
Low-Cost, High-Performance Catalyst Coated Membranes for Proton Exchange Membrane Water Electrolyzers

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Subcontractors:

- Giner Labs, Newton, MA
- National Renewable Energy Laboratory, Golden, CO

Project Start Date: October 1, 2018
Project End Date: December 31, 2020

Overall Objectives

- Develop advanced manufacturing techniques capable of producing high-performance, low-cost catalyst coated membranes (CCMs) and constituent components for proton exchange membrane water electrolyzers (PEMWEs) with a 6-fold decrease in overall CCM manufacturing cost (as defined as cumulative process time per m² of CCM produced), relative to the pre-project baseline process.

Fiscal Year (FY) 2019 Objectives

- Identify, develop, and demonstrate scalable processes for producing PEMWE CCMs and subcomponents (membranes, powder catalysts, electrodes) at an overall 2x lineal fabrication rate relative to the baseline process and at 0.25 m fabrication width.

- Identify and integrate specific material sets that are compatible with the processes and capable of achieving interim performance, process rate, and total platinum group metal (PGM) loading targets.

Technical Barriers

This project addresses the following technical barriers from the Hydrogen Production section of the Fuel Cell Technologies Office Multi-Year Research, Development, and Demonstration Plan¹:

- Manufacturing
- Capital Cost
- System Efficiency and Electricity Cost.

Contribution to Achievement of DOE Milestones

This project will contribute to achievement of the following DOE milestones from the Hydrogen Production section of the Fuel Cell Technologies Office Multi-Year Research, Development, and Demonstration Plan:

- Milestone 2.4: Develop technologies for producing hydrogen through electrolysis at centralized facilities using renewable power for a cost \leq \$3.00/gge at the plant gate. (Q4, 2015)

FY 2019 Accomplishments

- Identified, developed, and demonstrated advanced pilot-scale fabrication processes capable of producing membranes, anode and cathode powder catalysts and electrodes, and CCMs at an overall 2.9x lineal rate increase relative to the pre-project baseline, exceeding the 2.0x Year 1 project target.
- Demonstrated the pilot-scale fabrication processes of areal production rates of 4.3x the pre-project baseline, indicating feasibility for achievement of the final project target of 6x areal fabrication rate.

¹ <https://www.energy.gov/eere/fuelcells/downloads/fuel-cell-technologies-office-multi-year-research-development-and-22>

- Demonstrated a CCM fabrication process capable of producing CCMs and components at widths of 0.25 m or greater, which met the interim project target.
- Exceeded the final project targets with the performance of a CCM fabricated with the down-selected processes using a total PGM loading of 0.59 mg/cm². Validated performance of project CCMs by a second laboratory, with less than 15 mV average variation at 2 A/cm².
- Demonstrated that the project anode electrode technology is capable of yielding high performance with ultra-low Ir loadings of 0.15 mg/cm².
- Assessed the durability of the anode catalyst and electrode technology to be <4 μV/h at 80°C, 2 A/cm² with an electrode loading of ca. 0.42 mg Ir/cm², compatible with final project loading targets.
- Initiated development of roll-to-roll quality control/inspection methods for assessment of spatial variations of membrane thickness and catalyst loadings, with initial feasibility demonstrated for some component configurations.

INTRODUCTION

PEMWEs are electrochemical devices that generate hydrogen (H₂) and oxygen (O₂) gases from water and electrical energy feedstocks. PEMWEs are being investigated for several applications, including grid-scale energy storage for renewable energy curtailment avoidance, hydrogen fuels for fuel cell electric vehicles, low-carbon, renewable production of ammonia, and as a component of renewable liquid fuels (e.g., gasoline from electrochemical H₂ and CO via Fischer-Tropsch synthesis). However, commercial deployment of PEMWEs is limited due to relatively higher capital and operating costs than hydrocarbon reforming [1]. The higher costs of current commercial electrolyzers are due in part to (1) the use of significant quantities of expensive materials (Pt and Ir electrocatalysts and perfluorinated ion-conducting polymers) within the CCMs, (2) insufficient operating performance and durability of the CCMs (especially with low electrocatalyst loadings), and (3) high manufacturing costs of the CCM and constituent components due in part to non-optimized processes and low production volumes.

In this project, we propose to develop reduced-cost manufacturing techniques capable of fabricating PEMWE CCMs with state-of-the-art performance and ultra-low catalyst loadings. In combination, the higher manufacturing rates, ultra-low catalyst loadings, and high performance may address the three key cost barriers above and may enable significant decreases in both electrolyzer system capital costs and hydrogen production costs. If project targets are achieved, the resultant CCMs will be produced with an overall process with a 6x reduction in cumulative manufacturing time (minutes per m² of CCM produced) relative to the baseline process used prior to project initiation. Additionally, the CCM production processes will be demonstrated at widths of 0.5 m, capable of being integrated into next-generation, MW-scale large area water electrolyzer stacks. The CCMs will yield state-of-the-art performance (≥ 2 A/cm² at 1.75 V with 100 micron thick membranes, evaluated at 80°C cell temperature), enabling low-cost hydrogen and smaller, higher-power-density stacks with reduced capital costs. Finally, the CCMs will have ultra-low total catalyst loadings of ≤ 0.50 mg/cm² of PGM, enabling significant cost reductions relative to commercial technology while addressing an additional primary barrier for PEMWE water electrolyzers: limited global Ir supplies.

APPROACH

In this project, our approach is to develop advanced manufacturing processes for PEMWE components and CCMs through leveraging novel roll-to-roll precision process technologies at 3M Company, roll-to-roll electrode development at the National Renewable Energy Laboratory (NREL), and state-of-the-art material characterization capabilities. Initial development work will occur at laboratory and pilot scale, with the objective of identifying scalable process methods that enable reliable production of components at approximately 3x lineal rates, relative to the baseline process, at 0.25 m wide. Pilot-scale validated processes will then be transferred to production-scale equipment capable of fabricating CCMs at 0.50 m wide and at similar (or faster) lineal rates as pilot-scale, achieving the target 6x improvement in areal process rate.

Additionally, the project CCMs will achieve state-of-the-art performance and loading targets by integrating advanced components with higher performance and lower catalyst loading capability than many competitive materials and previous 3M technology. The keys to the improved performance and reduced loadings are utilization of 3M low equivalent weight (EW) perfluorosulfonic acid (PFSA) ionomers, PFSA membranes, nanostructured thin film (NSTF) powder catalysts, and dispersed NSTF electrodes. In laboratory testing, the NSTF powder catalyst and dispersed NSTF electrodes have improved cell performance by approximately 40 mV at 2 A/cm² relative to previous, “traditional” NSTF electrodes [2] with similar Ir loadings (Figure 1).

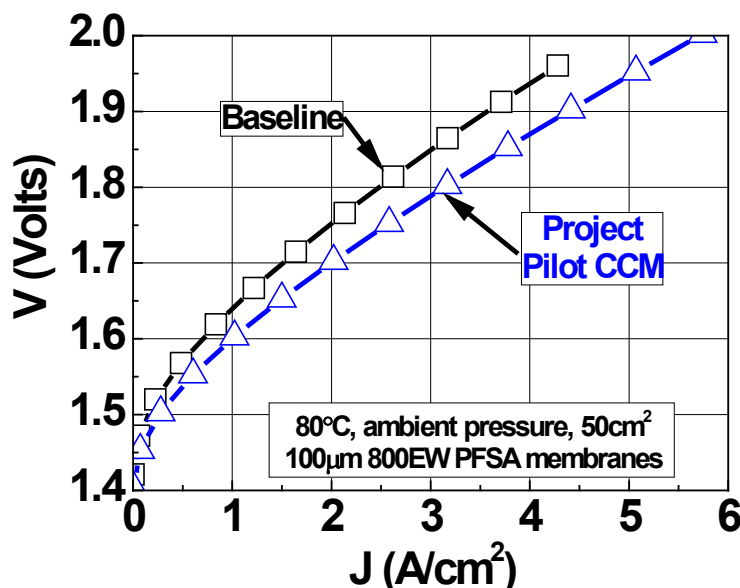


Figure 1. PEMWE polarization performance of pre-project baseline and project status pilot-scale CCMs. The baseline CCM anode and cathode are traditional Ir/NSTF and Pt/NSTF electrodes with 0.50 mg-Ir/cm² and 0.25 mg-Pt/cm², respectively. The project status CCM anode and cathode are dispersed NSTF electrodes with 0.49 mg-Ir/cm² and 0.10 mg-Pt/cm². Both CCMs contain 3M 800EW PFSA 100 μm membranes. Polarization curves measured at 80 °C cell temperature, 75 mL/min anode water flow, ambient pressure, 50 cm² cells, with 5 min dwell times per point.

RESULTS

Project Status

The primary objective this year was to identify, develop, and demonstrate pilot-scale processes suitable for production of high-performance, ultra-low-PGM-loading 3M PEMWE CCMs and all constituent components. The primary input raw materials for the overall process are commercially available 3M ionomer powder, Ir and Pt sputter targets, and perylene red 149 powder. The processes developed here will transform the input raw materials into the required output subcomponents: water electrolyzer membranes (consisting of 3M PFSA 800EW ionomer); oxygen evolution reaction and hydrogen evolution catalyst powders (consisting of 3M NSTF Ir and Pt powder catalysts); and anode and cathode electrodes (3M ionomer and NSTF powder catalysts). The final CCMs are fabricated by integration of the anode electrode, membrane, and cathode electrode.

Significant progress has been made toward the formal project targets, which consist of process rate, process width, PEMWE performance at three cell voltages, and total PGM loading, as summarized in Table 1. The CCM areal production rate status is currently 4.3x vs. the baseline process, calculated based on pilot process trials of each process step at demonstrated rates, which includes the CCM and all constituent processes listed above. The demonstrated CCM width is 0.25 m wide.

A CCM was fabricated with the improved processes (at 3.1x areal rate, 0.25 m wide), and the resultant PEMWE performance significantly exceeded the project targets. PEMWE polarization curves measured with the baseline and the pilot-scale CCMs are shown in Figure 1. The CCM produced 0.27, 2.6, and 5.0 A/cm² at

1.50, 1.75, and 1.95 V, respectively, which exceed final project targets and are improvements of 63%, 31%, and 20% relative to the baseline CCM. The 2019 status CCM's total PGM loading was 0.59 mg/cm², which is an improvement relative to the baseline CCM loading of 0.75 mg/cm² but higher than the project target of 0.50 mg/cm².

During the first project budget period, which occurred during FY 2019, the primary goal was demonstration of an overall CCM fabrication process of a 0.25 m wide CCM at 2x baseline linear rate. This goal was exceeded, with an overall CCM process demonstrated at 0.25 m wide and at a 2.9x linear rate relative to baseline.

Table 1. Project Status

Project Target	Target Value	Baseline	2019 Status
CCM Production Rate (m ² per cumulative process time)	>6x baseline	1 ^a	4.3 ^b
CCM Width (m)	>0.50	0.20 ^a	0.25 ^c
Current Density at 1.50 V (A/cm ²)	>0.25	0.16 ^a	0.27 ^c
Current Density at 1.75 V (A/cm ²)	>2	1.98 ^a	2.6 ^c
Current Density at 1.95 V (A/cm ²)	>4	4.2 ^a	5.0 ^c
Total PGM Loading (mg/cm ²)	<0.50	0.75 ^a	0.59 ^c

^a Baseline NSTF PEMWE CCM (0.50 mg-Ir/cm² and 0.25 mg-Pt/cm² traditional NSTF electrodes, 3M PFSA 800EW 100 μm).

^b Cumulative CCM pilot fabrication rate at 0.25 m web width with demonstrated processes.

^c Pilot-scale CCM (0.49 mg-Ir/cm² and 0.10 mg-Pt/cm² dispersed NSTF electrodes, 3M PFSA 800EW 100 μm) produced at 3.1x areal rate and 0.25 m wide.

Membrane Development

Significant progress has been made toward development of improved processes used for fabricating electrolyzer membranes. The work consisted of several process experiments that occurred at laboratory, pilot, and production scale. The result was demonstration of an overall PEMWE membrane (100 μm thick and 0.30 m wide) fabrication process with an areal process rate of up to 16.7x relative to the baseline CCM membrane process, which significantly exceeded project process targets for this component.

One key development area was identification of membrane dispersion coating and drying process methods that enable facile production of 100 μm thick electrolyzer membranes. Due to limited solubility of the ionomer in typical alcohol/water solvent systems, the as-cast wet membrane films are relatively thick and contain significant amounts of solvent, which must be removed during the drying step. Evaporative solvent removal can result in significant surface drying defects due to the requirement of rapid solvent evaporation from the film surface at meaningful production rates. Additionally, removal of the solvent during drying can induce severe in-plane film contraction, which can induce very severe curl of the membrane, which is exacerbated as the membrane thickness and width increase. Figure 2 (left) is an example of a water electrolyzer membrane (on polyimide substrate) using an initial set of coating and drying conditions, where the 5-inch-wide membrane film curled severely during the process. Figure 2 (right) is a 12-inch-wide membrane (on polyimide substrate) produced using an improved fabrication processes developed within this project, which has relatively much lower curl and lays flat.

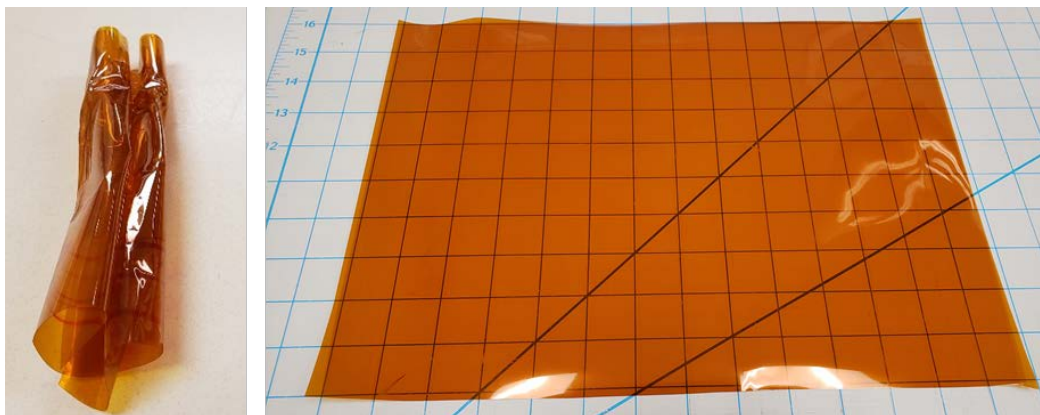


Figure 2. Left: Highly curled water electrolyzer membrane on polyimide liner, ca. 5-inch-wide coating. Right: 12-inch-wide, low-curl water electrolyzer membrane on 14-inch-wide polyimide liner. Both membranes are approximately 100 μm thick.

NSTF Powder Catalyst and Dispersed Electrode Development

NSTF catalyst fabrication has typically consisted of roll-to-roll (1) vacuum sublimation deposition of a thin film of perylene red 149 (PR149) onto a substrate, (2) vacuum annealing to convert the PR149 thin film to an array of oriented, microstructured whiskers used as catalyst supports, and (3) vacuum deposition (i.e., physical vapor deposition) of catalytic metals (e.g., Ir, Pt) onto the PR149 whisker supports to form nanostructured catalysts [2]. The result of this typical process is a roll-good web of a NSTF electrode, consisting of catalyst dispersed uniformly across the substrate, suitable for direct formation of a CCM with “traditional” NSTF electrodes by thermal lamination [2]. In this project, the above catalyst and electrode process is modified to enable fabrication of NSTF powder catalysts (Figure 3, left) and dispersed NSTF electrodes. As a result of the catalyst and electrode process development conducted to date, the overall catalyst and electrode areal fabrication rates for the anode and cathode are 2.2x and 2.3x of the baseline process rates, respectively.

A first key area focused on process development for NSTF catalyst powder. Key goals included increasing the rates and batch sizes of the vacuum processes (1–3 above) and up-scaling of the powder catalyst process(es). Several process experiments were conducted on a production vacuum coater to develop improved understanding of process variable sensitivities and limits for the PR149 deposition, PR149 annealing, and metal deposition. Experiments determined that the PR149 deposition, annealing, and metallization steps could be conducted at factors at or exceeding 4x the baseline rate, with resultant support whiskers retaining the expected morphology (Figure 3, right). In separate experiments, the whisker support process was demonstrated feasible with batch sizes up to 2.5x the baseline batch size.

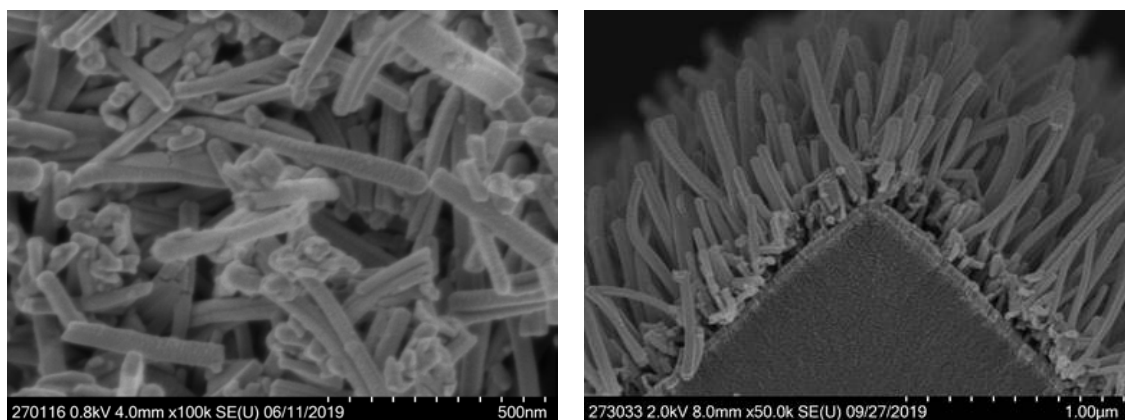


Figure 3. Left: Scanning electron microscopy (SEM) micrograph of NSTF catalyst powder. Right: SEM micrograph of catalyzed PR149 support whiskers with 4x faster fabrication rate.

A batch of high-production-rate Ir/NSTF catalyst was fabricated and its electrochemical surface area was assessed by in-cell cyclic voltammetry. Due to the (largely) metallic nature of the as-fabricated Ir/NSTF catalyst, the surface area can be approximately estimated by integration of the hydrogen underpotential deposition (H_{UPD}) charge and assuming a specific charge density ($220 \mu\text{C}$ per cm^2 of Pt assumed here, similar to polycrystalline Pt). The electrochemical surface area measurements indicated that the high-rate Ir/NSTF catalyst yielded specific surface areas in trend with the baseline process (Figure 4). The same high-rate Ir/NSTF catalyst was integrated into the Project Status Pilot CCM and yielded expected oxygen evolution performance as shown in Figure 1.

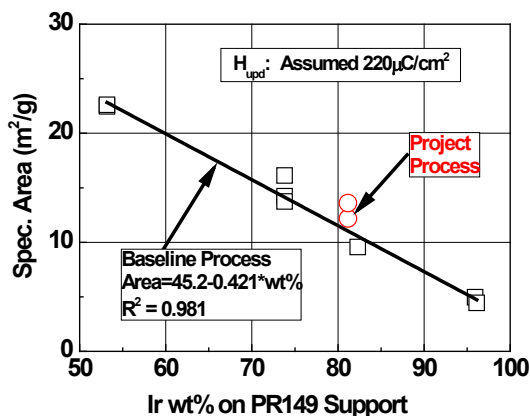


Figure 4. Specific area of Ir/NSTF catalysts with baseline or high-rate project processes.

Initial dispersed NSTF electrode development at 3M and NREL consisted of laboratory-scale coating experiments, ink rheology studies, application of a coating model to determine entitlement dispersion coating thicknesses and rates, and formulation sensitivity studies. Figure 5 summarizes the impact of a monotonic solvent system variation on the resultant dispersed Ir/NSTF anode electrode Ir loading uniformity and reproducibility, conducted at NREL. Solvent system #4 enabled electrode coatings within 5% of the loading target and with areal Ir uniformity less than 6% standard deviation. In comparison, solvent systems #5 and #6 had poorer reproducibility than solvent system #4, and solvent system #6 was much less reproducible.

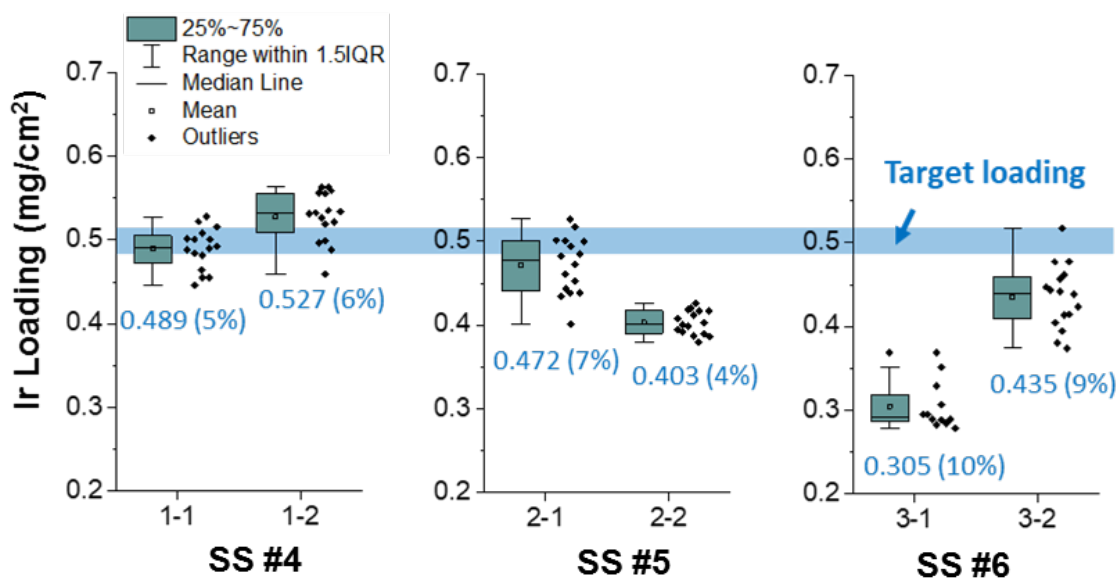


Figure 5. Lab-scale Ir/NSTF electrode loading uniformity and reproducibility as a function of solvent system.

In PEMWE cell tests, the performance of the dispersed Ir/NSTF electrodes was only modestly sensitive to the ranges of formulation variables assessed at 3M. Figure 6 (left) summarizes the cell voltage at 2 A/cm² for electrodes coated with three different ionomer:catalyst ratios and two different solvent systems. Overall, the voltage varied by ~20 mV across the experiment formulation variables, but no statistically significant variation with formulation was determined. The performance of the dispersed Ir/NSTF anode electrodes was also found to be highly robust to electrode coating method and rate, with essentially equivalent performance obtained with electrodes coated at 3M at laboratory scale, at NREL at laboratory scale, or at 3M at pilot scale with accelerated fabrication rates (Figure 6, right).

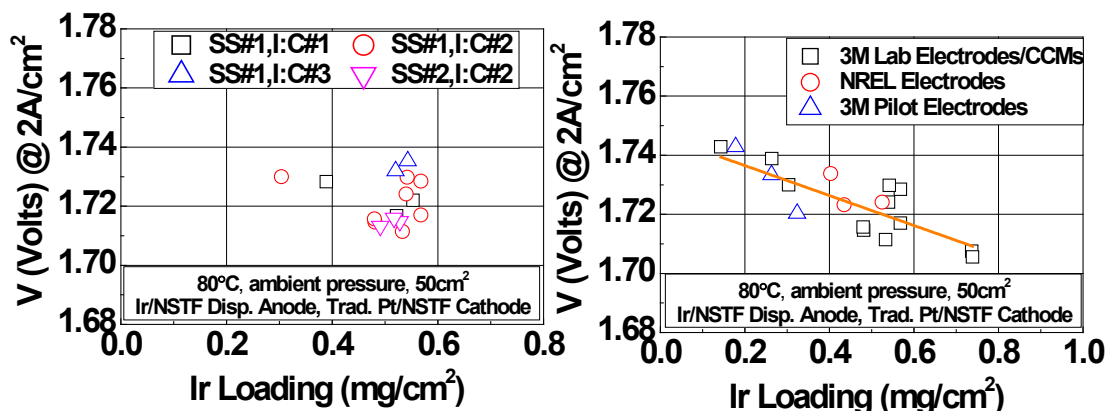


Figure 6. PEMWE performance in electrode formulation studies. Left: Dispersed Ir/NSTF anode electrodes with three different ionomer:catalyst ratios and two different solvent systems. Right: Dispersed Ir/NSTF anode electrodes fabricated within 3M laboratory, NREL laboratory, or 3M pilot scale. Electrodes tested at 3M in 50 cm² cells at 80 °C, ambient pressure, with traditional NSTF cathodes (0.25 mg-Pt/cm²) and 100- μ m-thick 3M PFSA 800EW membranes.

In addition to the formulation and process robustness noted above, both lab- and pilot-coated anode electrodes were found to effectively utilize the Ir/NSTF powder catalyst across a range of loadings, including ultra-low Ir loadings of 0.15 mg/cm². Figure 7 compares the PEMWE polarization curves for lab- and pilot-coated electrodes with Ir loadings ranging from 0.15 to 0.32 mg/cm². As loadings were varied through the range tested to date, polarization curves were essentially parallel to each other and shifted slightly as expected due to the absolute oxygen evolution reaction activity variation with loading. Additional experiments are planned to determine the performance sensitivity at further reduced loadings and to assess the durability of ultra-low-loaded anode electrodes.

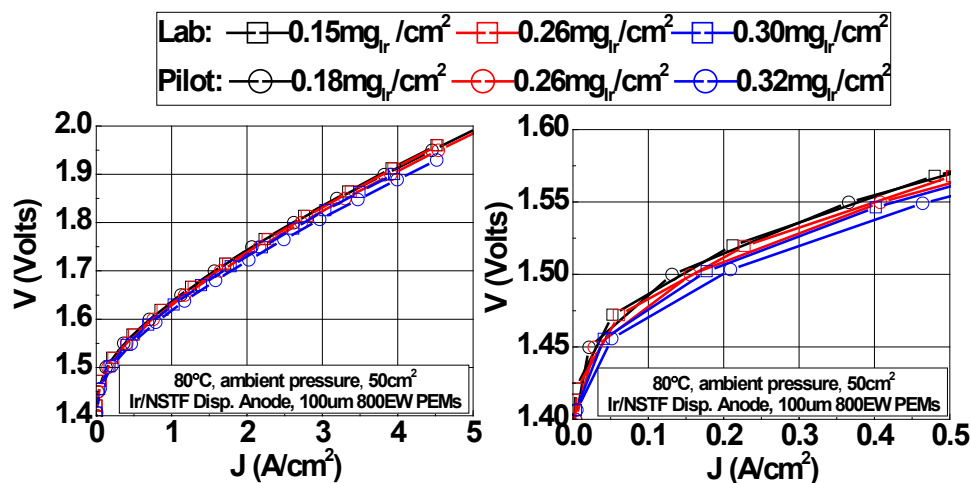


Figure 7. PEMWE polarization curves of laboratory- vs. pilot-coated dispersed Ir/NSTF electrodes. Left: Full range polarization curve. Right: Kinetic region of polarization curves. Electrodes tested in 50 cm² cells at 80 °C, ambient pressure, with traditional NSTF cathodes (0.25 mg-Pt/cm²) and 100- μ m-thick 3M PFSA 800EW membranes.

CCM Development

To date, CCM development has consisted of process experiments at laboratory and pilot scale, with the objective of defining sets of process conditions that result in acceptable performance and quality at project-compatible fabrication rates. Figure 8 (left) compares the PEMWE performance of laboratory, baseline fabricated CCMs to pilot process CCMs fabricated at rates of 1.4x, 4.1x, and 6.8x the baseline areal rates. Over similar anode loading ranges, laboratory and pilot CCMs yielded similar cell voltage at 2.0 A/cm². One caveat to the comparison is that different cathode electrodes were used between the lab and pilot CCMs (lab: traditional Pt/NSTF electrodes with 0.25 mg-Pt/cm² loadings; pilot: dispersed Pt/C electrodes with 0.05 mg-Pt/cm²). However, the use of different cathode electrodes and loadings within this range is not expected to impact the voltage by more than a few millivolts due to the very fast kinetics of the cathode hydrogen evolution reaction.

Initial stack integration activities of project CCMs has been initiated at Giner Labs in preparation for stack testing next year. CCMs with 50 cm² active area were fabricated at 3M and tested at both 3M and Giner Labs. The CCMs contained identical dispersed NSTF anode electrodes (0.32 mg-Ir/cm²), traditional NSTF cathode electrodes (0.25 mg-Pt/cm²), and 3M 800EW PFSA 100- μ m-thick membranes. Polarization curve performances of replicate MEAs tested at each site are shown in Figure 8 (right). At current densities of 0–1 A/cm², the performance measured at 3M was appreciably higher than that measured at Giner Labs; possible factors include differences in cell assembly and test cell type. However, at current densities of 2 A/cm² or higher, the measured performances at each site were similar and perhaps within measurement error. At 2 A/cm², the average cell voltage measured at 3M was 15 mV lower than measured at Giner, an acceptable difference at this stage of the project.

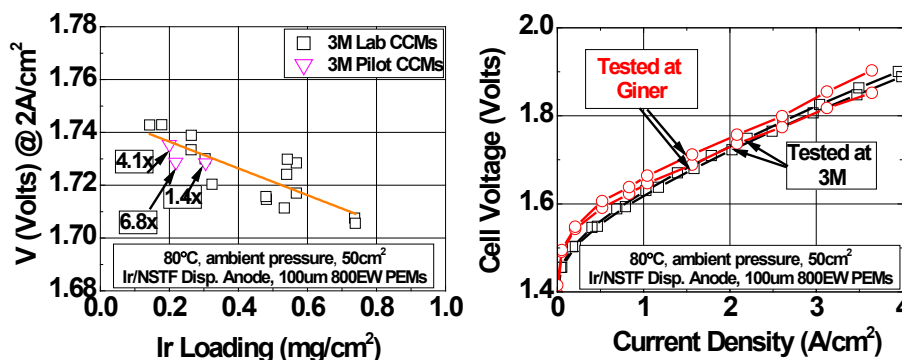


Figure 8. Left: PEMWE performance of CCMs fabricated at laboratory or pilot scale. Right: PEMWE polarization curves measured at 3M or Giner Labs.

Lastly, durability assessments of project CCMs and components has been initiated. Figure 9 summarizes a durability test conducted with a laboratory-fabricated CCM comprising a dispersed Ir/NSTF anode (0.42 mg/cm²), a traditional Pt/NSTF cathode (0.25 mg/cm²), and a 3M 800EW 100 μ m PFSA membrane. The CCM was tested at 2 A/cm² in a 50 cm² cell for approximately 2,000 hours at 80°C cell temperature and ambient pressures, with polarization curves recorded every 500 hours. Using the voltage at the end of each 500-hour steady-state test, the cell voltage *decreased* approximately 8 mV between 500 hours and 1,950 hours, indicating that the performance improved slightly with time. The cause for the increasing performance with time is not currently understood and is being investigated outside of this project. This initial result is suggestive that the decay rate of the NSTF powder catalyst and electrode technology may be considerably lower than the <4 μ V/h DOE target. Durability assessments of pilot- and production-scale CCMs will commence next year at both 3M and Giner Labs.

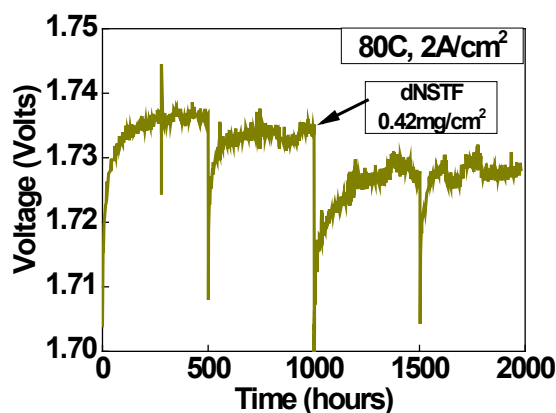


Figure 9. PEMWE durability test of dispersed Ir/NSTF anode with 0.42 mg-Ir/cm² loading

CONCLUSIONS AND UPCOMING ACTIVITIES

Laboratory- and pilot-scale process development for fabrication of PEMWE CCMs and constituent components has resulted in substantial reductions in process time, exceeding the goals for this year. On an overall CCM process basis, lineal and areal process rates have been improved 2.9x and 4.3x, respectively, through integration of advanced processing methods coupled with state-of-the-art characterization. The process routes identified have demonstrated capability of producing CCMs at 0.25 m wide (vs. 0.20 m baseline) and are currently estimated to be feasible at the 0.50-m-wide project target with additional process development. Additionally, the CCMs and constituent components fabricated with the pilot-scale processes yield state-of-the-art performance, exceeding final project targets, but with modestly higher catalyst PGM loadings than the allowable target level.

Future work will consist of additional process development with the primary focus of scaling the pilot-scale processes to production scale, capable of producing CCM at 0.50 m wide at 6x areal fabrication rate and meeting project performance and loading targets. The resultant CCM will be integrated into a short stack and evaluated for performance and durability at Giner Labs.

FY 2019 PUBLICATIONS/PRESENTATIONS

1. A. Steinbach, G. Thoma, A. Haug, M. Lindell, K. Struk, F. Sun, K. Lewinski, M. Yandrasits, M. Kurkowski, and D. Gobran, “Low-cost, High Performance Catalyst Coated Membranes for PEM Water Electrolyzers,” poster presentation at the DOE Hydrogen and Fuel Cells Program Annual Merit Review and Peer Evaluation Meeting, Washington, DC, April 2019.

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1. Hydrogen production and capital costs from U.S. Department of Energy H₂A Production Models. Current Forecourt Hydrogen Production from Natural Gas (1,500 kg per day) v. 3.101.201, Current Forecourt Hydrogen Production from PEM Electrolysis v. 3.101, Future Forecourt Hydrogen Production from PEM Electrolysis version 3.101. Accessed March 2018: https://www.hydrogen.energy.gov/h2a_prod_studies.html.
2. M.K. Debe, “Tutorial on the Fundamental Characteristics and Practical Properties of Nanostructured Thin Film (NSTF) Catalysts,” *J. Electrochem. Soc.* 160, no. 6: F522–F534.