
Fuel Cell Membrane Electrode Assemblies with Platinum-Group-Metal-Free Nanofiber Cathodes

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Subcontractors:

- Pajarito Powder, LLC, Albuquerque, NM
- eSpin Technologies, Inc., Chattanooga, TN

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Overall Objectives

- Fabricate, characterize, and evaluate nanofiber mat electrode membrane-electrode-assemblies (MEAs) with platinum group metal (PGM)-free oxygen reduction reaction (ORR) cathode catalysts for H₂/air fuel cells.
- Use state-of-the art catalyst powders provided by Pajarito Power, LLC.
- Generate useful correlations and insightful understandings regarding the relationship between fiber electrode composition, morphology, and structure, the hydrophobicity/hydrophilicity of the cathode binder, and MEA performance (both short-term and long-term).
- Identify electrospun nanofiber mat cathode/anode composition and morphology for MEAs that meet DOE's 2020 current density and durability targets.

Fiscal Year (FY) 2019 Objectives

- Prepare PGM-free catalyst powders that are targeted in terms of size, activity, efficiency,

and surface functionality for incorporation in submicron-diameter electrospun fibers.

- Identify the electrospinning conditions to fabricate nanofiber mat cathodes using PGM-free catalyst powder with a blended polymer binder composed of perfluorosulfonic acid (PFSA) ionomer and polyvinylidene fluoride (PVDF).
- Characterize and evaluate the short-term and long-term performance of nanofiber mat electrodes and MEAs with PGM-free ORR cathode catalysts in a H₂/air fuel cell.

Technical Barriers

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

- (A) Power density (fabricating MEAs that generate high power at a PGM-free cathode catalyst loading <4.0 mg/cm²).
- (B) Durability (aging and degradation of fuel cell electrodes).
- (C) Cost (lowering the material and manufacturing costs of high-performance electrodes and MEAs).

Technical Targets

This project is conducting experimental studies on the fabrication and performance of nanofiber electrode H₂/O₂ and H₂/air fuel cell MEAs that utilize a PGM-free cathode catalyst. Insights gained from these studies will be applied toward the design of MEAs that meet the following DOE targets:

- Meet or exceed a MEA current density of 0.044 A/cm² at 0.9 V when tested under H₂/O₂.
- Achieve cathode durability in an MEA of 5,000 hours under cycling conditions.

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

FY 2019 Accomplishments

- VariPore and metal organic framework (MOF)-based PGM-free catalysts were synthesized at Pajarito Powder and delivered to Vanderbilt University for nanofiber electrospinning experiments.
- Nanofiber mat cathodes with hard template PGM-free catalyst were successfully electrospun, with a series of binders: (1) Nafion/PVDF, where the Nafion/PVDF weight ratio varied from 1/1 to 3/1, and (2) Nafion/poly(ethylene oxide) (PEO).
- MEAs with the nanofiber mat cathodes were prepared and tested in H_2/O_2 and H_2 /air fuel cells.
- The initial and long-term (50 hours) power output of MEAs with nanofiber and conventional slurry cathodes was observed.
- For PGM-free catalyst nanofiber cathode MEAs with Nafion/PVDF binders, where the weight ratio of Nafion to PVDF is $<4/1$, constant power output was observed for 50 hours vs. a 45% power decrease for a conventional slurry MEA with the same catalyst and a neat Nafion binder.
- The use of Nafion/PVDF binder in a PGM-free nanofiber cathode lowered the power output but improved durability, with no loss in power for more than 50 hours.

INTRODUCTION

One strategy for lowering the platinum content in proton exchange membrane fuel cells is to use inexpensive PGM-free powders as the cathode catalyst. PGM-free ORR catalysts are typically carbon-based powders with metal/nitrogen/carbon (Me/N_x/C_y) catalytic surface sites, where the metal ion is often cobalt or iron. The ORR activity of these catalysts is lower than that of Pt, but they can be used at higher loadings to compensate for slower oxygen reduction kinetics. Prior studies have reported poor durability of MEAs with PGM-free catalysts in hydrogen/air fuel cells due to a combination of factors including a loss of the carbon support material; loss of metal ions from the catalyst, which lowers catalytic activity and binder conductivity; water flooding, which impedes oxygen transport; and the generation of peroxide species, which degrades the catalyst and binder.

Pintauro and co-workers have successfully electrospun nanofiber mat electrodes using Pt/C catalyst powder and binders of Nafion + poly(acrylic acid) or Nafion + PVDF [1]. When incorporated into an MEA, fiber mat cathodes with a carbon-supported Pt or Pt-alloy catalyst powder work exceptionally well with high power and excellent durability. Preliminary nanofiber electrode MEA tests with a PGM-free cathode catalyst and a hydrophobic Nafion + PVDF binder showed stable long-term power output, although the initial power densities were reduced as compared to those with a neat Nafion binder [2]. In the present project, highly active PGM-free oxygen reduction reaction catalysts developed at Pajarito Powder, LLC, have been integrated with advanced nanoparticle/polymer electrospinning for the fabrication of high power and durable PGM-free fuel cell cathodes that meet DOE's 2020 performance targets when integrated into a MEA.

APPROACH

The research approach for this project is as follows: (1) prepare PGM-free catalyst powders that are targeted in terms of size, activity, and surface functionality for incorporation in submicron-diameter electrospun fibers, and (2) fabricate, characterize, and evaluate nanofiber mat cathodes and MEAs with PGM-free ORR cathode catalysts for H_2 /air fuel cells. PGM-free nanofiber cathodes will be prepared with: (1) a catalyst loading of 0.5–3.0 mg/cm²; (2) different catalyst binders, either Nafion + PEO or Nafion + PVDF, where the latter is used to adjust the hydrophobicity of the binder; (3) different catalyst/binder weight ratios in the cathode fibers; and (4) different cathode mat thicknesses and fiber mat electrode porosities. The correct choice of catalyst powder and nanofiber catalyst binder (blend of hydrophilic [Nafion] and hydrophobic [PVDF] polymers) will be identified in terms of: (1) spinning well-formed nanofibers with a good distribution of catalyst particles along the fiber length, and (2) creating a PGM-free fiber mat cathode MEA that generates high power in a hydrogen/air fuel cell, with little or no power loss during a long-term constant current or constant voltage durability tests.

RESULTS

Nanofiber cathodes were prepared with VariPore baseline Fe-based catalyst powder supplied by Pajarito Powder. Figure 1 shows a scanning electron microscope (SEM) image of electrospun mats with a catalyst/Nafion/PVDF fiber composition of 50:33:17 wt %.

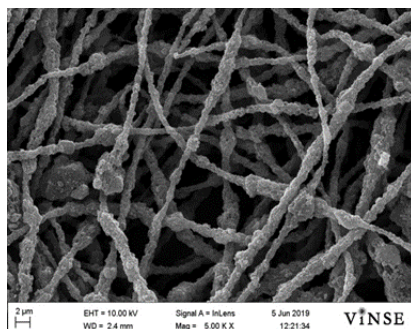


Figure 1. Top-down SEM image of PGM-free catalyst nanofibers with a 2/1 Nafion/PVDF binder

The effect of cathode binder composition on initial fuel cell performance and cathode durability after a constant voltage hold (at 0.5 V) was evaluated with two Nafion/PVDF weight ratio binders (2/1 and 3/1 Nafion/PVDF). Figure 2a compares beginning-of-life (initial) polarization curves for the two fiber cathode MEAs and a sprayed cathode MEA with neat Nafion binder (from Pajarito Powder). The initial power output of the nanofiber cathode MEAs with Nafion/PVDF binder was lower than that of the neat Nafion sprayed MEA. After 40 hours of constant voltage operation (0.5 V), the performance of both nanofiber cathode MEAs improved, as shown in Figure 2b. The maximum power densities are listed in Table 1.

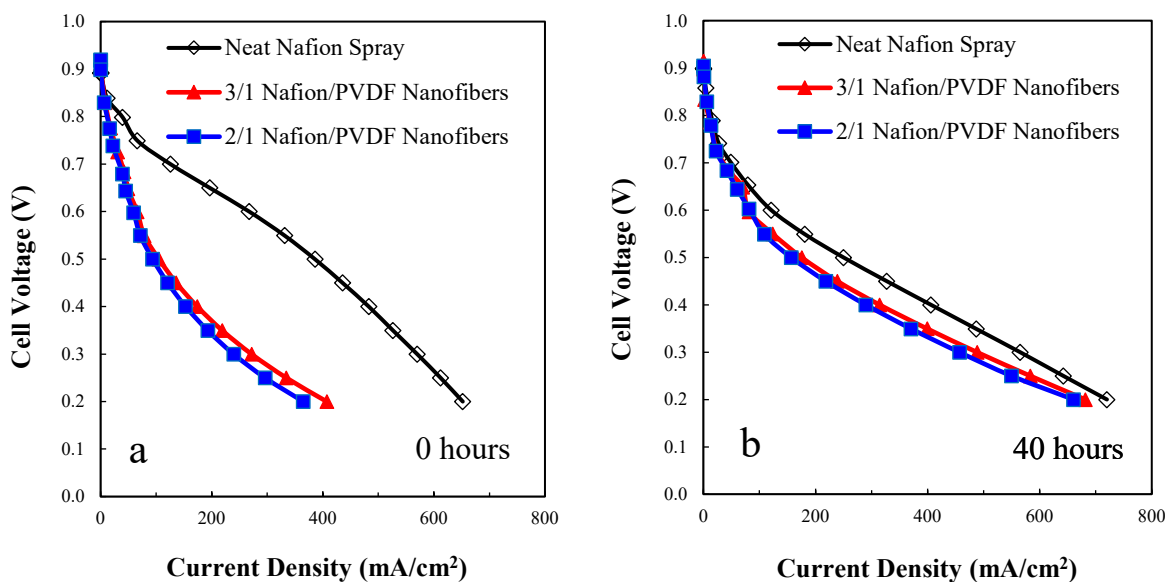


Figure 2. H₂/air fuel cell polarization curves for nanofiber and sprayed cathode MEAs with a PGM-free cathode catalyst. (a) Initial fuel cell performance and (b) fuel cell performance after 40 hours of constant voltage operation at 0.5 V. Cathode catalyst loading was 3.0 mg/cm² for all MEAs. A sprayed Pt/C anode was used for all MEAs at 0.1 mg_{Pt}/cm², with neat Nafion binder. Fuel cell operating conditions: 80 °C, 100% RH, 1 atm backpressure, and 125/500 sccm H₂/air.

Table 1. Summary of H₂/Air Fuel Cell Performance for MEAs with Nanofiber Mat or Sprayed Gas Diffusion Electrode Cathodes with PGM-Free Catalyst (fuel cell data at 80 °C, 100% RH, 1 atm backpressure, and 125/500 sccm H₂/air)

Operation Time	Cathode Binder (w:w)	Max. Power Density (mW/cm ²)
0 hours	Neat Nafion spray	196
	3/1 Nafion/PVDF nanofibers	84
	2/1 Nafion/PVDF nanofibers	74
40 hours	Neat Nafion spray	170
	3/1 Nafion/PVDF nanofibers	146
	2/1 Nafion/PVDF nanofibers	137

The long-term power output of three nanofiber cathode MEAs and one sprayed cathode MEA with neat Nafion is shown in Figure 3. The initial high performance of the sprayed cathode MEA degraded over time, with nearly a 50% decrease in power density at 0.5 V after 50 hours. The initial power output of the nanofiber cathode MEA with a Nafion/PEO binder was comparable to that of the sprayed cathode MEA with neat Nafion binder. In contrast, the power output of the nanofiber cathode MEAs with a Nafion/PVDF binder increased after start-up and reached a maximum/constant power density after ca. 10 hours of operation. The more hydrophilic 3/1 Nafion/PVDF binder produced more power, as expected.

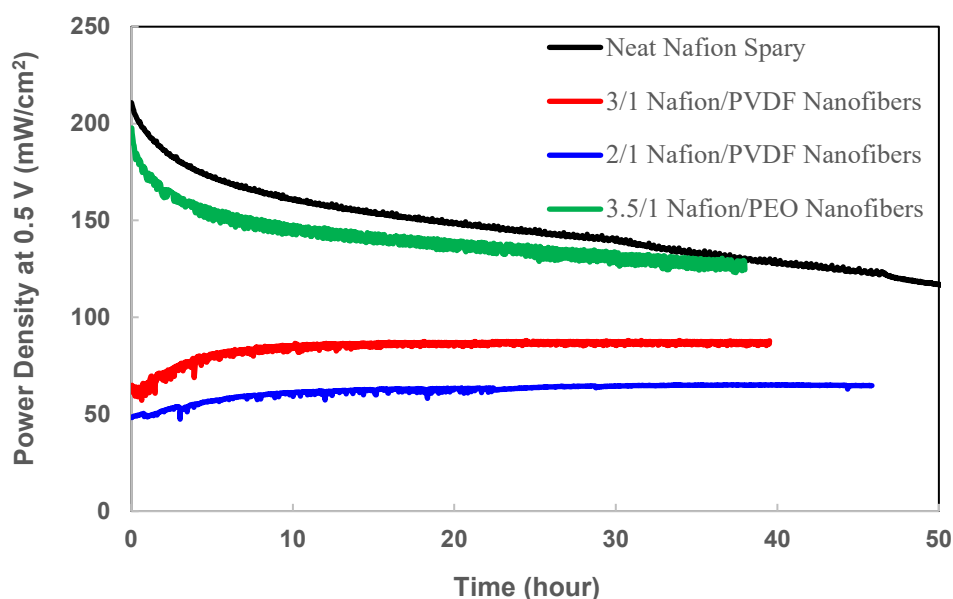


Figure 3. H₂/air fuel cell power density at 0.5 V vs. time for 40–50 hours with MEAs using PGM-free catalyst at 3.0 mg/cm² and either a nanofiber cathode (with a 2/1 Nafion/PVDF, 3/1 Nafion/PVDF, or Nafion/PEO binder) or a sprayed cathode with neat Nafion. Fuel cell operating conditions: 80 °C, 100% RH, 1 atm backpressure, 125/500 sccm H₂/air.

The effect of cathode catalyst loading on long-term power output for nanofiber cathodes at different catalyst loadings for a fixed binder composition of 3/1 Nafion/PVDF is shown in Figure 4. As expected, the power density increased by a factor of ~2 when the cathode catalyst loading was increased from 0.73 to 1.5 mg/cm². Further increasing the cathode catalyst loading to 3.0 mg/cm² produced only a small (~10%) increase in power for the nanofiber cathode MEA. These results indicate that a Nafion/PVDF binder cannot accommodate a high catalyst loaded (thick) fiber mat cathode, due presumably to the low proton conductivity of the blended Nafion/PVDF binder.

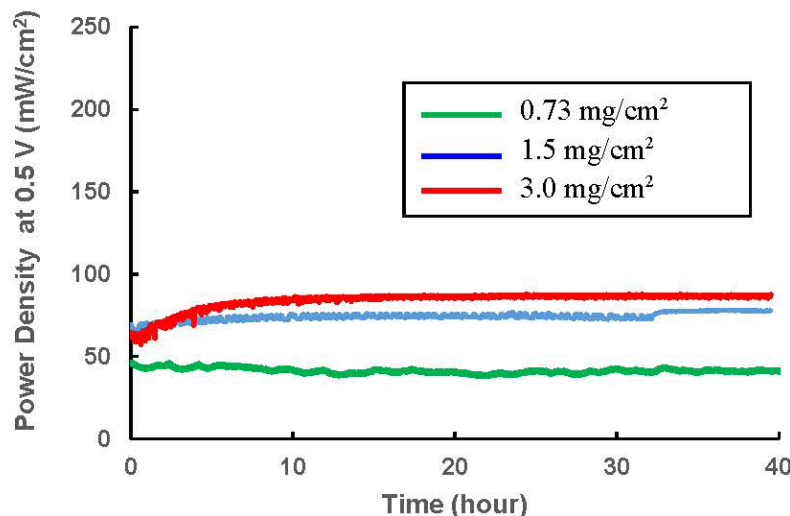


Figure 4. The effect of PGM-free cathode catalyst loading on long-term H₂/air fuel cell performance for a 3/1 Nafion/PVDF nanofiber cathode binder. Fuel cell operating conditions: 80 °C, 100% RH, at 1 atm backpressure, 125/500 sccm H₂/air.

The second catalyst thrust, using ZIF-8 MOF-based catalysts based on technology licensed from INRS, began with promising performance displayed in a slurry-based MEA and with the much-reduced catalyst particle sizes needed for electrospinning. Pajarito staff recovered the MOF-derived catalyst synthesis approach, which includes: (1) in-house synthesis of MOF using a mechanochemical synthesis approach at ~200 gram/batch scale, (2) mixing of the MOF with additional catalyst precursors including metal salts and complexing agents such as phenanthroline, (3) pyrolysis in an inert atmosphere, (4) catalyst particle attrition, (5) excess metal leaching to enhance stability, (6) ammonia pyrolysis, and (7) catalyst particle attrition. The resulting materials were characterized using a range of techniques, including agglomerate size analysis by dynamic light scattering. Briefly, 300 nm agglomerates were achieved using the MOF approach compared to 650 nm for the catalysts made using Pajarito's VariPore hard-templated catalysts, as shown in Figure 5. These catalysts were tested in slurry-based MEAs using gas diffusion electrode, with promising performance of over 20 mA/cm² achieved at the beginning and dropping to 10 mA/cm² over 2 hours of polarization curves in Figure 5 (right).

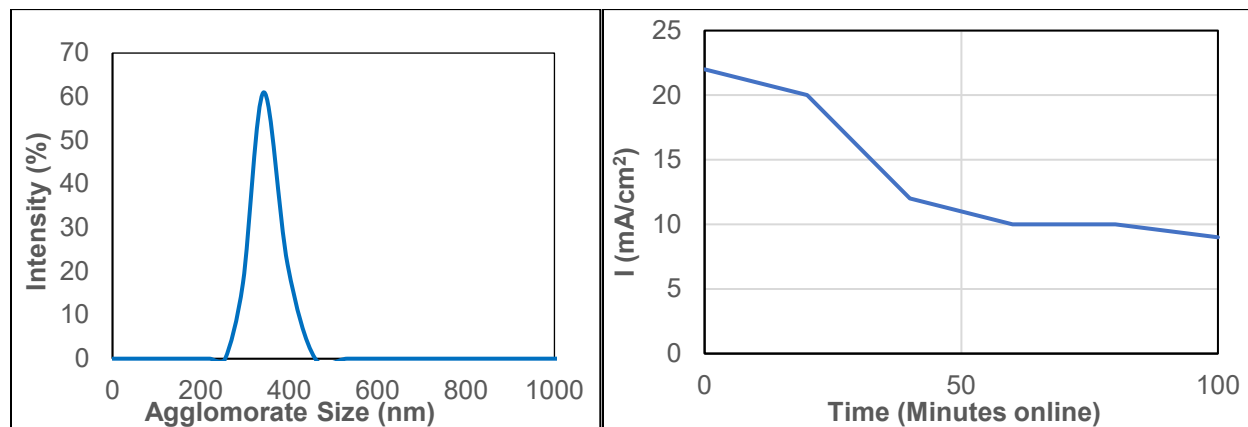


Figure 5. Left: MOF-derived catalyst agglomerate size measurement by dynamic light scattering, in dionized water, 0.2 wt % solids. Right: Summary of performance at 0.9 V from H₂/O₂ fuel cell polarization curves for sprayed cathode MEAs with a PGM-free cathode catalyst. Cathode catalyst loading was 2.0 mg/cm², a sprayed Pt/C anode was used at 0.1 mg_{Pt}/cm², with neat Nafion 1100 at 1:1 ionomer to catalyst ratio. Fuel cell operating conditions: 80 °C, 100% RH, 0.5 atm O₂ partial pressure, and 250/500 sccm H₂/O₂ in a 5 cm² serpentine cell.

CONCLUSIONS AND UPCOMING ACTIVITIES

Nanofiber cathode MEAs with a Nafion/PVDF binder stabilize the power output of a PGM-free cathode MEA in a H₂/air fuel cell. Excellent cathode durability is achieved for 50 hours of constant voltage operation at the cost of lower power output. There is no substantial increase in power with fiber cathode catalyst loading above 1.5 mg/cm², due presumably to the low proton conductivity of the Nafion/PVDF binder (i.e., the back of the cathode, furthest away from the anode, is not being utilized when the fiber mat is too thick). There is an increase in steady-state power output of a nanofiber cathode MEA (3.0 mg/cm² cathode loading) when the Nafion content in a Nafion/PVDF binder is increased from 1/1 to 3/1.

Future work will focus on: (1) synthesis and use of smaller MOF-based catalyst particles in electrospun nanofibers, (2) replacement of Nafion with low-equivalent-weight PFSA ionomers, (3) using different PVDF polymers in the fibers, and (4) determining the effect of catalyst/binder ratio on nanofiber cathode performance.

FY 2019 PUBLICATIONS/PRESENTATIONS

1. Peter N. Pintauro, “Nanofiber Electrodes in a Hydrogen/Air Fuel Cell: Cathode Durability Studies,” invited talk at Electrolysis and Fuel Cell Discussions: Towards Catalysts Free of Critical Raw Materials for Fuel Cells and Electrolyzers, La Grande Motte, France (September 15–18, 2019).

REFERENCES

1. M. Brodt, R. Wycisk, N. Dale, and P. Pintauro, “Power Output and Durability of Nanofiber Fuel Cell Cathodes with PVDF and Nafion/PVDF Binders,” *J. Electrochem. Soc.* 163 (2016): F401–F410.
2. J. Slack, B. Halevi, G. McCool, J. Li, R. Pavlicek, R. Wycisk, S. Mukerjee, and P. Pintauro, “Electrospun Fiber Mat Cathode with PGM-Free Catalyst Powder and Nafion/PVDF Binder,” *ChemElectroChem* 5 (2018): 1537–1542.