2014 Annual Merit Review DOE Hydrogen and Fuel Cells and Vehicle Technologies Programs High Performance, Durable, Low Cost Membrane Electrode Assemblies for Transportation Applications

> Andrew Steinbach 3M Company June 18th, 2014



Project ID: FC104

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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/cm²
- Electrocatalyst, Support Durability: < 40% Activity, ECSA Loss

MEA (2017)

- Q/∆T: 1.45 kW/°C
- Cost: \$9 / kW
- Durability w/cycling: 5000 hrs
 - Performance @ 0.8V: 0.300 A/cm²

2

Perf. @ Rated Power: 1 W/cm²

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	Barriers	MEA, Catalys	t Targets Address	sed
	Approaches This Year	Addressed	2017 Targets	Target Values	Obj.
1.	Improve MEA Robustness for Cold Startup and Load Transient via	B. Cost	Q/AT	1.45kW / °C	3,4
	Materials Optimization, Characterization and Modeling.	C. Performance	Cost	\$9 / kW	3,4
2.	Evaluate Candidate MEA and	A. Durability			
	Component Durability to Identify Gaps; Improve Durability Through		Durability with cycling	5000 hours w/ < 10% V loss	2,3,4
	Material Optimization and Diagnostic Studies.		Performance @ 0.8V	0.300A/cm ²	3,4
3.	Improve Activity, Durability, and Rated Power of MEAs based on Pt ₃ Ni ₇ /NSTF Cathodes via Post-Processing	A. Durability B. Cost C. Performance	Performance @ rated power	1W/cm²	3,4
4.	Optimization and Characterization. Integrate MEAs with High Activity, Rated Power, and Durability with Reduced Cost.	A. Durability B. Cost C. Performance	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 <u>nanos</u>tructured <u>thin film</u> (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.

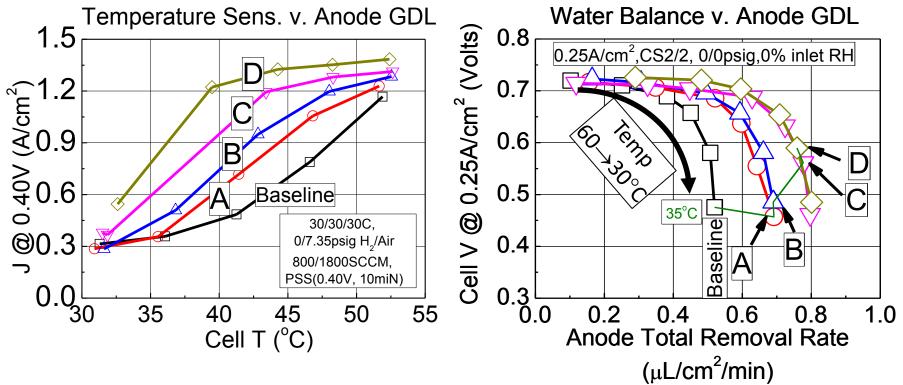
- 1. Place appropriate emphasis on key commercialization and DOE barriers.
- 2. Through advanced diagnostics, identify mechanisms of unanticipated component interactions resulting from integration of low surface area, low PGM, high specific activity electrodes into MEAs.

	Q	Project Milestone MS 1.1, 2.1, 5.1 based on 4-5 Project Goals (See Backup Slides)	% Complete (Apr. '14)	Status Against DOE 2017 Targets		
MS ID	T R			Characteristic	2017 Targets	Status, '13/'14
		BUDGET PERIOD 1 (Sept. '12-May '14)	Q/ΔT (kW / °C)	1.45	1.56/1.56	
6.1	2	Baseline MEA: Short Stack Eval. Complete.	CANCELLED			(0.670V) 6 / 5
1.1	7	Comp. Cand. Meet Interim Perf./Cost Goals.	75% (3 of 4)	Cost (\$ / kW)	9	(PGM only @ \$35/g _{Pt})
2.1	7	Comp. Cand. Meet Interim Cold-Start Goals.	75% (3 of 4)	Durability with	5000	NA
5.1	7	Comp. Cand. Meet Interim Durability Goals.	66% (8 of 12)	cycling (hours)	3000	INA
3.1	7	GDL Pore Network Model Validation With	500/ (1 - 6 2)	Performance @ 0.8V (mA/cm ²)	300	203/125
		≥ 2 3M Anode GDLs. Interim BOC MEA: Short Stack Eval.	50% (1 of 2)	Performance @ rated	1000	871/932
6.2		Complete.	10% (1 of 3)	power (mW/cm ²)		(0.670V)
4.1		2014(Mar.) Best of Class MEA Meets G/NG	<u>100%</u>	PGM total content (g/kW (rated))	0.125	0.157/0.138 (0.670V)
4.1 Go/		$1) \leq 0.135 \text{mg}_{\text{PGM}}/\text{cm}^2 \text{ (Total)}$	0.129mg/cm ²	PGM total loading		
G0/ No-Go		2) Rated Power, Q/ΔT:		$(mg PGM / cm^2)$	0.125	0.137/0.129
		≥0.659V@ 1.41A/cm ² , 90°C, 1.5atm H ₂ /Air	0.668V	electrode area)		

3M High Performance, Durable, Low Cost MEAs. 2014 DOE Hydrogen, Fuel Cells, Vehicles Program AMR, June 16-20 ⁴

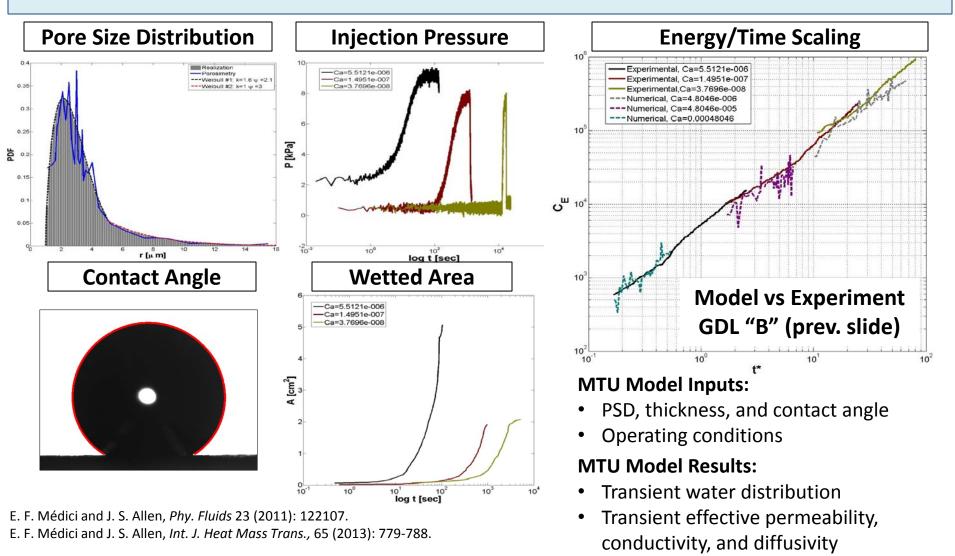
Improved Robustness for Cold Startup, Load Transient (Task 2):

New Anode GDLs Improve Startup Capability - Higher H₂O Removal Out Anode



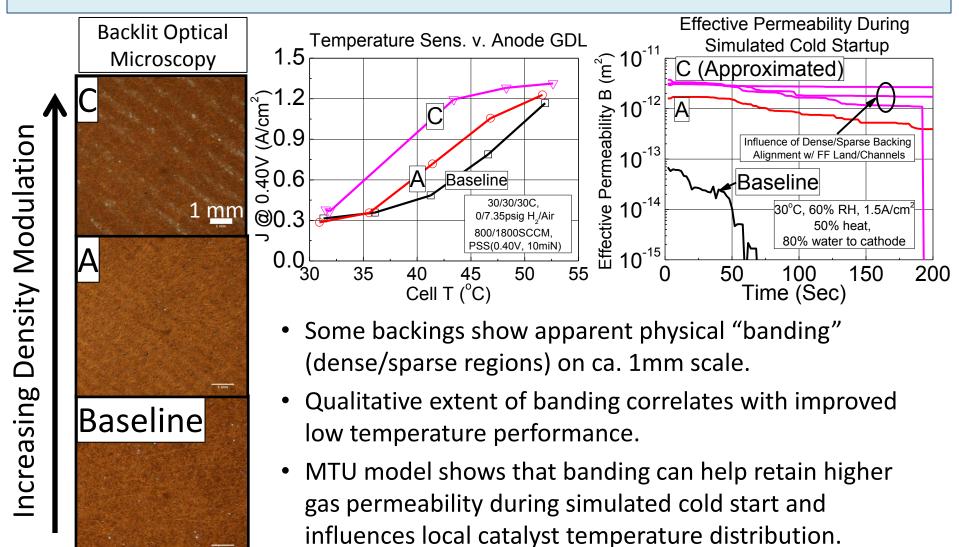
- New anode GDL candidates show good promise for improving cold-start capability.
- Improvements in low T performance as the anode GDL is varied correlate with higher anode water removal rates @ 0.25A/cm².
- As T decreases, performance loss occurs as anode water removal rate limit occurs.

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



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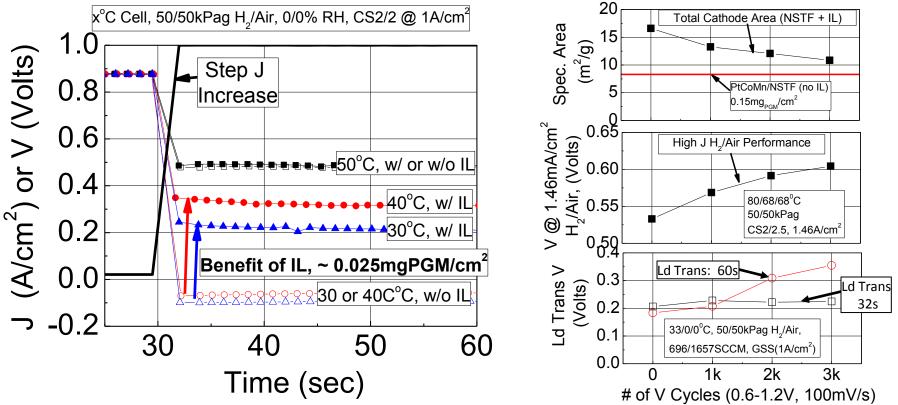
Cold Startup Modeling (Task 3): Possible Backing Structural Factor Identified Which Correlates with Improved Low T Response; MTU Modeling Provides Insight



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

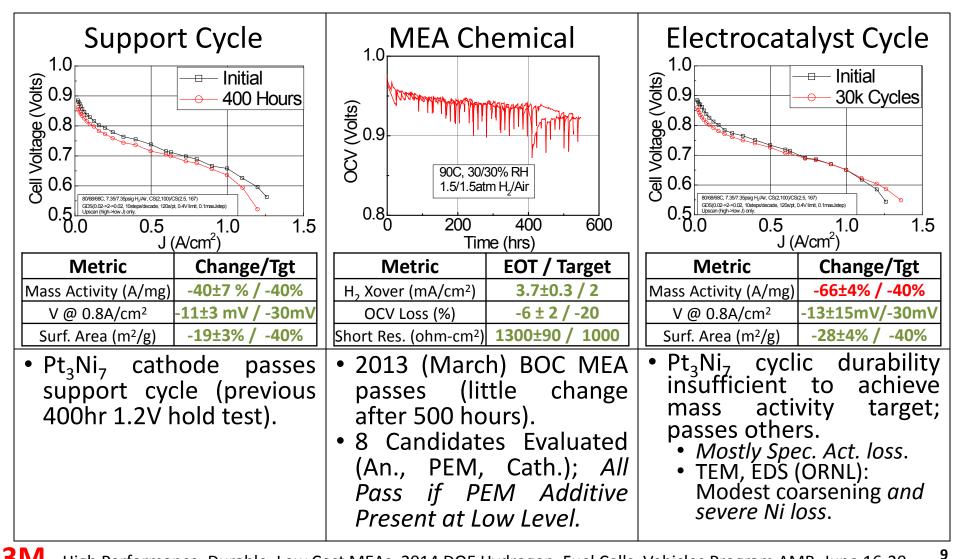
Cathode Interlayer Developed: 20°C Improvement in Operating Window, and Is Durable



- 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.

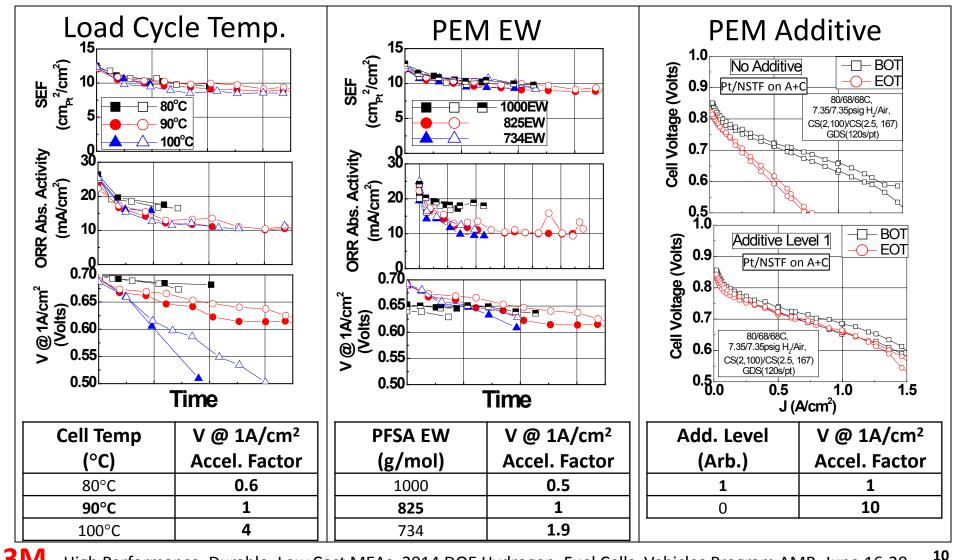
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Component Durability Evaluation (Task 5): Component Candidates Generally Show Acceptable Durability; Cathode Cyclic Durability Insufficient



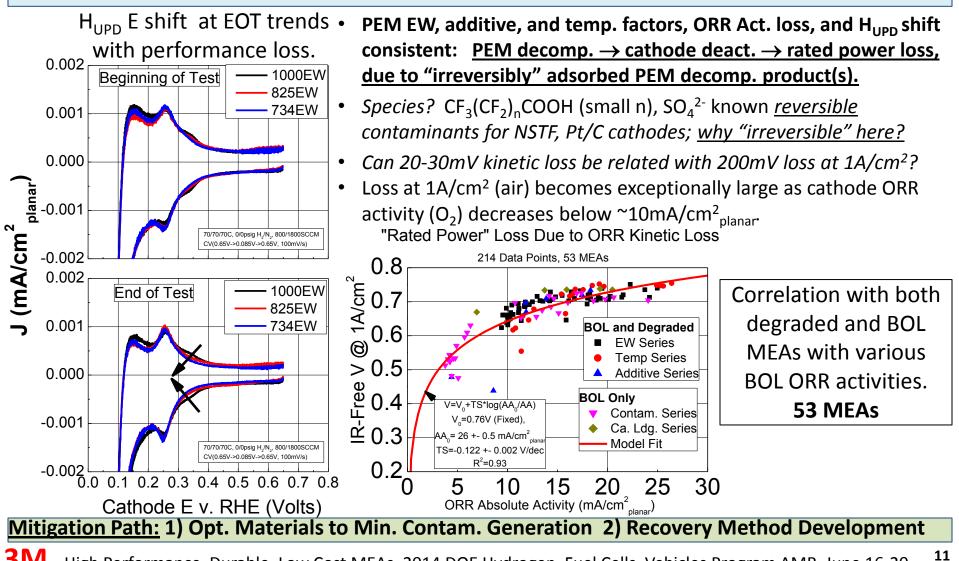
MEA Rated Power Durability (Task 5): 3 Primary Factors To Date

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



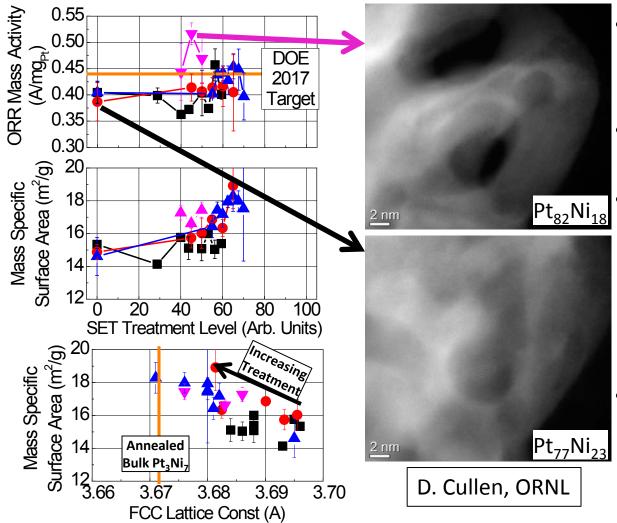
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MEA Rated Power Durability (Task 5): Voltammetry Suggests Accumulation of Anionic Contaminant; Rated Power Loss Due to ORR Kinetic Loss



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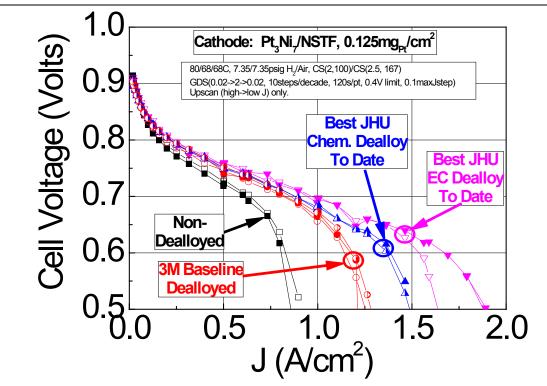
Improved Activity, Rated-Power Capable ORR Catalysts (Task 1.1): SET (Annealing) Improves Activity, Area of Pt₃Ni₇/NSTF Cathodes



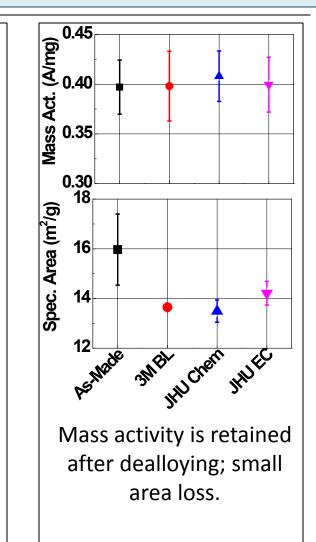
- Annealing optimization:
 - +30% mass activity, in MEA.
 - +20% specific area.
- DOE Mass Activity target exceeded.
- Increasing grain size, decreasing lattice constant (XRD) correlates with specific area gains.
 - Alloy homogenization, defect reduction.
- ORNL TEM: annealing improves in-situ nanoporosity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

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

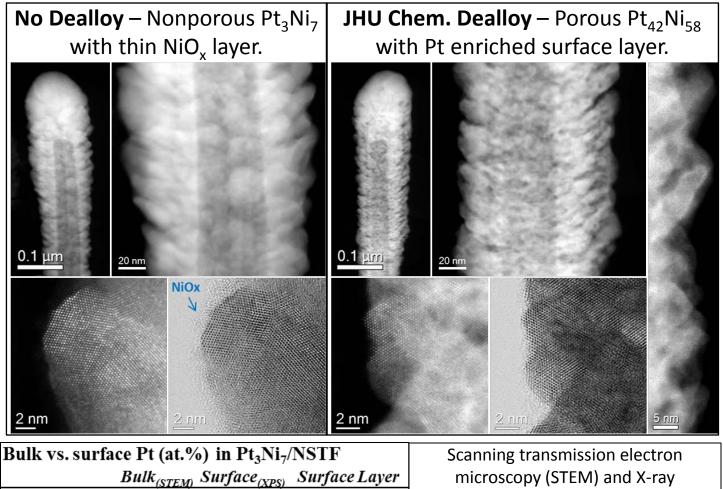


- JHU dealloying development has substantially increased rated power capability with Pt₃Ni₇ cathodes.
 - Best Chem/EC: +20/+40%% J @ 0.60V
- Optimization for volume production needed.



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

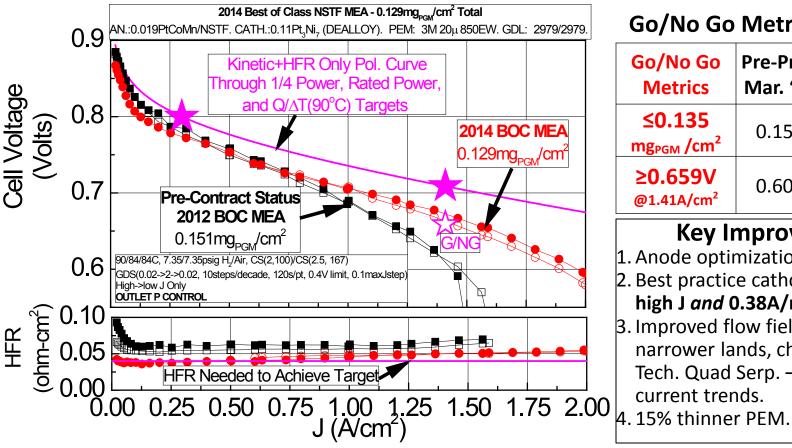
Dealloying Transforms $Pt_3Ni_7/NSTF$ Surface from NiO_x to Pt Rich; Forms Nanoporosity



	(STEM)	$\approx m f m c c_{(XPS)}$	Sulface Buyer	
No Dealloy	30	20	Ni Oxide	photoelectron spectroscopy (XPS) –
JHU Chem.	42	53	Pt-rich	ORNL, D. Cullen, H. Meyer
Deuteuree				- Ina san Fuel Celle Mahieles Dressen AA

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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.

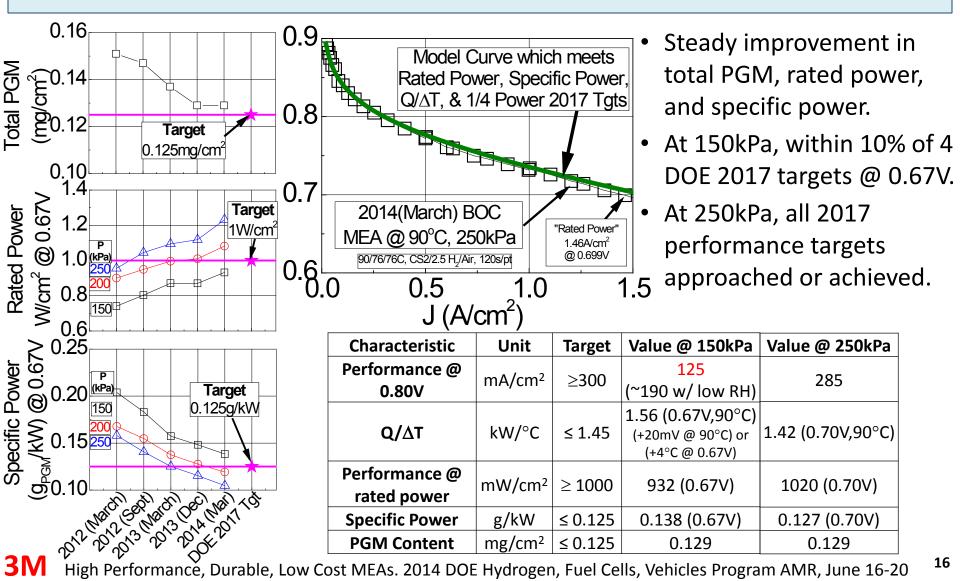
- 2. Best practice cathode dealloying
 - high J and 0.38A/mg mass activity.
- 3. Improved flow field w/ modestly narrower lands, channels than FC Tech. Quad Serp. – in line with

Path to 2017 MEA Performance, Loading Targets:

1) Increase 0.80V H₂/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). 15

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



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. Pt₃Ni₇/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 \rightarrow Identify Key A. GDL Factors. Task 4 - Best of Class MEA Integration Activities •Best of Class Component Integration Towards Project Goals: $(\leq 0.125 \text{mg}_{PGM}/\text{cm}^2; \text{ Rated Power, } Q/\Delta T: 0.709 \text{V} @ 1.41 \text{A}/\text{cm}^2 @ 90^{\circ}\text{C}).$ 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)

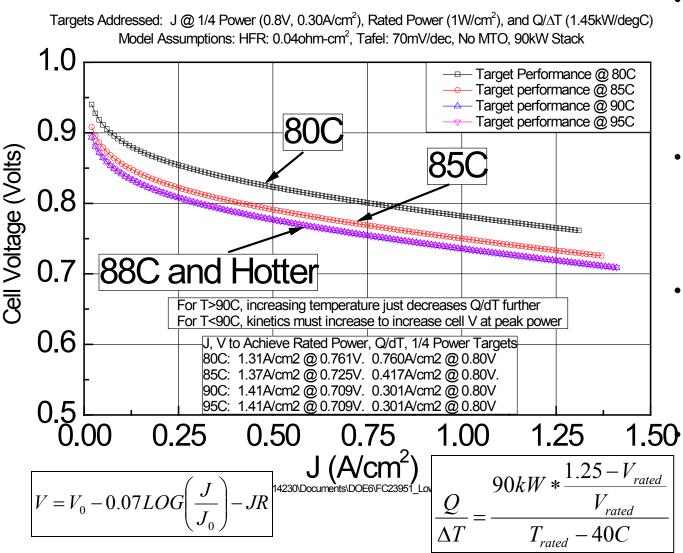
- Annealing: 30% mass activity gain, via method development and improved structural understanding. Dealloying: +20-40% lim. J over baseline method. Annealing & Dealloying integration, process feasibility are key next steps.
- MEA integration substantial gains in specific power (+47% kW/g v. pre-proj.)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

Instruction

Technical Back-Up Slides

Target Polarization Curve Calculation

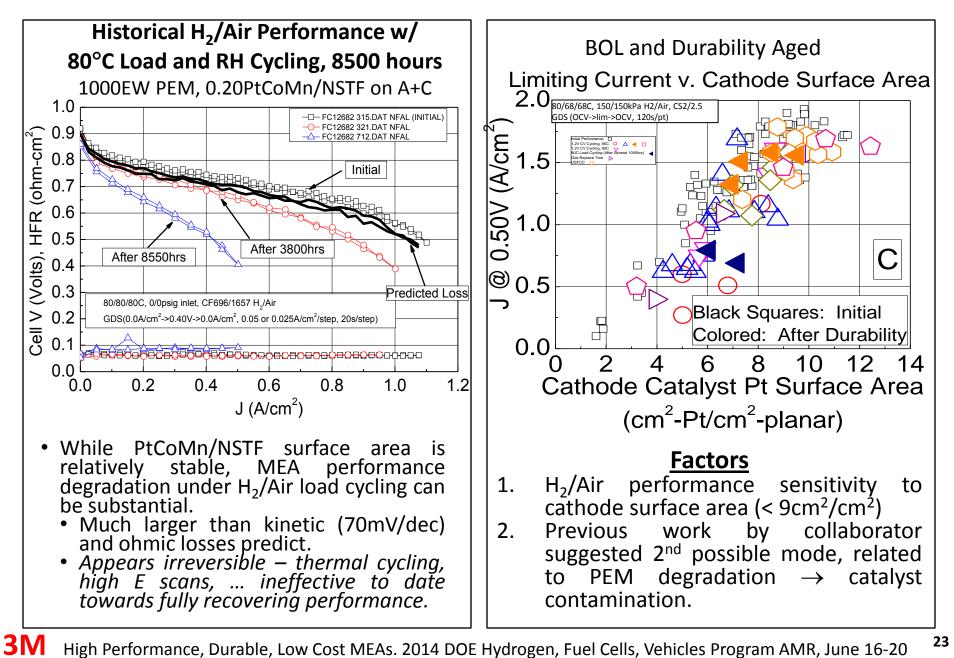
Performance Needed To Simultaneously Achieve DOE2017 MEA Targets At Various Cell Temperatures



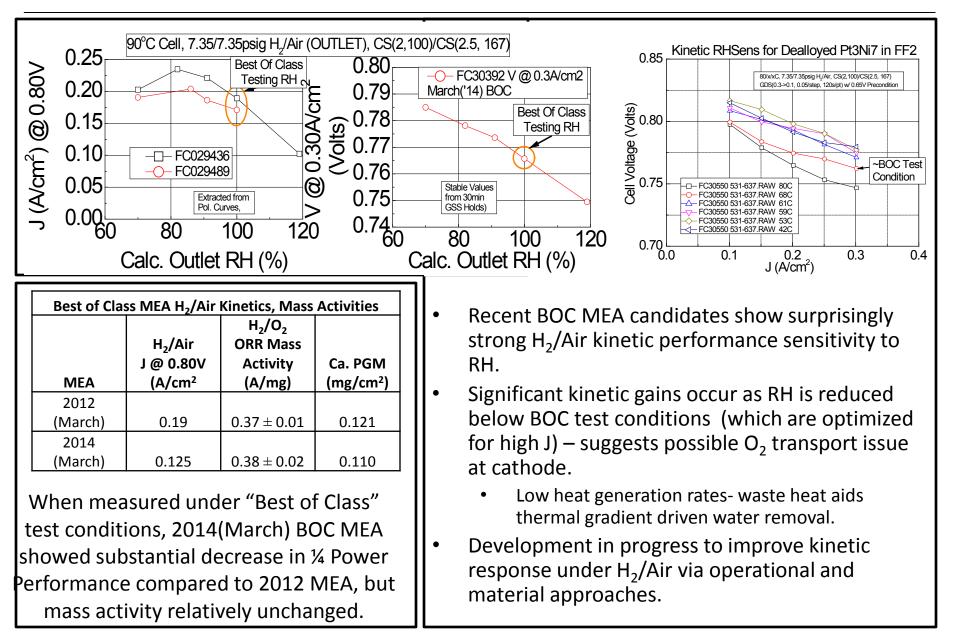
- Polarization curves calculated which simultaneously meet ¼ power, Q/ΔT, and rated power targets.
- Required performance *decreases* as cell temperature *increases* to 88°C (Q/<u>AT</u>)
- Q/ Δ T target puts strict requirements on:
 - Cell T (≥88°C)
 - HFR (≤0.04ohm-cm²)

Peak power (1W/cm²) occurs at < 1.5A/cm² and >0.70V.

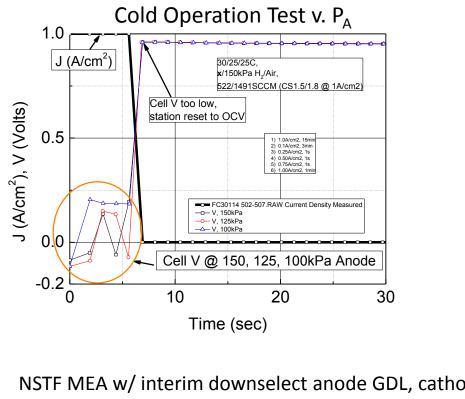
MEA Rated Power Durability – Background

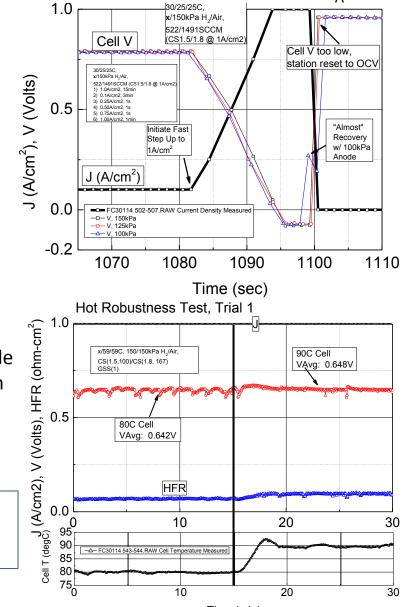


2014 (March) Best of Class MEA – Kinetic Analysis



Task 6 – Short Stack Evaluation – Robustness Metrics





Cold Transient Test v. P_A

 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/cm²(interim DS)

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Cold Startup: Effective Properties

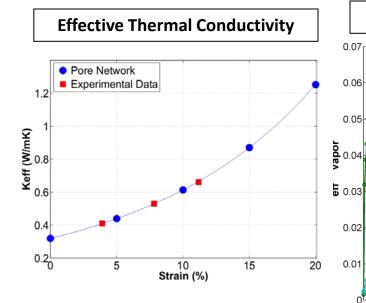
Transient Effective Diffusivity

With MPL

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

No MPL

100



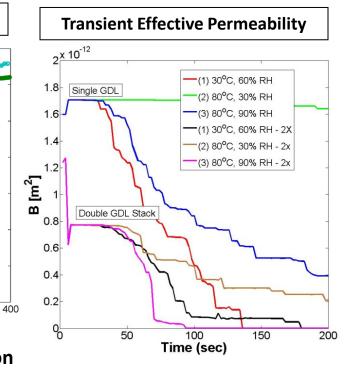
Model prediction and experimental measurement [1] of effective thermal conductivity for a dry GDL under strain. MTU Pore Network Model accounts for change in contact resistance due to GDL compression.

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

200

t [sec]

300



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)