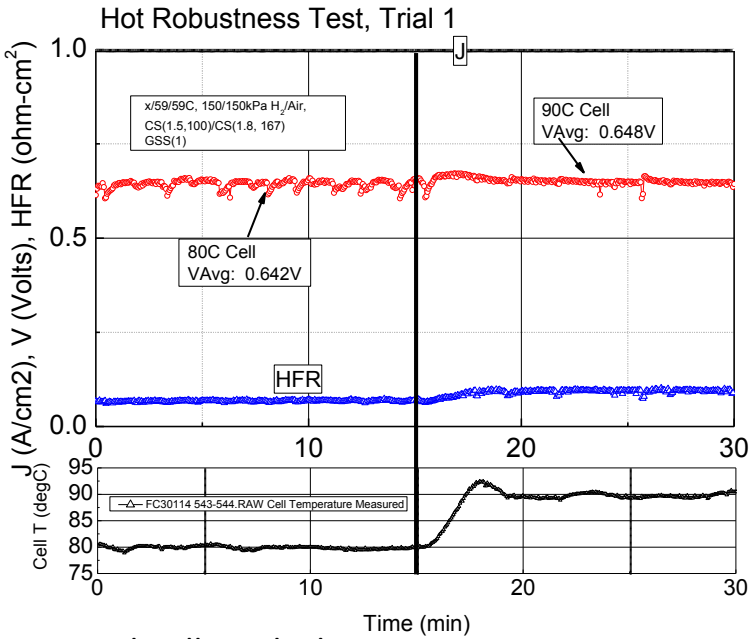
When measured under "Best of Class" test conditions, 2014(March) BOC MEA showed substantial decrease in ¼ Power Performance compared to 2012 MEA, but mass activity relatively unchanged.

- Recent BOC MEA candidates show surprisingly strong H_2/Air kinetic performance sensitivity to RH.
- Significant kinetic gains occur as RH is reduced below BOC test conditions (which are optimized for high J) – suggests possible O_2 transport issue at cathode.
  - Low heat generation rates- waste heat aids thermal gradient driven water removal.
- Development in progress to improve kinetic response under H_2/Air via operational and material approaches.

Task 6 – Short Stack Evaluation – Robustness Metrics







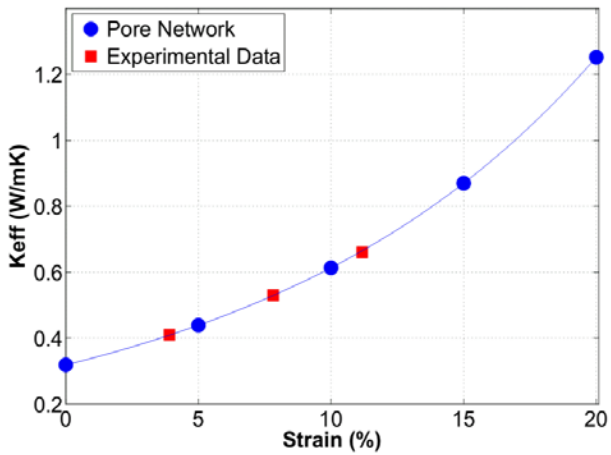
- NSTF MEA w/ interim downselect anode GDL, cathode interlayer from Task 2 "almost" passes cold operation and cold transient tests (above).
- Easily passes Hot Operation test (right).

CCM: 0.05PtCoMn/0.15PtCoMn, 3M 20u 825EW
Anode GDL: X+PTFE, MPL (interim DS).
Cathode IL: 2979+ "B" IL @ ca. 0.03mgPt/cm^2(interim DS)

Cold Startup: Effective Properties

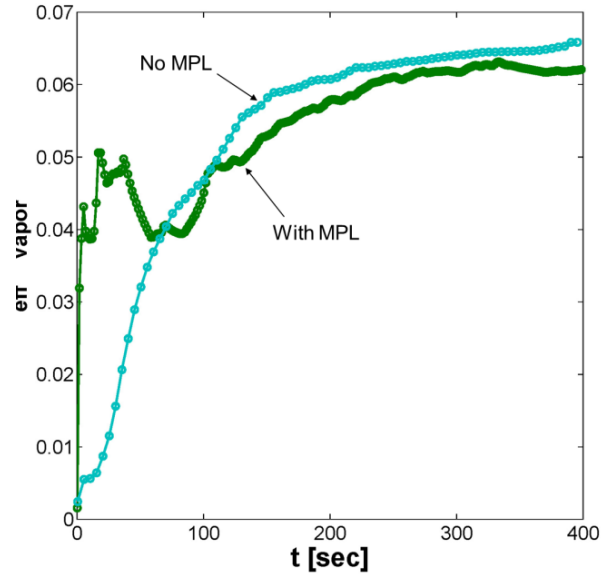
Cold Startup Modeling (Task 3): MTU Pore Network Model Calculations of GDL Effective Properties.

Effective Thermal Conductivity



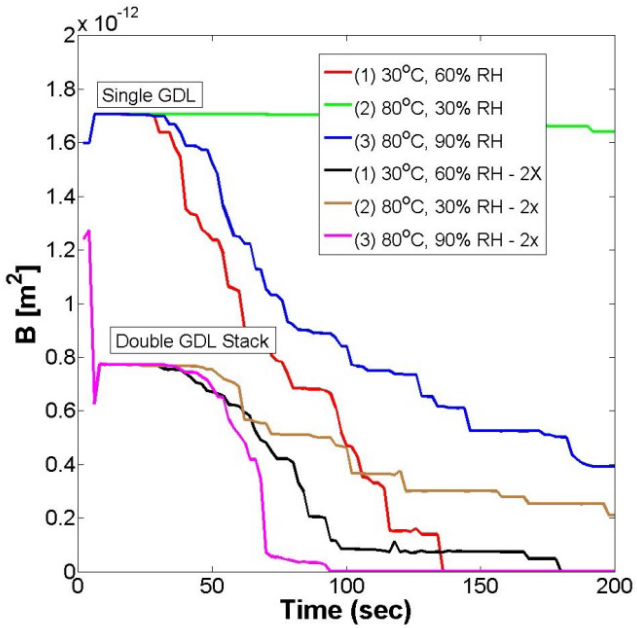
Model prediction and experimental measurement [1] of effective thermal conductivity for a dry GDL under strain. MTU Pore Network Model accounts for change in contact resistance due to GDL compression.

Transient Effective Diffusivity



Toray T060 w/ and w/o MPL on cathode side at 1.5A/cm² with 50% heat and 50% water.

Transient Effective Permeability



Freudenberg H2315 at 1.5A/cm² with 50% heat and 80% water on cathode for a range of conditions. Steady-state effective permeabilities were also calculated for Toray T060 and found to correspond to experimental values [2].

1. Burheim, Pharoah, Lampert, Vie, and Kjelstrup, *J. Fuel Cell Sci. Tech.,* **8**(2): 021013 (2011)
2. Gostick, Fowler, Pritzker, Ioannidis, and Behra, *J. Power Sources* ,**162**(1): 228-238 (2006)