Low-cost, High Performance Catalyst Coated Membranes for PEM Water Electrolyzers

U.S. DOE 2019 Annual Merit Review and Peer Evaluation Meeting
Washington, DC
April 29, 2019

Andrew J. Steinbach
3M Company, St. Paul, MN

Project ta026

Project Overview

Timeline

Project Start: 10/1/2018
Project End: 12/30/2020

Barriers

F. **Capital Cost**
K. **Manufacturing**

Budget

Total DOE Project Value:	$2.325MM*
Total Funding Spent:	$0.097MM*
Cost Share Percentage:	23.25%

*Includes DOE, contractor cost share and FFRDC funds as of 1/31/19

Technical Targets

CCM Production Rate (area/time):	6x Baseline
CCM Width:	$\geq$ 0.50 m
Current Density at 1.50V:	$\geq$ 0.25
Current Density at 1.75V:	$\geq$ 2
Current Density at 1.95V:	$\geq$ 4
Total PGM Loading (mg/cm^2):	$\leq$ 0.50

Partners

National Renewable Energy Laboratory (M. Ulsh, S. Mauger, P. Rupnowski)
Giner (H. Xu)

Status versus Project Targets

Project Target	Target Value	Baseline	2019 Status
CCM Production Rate (m^2 per cumulative process time)	$\geq$ 6x baseline	1[1]	0.7[2]
CCM Width (m)	$\geq$ 0.50	0.25[1]	0.10[3]
Current Density at 1.50V (A/cm^2)	$\geq$ 0.25	0.16[1]	0.28[4]
Current Density at 1.75V (A/cm^2)	$\geq$ 2	1.98[1]	2.4[4]
Current Density at 1.95V (A/cm^2)	$\geq$ 4	4.2[1]	4.5[4]
Total PGM Loading (mg/cm^2)	$\leq$ 0.50	0.75[1]	0.70[4]

GREEN: Meets or exceeds target. YELLOW: Within ca. 15% of target.

[1]Traditional NSTF PEMWE CCM with laminated electrodes; 0.50mg_{Ir}/cm^2 and 0.25mg_{Pt}/cm^2. [2]Estimated production rate at 8" web width. [3] Lab-scale CCM fabrication. [4] Lab-scale CCM; 0.45 mg_{Ir}/cm^2 and 0.25 mg_{Pt}/cm^2 electrode loadings.

- Baseline process is based on experimental pilot-scale CCM based on first generation laminated NSTF electrodes and first generation crossover-mitigated membrane. Project rates set relative to baseline.
  - Absolute rates, yields, and costs are 3M Confidential and will not be publicly disclosed.
- CCM production rate is cumulative of all constituent process steps on capital-intensive equipment
  - Includes core processes - does not include low-capital process steps, e.g. web slitting.
- Current rate status is 0.7x, based on *estimated* rates for similar process and rates as baseline.
- Performance targets achieved with lab. CCMs; project focus is process development, not materials.
- Loading target likely achievable with lower loading cathode.

Project Objective, Relevance, and Approach

Overall Project Objective

Develop reduced-cost, roll-to-roll manufacturing processes for high performance membranes, catalysts, electrodes and catalyst coated membranes (CCMs) for PEM water electrolyzers.

Project Relevance

Electrolyzer system capital cost is a key commercialization barrier for renewable H_2.

Electrolyzer capital costs can be reduced through development of high performance PEMWE CCMs with both low material and low manufacturing costs made possible with roll-to-roll continuous manufacturing.

Current manufacturing costs are high due to non-optimized processes and small current CCM market sizes which inhibit manufacturing process investment.

Project CCM and component manufacturing processes will be:

- **Scalable and low-cost (6x process rate increase per m^2 vs. baseline; 0.5m wide)**
- **Capable of producing CCMs with high performance and low total PGM content ($\geq$ 2A/cm^2 at 1.75V at < 0.50 mg_{PGM}/cm^2 total loading)**

Overall Project Approach

1. Improve fundamental understanding of key material and process factors limiting fabrication rates and quality at laboratory scale.
2. Optimize component processes at lab and pilot scale for increased rate and width-scalabilty.
3. Translate lab/pilot processes to “production” scale (0.5 m width).

Approach – Project Schedule

Budget Periods	Budget Period 1					Budget Period 2			
Task/Project Quarter	Q0	Q1	Q2	Q3	Q4	Q5	Q6	Q7	Q8
Task 1: Laboratory/Pilot Development					GNG1				
Subtask 1.1 Membrane Process Development				M1.1.1					
Subtask 1.2 Catalyst Process Development	**M1.2.1**		M1.2.2		M1.2.3				
Subtask 1.3 Electrode Process Development					M1.3.1				
Subtask 1.4 CCM Process Development					M1.4.1				
Subtask 1.5: Performance Assessment				M1.5.1	M1.5.2				
Subtask 1.6: Inspection Development				M1.6.1	M1.6.2				
Subtask 1.7: Process Cost Model		M1.7.1			M1.7.2				
Task 2: Production Process Development									
Subtask 2.1: CCM Production Process Development						M2.1.1			
Subtask 2.2: CCM Production							M2.2.1		
Subtask 2.3: CCM Inspection									
Subtask 2.4: CCM Performance Assessment								M2.4.1	M2.4.2
Subtask 2.5: Production Process Cost Model									M2.5.1

AMR Submission Date

Task Breakdown

- Task 1 (Budget period 1) – development of individual component scalable processes at lab/pilot scale, performance assessment, inspection/QC development, and cost modeling
- Task 2 (Budget period 2) – scale processes to width, performance assessment (in short stack), and final cost model.

Budget Period 1

- Smaller laboratory /pilot-scale process development
- Downselect CCM construction
- Identify preferred processes
- ***Demonstrate process at 2x baseline cumulative lineal rate, 0.25m wide.***

Budget period 2

- Transfer processes to wider-width pilot / production lines.
- Validation in stack
- ***Demonstrate process at 6x baseline cumulative areal rate, 0.50m wide.***

Approach – Critical Success Factors and Approaches

Membrane Process

Objective: develop an overall membrane process for solution casting mitigated membranes at 100µm (dry) thickness at > 0.5m wide with higher linear rates

Development Areas:

1. Mitigation optimization for process compatibility
2. Formulation, drying optimization.

Approach:

1. Laboratory formulation and coating/drying modeling and experiment
2. Pilot-scale process trials for validation and optimization
3. Assessment by SEM, PEMWE cell testing

Catalyst Process

Objective: develop an overall catalyst fabrication process with 5x larger batch sizes and 4x faster support fabrication

Development Areas:

1. Organic sublimation deposition optimization
2. Physical vapor deposition optimization

Approach:

1. Sublimation and whisker growth factor sensitivity studies (lab and pilot)
2. PVD power/cooling studies
3. Assessment by SEM, PEMWE cell testing.

Electrode/CCM Process

Objective: development of coating processes for new dispersed NSTF electrodes at 0.50m wide at target lineal rate

Development Areas:

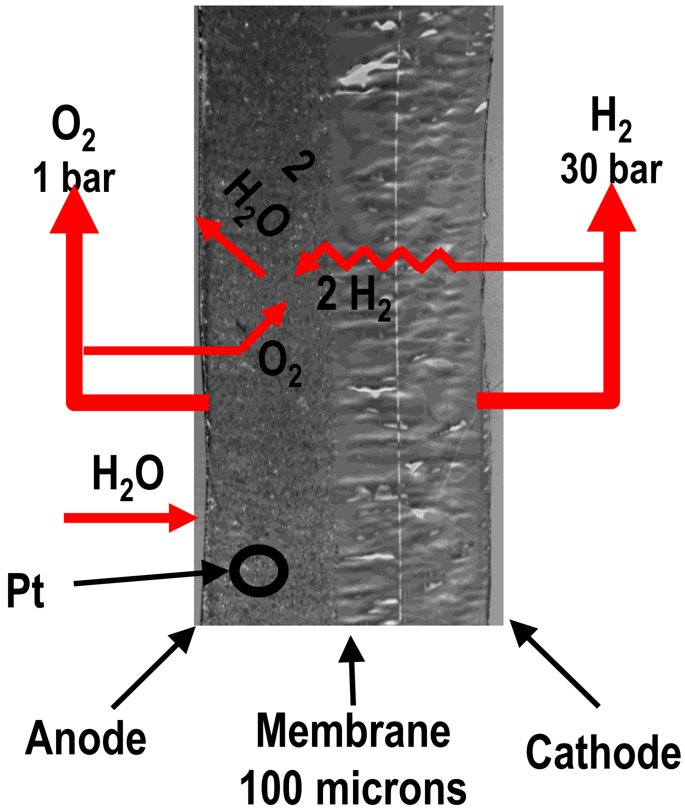
1. Ink formulation optimization
2. Coating method development

Approach

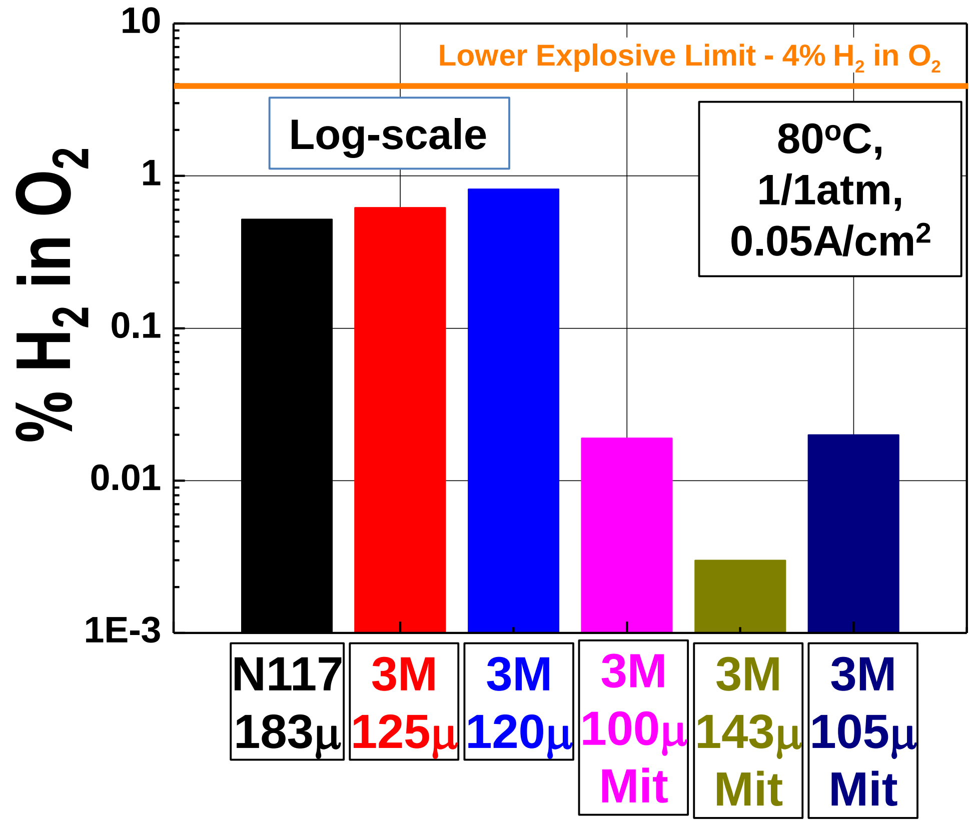
1. Ink rheology characterization
2. Lab-scale coating and drying trials (rod-coating, knife coating)
3. Assessment by optical microscopy, XRF, SEM, PEMWE cell testing.

Approach – Low Cost H_2 Crossover Mitigation

Mitigated CCM



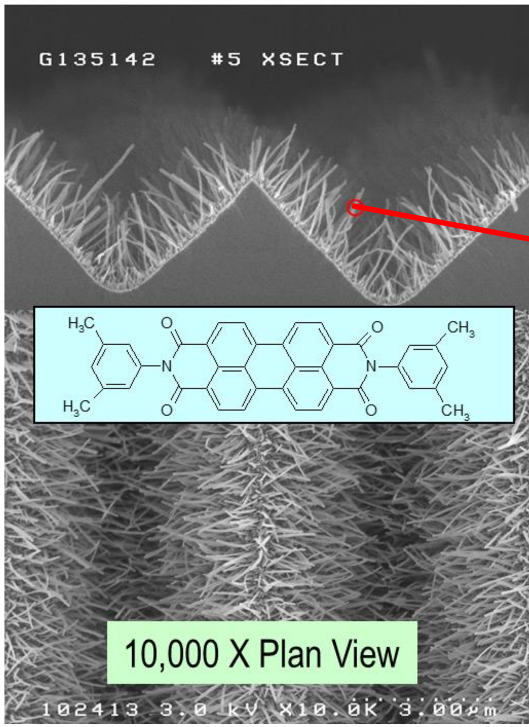
Crossover Mitigation



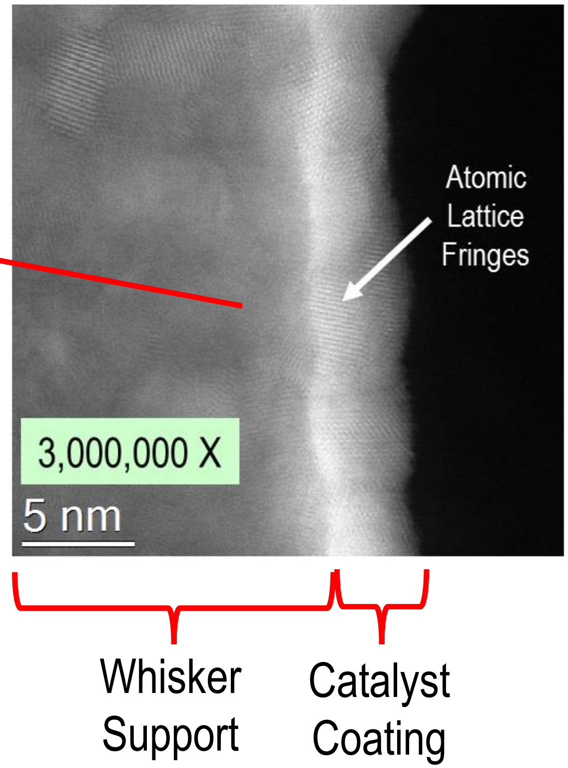
- H_2 crossover from cathode to anode is a barrier to thinner membranes.
- Project mitigation approach is recombination catalyst (high surface area Pt) in PEM.
- Pt mitigation reduces crossover 1-2 orders of magnitude, well below H_2 LEL.
- Pt mitigation loading is compatible with meeting project loading, performance, and process targets.
- Membrane fabrication processes are roll-to-roll and continuous.

Approach – Nanostructured Thin Film (NSTF) Powder Catalysts

NSTF Support On Growth Substrate



NSTF Catalyst On NSTF Support



NSTF Catalyst Powder

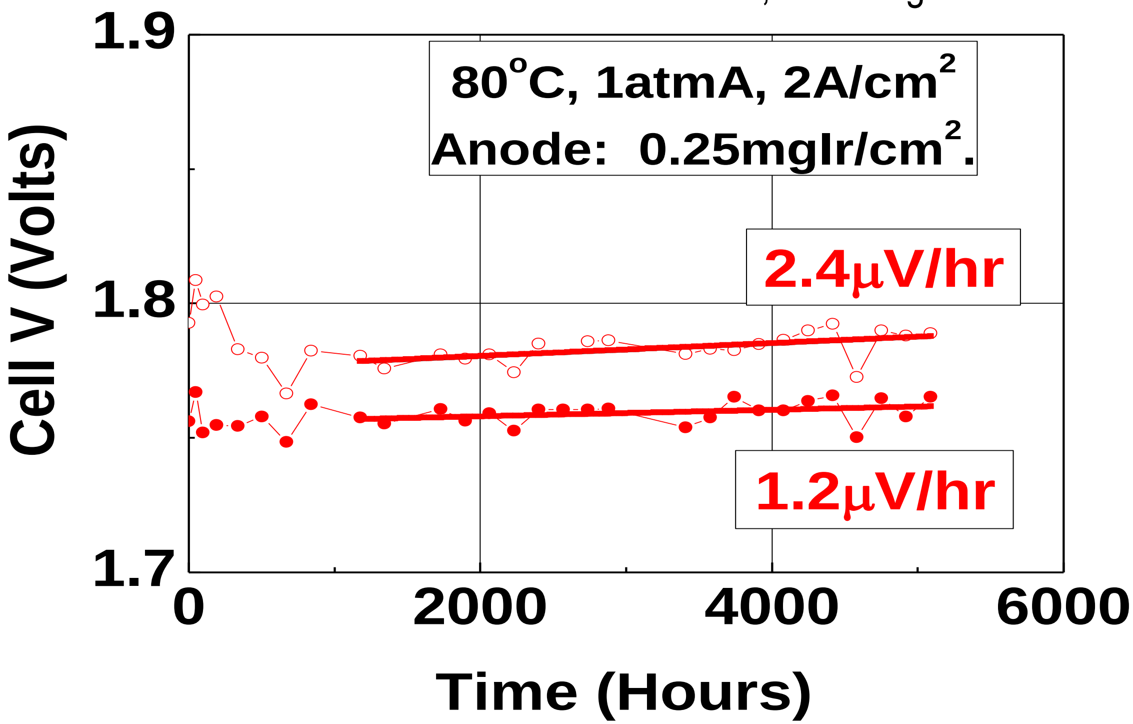
- NSTF catalysts consist of nm-scale catalyst metal films on crystalline organic supports.
- NSTF catalysts are stable at oxygen evolution potentials.
- NSTF catalyst powder enables increased specific area and performance.
- Support, catalyst, and powder processes are roll-to-roll and semi-continuous.

Approach – NSTF Durability

Durability of 3M Traditional NSTF CCM (Pre-Project)

Anode: 250Ir/NSTF, traditional. Cathode: 250Pt/NSTF, traditional.

PEM: 3M 825EW 100 micron, with mitigation.

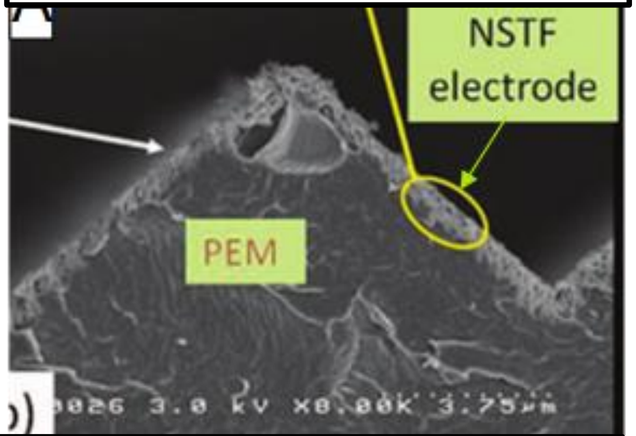


- Decay rates of ca. 10 μV/hr are likely required for 7 year lifetimes (lower in future).
- Ir dissolution is one main degradation mode, resulting in loss of area and performance.
- 3M CCMs with Traditional Electrodes: < 2.5 μV/hr degradation rates with just 0.25mg/cm^2.
- Durability of project CCMs with dispersed NSTF electrodes is under assessment (3M and Giner).

Approach – "Dispersed" Electrodes from NSTF Powder Catalyst

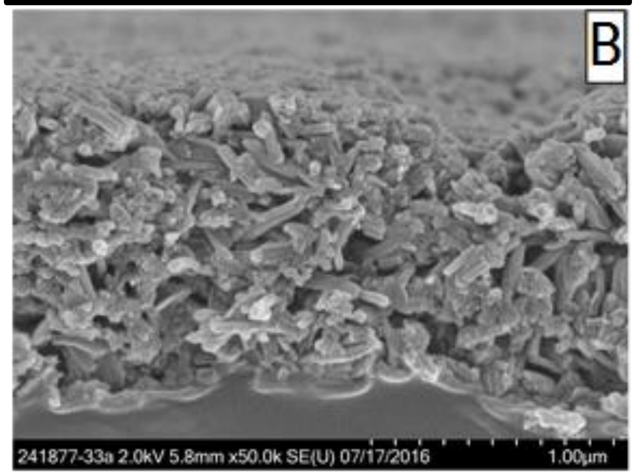
"Traditional" NSTF Electrode

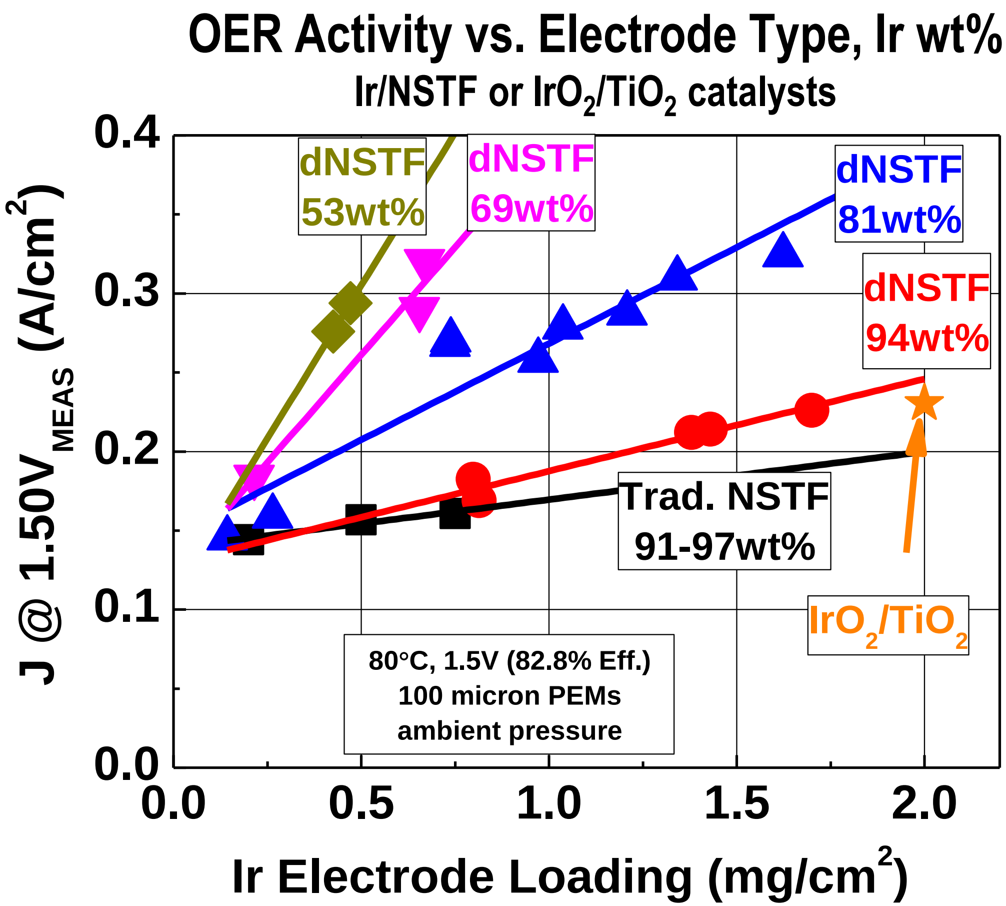
NSTF Laminated into Membrane



Dispersed NSTF Electrode

NSTF Powder Catalyst, Ionomer



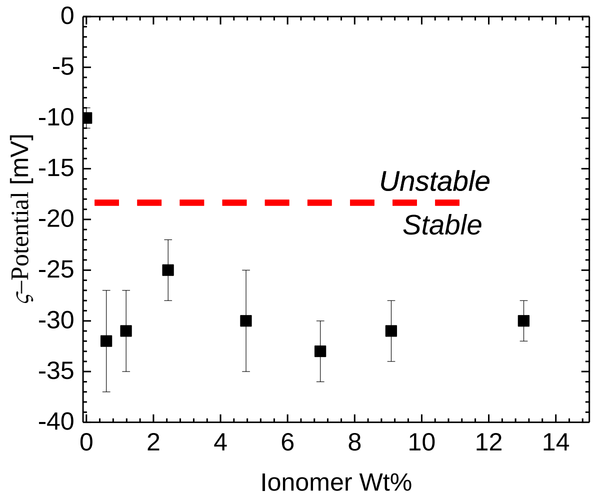


- Dispersed electrodes based on NSTF powder catalyst enable much higher activity than traditional NSTF electrodes
- Dispersed format enables use of lower Ir wt%., higher specific area NSTF catalysts in electrodes.

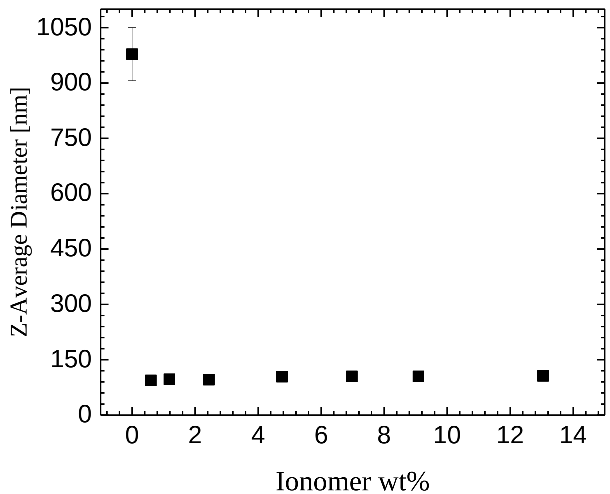
Approach – Ink Formulation Studies (NREL)

Electro-steric Stabilization Effects of Nafion on IrO_2 Catalyst Ink

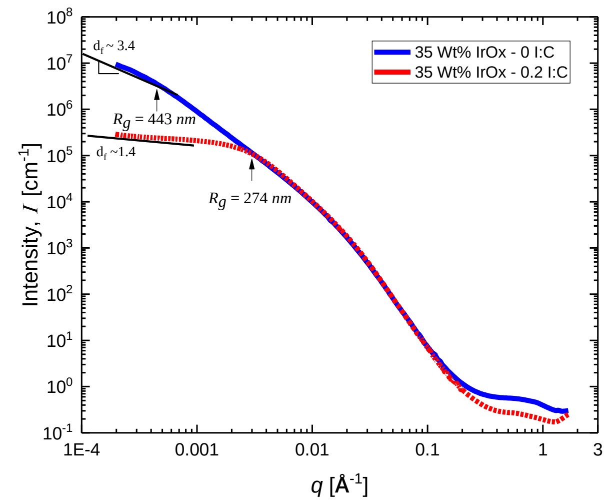
Zeta Potential



Dynamic Light Scattering (DLS)



USAXS of Concentrated Ink



- Zeta potential measurements show Nafion is adsorbing on catalyst particle surface and providing electrostatic stabilization
- Stabilization of IrO_2 leads to significant decrease in effective catalyst particle size
- USAXS measurements of concentrated inks verify DLS and zeta potential measurements of dilute inks
- Work above under project TA008 (S. Mauger). Formulation studies with Ir/NSTF catalysts under this project to be initiated Q2CY19.

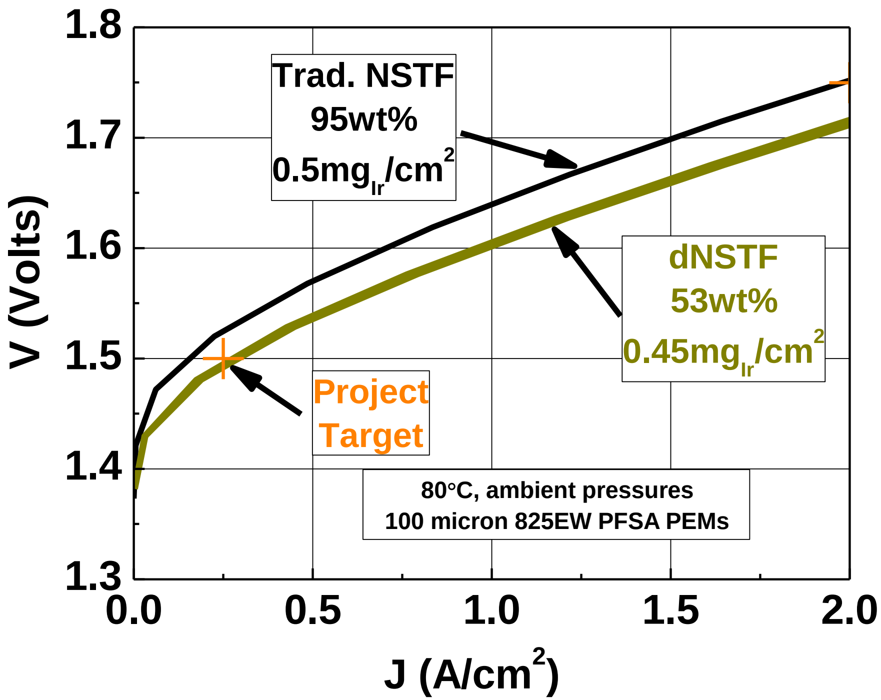
BP1 Milestones and Go/No-Go

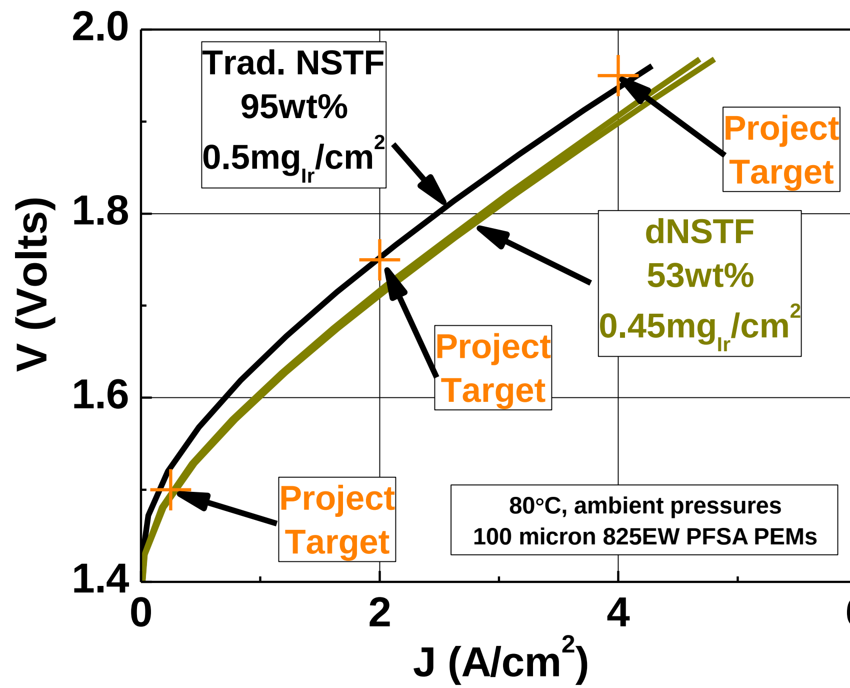
Task Number, Title	Type (M/G), Number	Milestone Description/ Go/No-Go Decision Criteria	Status	Date (Q)
1.2 Catalyst	M1.2.1	$10g_{Ir}$ of Ir/NSTF catalyst powder produced.	100%	0
1.7 Cost Model	M1.7.1	Cost model of baseline laboratory/pilot scale CCM developed.	100%	1
1.2 Catalyst	M1.2.2	Support process demonstrated with 2.5x larger batch size and 2x faster lineal-rates than baseline.	40%	2
1.1 Membrane	M1.1.1	Pilot-scale membrane fabrication process demonstrated with 100±10μm thickness, > 0.3m wide, at target-compatible lineal rate.	20%	3
1.5 Performance	M1.5.1	Equivalent CCM performance at 3M and test partner site.	0%	3
1.6 Inspection	M1.6.1	Uniformity and defect inspection system downselected.	5%	3
1.2 Catalyst	M1.2.3	Support process demonstrated with 5x large batch size and 4x faster lineal-rates than baseline.	5%	4
1.3 Electrode	M1.3.1	Pilot-scale electrode process demonstrated with anode electrode loading variation of < 10%, at least 0.25m wide, at target-compatible lineal rate.	5%	4
1.4 CCM	M1.4.1	Pilot-scale CCM process produces CCM with > 0.25m wide and total PGM loading < 0.60mg/cm^2 at target-compatible lineal rate.	0%	4
1.5 Performance	M1.5.2	Pilot-scale CCM produces 1) > 0.20 A/cm^2 at 1.5 V, 2) > 2.0 A/cm^2 at 1.80 V and 3) > 4 A/cm^2 at 2.1V	0%	4
1.6 Inspection	M1.6.2	Inspection of pilot-scale CCM completed and report generated.	0%	4
1.7 Cost Model	M1.7.2	Pilot-scale CCM process model indicates cost target feasibility.	0%	4
BP1 GNG1		**Pilot-scale CCM fabrication process produces CCMs with total PGM loadings of < 0.60 mg/cm^2 and widths > 0.25m at > 2x net-effective lineal rate than the baseline process, which generates 1) > 0.20 A/cm^2 at 1.5 V, 2) > 2.0 A/cm^2 at 1.80 V and 3) > 4 A/cm^2 at 2.1V.**	0%	4

Project on track (Q1 end is March 31st, 2019).

Initial focus is laboratory scale development of processes and R2R inspection methods.

Accomplishments and Progress – Lab CCM Meets Performance Targets



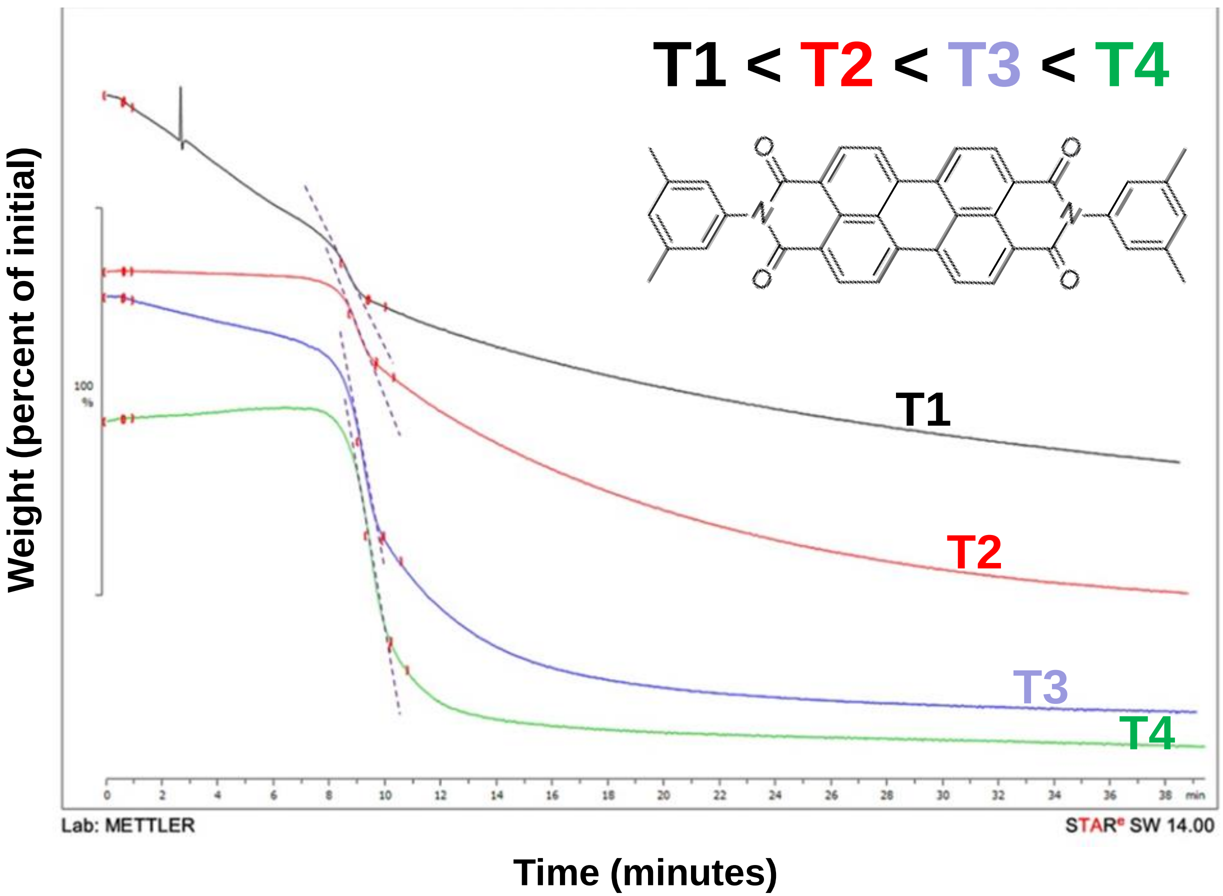


Project Target	Target Value	Baseline	2019 Status
Current Density at 1.50V (A/cm^2)	≥ 0.25	0.16[1]	0.28[4]
Current Density at 1.75V (A/cm^2)	≥ 2	1.98[1]	2.4[4]
Current Density at 1.95V (A/cm^2)	≥ 4	4.2[1]	4.5[4]
Total PGM Loading (mg/cm^2)	≤ 0.50	0.75[1]	0.70[4]

GREEN: Meets or exceeds target. YELLOW: Within ca. 15% of target.
[1]Traditional NSTF PEMWE CCM with laminated electrodes; $0.50 mg_{Ir}/cm^2$ and $0.25 mg_{Pt}/cm^2$. [2]Estimated production rate at 8" web width. [3] Lab-scale CCM fabrication. [4] Lab-scale CCM; $0.45\ mg_{Ir}/cm^2$ and $0.25\ mg_{Pt}/cm^2$ electrode loadings.

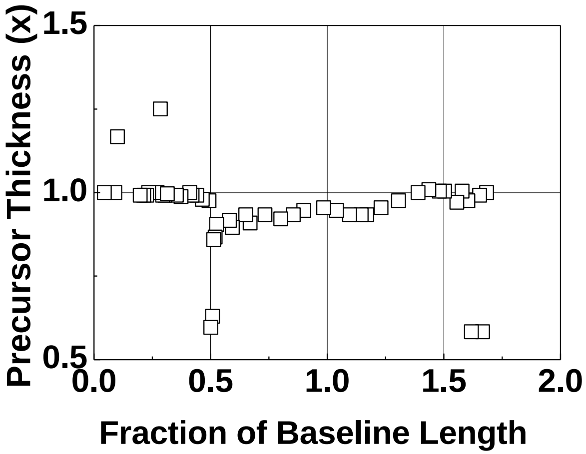
- Dispersed Ir/NSTF electrodes yield 40 mV improvement at $1A/cm^2$ vs. traditional NSTF electrodes
- Lab CCM meets project performance targets, but at higher total loading than project target.
- Achievement of project target needs to be demonstrated with CCM produced via final project production process.

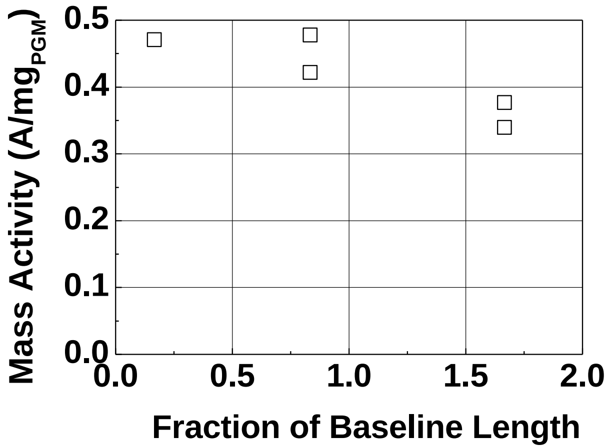
Vacuum Thermogravimetric Analysis of PR149

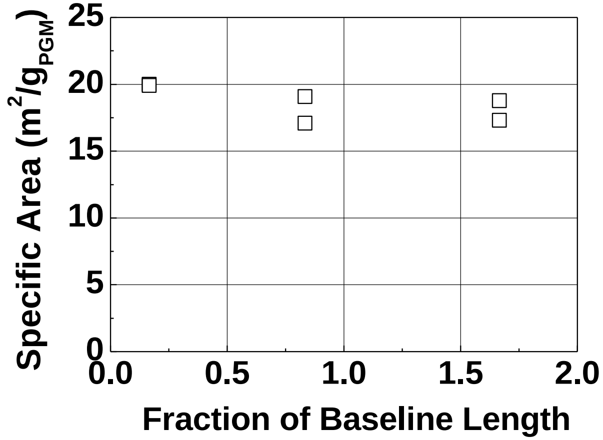


- Initial work has focused on determining key process and material factors to enable required increases in perylene red 149 deposition rate.
- Vacuum thermogravimetric analysis was used to quantify sublimation rate vs. temperature under vacuum.
- Sublimation rate increased with temperature, as expected, but must be balanced against thermal decomposition.
- Development of deposition rate model in progress based on sublimation data in progress.

Pilot Process Trial of Extended Batch Length Support Process







- Process trial conducted to examine support process with extended roll-to-roll batch length with all deposition and annealing parameters at baseline conditions.
  - Run length of 1.7x of baseline completed – halted because of time of day
- Supports were metallized with UTF 28PtNi (FC143), tested for ORR activity and specific area in fuel cell tests as one measure of whisker quality, and examined by SEM.
  - Potential issue with whisker quality identified at 1.7x of baseline length. ORR mass activity decreased modestly, but area largely within spec.
  - SEM characterization (not shown) revealed non-standard support morphology at 1.7x length.
  - Characterization of source and deposited materials for physical and chemical changes in progress.

Accomplishments and Progress – Process Time Model (3M)

Baseline Process (Traditional NSTF)	
	Areal Process Rate (Rel. To Baseline)
Overall	**1.0**
Component Breakdown	
Membrane	1.0
Anode Electrode	1.0
Cathode Electrode	1.0
CCM	1.0

Current Status (Dispersed NSTF) - *Estimated*	
	Areal Process Rate (Rel. To Baseline)
Overall	**0.7**
Component Breakdown	
Membrane	2.0
Anode Electrode	0.4
Cathode Electrode	0.3
CCM	1.0

CCM Concept #1 Target	
	Areal Process Rate (Rel. To Baseline)
Overall	**7.7**
Component Breakdown	
Membrane	30.2
Anode Electrode	5.4
Cathode Electrode	3.2
CCM	7.6

CCM Concept #2 Target	
	Areal Process Rate (Rel. To Baseline)
Overall	**9.1**
Component Breakdown	
Membrane	30.2
Anode Electrode	6.1
Cathode Electrode	3.9
CCM	22.7

- Process map and process rate model developed for 3M PEMWE CCMs.
- Component and CCM rates are cumulative of all constituent processes.
- Baseline process based on demonstrated process times for 1st generation traditional NSTF CCM.
- Current rate status is 0.7x, based on *projected* production of dispersed NSTF CCMs using current constituent component rates - *not demonstrated at pilot scale*.
- Two CCM concepts modeled which exceed the project areal rate target of 6x.

Absolute rates, yields, and costs are 3M Confidential and will not be publicly disclosed.
3M will provide limited rate information to DOE project manager for validation.

Collaborations

- **3M - Component Process Development and Cost Model**
  - A. Steinbach (PI), Mike Yandrasits, N. Petkovich, G. Thoma, D. Rowe, K. Struk, A. Haug, J. Abulu, C. Thomas, K. Lewinski, F. Sun, P. Crain, M. Burch, and J. Phipps.
- **National Renewable Energy Laboratory – Process and Inspection Development**
  - M. Ulsh, S. Mauger, P. Rupnowski
- **Giner, Inc. – Component Performance Validation**
  - H. Xu

Response to Reviewers’ Comments

This project was not reviewed last year.

Remaining Challenges and Barriers

1. Dispersion coating of “thick” electrolyzer membrane films may require tailoring of solvent systems and drying profiles, relative to fuel cell membranes, to mitigate drying defects.

2. Achievement of project catalyst targets will require increased rate of organic sublimation deposition without increased precursor thermal degradation.

3. Electrode inks comprising high-aspect ratio catalysts may have different rheological properties than electrodes comprised of spherical nanoparticles or supported nanoparticles. Coating formulations and processes developed for nanoparticle catalysts may not be applicable and may require optimization for high-aspect ratio catalysts.

4. Coating and other fabrication processes at 0.5m widths have not yet been demonstrated. Process tolerances (e.g. thickness uniformity) at relatively wider widths may be more difficult to achieve.

Key Future Work – Q2CY19-Q1CY20

- Completion of laboratory membrane coating studies and initiation of pilot-scale coating trials towards increased rate and thickness milestones.
- Pilot-scale catalyst process optimization, including demonstration of 4x lineal rate for support process.
- Initiation and completion of ink formulation and rheological studies at lab-scale, and initiation of pilot-scale coating trials.
- CCM fabrication studies at laboratory scale, pathway downselect, and pilot-scale trials towards achievement of project Go/No-Go.

Any proposed future work is subject to change based on funding levels

Summary

- Project objective is to reduce PEM water electrolyzer capital cost barriers by developing reduced-cost manufacturing processes for high performance catalysts, membranes, electrodes, and CCMs.
- Project performance targets have been met with laboratory scale CCMs, but at modestly higher catalyst loadings than project target.
- Process development work has been initiated, focusing on laboratory and pilot-scale studies of whisker support fabrication, membrane coating trials, electrode ink formulation studies, and initiation of QC inspection development.
- A process cost model has been developed, which provides pathways for achieving the project manufacturing rate target.

Technical Backup Slides

Reviewer Slides - Technology Transfer

- 3M commercially sells electrochemical components through the Advanced Materials Division.
- 3M technology and product development occurs within formal New Technology Introduction and New Product Introduction frameworks.
- 3M samples developmental electrochemical components to selected partners based on strategic alignment.

Reviewer Slides – Team Roles

3M will lead and conduct process development work for membranes, catalysts, electrodes, and CCMs. 3M will conduct material assessment at single cell level. 3M will generate a cost model based on the process development work, and is responsible for overall project management.

NREL will conduct electrode ink formulation studies, CCM integration studies, and develop relevant inspection techniques for CCM and component roll-goods.

Giner will conduct limited performance and durability assessments of CCMs at single cell level, including characterization of hydrogen crossover and accelerated stress testing and subsequent characterization. Giner will integrate final production CCMs into a short stack for performance and limited durability tests.

Reviewer Slides – BP2 Milestones

Task Number, Title	Type (M/G), Number	Milestone Description/ Go/No-Go Decision Criteria	Status	Date (Q)
2.1 CCM Process	M2.1.1	Production-scale CCM fabrication process produces CCM $\geq$ 0.50m wide at target-compatible lineal rate.	Not started	5
2.2 CCM Process	M2.2.1	50m^2 of CCM produced with > 0.50m width and total PGM loading $\leq$ 0.50mg/cm^2 at target-compatible lineal rate.	Not started	6
2.4 CCM Performance	M2.4.1	Production-scale CCM process produces 1) $\geq$ 0.25 A/cm^2 at 1.5 V, 2) $\geq$ 2.0 A/cm^2 at 1.75 V and 3) $\geq$ 4 A/cm^2 at 1.95V.	Not started	7
2.4 CCM Performance	M2.4.2	Production CCM short stack operated for 500 hours at 2A/cm^2.	Not started	8
2.5 Cost Model	M2.5.1	Production-scale manufacturing rate (m^2 per cumulative process time) is 6x higher than baseline.	Not started	8
Project Target	Goal	Production-scale CCM fabrication process produces CCMs with total PGM loadings of $\leq$ 0.50 mg/cm^2 and widths $\geq$ 0.50m at $\geq$ 6x manufacturing rate which generate: 1) $\geq$ 0.25 A/cm^2 at 1.5 V, 2) $\geq$ 2.0 A/cm^2 at 1.75 V and 3) $\geq$ 4 A/cm^2 at 1.95V.	Not started	8