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

U.S. DOE 2020 Annual Merit Review

May 21, 2020

<u>Andrew J. Steinbach</u>

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:	$1.602MM**
Cost Share Percentage:	23.25%

*Includes DOE, contractor cost share and FFRDC funds as of 3/31/20

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, Inc. (H. Xu, F. Yang)

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)**

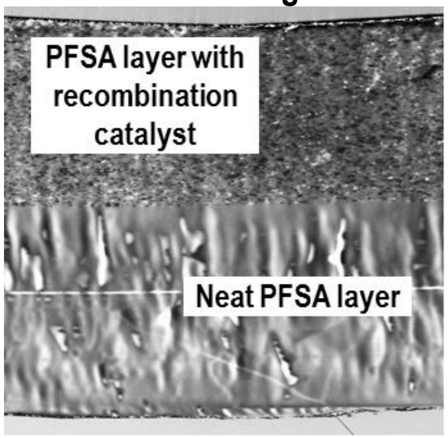
Overall Project Approach

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).

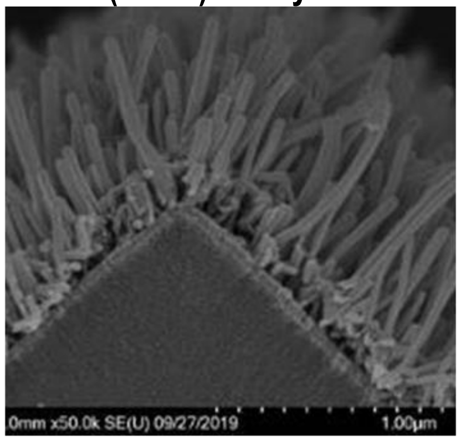
Project Objective, Relevance, and Approach

Project component technologies provide unique combination of high efficiency, durability, and Ir utilization critical for wide-spread deployment of PEM water electrolysis.

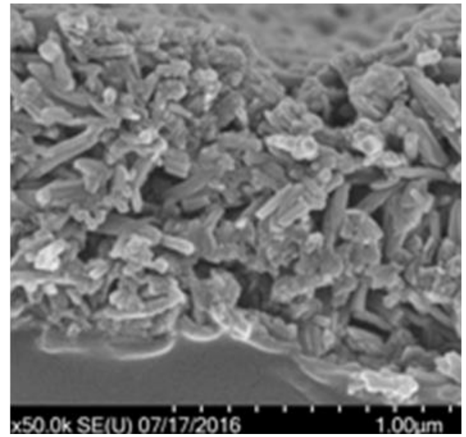
Membranes with H_2 Crossover Mitigation



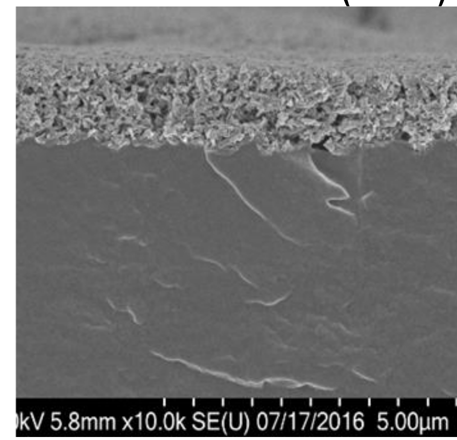
Nanostructured Thin Film (NSTF) Catalysts



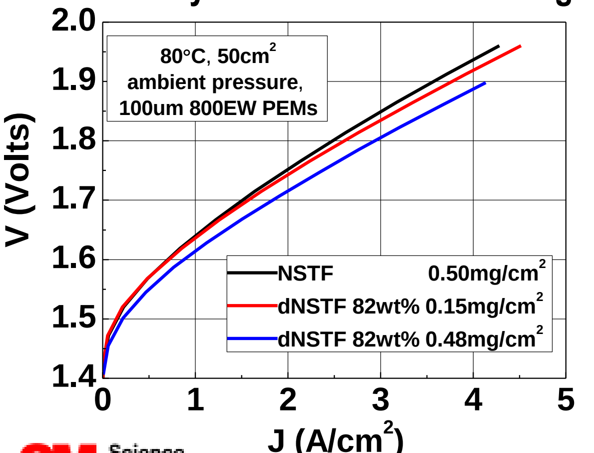
Dispersed NSTF Powder Electrodes



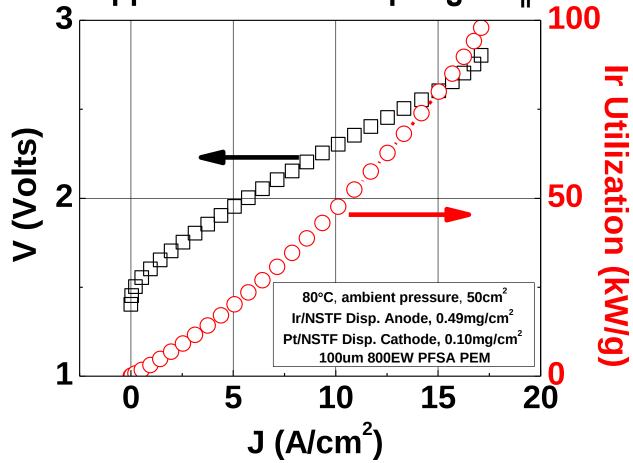
Dispersed NSTF Catalyst Coated Membranes (CCMs)



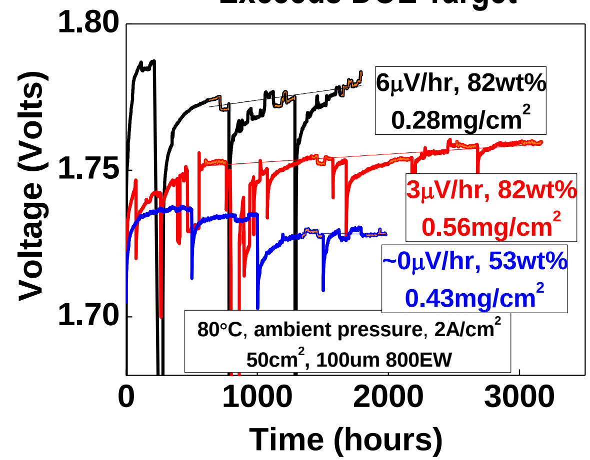
Dispersed NSTF: Similar or Improved Efficiency w/ 70% Lower Ir Loading



Pilot-Scale CCM Ir Utilization Approaches 100 kW per gram$_{Ir}$



Durability Approaches or Exceeds DOE Target



Status versus Project Targets

Project Target	Target Value	Baseline	2019 Status	2020 Status
CCM Production Rate (m^2 per cumulative process time)	$\geq$ 6x baseline	1[1]	0.7[2]	5.3[5]
CCM Width (m)	$\geq$ 0.50	0.25[1]	0.10[3]	0.30[5]
Current Density at 1.50V (A/cm^2)	$\geq$ 0.25	0.16[1]	0.28[4]	0.24[6]
Current Density at 1.75V (A/cm^2)	$\geq$ 2	1.98[1]	2.4[4]	2.4[6]
Current Density at 1.95V (A/cm^2)	$\geq$ 4	4.2[1]	4.5[4]	4.8[6]
Total PGM Loading (mg/cm^2)	$\leq$ 0.50	0.75[1]	0.70[4]	0.63[6]

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. [3,4] Lab-scale CCM with 0.45 mg_{Ir}/cm^2 and 0.25 mg_{Pt}/cm^2 electrode loadings.

[5]CCM pilot fabrication rate at 0.30m wide. [6]Pilot-scale CCM with 0.50 mg_{Ir}/cm^2 and 0.13 mg_{Pt}/cm^2 electrode loadings.

- Current rate status is 5.3x, based on *demonstrated* rates of individual process steps.
    - Project rates set relative to pre-project "traditional NSTF" PEMWE CCM technology baseline (pilot scale).
    - CCM production rate is cumulative of all constituent process steps on capital-intensive equipment
        - Development focuses on core processes – excludes low-capital, routine process steps, e.g. web slitting.
- CCM areal production rate target of 6x likely achievable with width scaleup to 0.30 to 0.50m wide, assuming lineal rates already demonstrated are maintained.
- Performance targets approached or exceeded with pilot CCM.

Overall 7.6x rate increase since 2019; project on-track to meeting targets.

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.***

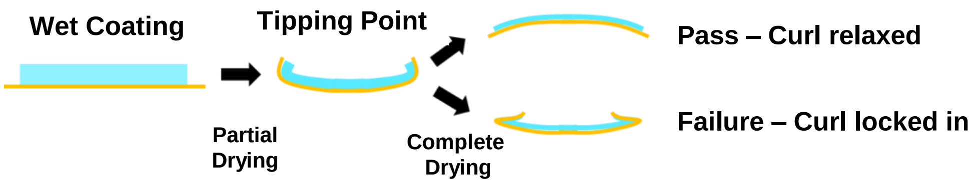
Project delays due to COVID-19 anticipated.

Accomplishments and Progress – Wide PEM Process Developed

- PEM process consists of dispersion coating onto a substrate, drying, and annealing.
- Key limiting factor for 100μm thick electrolyzer PEMs was curl during drying.

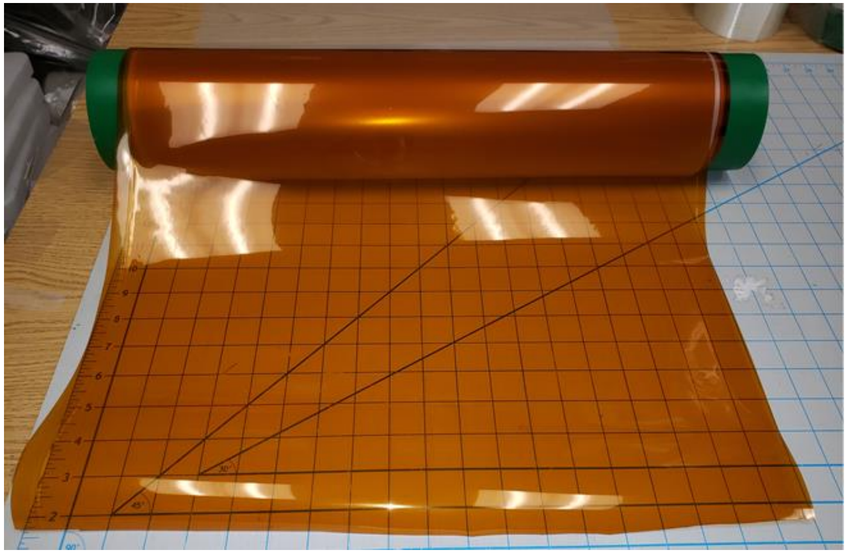
Membrane from Baseline Process
Curl Failure at 4” wide, 100μm

- Mechanism: Large lateral stresses during drying.
  1. Edges dry first, binding contracting, drying PEM to substrate.
  2. If web curls beyond “tipping point”, web locks on tacky coating.



- Curl failure resolved via modified process.
- Modified process enabled fabrication of 0.48m wide electrolyzer PEM at production scale and accelerated areal rate (20.6x of baseline).

0.48m Wide, 825EW 100μm Membrane Produced with Advanced Process at 20.6x Areal Rate

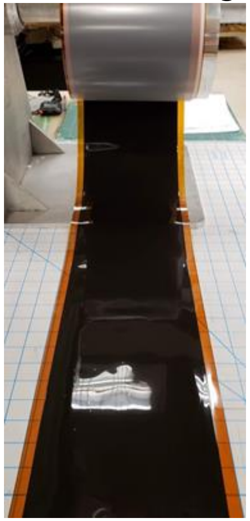


New PEM process is 20.6x faster; approaches project width target.

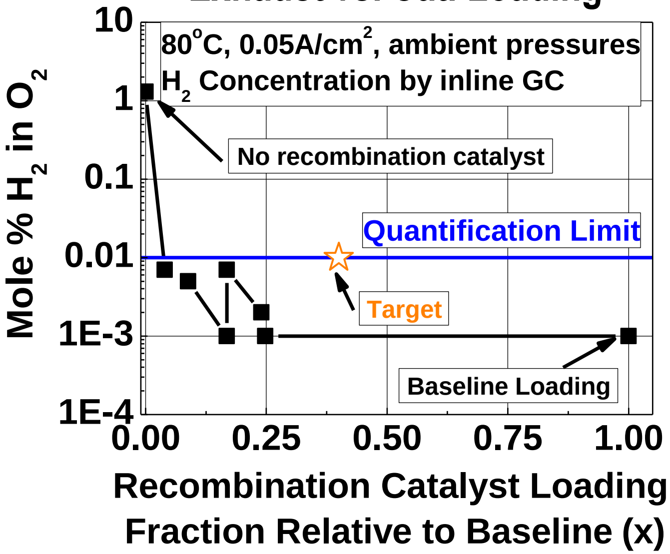
Accomplishments and Progress – Crossover-Mitigated PEM Development

- H_2 crossover from cathode to anode is a limiting factor for thin electrolyzer membranes.
- Recombination (H_2 + O_2) catalyst in PEM reduces net H_2 crossover 2 orders of magnitude vs. w/o additive, to below limit of quantification.
- Effective with as little as 4% catalyst loading relative to pre-project baseline.
- Internal target of < 40% loading met.

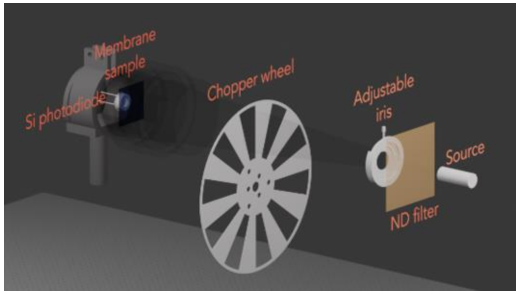
PEM with H_2 Crossover Mitigation



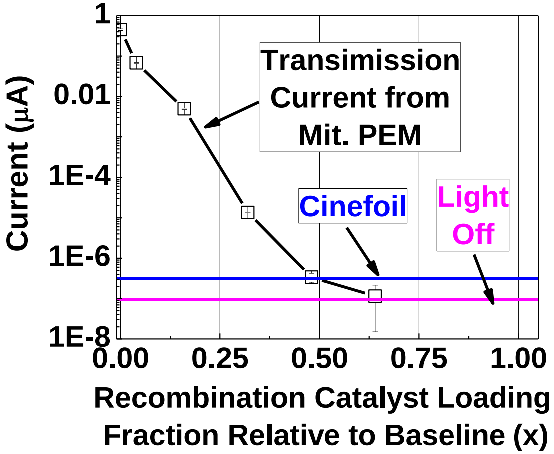
H_2 Concentration In Anode Exhaust vs. Cat. Loading



Optical Transmission Spectroscopy



Transmission vs. Cat. Loading



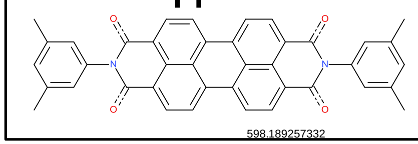
- QC / Inspection development has utilized optical transmission spectroscopy to detect recombination catalyst loading and uniformity.
- To date, bench method yields quantitative catalyst loading signal at levels approaching project target.
- Next: mapping development.

Lower-loading mitigated PEM and QC/Inspection feasible.

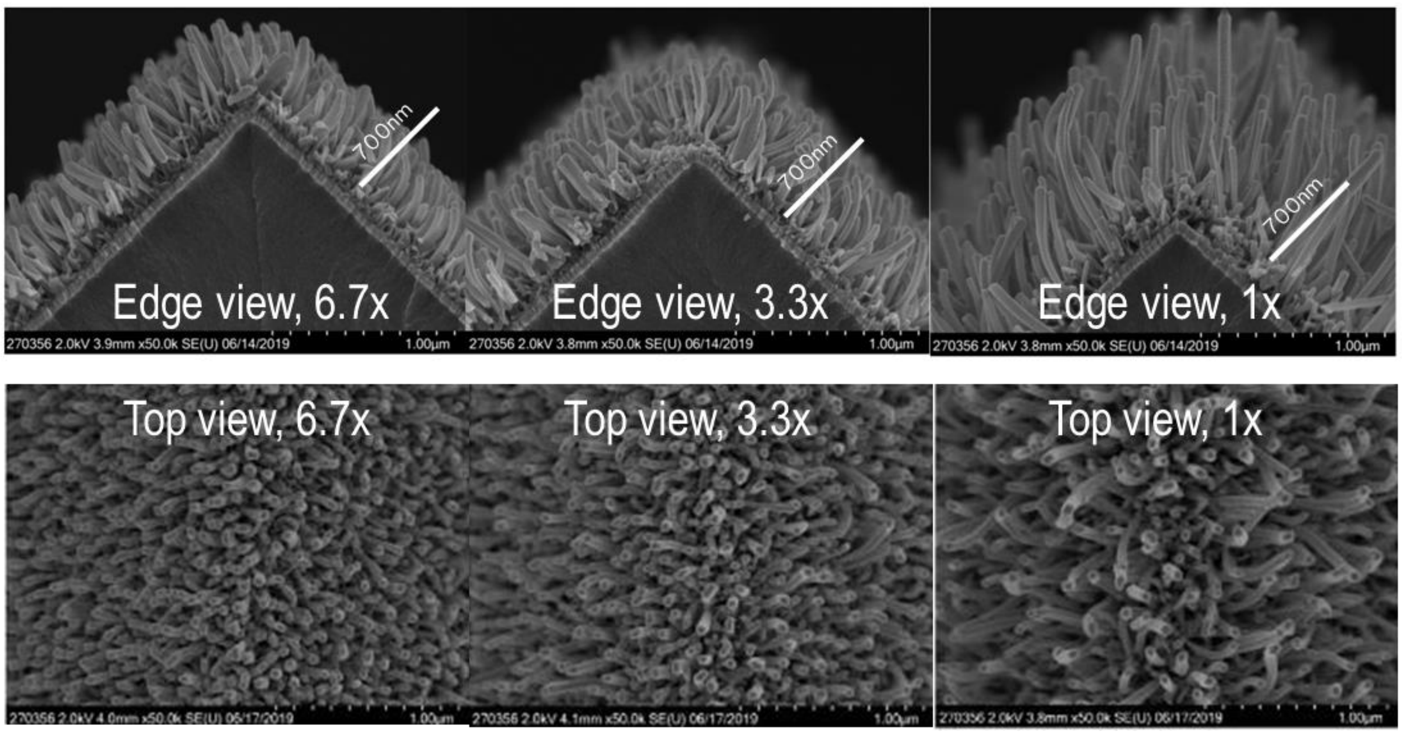
Accomplishments and Progress – Accelerated Catalyst Support Process

- NSTF support process consists of 1) vacuum sublimation deposition of support precursor (PR149), and 2) vacuum thermal annealing to form support whiskers.
- Process development enabled production of supports at 6.7x of baseline rate.
- The accelerated processes produced supports which were shorter and had higher areal number density than the baseline rate, resulting in higher surface area.

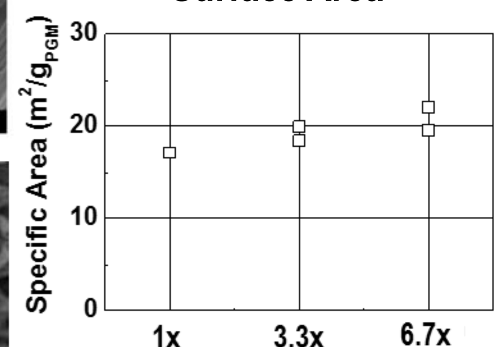
PR149 Support Precursor



PR149 Support Whiskers Annealed at 1, 3.3, and 6.7x of Baseline Rate



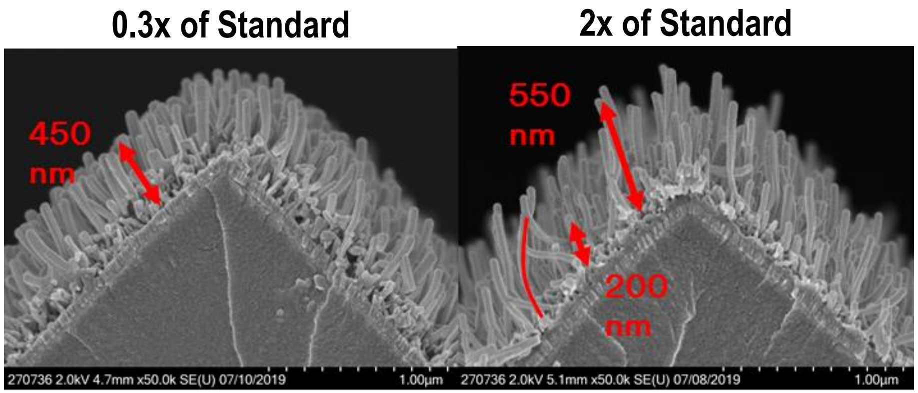
Supports from Accelerated Process Have Enhanced Surface Area



Support process rate increased 6.7x; yields increased surface area.

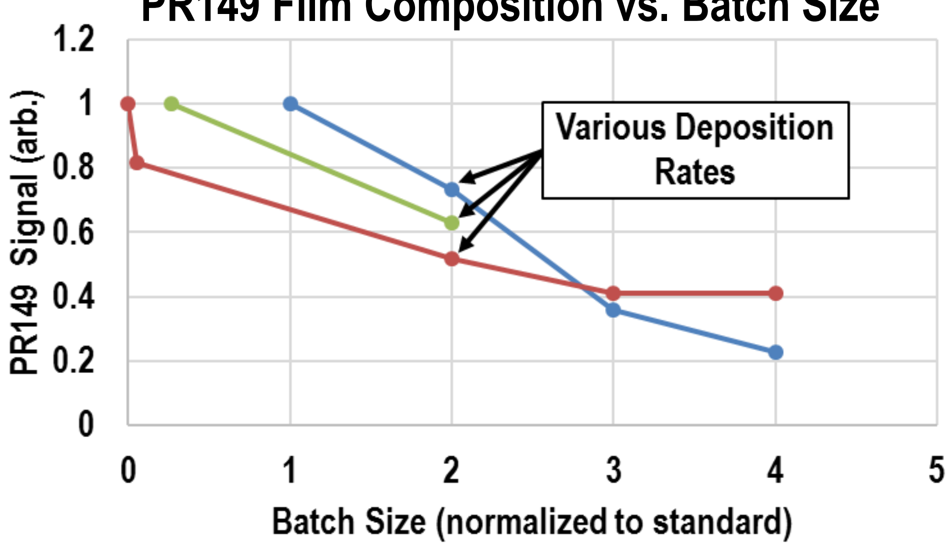
Accomplishments and Progress – Catalyst Support Process Batch Size

SEM of Support Whiskers vs. Batch Size



- "Large" batch sizes are critical for further process time and cost reductions.
- Supports produced with "large" batch sizes have defects which *may* impact performance.
  - Higher length variability
  - Lower areal number density
- Thermal degradation of PR149 in sublimation source suspected as limiting factor.

PR149 Film Composition vs. Batch Size

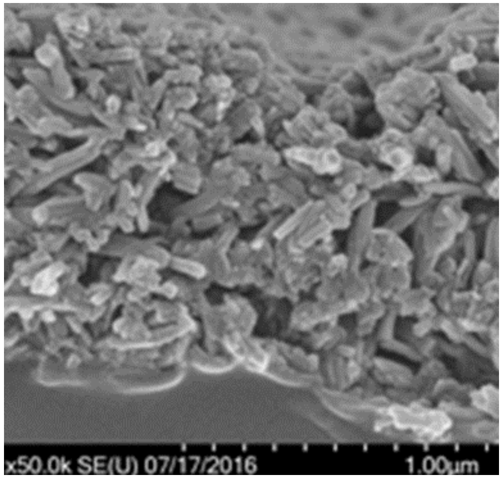


- New analytical methods identified which allowed for direct compositional analysis of deposited PR149 films.
- Analysis indicated decreasing proportion of PR149 with increasing batch size(time), consistent with hypothesis.
- New analytical methods will provide critical feedback for "large" batch development.
- Potential mitigation routes identified and to be explored.

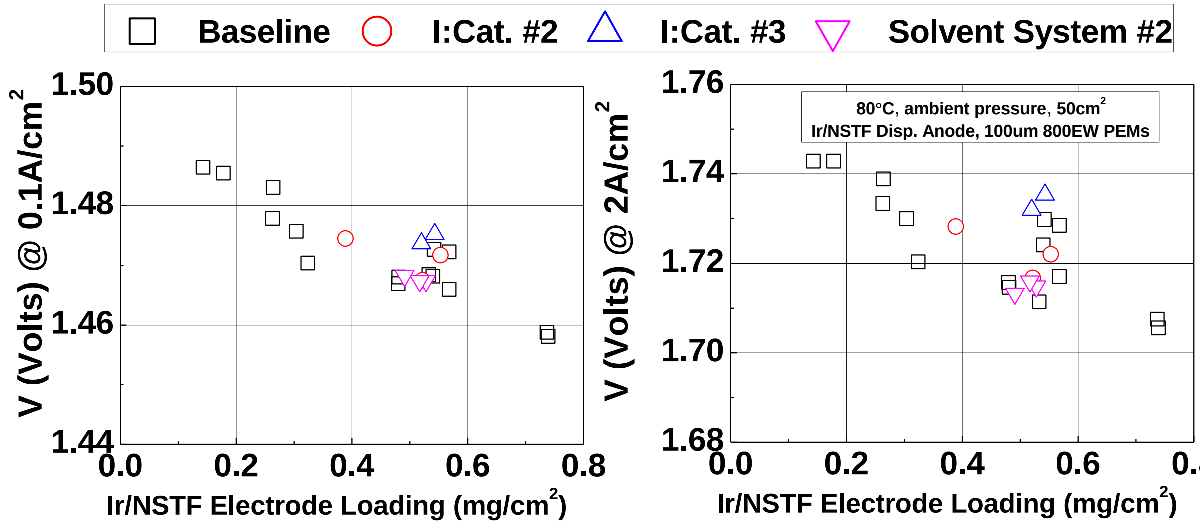
Limiting factor for "large" catalyst batch size and potential mitigation identified.

Accomplishments and Progress – NSTF Dispersed Anode Formulation

Dispersed NSTF Electrode

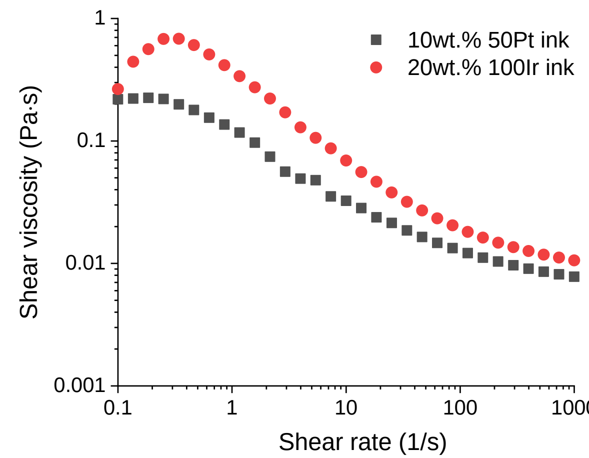


Performance vs. Ionomer:Catalyst Ratio, Solvent System



- Dispersed NSTF electrodes fabricated by dispersion coating (NSTF powder catalyst, ionomer, solvents) and drying.
- Performance was relatively insensitive to ionomer:catalyst and solvent system variations, enabling formulation development to focus primarily on processability and quality.
- NSTF electrode dispersions have low viscosity at relevant catalyst concentrations, conceptually allowing for high-rate coating.

Ink Viscosity vs. Shear Rate



Anode electrode performance is robust to formulation variation.

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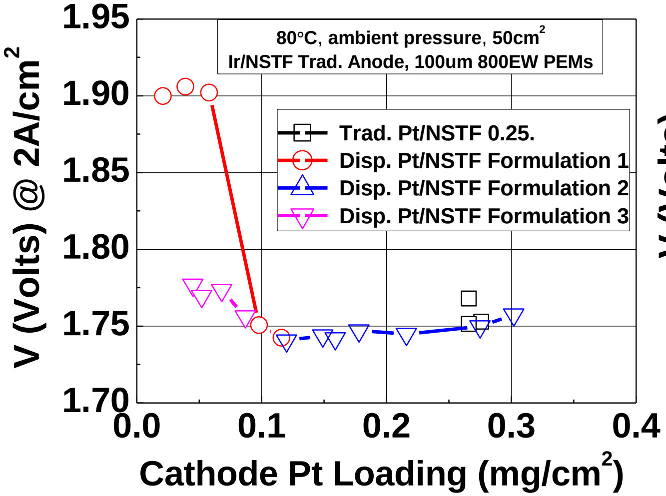
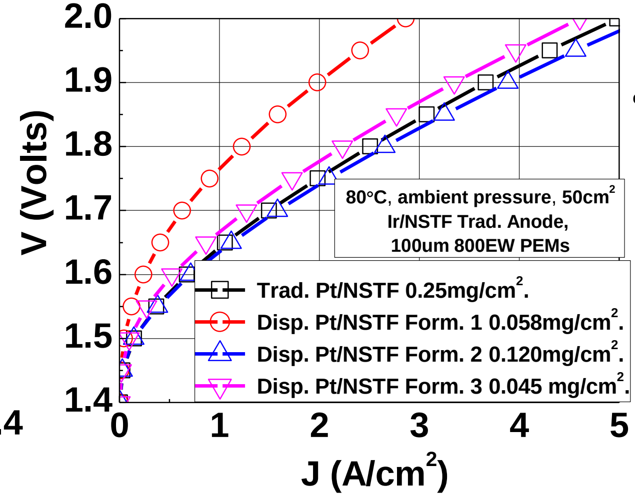
Accomplishments and Progress – NSTF Dispersed Cathode Formulation

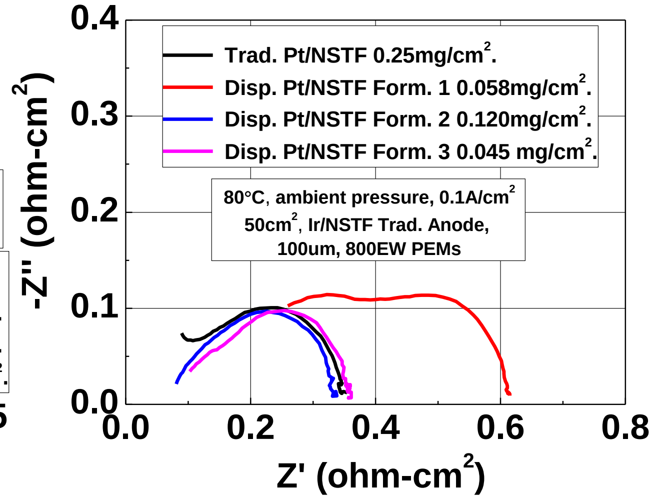
Performance vs. Loading, Formulation



Performance vs. Formulation



Impedance vs. Formulation



- New this year: dispersed NSTF PEMWE *cathodes.*
- Performance with initial formulation depended strongly on electrode loading.
  - Polarization and impedance measurements suggest that at low loading, initial formulation suffered from poor CCM areal utilization (30-50%), potentially due to insufficient in-plane conductivity.
- Low loading performance improved significantly with electrode formulation optimization.
- With to-date optimal formulations 2 and 3, performance is comparable or improved relative to traditional NSTF baseline, and with at least 2x lower Pt loading.

Optimized electrode formulation critical for low-loading HER electrodes.

Accomplishments and Progress – NSTF Electrode Process Development

0.25m Wide Electrode Roll Goods at 4x Lineal Rate

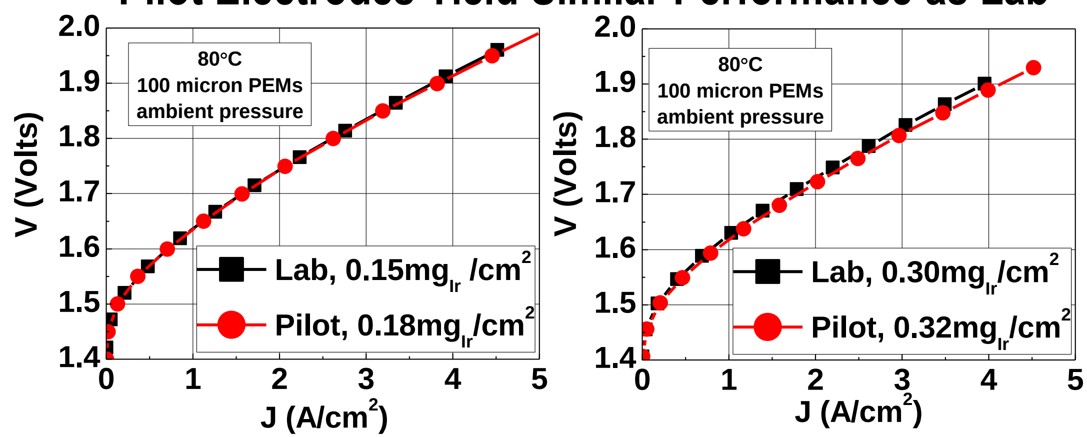
Anode: 0.50mg/cm^2 Ir/NSTF

Cathode: 0.13mg/cm^2 Pt/NSTF

- Electrode process consists of dispersion coating (NSTF powder catalyst, ionomer, solvents) onto liner and drying.
- 0.25m wide electrode coatings were visually uniform and high-rate capable (4x lineal rate demonstrated, exceeded target).

- Pilot-coated anode electrodes have generally yielded similar performance as lab-coated, even with loadings < 0.20mg/cm^2.

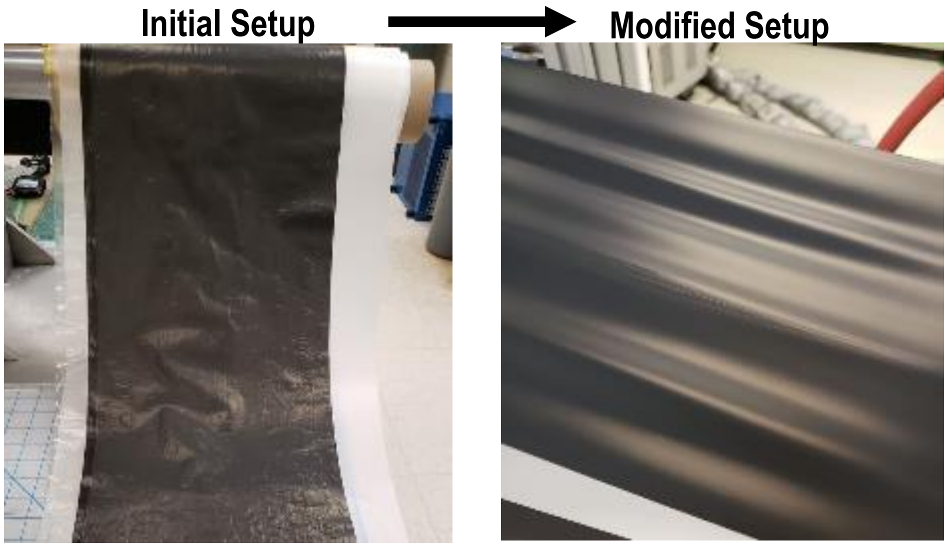
Pilot Electrodes Yield Similar Performance as Lab



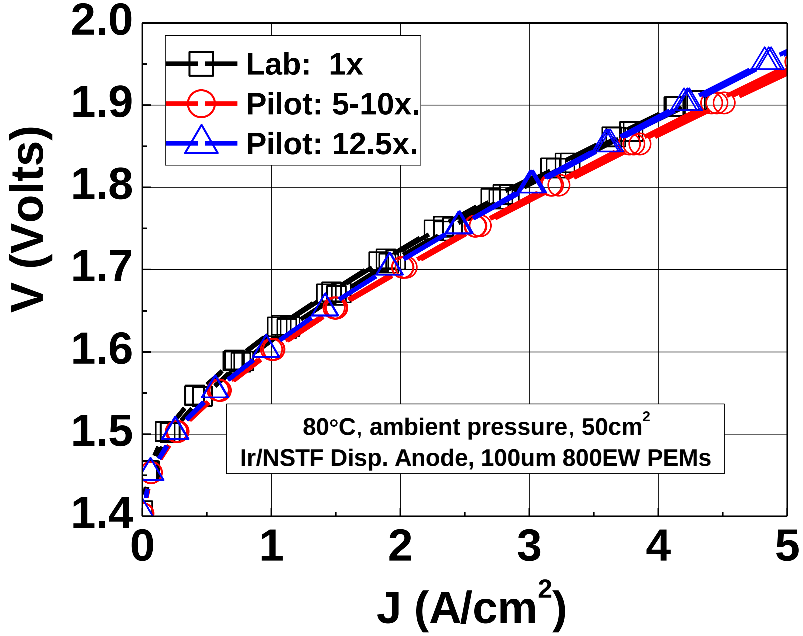
Electrode coating/drying process accelerated 4x; yields expected performance.

Accomplishments and Progress – CCM Process A (Lamination)

0.30m Wide CCM Roll Goods at 12.5x Lineal Rate



Performance of Lab vs. Pilot CCMs



- CCM Process A consists of thermal transfer of the anode and cathode electrodes from liner to the PEM.
- New lamination process developed with capability of meeting project 0.5m width target and rate target.
- Initial setup resulted in numerous visual defects (left), substantially resolved by setup modification (right).
- Several meters of 0.30m wide CCM produced.

- Performance of pilot CCMs produced at 5-10x or 12.5x of baseline rate were comparable or improved relative to lab lamination (1x).

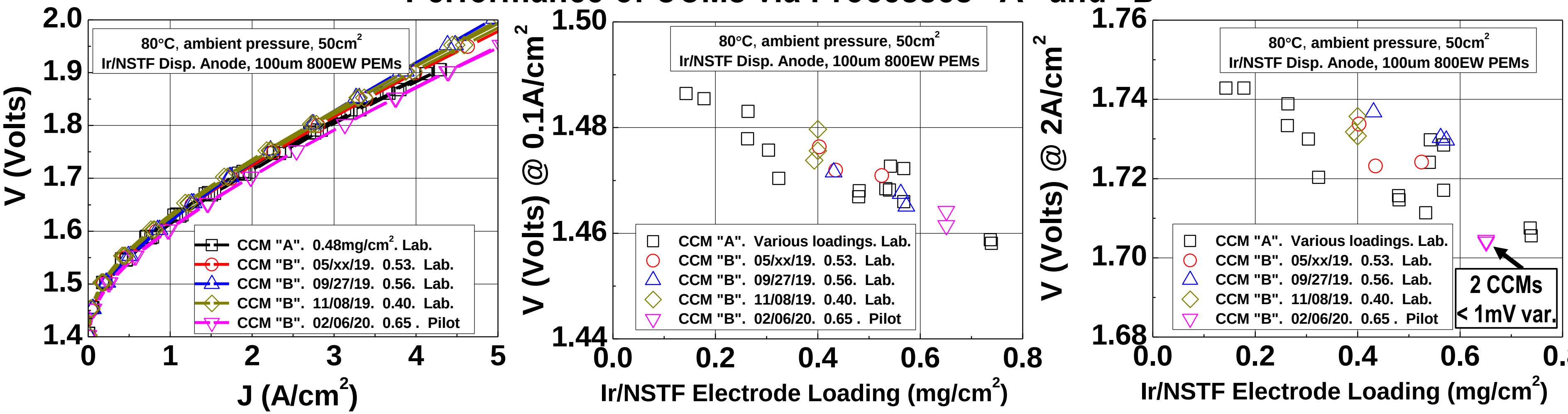
CCM Process A rate increased > 10x; achieves expected performance.

Accomplishments and Progress – CCM Process B (Direct Coat)

- CCM Process B consists of coating the anode and cathode electrodes directly onto the PEM.
  - Conceptual benefits: less waste; reduction of process step.
- Electrode coating is uniform, but membrane distortion from solvents is key challenge (right).
- Lab Process B CCMs' performance slightly lower than Lab Process A
- R2R Pilot Process B CCM performance was improved vs. lab CCMs and highly reproducible.

Pilot Electrode Coating on PEM (NREL)

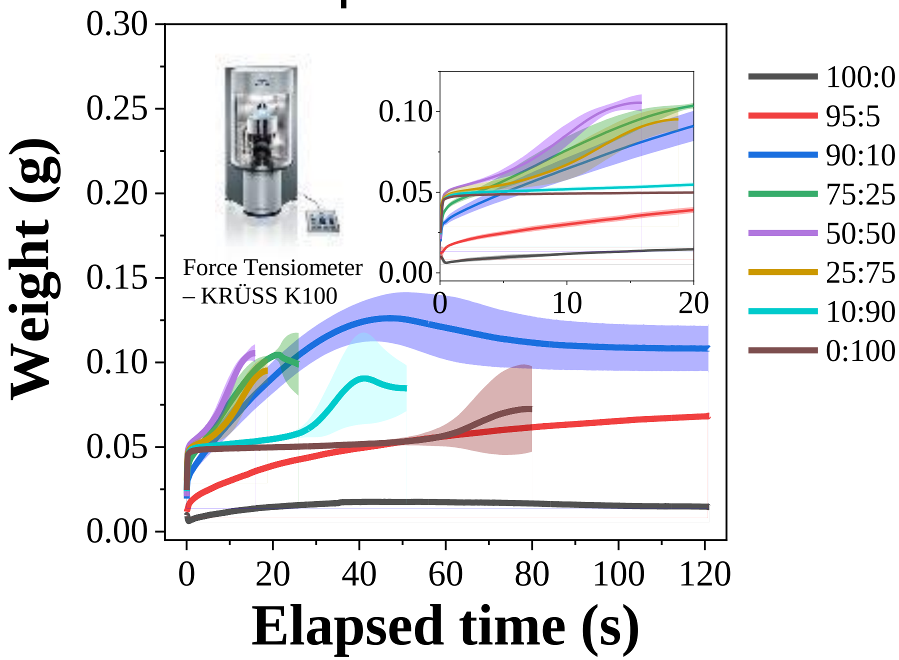
Performance of CCMs via Processes "A" and "B"



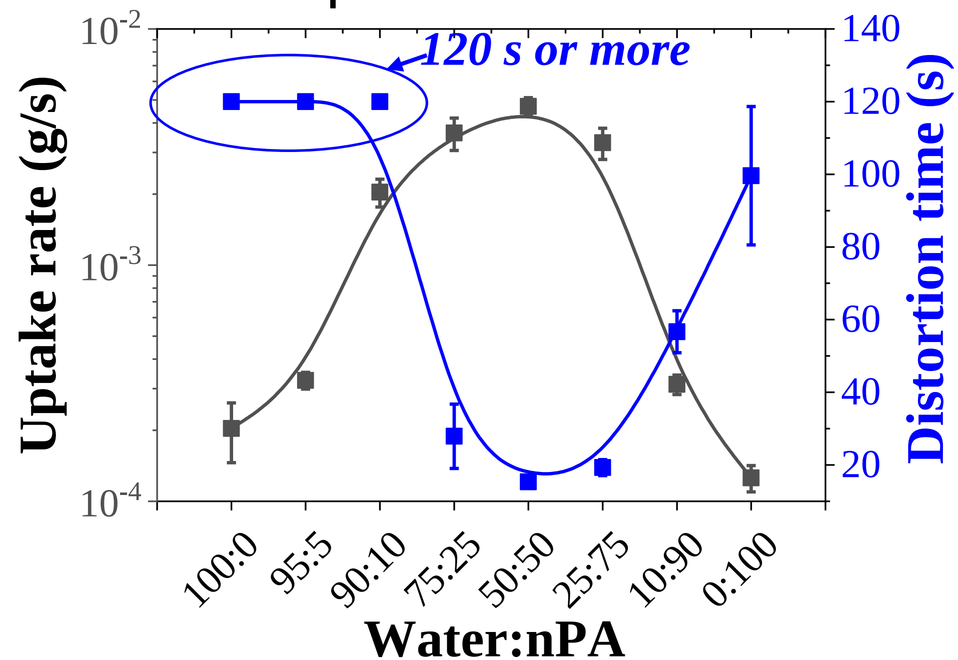
New direct coat CCM pilot process yields good performance.

Accomplishments and Progress – Membrane Solvent Uptake

Solvent Uptake Measurements



Solvent Uptake Rate vs. nPA Content



- Solvent uptake measurements into PEM conducted vs. water:alcohol ratio to determine if solvent system adjustments can reduce PEM swelling during CCM Process “B” .
- Uptake rate and time to membrane distortion depended strongly on water:nPA ratio.
- Pure solvents had lowest rates and longest times to distortion, but are more challenging for ink formulation.
- Uptake phenomena varies between pure water and pure nPA, likely due to varying absorption kinetics with the hydrophobic backbone and hydrophilic acidic regions of the membrane.

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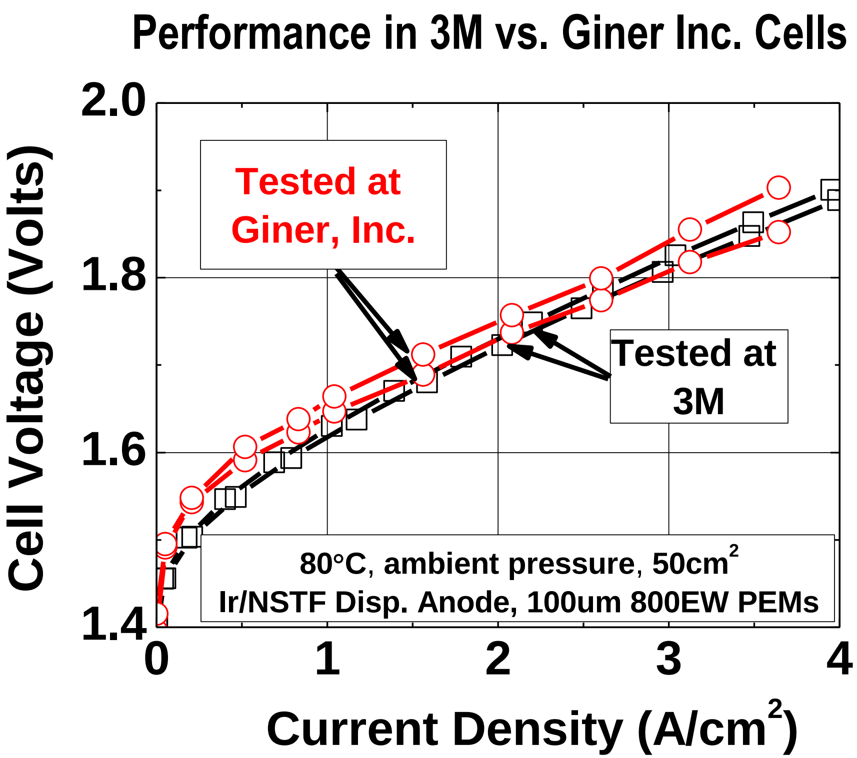
Solvent properties strongly influence uptake rate into PEM.

Accomplishments and Progress – Stack Integration

- Final project CCM to be integrated into short stack at Giner Inc. and evaluated for performance and short-term durability.
- Initial integration work has focused on CCM integration into Giner Inc. hardware at single cell scale.
- Project CCMs (laboratory-fabricated) tested at Giner Inc. exhibited:
  - higher activation losses than at 3M
  - similar or higher cell voltage at typical operating current densities (1.5 -3.5 A/cm^2).
- Average site-site difference of 14mV at 2A/cm^2 met project milestone (M1.5.1, $\leq$ 30mV).
  - Potential factors include differences in cell temperature control methods; 3M tested cells may be slightly hotter.



Project technology performance validated at two sites.

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) - *Demonstrated*	
	Areal Process Rate (Rel. To Baseline)
Overall	**5.3**
Component Breakdown	
Membrane	20.6
Anode Electrode	2.9
Cathode Electrode	2.4
CCM	17.3

- Process map and process rate model developed for components and 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 5.3x based on demonstrated trials at pilot/production scale.
- Membrane and CCM processes increased > 15x vs. baseline.
- Overall anode and cathode electrode processes increased 2.9 and 2.4x vs. baseline, respectively.

Absolute rates, yields, and costs are 3M Confidential and will not be publicly disclosed.
3M has provided quantified information to DOE for validation.

Collaborations; Response to Reviewers' Comments

Collaborations

- **3M - Component Process Development and Cost Model**
    - A. Steinbach (PI), M. Yandrasits, G. Thoma, D. Gobran, A. Haug, M. Lindell, F. Sun, K. Struk, J. Abulu, C. Duru, C. Thomas, K. Lewinski, P. Crain, M. Burch, A. Marcella, P. Murria, A. Gharcharlou, J. Phipps, W. Kolb, P. Hines, S. Javid, M. Hammes
- **National Renewable Energy Laboratory – Process and Inspection Development**
    - M. Ulsh, S. Mauger, J. Park, P. Rupnowski, B. Green, M. Liu
- **Giner, Inc. – Component Performance Validation**
    - H. Xu and F. Yang

Response to Reviewers' Comments

- **This project was not reviewed last year.**

Remaining Challenges and Barriers; Future Work (Q2CY20-Q4CY20)

Remaining Challenges and Barriers

1. Many fabrication processes have been demonstrated at 0.3m wide, less than the 0.5m target. Process tolerances at relatively wider widths may be more difficult to achieve.
2. Project CCMs have not yet achieved all performance targets at target total catalyst loading.
3. CCM Process "B" has challenges associated with membrane distortion during coating.
4. Remaining project work is delayed due to COVID-19; project schedule is not certain.

Future Work

1. Scaleup of component processes to production scale, at 0.5m wide and target rates.
2. Completion of QC/Inspection development for membranes, electrodes and CCMs.
3. Electrode formulation optimization for CCM process "B" to minimize solvent uptake rate and extent.
4. Production of 15 m^2 of CCM at 0.5m wide and 6x rate relative to baseline.
5. Integrate production CCM into short stack and assess performance and durability.

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

Summary

- Project process development has reduced process time (proportional to cost) 5.3x relative to baseline technology processes, and is on track to meet the project target of 6x.

- The project CCMs enable ultra-low Ir loadings with improved performance relative to baseline 3M technology, and have durability which approaches or exceeds DOE targets.

- New “direct coating” CCM fabrication method development has resulted in equivalent performance as the incumbent lamination method and reduces the number of process steps.

- The project CCM performance has been validated at Giner Inc., the project OEM partner.