2013 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 May 15th, 2013



Project ID: FC104



DOE Hydrogen Program

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Project Overview

Timeline

- Project start: 9/1/12
- Project duration: 3 years
- Percent Complete: 20%

Budget

- Total project funding \$4.307MM
 - \$3.445 MM DOE
 - \$0.862 MM Contractor
- Funding Received FY12: \$2.859MM
- Funding for FY13: \$1.04MM (Est. non-FFRDC expend.; DOE share)

Partners

- Lawrence Berkeley Nat'l Lab.(A. Weber)
- Michigan Technological Univ. (J. Allen)
- Johns Hopkins Univ. (J. Erlebacher)
- Oak Ridge Nat'l Lab. (D. Cullen)
- Argonne Nat'l Lab. (R. Ahluwalia)

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

2

• Rated Power: 1W/cm²

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Relevance and Approach

Relevance (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 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, and flow fields for best overall MEA performance, durability, robustness, and cost. <u>Integration</u>: Includes optimization of existing

Primary Focus Topics:

and flow fields for best overall MEA performance, Integration: Includes optimization of existing components and processes via reasonable and known means – NO COMPONENT DEVELOPMENT.

- NSTF Cathode Post-Processing Optimization (Dealloying, Annealing)
- NSTF Anode Catalyst Composition , PGM Content Sensitivity
- PEM-Electrode Integration Studies
- Anode GDL Characterization, Modeling for Cold-Startup Optimization
- Integration of 2012, 2013(March) Best of Class NSTF MEAs
- Project Initiation at 3M and Partners
- MEA Integration Diagnostics (Segmented Cell; HOR Kinetic Studies; Water Balance)

Relevance and Approach – Project Tasks

- Tasks Address Barriers of Durability, Cost, and Performance
- <u>Strong Emphasis on Cold-Startup</u>, Load Transient (2,3), and Performance Durability (5).

Task	Task Description	Status/	Α.	В.	С.
	lask Description	Timing	Durability	Cost	Perform.
1	Component integration towards MEA ¼ power,	In Progress/			
L	rated power, and $Q/\Delta T$ targets.	On Target			
2	GDL and interfacial layer integration towards	Starting/			
	cold start up and transient response targets.	Delayed			
3	Water management modeling for cold start	In Progress/			
		On Target			
4	Overall Best of Class MEA Integration;	In Progress/			
	component interaction mechanism studies.	On Target			
5	Component/MEA durability evaluation;	Started/			
	Rated-power performance loss mitigation.				
6	Short stack eval. of integrated MEAs for rated	Not Started/			
	power, cold/freeze-start, transient response.	Delayed			
7	Drojact management	In Progress/			
	Project management	On Target			
8	Polative cost and manufacturing accessment	Not Started/			
	Relative cost and manufacturing assessment	On Target			

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Milestone, Go/No-Go Goals and Status

Q1 Q2 Q3 Q4 Q5 Q6 Q7 Q8 Q9 Q10Q11Q12Q13

	i _	Kick off						Go NG				End			
Milestone ID	Project Quarter					Pr	oject	Miles	one					M /	lar. '13 Statu <u>% Complet</u>
			BU	U DGI	ET P	ERI	OD 1	(Sept	'12 -	June	'14)				
6.1	2	Baseline MEA: Short Stack Evaluation Complete.											25%		
1.1	7	Componer	Component Candidates Meet Interim Performance/Cost Goals Component Candidates Meet Interim Cold-Startup Goals								33%				
2.1	7	Componer									5%				
5.1	7	Componer	nt Ca	ndida	ates N	Meet	Interi	im Du	rabil	ity Go	oals				20%
3.1	7	GDL Mod	GDL Model Validation With 2 or More 3M Anode GDLs									20%			
6.2	7	Interim Be	est of	Clas	s ME	EA: S	Short	Stack	Eval	uatior	n Comj	plete.			0%
4.1 Go/No-	7	Interim Best of Class MEA Meets Go/No-Go Goals: 1) $\leq 0.135 \text{mg}_{PCM}/\text{cm}^2$ (Total)							0.1	<u>99%</u> 137mg _{a a s} /ci					
Go		2) Rated	Pow	er. O	/ Δ Τ:	0.65	, 9V@	1.41A	$/\mathrm{cm}^2$.	90°C	. 1.5at	tm H	/Air		0.658V
			BU	DGE	ET P	ERIC	DD 2	(June	'14 –	Aug.	'15)		-		
1.2	1.2 11 Component Candidates Meet Project Performance/Cost Goals									0%					
2.2	11	Componer	nt Ca	ndida	ates N	Meet	Proje	ect Co	d-Sta	irtup	Goals				0%
5.2	11	Component Candidates Meet Project Durability Goals							0%						
4.2	11	Best of Cl	lass I	MEA	Mee	ets Al	ll Proj	ject G	oals						0%
3.2	12	MEA Coo	ol Sta	rt M	odel	Vali	datio	n with	2 or 1	more 3	3M MI	EAs.			0%
6.3	12 Best of Class MEA: Short Stack Evaluation Complete.									0%					
8.1	12	12 Relative Cost Savings Report – Final Best of Class MEA Relative to 2012 MEA.								0%					
0	10	Final Dost	t of (ME	A Sh	ort St	ook D	alivo	rad ta	Fyalı	iatio	n Site		0%

5

Improved Activity, Rated-Power Capable ORR Catalysts (Task 1.1): Post-Process Optimization (<u>Surface Energetic Treatment</u> (SET))



- Mass Activity of previous generation Pt₃Ni₇/NSTF increased significantly after SET.
 - SET: NSTF-compatible continuous annealing process.
 - PREVIOUS WORK DE-FG36-07GO17007.
- Current generation Pt₃Ni₇/NSTF activity, as-deposited, higher than previous, but benefit of SET not yet demonstrated.

6

Focus of current work is determination of factors to achieve entitlement activity.

Improved Activity, Rated-Power Capable ORR Catalysts (Task 1.1): SET Induces Significant Structural Changes of Pt₃Ni₇/NSTF Cathodes



- To date, mass activity relatively unaffected by SET process parameters evaluated.
- Monotonic changes
 observed in specific
 area, crystallite size,
 and lattice constant.

MEA evaluation of larger grained materials in progress.

7

Improved Activity, Rated-Power Capable ORR Catalysts (Task 1.1): TEM Confirms Grain Growth After SET



- Preliminary 3M TEM imaging confirms significant grain growth after SET.
- Analysis at ORNL in progress to quantify surface faceting and surface composition.
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8

Improved Activity, Rated-Power Capable ORR Catalysts (Task 1.1): Post-Process Optimization (<u>Dealloying</u>) @ Johns Hopkins (J. Erlebacher)

Objective: Dealloying Optimization-Improve Peak Power, Maintain Activity, w/ <u>Scalable</u> Process.



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Improved Activity, Rated-Power Capable ORR Catalysts (Task 1.1): Microscopy Reveals Structural Evolution of Pt₃Ni₇/NSTF (ORNL, D. Cullen)



OAK RIDGE NATIONAL LABORATORY

Managed by UT-Battelle for the Department of Energy

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- Dramatic porosity increase, Ni loss after MEA conditioning.
 - Current practice dealloying induces less porosity, Ni loss than MEA conditioning.

Dealloying Development Needed to Achieve MEA-Conditioned State, <u>Ex-Situ</u>



Durable, Ultra-Low PGM NSTF Anode Catalyst (Task 1.2):

PGM Content and Composition Sensitivity Study Completed



- Pt, PtCoMn, and Pt_3Ni_7 at $0.02mg_{PGM}/cm^2$ comparable to baseline $0.05mg_{PGM}/cm^2$ PtCoMn.
- Project Goal of ≤ 0.02mg_{PGM}/cm² Achieved.
- At further reduced PGM, performance has significant loading, composition dependence.
 - 0.01mg_{PGM}/cm²: Pt₃Ni₇, PtCoMn >> Pt
 - $0.005 \text{mg}_{\text{PGM}}/\text{cm}^2$: $\text{Pt}_3 \text{Ni}_7$ >> PtCoMn

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Durable, Ultra-Low PGM NSTF Anode Catalyst (Task 1.2): Support Optimization Needed for Ultra-Low PGM NSTF Anodes





Typically-used NSTF support not optimized for ultra-low PGM anodes.

Modified NSTF generated.

Performance Improvement with Modified Support – Further Gain Possible?

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Durable, Improved Conductivity PEMs (Task 1.3):

Multi-Factor Systematic PEM Variable Study Completed



- Factors: PEM EW(3), additive(2), 3M support(2), thickness(3); cathode composition(2).
- Two Primary Observations
 - 1. PtCoMn: Performance Loss w/ Support and/or EW > 825 (Largely Non-Ohmic).
 - **2. Pt₃Ni₇**: Most Trends Similar to PtCoMn, but <u>More Accentuated</u>.

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Durable, Improved Conductivity PEMs (Task 1.3): PEM "Effective" EW Correlation Identified; Dealloying Target Composition Identified



Durable, Improved Conductivity PEMs (Task 1.3): Perf. Variation

with PtCoMn/NSTF May Be Influenced by Active Area Utilization



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15

Water Management Modeling for Cold Start (Task 3):

Understanding Influence of Anode Backing on NSTF MEA Cold-Startup



Water Management Modeling for Cold Start (Task 3): Material Property Measurements Initiated at MTU(J. Allen), LBNL (A. Weber)

PTL Percolation Measurements GDL C Backing GDL Capillary Pressure/Saturation Measurements - GDL C Backing

17



- Material property measurements in progress; results to be incorporated into existing MTU, LBNL models.
- Methods include: Liquid percolation, capillary pressure/saturation, contact angle, adhesion force, breakthrough pressure, tomography, thermal conductivity,...

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Water Management Modeling for Cold Start (Task 3): GDL, MEA Modeling Initiated at MTU(J. Allen), LBNL (A. Weber)



Parametric modeling study initiated on effect of backing solid phase distribution on thermal, water transport.

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Best of Class Component Integration (Task 4.1): Go/No-Go Targets Approached - 2013 3M NSTF Best of Class MEA in Improved Flow Field



Path to Target: 1) Reduce HFR (Dealloying, Thinner Supp. PEM). 2) Increase Activity (SET)

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Collaborations

Johns Hopkins University (Jonah Erlebacher) – Subcontractor

•Task 1 - $Pt_3Ni_7/NSTF$ dealloying optimization for improved peak power.

Lawrence Berkeley National Laboratory (Adam Weber) – Subcontractor

- •Task 3 Cold startup MEA modeling.
- •Task 3 GDL characterization.

Michigan Technological University (Jeffrey Allen) – Subcontractor

- •Task 3 Integration of 3M anode GDLs into GDL network model.
- •Task 3- GDL characterization.

Oak Ridge National Laboratory (David Cullen) – Subcontractor

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

Argonne National Laboratory (Rajesh Ahluwalia) – Collaborator

- •Task 1 NSTF HOR/HER kinetics characterization study.
- •3M data provided in support of Fuel Cells Systems Analysis project

Key Future Work – FY13, FY14

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

Dealloying, SET Optimization for Improved Peak Power, Activity w/ Pt₃Ni₇/NSTF.
PEM Integration Towards Confirmation, Resolution of Area Under-utilization.
Further Support Optimization for Ultra-Low PGM Anodes; Durable Anode Incorporation.
Systematic Study of Flow Field Land, Channel Widths on Rated Power Response.

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

•Initiation of Anode GDL and Cathode Interlayer Optimization.

Task 3 - Water Management Modeling for Cold Start

•Finalize Material Property Measurements, Initiate Modeling with 3M-Specific Materials.

Task 4 - Best of Class MEA Integration Activities

 Best of Class Component Integration Towards Interim BOC MEA, Go/No-Go Criteria: (≤ 0.135mg_{PGM}/cm²; Rated Power, Q/∆T: 0.659V @ 1.41A/cm²).
 Improvement in Dealloyed, SET Cathode Critical

Task 5 - Durability Evaluation and Performance Degradation Mitigation

•Influence of Post-Processing on Pt₃Ni₇/NSTF Electrocatalyst Durability.

•Irreversible Peak Power Loss Mitigation Study Initiation (Material, Operational Factors).

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

- Finalize Identification of Short Stack Testing Provider.
- Complete Short Stack Testing of Interim Best of Class MEA.

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Summary

Performance, Cost, Durability Targets, Go/No-Go Criteria, March 2013 Status											
	Performance @ 1/4 Power, Rated power, and	Ι Q/ΔT]	Fargets								
Goal ID	Project Goals (units)	2013 Status (Rep. MEA)	Go/No- Go or								
		DOE	NEW	Interim							
1	Performance @ 0.80V (A/cm ²); single cell, ≥80°C cell temperature (50, 100, 150kPag Reactant Pressures)	0.300	0.292 ^A	≥0.300							
2	Performance at Rated Power, $Q/\Delta T$: Cell voltage at 1.41 A/cm ² (Volts): single cell. >88°C cell temperature. 50kPag [*]	0.709	0.658 ^A	0.659							
Cost Targets											
3	3 Anode, Cathode Electrode PGM Content (mg/cm ²) ≤ 0.125 0.137 ^A 0.13										
4	PEM Ionomer Content (effective ion. thickness, microns)	≤16	24 ^A	20							
	Cold/Freeze Startup, Power Transient T	argets									
5	Transient response (time from 10% to 90% of rated power); single cell at 50°C, 100% RH (seconds)	≤ 1	TBD	5							
6	Cold start up evaluated as single cell steady state J @ 30° C [to simulate cold start to 50% of rated power @ $+20^{\circ}$ C] (A/cm ²)	≥ 0.8	0.38 ^B	0.6							
7	Cold start up time @ -20°C; short stack (seconds)	≤ 30	27 ^C	30							
8	Unassisted start from -40°C (pass/fail); short stack	Pass @ -40°C	Pass @ $-20^{\circ}C^{\circ}$	Pass @ -30°C							
Durability Targets											
9	Cycling time under 80°C MEA/Stack Durability Protocol with \leq 30mV Irreversible Performance Loss (hours)	≥ 5000	600 ^{D,**}	2500							
10	Table D-1 Electrocatalyst Cycle and Metrics (Mass activity	≤-40	-67	≤-40							
	% loss; mV loss @ 0.8A/cm ² ; % initial area loss)	≤-30	-24	≤- 30							
		≤-40	-26 ^E	≤-40							
11	Table D-2 Catalyst Support Cycle and Metrics (Mass	≤-40	-10	≤-40							
	activity % loss; mV loss (a) 1.5A/cm ² ; % initial area loss)	≤-30	-10	≤-30							
		≤-40	-10 5	≤-40							
12	Table D-3 MEA Chemical Stability: 500 hours (H_2	≤2	-13±4	≤2							
	crossover (mA/cm ⁻); UCV loss (% Volts); Shorting	≤-20	-12±5	≤-20							
12	Teststance (0000-000))	>1000	NA^{-}	>1000							
13	1 able D-4 Memorane Mechanical Cycle: 20K Cycles (H_2 crossover (mA/cm^2): Shorting resistance (ohm cm^2))	≤ 2	16K±0.3K	≤ <u>3</u> >500							
	crossover (mA/cm), shorting resistance (onni-cm))	>1000	INA	>300							

	A: Mean or singular values for 3M 2013(March) Best o
	Class NSTF MEAs: Anode=0.02PtCoMn/NSTF,
_	Cathode=0.117Pt ₃ Ni ₇ /NSTF(Dealloy+SET),
	$(0.137 \text{mg}_{\text{PGM}}/\text{cm}^2 \text{ total}), 3M 825 \text{EW} 24 \mu \text{ PEM}, \text{Baseline}$
	2979/2979 GDLs, "New" FF2 Flow Field, operated at
_	90°C cell temperature with subsaturated inlet humidity
	and anode/cathode stoichs of 2.0/2.5 and at
_	50,100,150kPag anode/cathode reactant outlet pressures
	respectively.
_	B: Mean values for duplicate 3M NSTF MEAs:
_	Anode=0.05PtCoMn/NSTF,
	Cathode=0.10PtCoMn/NSTF, (0.15mg _{PGM} /cm ² total),
	3M 825EW 24µ PEM, Baseline 2979/2979 GDLs,
	Baseline Quad Serpentine Flow Field.
	C: OEM Stack testing results with 3M NSTF MEAs:
	Anode=0.10PtCoMn/NSTF,
	Cathode= 0.15 PtCoMn/NSTF (0.25 mg _{PGM} /cm ² total),
	3M ionomer in supported PEM, Baseline 2979/2979
	GDLs. OEM-specific enabling technology.
	D: Mean or singular values for 3M NSTF MEAs:
	Anode=0.05PtCoMn/NSTF,
	Cathode= 0.15 PtCoMn/NSTF, (0.20 mg _{PGM} /cm ² total),
	3M supported 825EW PEM, Baseline 2979/2979
	GDLs, Baseline Quad Serpentine Flow Field. Values
	with estimated standard deviation error tested in
	duplicate.
	E: Value for Single 3M NSTF MEA. Anode:
	0.05PtCoMn/NSTF. Cathode=0.107Pt ₃ N ₁₇ / NSTF
	(Dealloy+SET), 3M 825EW 24µ PEM, Baseline 29/9/
	2979 GDLs, Baseline Quad Serpentine Flow Field.
	*: Cell performance of 0.709V (a) 1.41A/cm ² with cell
	temperature of \geq 88°C simultaneously achieves the
	$Q/\Delta I$ and rated power targets of 1.45kW/°C and
	1000mW/cm ² , respectively.
	**: Single sample result. MEA failed prematurely due
	to experimental error.

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Instruction

Technical Back-Up Slides

Target Polarization Curves Calculation

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



- Calculated polarization curves 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.

Performance Progression – March '12 to March '13



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Water Management Modeling for Cold Start (Task 3):

GDL – MEA Model Integration

Water Transport in MEA model (Macro Scale)

- Effective liquid permeability "k"
- Effective vapor diffusion coefficient "D"



Water Transport in GDL Model

(Pore Scale)

- Poiseuille flow liquid transport
- Concentration dispersion vapor transport

Proposed Integration Method

- MTU will generate lookup tables of "k" and "D" of discrete volumes from the GDL model, as function of:
 - Position
 - Local conditions (T, RH, P)
 - Pore morphology (size, distribution)
- LBNL will modify MEA model to utilize lookup tables.

Area Utilization Including Assumptions



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Durability Evaluation and Perf. Degradation Mitigation (Task 5): Support, Electrocatalyst Durability of 0.107mg_{PGM}/cm² Pt₃Ni₇/NSTF



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28