Power for the Real World

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

> Andrew Steinbach 3M Company June 8th, 2016



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: 8/30/16*
 * Project extended from 8/30/15 (no-cost).

Budget

- Total DOE Project Value: \$4.606MM*
- Total Funding Spent: \$4.346MM*
- Cost Share Percentage: 20%

* Includes DOE, contractor cost-share, and FFRDC funds, as of 2/28/16.

Barriers

- A. MEA Durability
- B. Stack Material & Mfg Cost
- C. MEA Performance

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 (V. Banhardt)
- Argonne Nat'l Lab. (R. Ahluwalia)
- Los Alamos Nat'l Lab. (R. Mukundan, R. Borup)
- General Motors (B. Lakshmanan)



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 DOE 2020 MEA targets.

	Primary Objectives and	Barriers	MEA, Catalyst Targets Addressed		
	Approaches This Year	Addressed	2020 Target	Target Values	Obj.
1.	Produce Project Best of Class		Q/AT	1.45kW / °C	3,4
	Components and CCMs (to be used for		Cost	\$7 / kW	3,4
	stack testing) via Continuous, Pilot Mfg. Processes	C. Performance	Durability with cycling	5000 hours w/ < 10% V loss	2,3,4
2.	Validate Performance and Operational Robustness of Project Best of Class MEAs in Short Stack.	B. Cost C. Performance	Performance @ 0.8V	300mA/cm ²	3,4
3.	Evaluate Project Best of Class MEAs for		Performance @ rated power	1000 mW/cm ²	3,4
	Performance/Cost Modeling and Durability Under ASTs and Load Cycling.	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

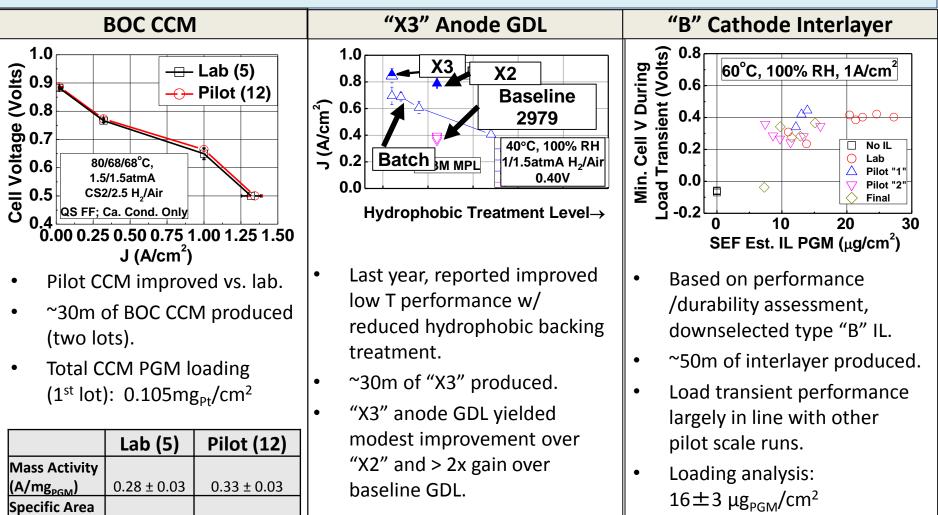
Approach: Optimize integration of advanced anode and cathode catalysts, based on 3M's <u>nanos</u>tructured <u>thin film</u> (NSTF) catalyst technology platform, with next generation PFSA PEMs, gas diffusion media, cathode interfacial layers, and flow fields for best overall MEA performance, durability,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

MG	Q	Project Milestone	0/ Commisto	Status Against DOE 2020 Targets			
MS ID	T R	MS 1.2, 2.2, 4.2, and 5.2 based on Achievement of Multiple Project Goals (See Backup Slides)	% Complete (Mar. '16)	Characteristic	2020 Targets	Status, '15 / '16	
BUDGET PERIOD 2 (June '14-Aug. '16)				Q/ΔT (kW / °C)	1.45	1.45	
1.2	15	Comp. Cand. Meet Project Perf./Cost Goals.	98%		<u>(@ 8kW/g)</u>	(@ 6.5/6.8* kW/g)	
2.2	15	Comp. Cand. Meet Project Cold-Start Goals.	50% (2 of 4)	Cost (\$/kW)	7	$5 / 5^*$ (PGM only @	
5.2	15	Comp. Cand. Meet Project Durability Goals.	91% (10 of 11)		,	\$35/g _{Pt} ; 0.692V)	
4.2		Best of Class MEA Meets All Perf./Cost,	84%	Durability with cycling (hours)	5000	In progress	
		Cold-Start, and Durability Project Goals	0170	Performance @ 0.8V (mA/cm ²)	300	304 / 310*	
3.2	12	Validation of Integrated GDL/MEA Model With ≥ 2 3M MEAs (Different Anode GDLs).	100%	Performance @ rated power (mW/cm ²)	1000	855 / 891* (0.692V, 1.45kW/°C)	
6.3	15	BOC MEA: Short Stack Eval. Complete.	40%	PGM total content	0.125	0.155 / 0.147*	
	1 1 2 1	Final Short Stack to DOE-Approved	400/	(g/kW (rated))		(0.692V, 1.45kW/°C)	
0		Location.	40%	PGM total loading (mg PGM / cm ²	0.125	0.133 / 0.131*	
				electrode area)	0.125	0.155 / 0.151	
				*: 2016 values from 201 include a cathode			

Best of Class Component Integration (Task 4.1):

Pilot Scale Component Fabrication





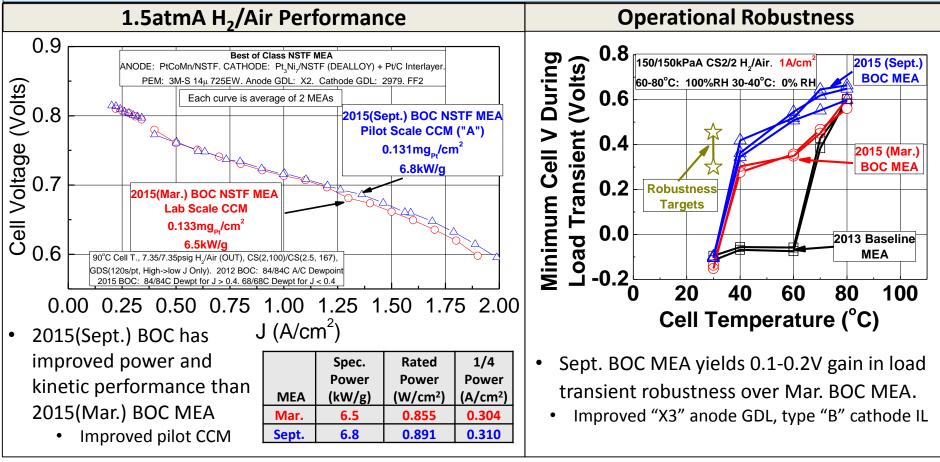
 (m^2/g_{PGM})

 11.8 ± 1.4

 14.5 ± 0.7

Best of Class Component Integration (Task 4.1):

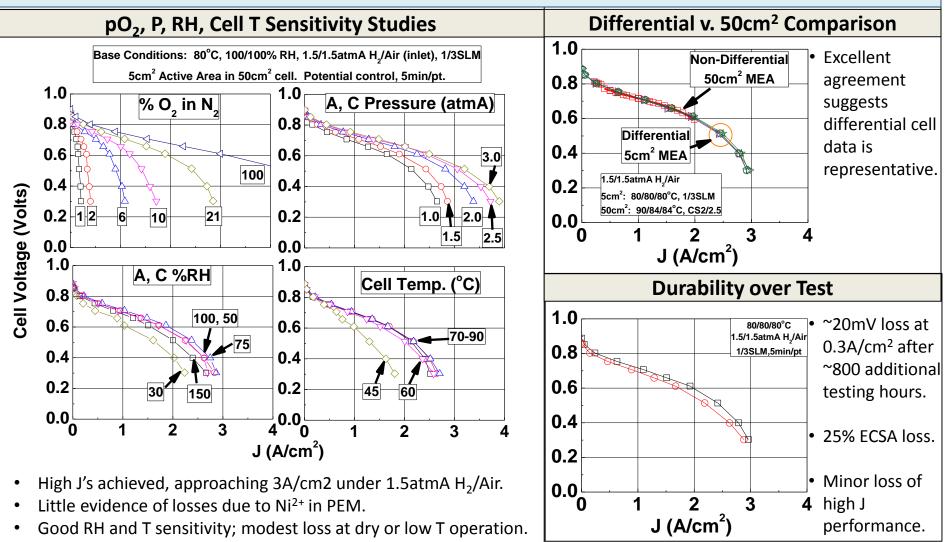
2015(Sept.) 3M NSTF Best of Class MEA Performance, Robustness



MEA	Anode Cat	PEM	Cathode Catalyst	CCM	Anode GDL/Cathode IL
2015(Mar.)	PtCoMn/NSTF, 15µg/cm ²	3M-S 725EW	Dealloyed PtNi/NSTF, 0.103mg/cm ²	Lab	"X2"/ 30% "A"(15µg/cm ²)
2015(Sept.)	PtCoMn/NSTF, 19µg/cm ²	14µ w/ add.	Dealloyed PtNi/NSTF, 0.096mg/cm ²	Pilot	"X3"/ 30% "B"(16µg/cm ²)

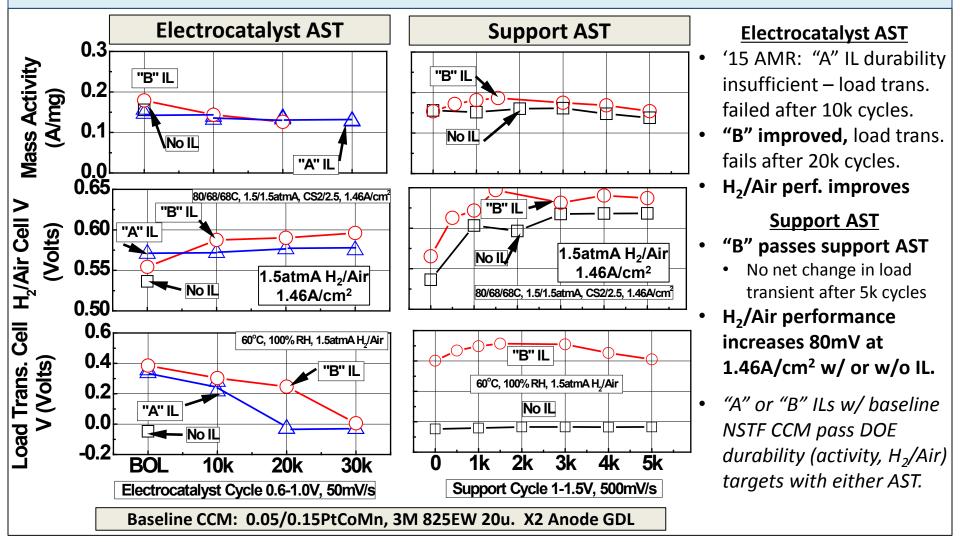
Best of Class Integration Diagnostics (Task 4.2):

2015(Sept.) BOC MEA Differential Cell Evaluation for ANL Model



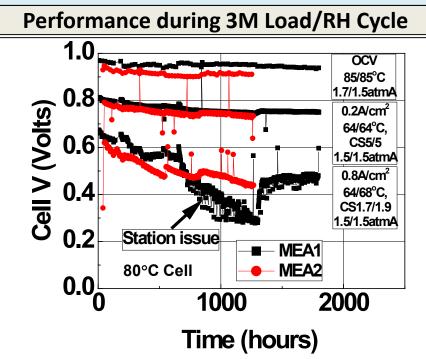
Cathode Interlayer Durability (Task 5):

AST Durability Evaluations of "B" Interlayer

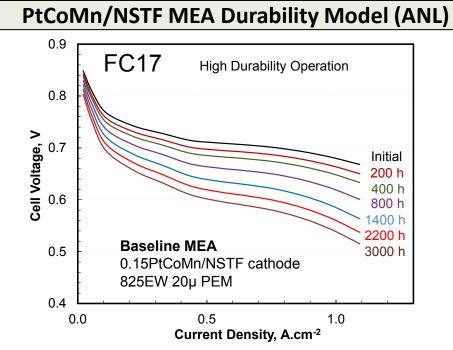


MEA Rated Power Durability (Task 5): Load/RH Cycle Evaluation of 2015 (Sept.) BOC MEAs; ANL Durability Modeling of NSTF MEAs

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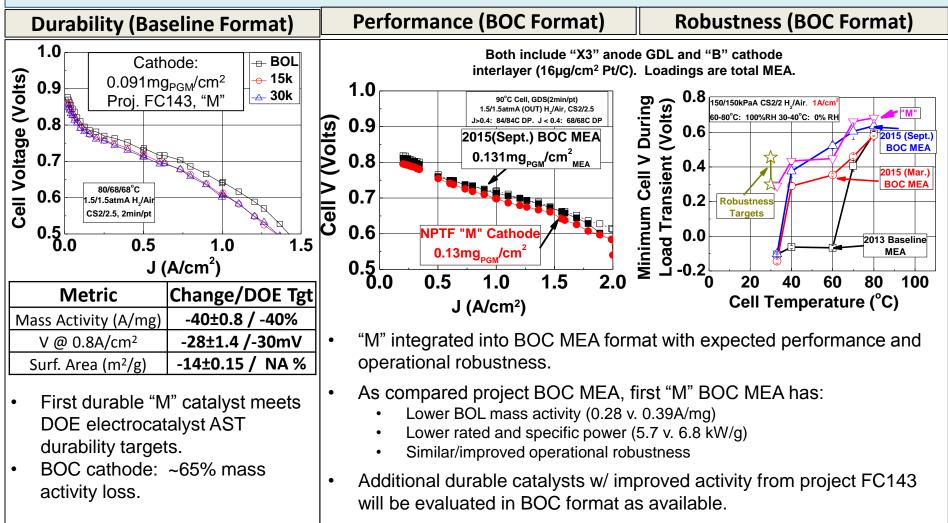
- BOC MEAs have completed > 1200 hours of 3M load/RH cycle testing.
- Significant performance decay during cycling due to both reversible and irreversible factors.
- Steady OCV no PEM breach.
- Tests ongoing and diagnostics conducted periodically.



- NSTF rated power degradation correlates to PFSA decomposition extent ('15 AMR).
 - 800 hours to predicted 10% irreversible voltage loss; 2300 hours to 20% loss.
 - Critical requirement for 5000 hour durability (10% V loss): limit cathode F⁻ to 0.7µg_{F-}/cm² (80% FER reduction)
 - Path: Decrease MEA FER and increase cathode durable activity and surface area.

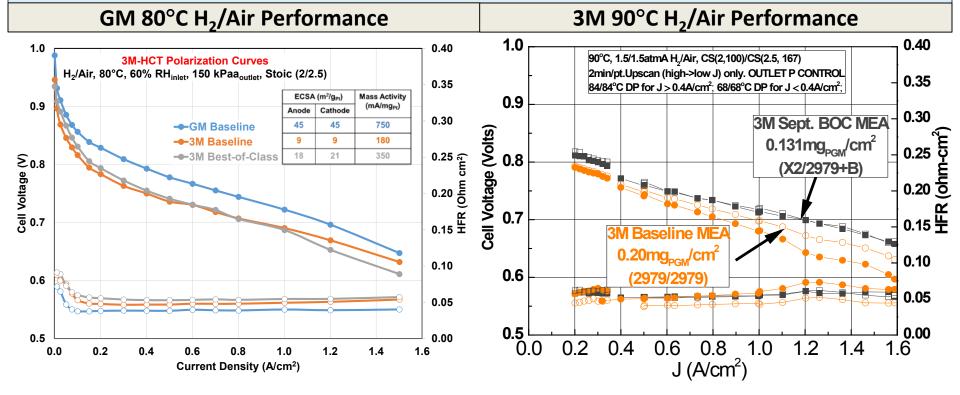
Best of Class Component Integration (Task 4.1):

New, Improved Durability NSTF "M" Cathode Integration



BOC MEA Short Stack Evaluation (Task 6):

Single Cell Testing at 3M, GM – H₂/Air Performance



- At 1.5 A/cm², order of performance 3M Baseline > 3M March BOC
- BOC mass activity, specific areas largely in-line w/ 3M expectation.

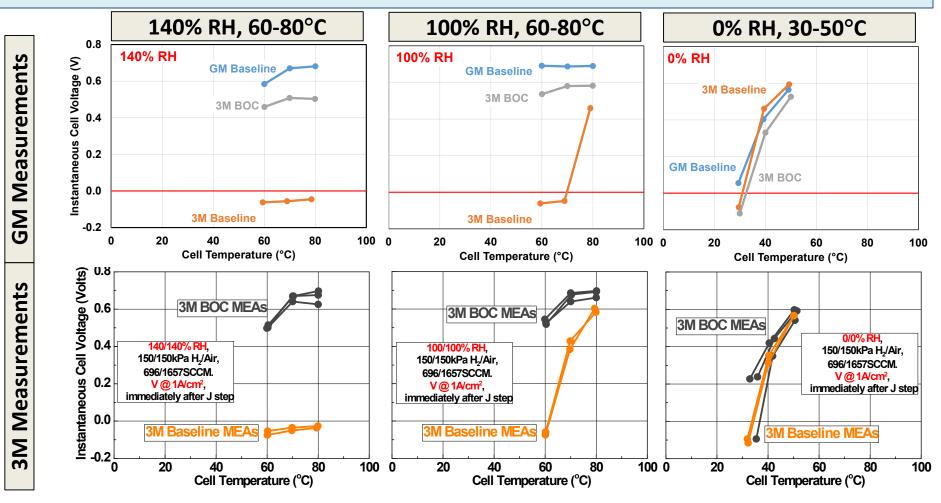
- 3M baseline MEA data consistent w/ GM
- BOC MEA data inconsistent at high current (GM: 60mV lower @ 1.5A/cm²)

3M Baseline MEA: 0.05/0.15PtCoMn, 3M 825EW 20µ. 3M 2979/2979 GDL 3M BOC MEA: 0.019/0.096PtNi, 3M 725EW 14µ. 3M "X3"/2979+"B"IL GDL



BOC MEA Short Stack Evaluation (Task 6):

Single Cell Testing at 3M, GM – Load Transients



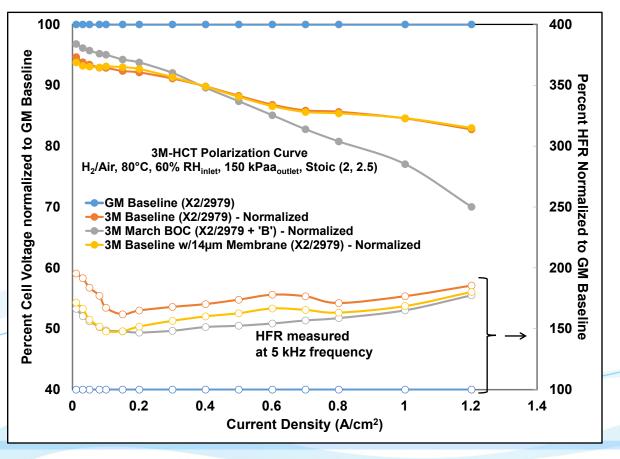
- Load transient results for 3M baseline and BOC MEAs similar between sites.
- Robustness improvement of BOC MEA largely confirmed at single cell level Applied to Life."

Science.

BOC MEA Short Stack Evaluation (Task 6):

Stack H₂/Air Performance Much Lower than Expected

Short Stack – 3M-HCT Polarization Curve H₂/Air, 80°C, 60% RH_{inlet}, 150 kPaa_{inlet}, Stoic (2/2.5)



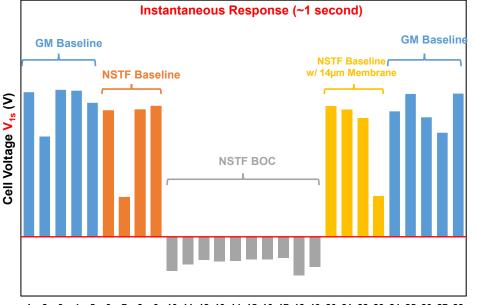
- Cell voltage of 3M CCMs from short stack testing have been normalized to the GM Baseline performance
- 3M BOC CCMs show a ~3% improvement in low current density performance over the 3M Baseline Cells
- At 1.2 A/cm², performance of 3M BOC CCMs are ~70% of that observed with GM Baseline Cells

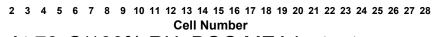


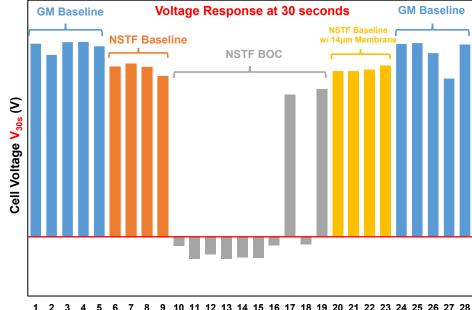
BOC MEA Short Stack Evaluation (Task 6):

Stack Load Transient Performance Much Lower than Expected

100% RH_{inlet}, 70°C, H₂/Air, 150 kPaa_{inlet}, Transient from 0.02 to 1.0 A/cm²





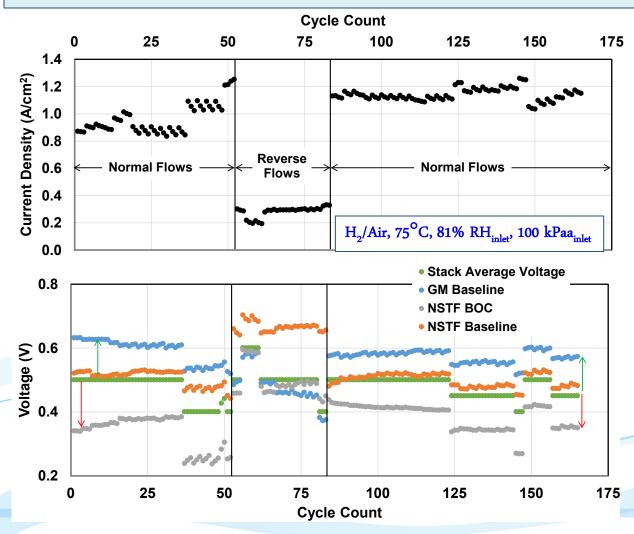


Cell Number

- At 70°C/100% RH, BOC MEA instantaneous voltage after load transient was negative (failed)
- Most BOC cells did not recover to positive cell voltages within 30 seconds.
- Unexpectedly, NSTF baseline CCMs (no cathode interlayer) pass

More optimization of NSTF MEAs with the stack platform is needed to be competitive with conventional catalyst for steady state and load transient performance.

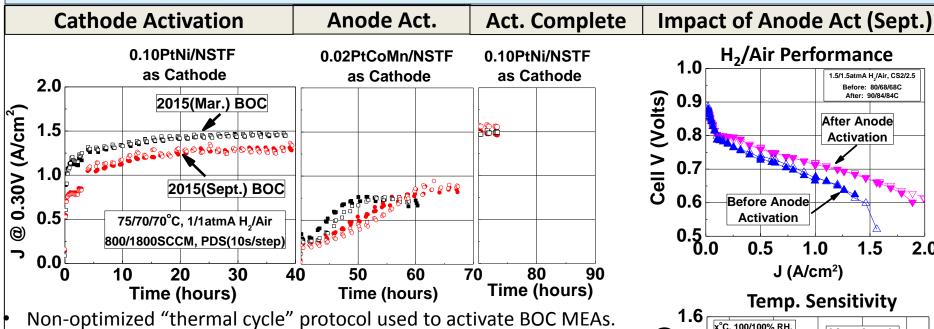
BOC MEA Short Stack Evaluation (Task 6): Possible Cause for Low Stack Performance: Stack Conditioning Method May Not Be Effective



- For a given stack current density, NSTF BOC Cells show lower cell voltages than the Stack Average Voltage
- This scenario did not change during the entire stack test duration
- Not much improvement in performance observed after reverse flow conditioning
- Ineffective or a non-optimized thermal cycle break-in process at the stack level, likely prevents the effective conditioning and performance of the NSTF BOC Cells



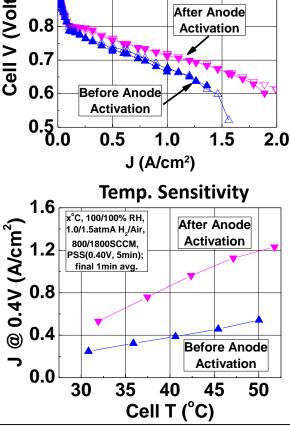
Best of Class Integration Diagnostics (Task 4.2): Best of Class MEA Activation Required for Entitlement Performance, Robustness



- Slow voltage and temperature cycles (1.5 hours per complete cycle).
- Both electrodes are activated (operated as cell cathodes)
- After anode activation, substantial improvement in $80^{\circ}C H_{2}/air$ performance and at low temperature.
 - ~60mV at 1.5A/cm² 2x J between 35-50°C

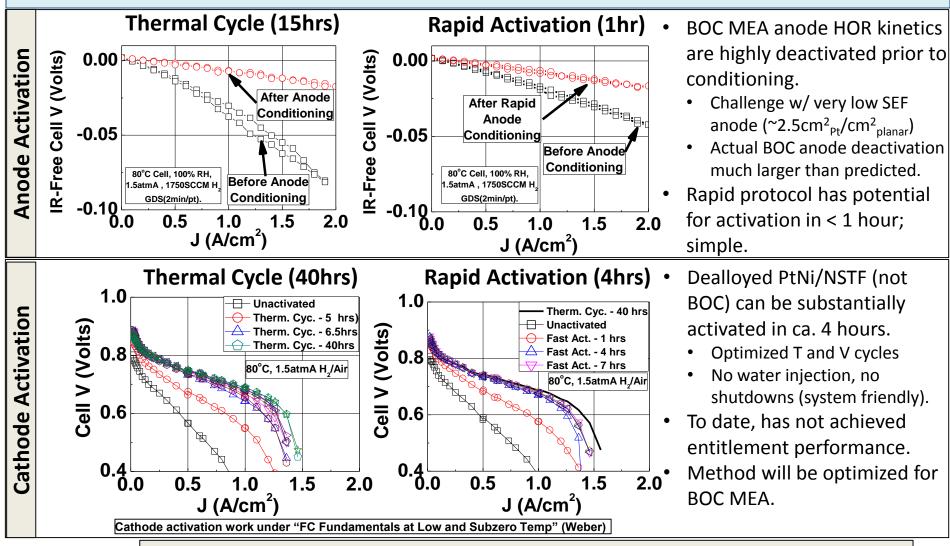
Likely contributors to poor stack performance to date:

- "Thermal cycle" protocol not effective in GM stack. 1.
- 2. Slower activation of Sept. BOC MEAs (cause under investigation)



Best of Class Integration Diagnostics (Task 4.2):

Rapid NSTF MEA Activation Development



3 Science. Applied to Life.[™] Rapid, stack friendly activation development is key remaining integration task 17

Response To Reviewers' Comments

- "Very good progress and a good deal of work have been accomplished in the last year. Key procedures to improve ... apparently promise that, in subsequent research efforts, most of the performances will be at 2020 levels. However, several problems ... are not completely solved: the necessity of using an interlayer with the thickness of another catalytic layer, the dealloying procedure, and the problem with Ni leaching due to the Kirkendall effect. The third point has not been considered at all."
 - Agreed, additional materials (e.g. interlayer) and additional processing (e.g. dealloying) are undesirable from a cost/yield perspective. Tradeoff analysis for this approach vs. others, considering power density, durability, cost (material, process, yield), and end-use system requirements, is complex and not readily assessable.
 - Interlayer thickness is ca. 1-2 μm thick (low loading) and imposes little apparent transport loss (compare 2015(Jan.) to 2015 (Mar.) BOC in '15 AMR presentation for interlayer transport impact).
 - Transition metal stability in porous metal electrocatalyst has always been a key concern, but believed to be tractable. "M" is promising (see FC143).
- "... the key issues have still not been mitigated sufficiently to enable this new catalyst to replace more conventional MEAs, primarily because 3M has not been willing to make any significant changes to the original NSTF catalyst layer structure. ..."
 - Our assessment remains that the project approach will achieve sufficient robustness in stack format.
 - Per the 2011 FOA, component development was not allowed; our work here was limited to modest modifications of existing components using known means. Development of a modified NSTF electrode structure was deemed out of scope.
 - An "advanced" NSTF electrode with improved intrinsic robustness is in early development (outside this project). Many factors not yet understood, but operational robustness is improved.



Collaborations

- **3M** Project management; Materials and process optimization; MEA integration
 - <u>A. Steinbach</u>, D. van der Vliet, C. Duru, D. Miller, I. Davy, M. Kuznia (Core)
 - Cathode Integration: A. Hester, D. Lentz, S. Luopa, D. Tarnowski, B. Smithson, C. Studiner IV, A. Armstrong, M. Stephens, J. Bender, M. Brostrom
 - PEM Integration: M. Yandrasits, D. Peppin, G. Haugen, R. Rossiter
 - Anode GDL/Cathode IL: M. Pejsa, A. Haug, J. Abulu, J. Sieracki
 - Durability: A. Komlev
- Michigan Technological University GDL char. and PNM modeling; model integration
- <u>J. Allen</u>, E. Medici, V. Konduru, C. DeGroot
- Johns Hopkins University Pt₃Ni₇/NSTF dealloying method studies
 - J. Erlebacher

Lawrence Berkeley National Laboratory – GDL char. and MEA modeling; model integration

- <u>A. Weber</u>, J. MacDonald, I. Zenyuk, A. Kusoglu, S. Shi
- Oak Ridge National Laboratory Materials characterization (TEM, XPS)
- <u>D. Cullen</u>, H. Meyer III
- Los Alamos National Laboratory Accelerated Load Cycle Durability Testing
- <u>R. Borup</u>, R. Lujan, R. Mukundan
- Argonne National Laboratory Kinetic, rated power durability, and performance modeling.
- <u>R. Ahluwalia</u>, X. Wang, J-K Peng
- **General Motors** Stack Testing
- <u>B. Lakshmanan</u>, N. Ramaswamy



Remaining Barriers

- A. 2015(Sept.) Best of Class MEA does not achieve the DOE 2020 loading and specific power targets.
- B. Operational robustness of enhanced durability "B" interlayer is not maintained after 30k Electrocatalyst AST cycles.
- C. 2015(Sept.) BOC MEA is not sufficiently durable to achieve MEA load cycle durability targets (10% V loss after 5000 hours).
 - 1. Dealloyed $Pt_3Ni_7/NSTF$ cyclic durability insufficient
 - 2. PFSA decomposition leading to cathode deactivation.
- D. Operational robustness of 2015(Sept.) BOC MEA has not been demonstrated to be acceptable for automotive traction applications.
- E. Rapid break-in conditioning method not yet implemented w/ BOC MEAs.



Key Future Work – FY16 (Through Aug. '16)

- A. Complete short stack testing to evaluate operational robustness of project BOC MEAs in relevant architecture.
 - 1. Determine method to enable rapid break-in conditioning of BOC MEAs, compatible with stack testing.
 - 2. Evaluate stack towards performance, cold/freeze startup, load transient.
- B. Complete evaluations of downselected Best of Class MEA:
 - 1. ANL performance model
 - 2. Load cycle durability and AST durability.
- C. Improve load cycle durability by integration of higher durability NSTF cathodes and experimental PEMs with reduced degradation contaminant impact.
- D. Complete assessment of relative cost savings of project Best of Class MEA to baseline.
- E. Complete project final report.



Summary

Operational Robustness (Cold Start; Load Transient)

 Integrated new anode GDL and improved durability "B" cathode interlayer into 2015 (Sept.) BOC MEA, yielding 0.1-0.2V improvement at intermediate T over 2015(Mar.) BOC MEA.

Durability (MEA Load Cycling; Electrocatalyst/Support ASTs)

- New "B" interlayer maintains operational robustness after Support AST and after 20k Electrocatalyst AST cycles. H₂/Air performance near 1.5A/cm² improves after ASTs.
- Load cycle evaluation of BOC MEAs show significant reversible and irreversible performance losses after 1200+ hours; tests ongoing.
- New "M" NSTF cathode passes DOE Electrocatalyst AST, but improved activity needed.

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

- Substantial gains in specific power (55% kW/g v. pre-proj.) due to improved absolute performance and PGM reduction. DOE 2020 targets for loading, rated power approached.
- Pilot scale components successfully fabricated.

Short Stack Evaluation of BOC MEAs

- To date, BOC MEA evaluated in GM short stacks have not demonstrated expected performance and robustness benefit over baseline.
- Insufficient conditioning of ultra-low PGM anode suspected
- Development of stack-compatible, rapid conditioning methods are in progress.



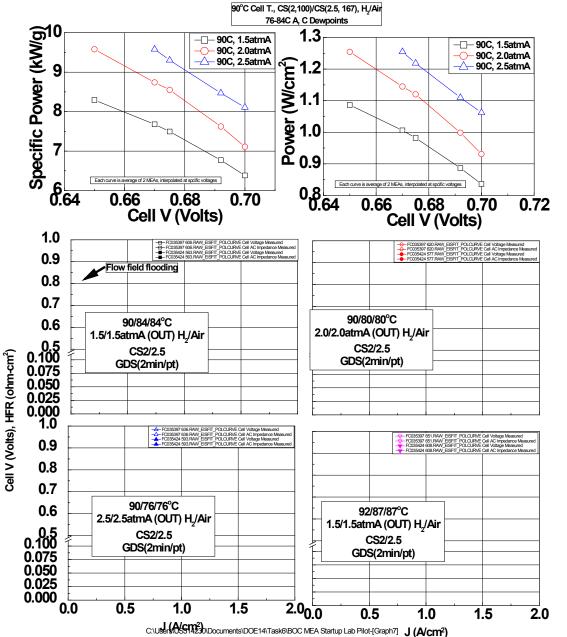
Technical Back-Up Slides

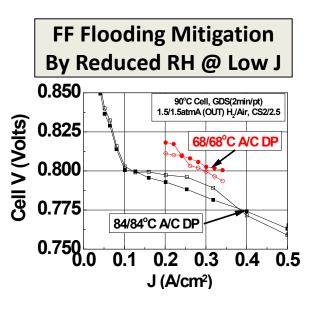
Project Goal Table

Table 10. Performance, Cost, Durability Targets, Current Project Status, and Go/No-Go and Goal Criteria								
Performance at ¼ Power, Performance at rated power, and Q/ΔT Targets								
Goal ID	Project Goals (units)	Target Value	Status (NEW since '15 AMR)	G/NG or Interim Goal Value				
1		0.300	0.310 ^A	0.250				
	Performance at 0.80V (A/cm ²); single cell, ≥80°C cell	NA	NA	≥0.300				
	temperature, 50,100,150kPag, respectively.	NA	NA	≥0.300				
2	Performance at Rated Power, $Q/\Delta T$: Cell voltage at 1.41A/cm ² (Volts); single cell, \geq 88°C cell temperature, 50kPag [*]	0.709	0.679 ^A	0.659				
	Cost Targets							
3	Anode, Cathode Electrode PGM Content (mg/cm ²)	≤ 0.125	0.131 ^A	0.135				
4	PEM Ionomer Content (effective ion. thickness, microns)	≤16	12 ^A	20				
Trans	ient response (time from 10% to 90% of rated power), Cold start	t up time to	50% of rated	power at -				
	20°C, +20°C), and Unassisted start							
5	Transient response (time from 10% to 90% of rated power); single	≤ 1	PASS	5				
	cell at 50°C, 100% RH (seconds)	51	(0%RH) ^A	3				
6	Cold start up time to 50% of rated power at +20°C; evaluated as single cell steady state J at 30°C (A/cm ²)	≥ 0.8	0.7 ^A	0.6				
7	Cold start up time at -20°C; short stack (seconds)	≤ 30	27 ^C	30				
8	Unassisted start from -40°C (pass/fail); short stack	Pass at -	Pass at	Pass at				
		40°C	-20°C ^C	-30°C				
MEA	Durability with cycling, Electrocatalyst Cycle, Catalyst Support	Cycle, MEA	Chemical St	ability, and				
	Membrane Mechanical Targets		-					
9	Cycling time under 80°C MEA/Stack Durability Protocol with ≤ 30mV Irreversible Performance Loss (hours)	≥ 5000	TBD ^A	2500				
10	Table D-1 Electrocatalyst Cycle and Metrics (Mass activity %	≤-40	-40±0.8	≤-40				
	loss; mV loss at 0.8A/cm ² ; % initial area loss)	≤-30	-28±1.4	≤- 30				
		≤-40	-14±0.2 ^F	≤-40				
11	Table D-2 Catalyst Support Cycle and Metrics (Mass activity %	≤-40	-40±7	≤-40				
	loss; mV loss at 1.5A/cm ² ; % initial area loss)	≤-30	$-11\pm 3(0.8)$	≤-30				
		≤-40	-19±3 ^E	≤-40				
10	Table D-3 MEA Chemical Stability: 500 hours (H ₂ crossover	≤2	PASS	≤2				
	Γ able D-5 minimum Chemiean Stability. 500 hours (11) clossover	<u> ~</u>	1 100					
12		<-20	_4	<_20				
12	(mA/cm ²); OCV loss (% Volts); Shorting resistance (ohm-cm ²))	≤-20 ≥1000	-4 PASS ^B	≤-20 >1000				
12		≤-20 >1000 ≤2	-4 PASS ^B 20.1k ^{A (PEM}	≤-20 >1000 ≤3				

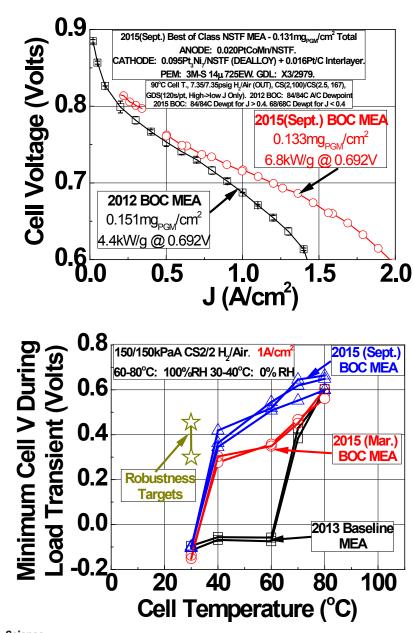
A: Mean values for duplicate 3M 2015(Sept.) Best of Class NSTF MEAs: Anode=0.02PtCoMn/NSTF, Cathode= 0.095Pt₃Ni₇/NSTF + 0.016 Pt/C IL, (0.131 m_{PGM}/cm² total), 3M-S 725 EW 14 μ PEM, X2/2979+IL Anode/Cathode, 3M "FF2" flow fields, operated at 90°C cell temperature with subsaturated inlet humidity and anode/cathode stoichs of 2.0/2.5 and at stated anode/cathode reactant outlet pressures, respectively. B: Mean value for duplicate 3M 2015(Mar.) Best of Class MEAs. Analogous result for 2015(Sept.) MEAs is expected. C: OEM Stack testing results with 3M NSTF MEAs: Anode=0.10PtCoMn/NSTF, Cathode=0.15PtCoMn/NSTF, (0.25mg_{PGM}/cm² total), 3M ionomer in supported PEM, Baseline 2979/2979 GDLs. OEM-specific enabling technology. E: Value for Replicate 3M NSTF MEAs. Anode: 0.05PtCoMn/NSTF. Cathode=0.107 or 0.125 Pt₃Ni₇/ NSTF(Dealloy+SET), 3M 825EW 24µ PEM w/ or w/o additive, Baseline 2979/2979 GDLs, w/ or w/o Edge Protection, Quad Serpentine Flow Field. E: Value for Replicate 3M NSTF MEAs. Anode: 0.05PtCoMn/NSTF. Cathode: "M", 0.091mg_{PGM}/cm², 3M 825EW 24µ PEM w/ or w/o additive, Baseline 2979/2979 GDLs, w/ or w/o Edge Protection, Quad Serpentine Flow Field. *: Cell performance of 0.709V at 1.41A/cm² with cell temperature of \geq 88°C simultaneously achieves the Q/ Δ T and rated power targets of 1.45kW/°C and 1000mW/cm², respectively. **: Single sample result. MEA failed prematurely due to experimental error.

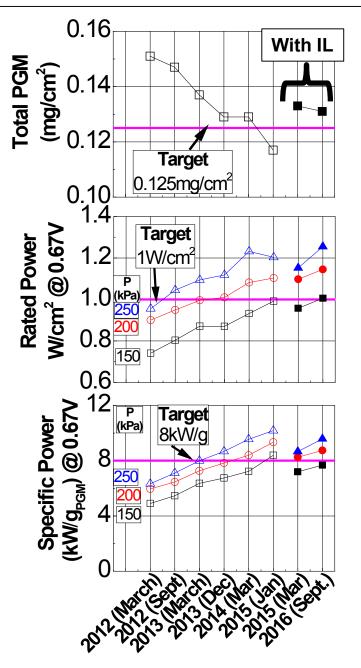
2015 (Sept.) BOC MEA Performance v. Pressure





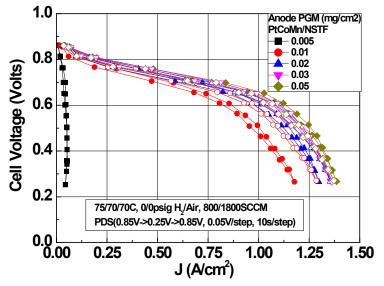
Technical Backup – Progression Over Project



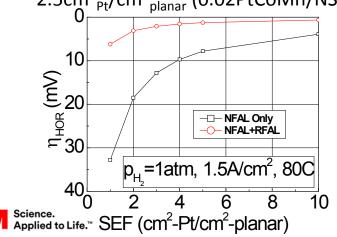


NSTF Anode Activation

1. Early project work: little apparent impact with $0.02mg_{Pt}/cm^2$ PtCoMn/NSTF anode(all unactivated).



 Model prediction of ~10mV excess loss due to poor activation at 2.5cm²_{Pt}/cm²_{planar} (0.02PtCoMn/NSTF)

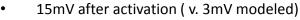


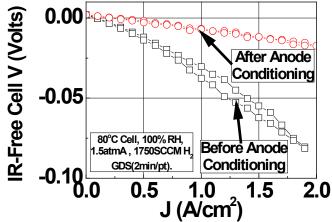
 NSTF HOR kinetic study concluded that thermal cycle activation increased NSTF HOR specific activity > 5x over unactivated, and 1 order of magnitude over Pt/C.

> Wang et al., "Kinetics of Hydrogen Oxidation and Hydrogen Evolution Reactions...", J. Electrochem. Soc. **160**(3) F251 (2013)

Electrode	E _{HOR} (kJ/mol)	i0 (mA/cm² _{Pt})
0.05PtCoMn/NSTF, Partially activated	38.9	489
0.05PtCoMn/NSTF, Fully activated	64.3	2727 ± 563
0.003Pt/C (5wt%)	NA	235-300

- 4. Actual HOR kinetics much lower than model prediction, or by early project FC tests (#1)
 - 60mV before activation (v. 15mV modeled)





Short Stack Design

Stack consisted of the following CCM MEAs

#	Туре	Anode Description	Membrane	Cathode Description	No. of Cells
1	3M Baseline CCM	PtCoMn/NSTF 0.05 mg _{Pt} /cm ²	3M 825EW 20 μm	PtCoMn/NSTF 0.15 mg _{Pt} /cm ²	4
2	3M 'Baseline' CCM with 14 μm membrane	PtCoMn/NSTF 0.05 mg _{Pt} /cm ²	3M-S 725EW 14 μm w/ additive	PtCoMn/NSTF 0.15 mg _{Pt} /cm ²	4
3	3M March BOC CCM	PtCoMn/NSTF 0.019 mg _{Pt} /cm ²	3M-S 725EW 14 μm w/ additive	Dealloyed Pt ₃ Ni ₇ /NSTF 0.096 mg _{Pt} /cm ² 3M 2979 w/ "B" Interlayer IL Loading – 0.016 mg _{Pt} /cm ²	10
4	GM Baseline CCM	Dispersed Pt/C 800EW Ionomer	18 μm PFSA	Dispersed Pt-alloy/C 800EW Ionomer	10

- Following GDLs were used
 - Anode 3M-X2 Low phobic GDL
 - Cathode 3M 2979
- Short stack stands were equipped with DI Water Flush lines for thermal cycle break-in process



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