Fuel Cell Membrane-Electrode-Assemblies with PGM-free Nanofiber Cathodes

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Project ID: # FC304

Overview

Timeline and Budget

- Project Start Date: 3/1/2019
- Project End Date: 2/28/2021
- Percent complete: 0%

- Total Project Budget: $1,100,043
- Total Recipient Share: $220,009
- Total Federal Share: $880,034
- Total Funds Spent: $0

Barriers and Targets

- Barriers Addressed:
  - The use of thick cathodes (high catalyst loading, with significant O_2 and H^+ mass transfer resistance).
  - Catalyst durability associate with metal leaching.
- Targets: MEA metrics:
  - Meet or exceed activity of 0.044 A/cm^2 at 0.9 V when tested under H_2/O_2.
  - Achieve a durability of 5,000 hours under cycling conditions.

Partners

- Pajarito Powder, LLC
- eSpin Technologies, Inc.
- Project Lead: Peter N. Pintauro, Vanderbilt

Project Relevance and Objectives

Project Relevance:

- The VU/Pajarito/eSpin team seeks to better understand and further improve the power output and durability of nanofiber mat fuel cell cathodes and MEAs with state-of-the-art PGM-free catalyst powders.

- There is a critical need to transition from conventional fuel cell electrodes (e.g., prepared by slot die coating) to novel electrode structures to improve MEA performance and durability. This is especially true for PGM-free ORR catalysts, where cathode catalyst loading with be high (i.e., cathodes will be thick, with the potential problem of significant O_2 and H^+ mass transfer resistance) and where catalyst durability, associate with metal leaching, is a problem.

Project 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 H_2/air fuel cells.

- Use state-of-the art catalyst powders provided by Pajarito Power, LC.

- Generate useful correlations and insightful understandings regarding the relationship between fiber electrode composition 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 the DOE's 2020 current density and durability targets:
    - A current density of 0.044 A/cm^2 at 0.9 V when tested under H_2/O_2
    - A durability of 5,000 hours (where the latter metric is estimated during by extrapolating accelerated stress test results).

Approach

1. Prepare PGM-free catalyst powders that are targeted in terms of size, activity, and surface functionality for incorporation in sub-micron diameter electrospun fibers.
    1. Three generations of PGM-free Fe-N-C powders will be examined, with increasingly smaller particle size, using MOF-based and hard-templated families of catalysts.
2. Fabricate and evaluate nanofiber and sprayed cathode MEAs with PGM-free catalyst powders, with hydrophilic ionomer and hydrophobic blended ionomer/PVDF binders.
3. Optimize the nanofiber cathode mat composition and mat morphology to maximize fuel cell power output and durability
4. Work closely with the ElectroCat Energy Materials Network (EMN) consortium to probe the structure of electrospun particle/polymer fibers and fiber mat cathodes, quantify and minimize cathode degradation mechanisms, identify structure/function properties of materials and electrodes, and model fuel cell operation/performance.
5. Prepare and evaluate nanofiber mat electrodes using commercial electrospinning equipment.

Collaborations – Team Members

Vanderbilt University (Prime) led by Peter Pintauro (project PI) and Dr. Ryszard Wycisk (technical contact)

- Electrospin nanofiber mat electrodes with different catalysts and binders (identify the ink composition and electrospinning conditions to make well-formed fibers)
- Fabricate MEAs with nanofiber mat and sprayed electrodes and screening MEAs in fuel cell tests, including constant power operation and start-stop cycling and load cycling ASTs.

Pajarito Power, LLC (Sub) led by Dr. Barr Zulevi (Project co-PI)

- Design and Synthesize high activity PGM-free ORR catalyst powders for incorporation into sub-micron diameter electrospun particle/polymer fibers.
- Perform sprayed electrode MEA tests

eSpin Technology, Inc. (Sub) led by Dr. Jayesh Doshi (project co-PI)

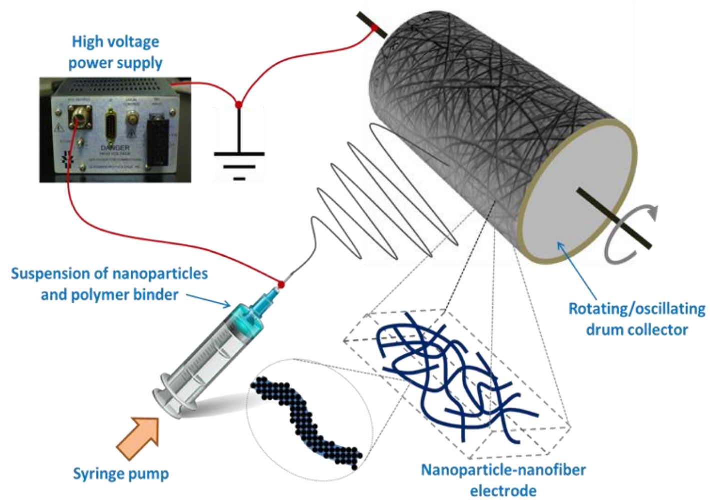
- Prepare electrospun particle/polymer cathode mats, based on the best formulations identified at Vanderbilt, which perform similar to Vanderbilt fiber cathodes in a fuel cell MEA.

Milestones and Go/No-Go Decision for Year 1

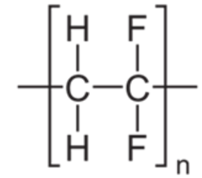
Milestone Description	Date
Deliver 10 g of Fe-MOF Gen-1 catalyst powders (50-300 nm diameter) to Vanderbilt and benchmark MEAs. Demonstrate that slurry electrode MEAs can generate at least 60 mA/cm^2 @ 0.8V	Q1
Demonstrate that nanofiber electrode MEAs with Gen-1 catalyst can generate at least 80 mA/cm2 @ 0.8V.	Q2
Deliver 10 g of Fe-MOF Gen-1A/B catalyst powders (50-300 nm diameter) to Vanderbilt and benchmark MEAs. Demonstrate that slurry electrode MEAs can generate at least 80 mA/cm^2 @ 0.8V	Q3
Demonstrate that nanofiber electrode MEAs with Gen-1 A/B catalyst can generate at least 100 mA/cm^2 @ 0.8V.	Q3
Go/No-Go Description	
For a nanofiber MEA with a PGM-free ORR catalyst cathode fabricated by electrospinning, demonstrate 0.025 A/cm^2 at 0.90 V (iR-corrected) in a H_2 /O_2 fuel cell operating at 1.0 bar partial pressure of O_2, 100% RH, and a cell temperature of 80 °C (≥5 cm^2 MEAs).	Q4

Prior Results: Electrospinning PGM-Free Catalyst into a Nanofiber Electrode

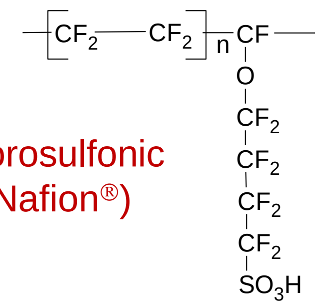
Pajarito PGM-free catalyst: ZIF-8 MOF (tetrahedrally-coordinated Zn ions, connected by imidazolate linkers) is ball milled with iron phenanthroline and then pyrolized in Ar and NH_3.

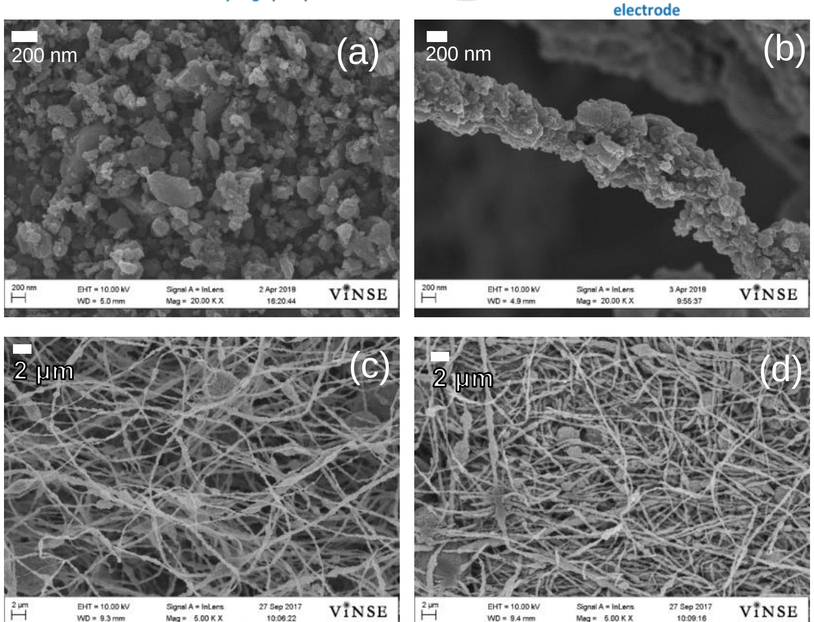


PVDF



PFSA = Perfluorosulfonic Acid Polymer (Nafion®)





SEM images of

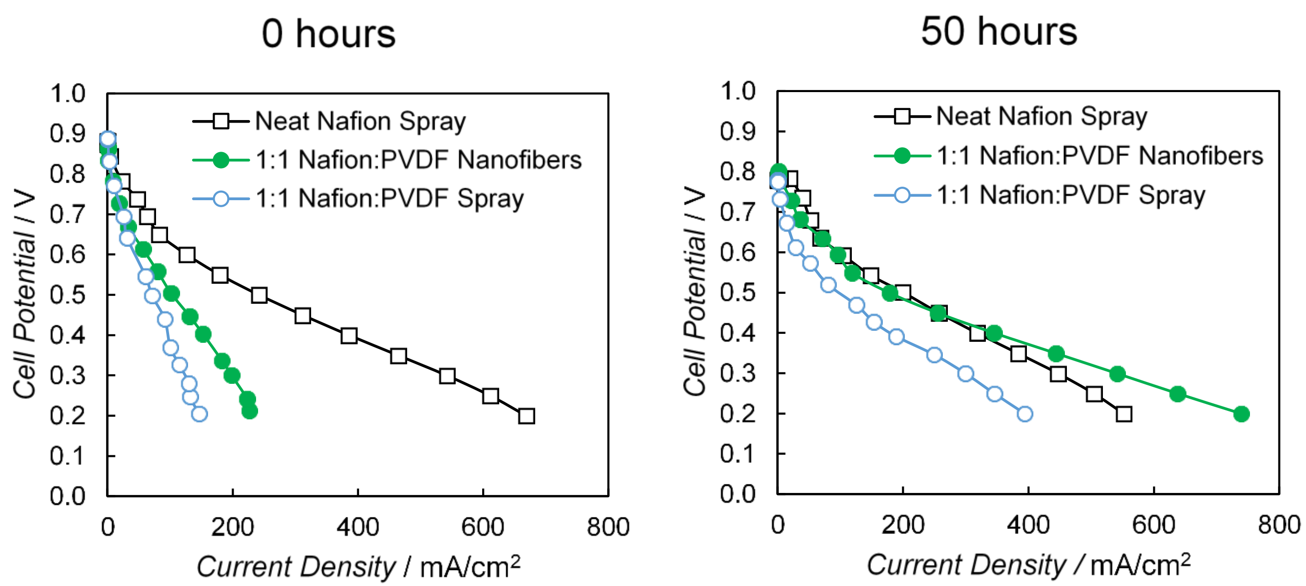
(a) the PGM-free catalyst particles after ultrasonicating to break up agglomerates

(b) a nanofiber composed of PGM-free catalyst:Nafion:PVDF (70:10:20 weight ratio)

(c) an electrospun mat of the same composition at 5,000x magnification

(d) an electrospun mat of the same composition after hot pressing at 140 °C and 4 MPa.

Prior Results: H_2/Air Fuel Cell Polarization Curves for Nanofiber and Sprayed Cathodes MEAs



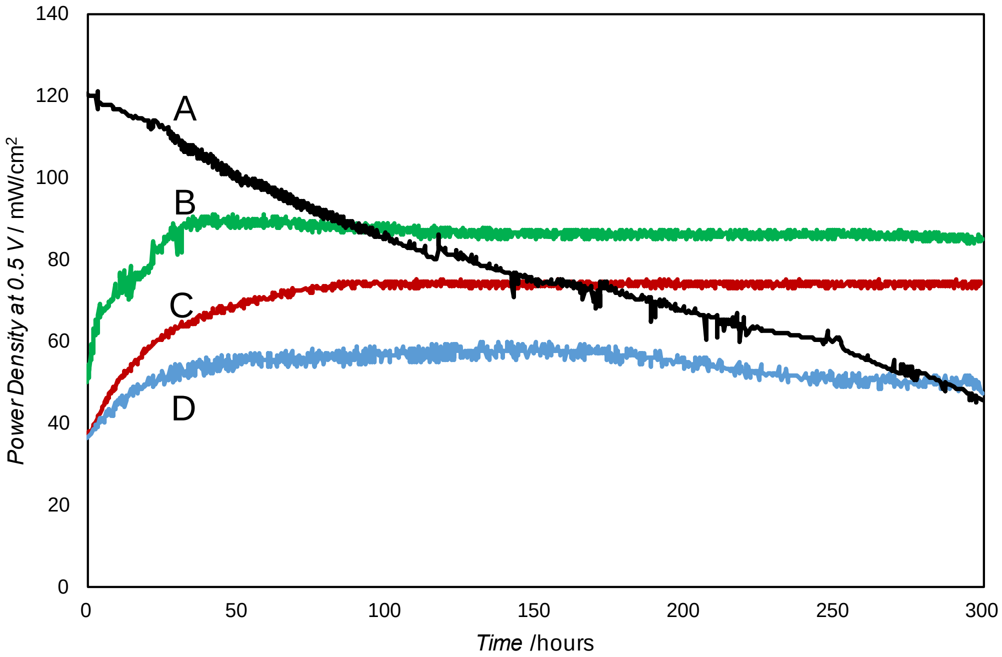
There was a significant improvement in power output over time for the nanofiber cathode (the nanofiber cathode requires a break-in period)

MEA Composition: PGM-free cathode catalyst (3.0 mg/cm^2), a Nafion 211 membrane, and a Pt/C sprayed anode (0.1 mg/cm^2 with a neat Nafion binder).

Fuel cell operating conditions: 80ºC, 100% relative humidity, 200 kPa (abs) backpressure, H_2/air feed gas flow rates of 125/500 sccm. All MEAs have an anode of Johnson Matthew 40% Platinum on carbon with a loading of 0.1mg$_{Pt}$/cm^2

J. Slack, B. Halevi , G. McCool , J. Li, R. Pavlicek, R. Wycisk, S. Mukerjee, P. N. Pintauro, "Electrospun Fiber Mat Cathode with PGM-free Catalyst Powder and Nafion/PVDF Binder", *ChemElectroChem,* **5**, 1537-1542 (2018).

Prior Results: H_2/air Fuel Cell Power Density at 0.5 V vs Time for 300 Hours



MEAs: PGM-free catalyst at 3.0 mg/cm^2.

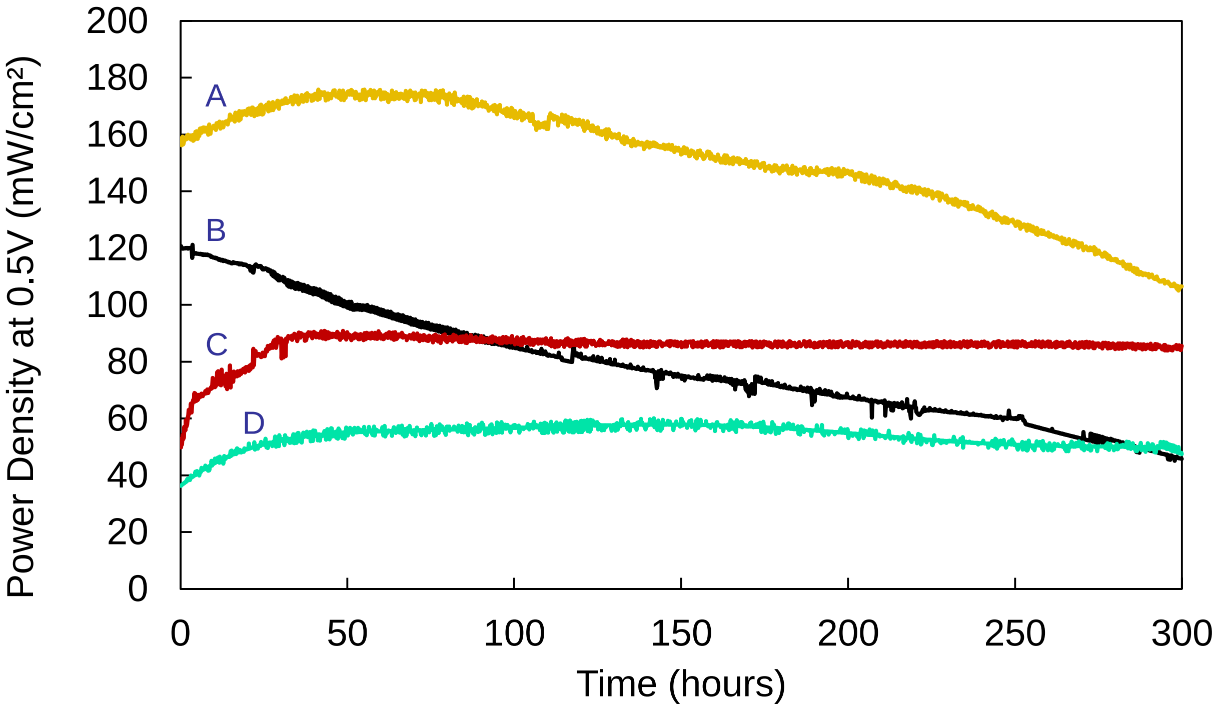
A: sprayed cathode MEA with a neat Nafion binder
B: nanofiber cathode MEA with a 1:1 Nafion:PVDF;
C: nanofiber cathode MEA with a 1:2 Nafion:PVDF;
D: sprayed cathode MEA with a 1:1 Nafion:PVDF binder.

A long break-in period is required for cathodes with a Nafion/PVDF binder: ca. 40- hours for a 1:1 Nafion:PVDF binder and ca. 70 hours for a 1:2 Nafion:PVDF binder

Long-term performance is dependent on binder and cathode morphology. Nanofibers with a 1:1 Nafion:PVDF binder works best.

Fuel cell operating conditions: 80ºC, 100% relative humidity, 200 kPa (abs) backpressure, 125 H_2 and 500 air (sccm) feed gas flowrate. All MEAs had a Nafion 211 membrane and a sprayed anode with Nafion binder and Johnson Matthey Pt/C HiSpec 4000 at $0.1 mg_{Pt}/cm^2$.

Prior Results: PGM-free Nanofiber Cathode MEA Durability

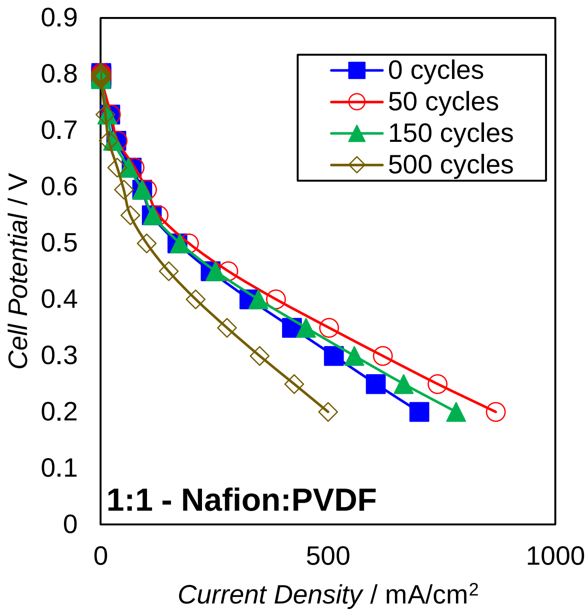


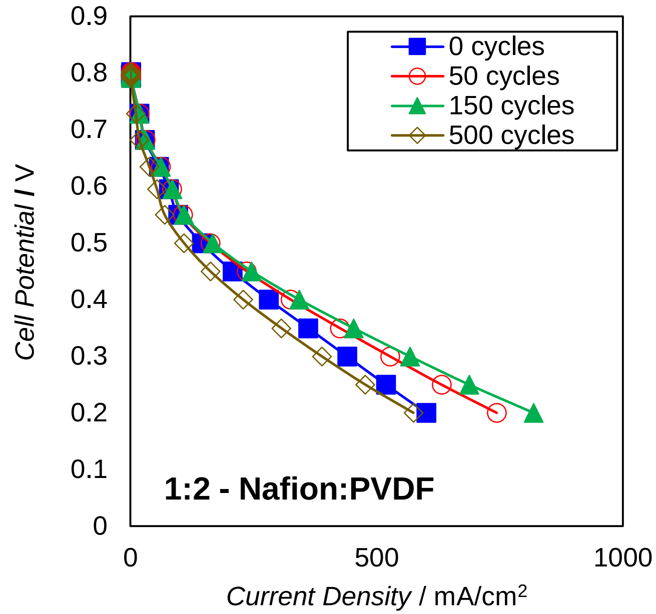
Conditions:
Feed gases: H_2/air – 125/500 sccm
Temperature: 80 °C
Back Pressure: 200 kPa (absolute)
Relative Humidity: 100%
Cathode catalyst loading: 3.0 mg/cm^2
Anode catalyst (Pt/C) loading: 0.1 mg/cm^2

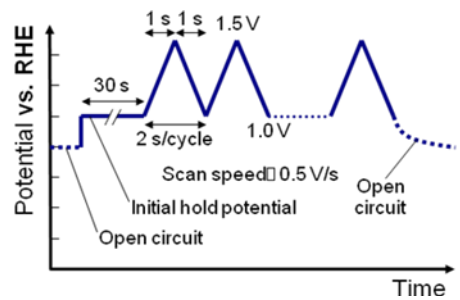
A: nanofiber cathode MEA with a Nafion binder (a hydrophilic binder)
B: sprayed cathode MEA with neat Nafion binder
C: nanofiber cathode MEA with a 1:1 Nafion:PVDF binder
D: sprayed cathode MEA with a 1:1 Nafion:PVDF binder.

- A hydrophilic Nafion binder produces higher power than a hydrophobic Nafion/PVDF binder.
- Hydrophilic binders show a power density decline over time
- One must find a hydrophilic/hydrophobic balance for the binder.
- A long break-in period is required for cathodes with a Nafion/PVDF binder: ca. 40- hours for a 1:1 Nafion:PVDF binder.

Prior Results: A start/stop carbon corrosion voltage cycling accelerated stress test

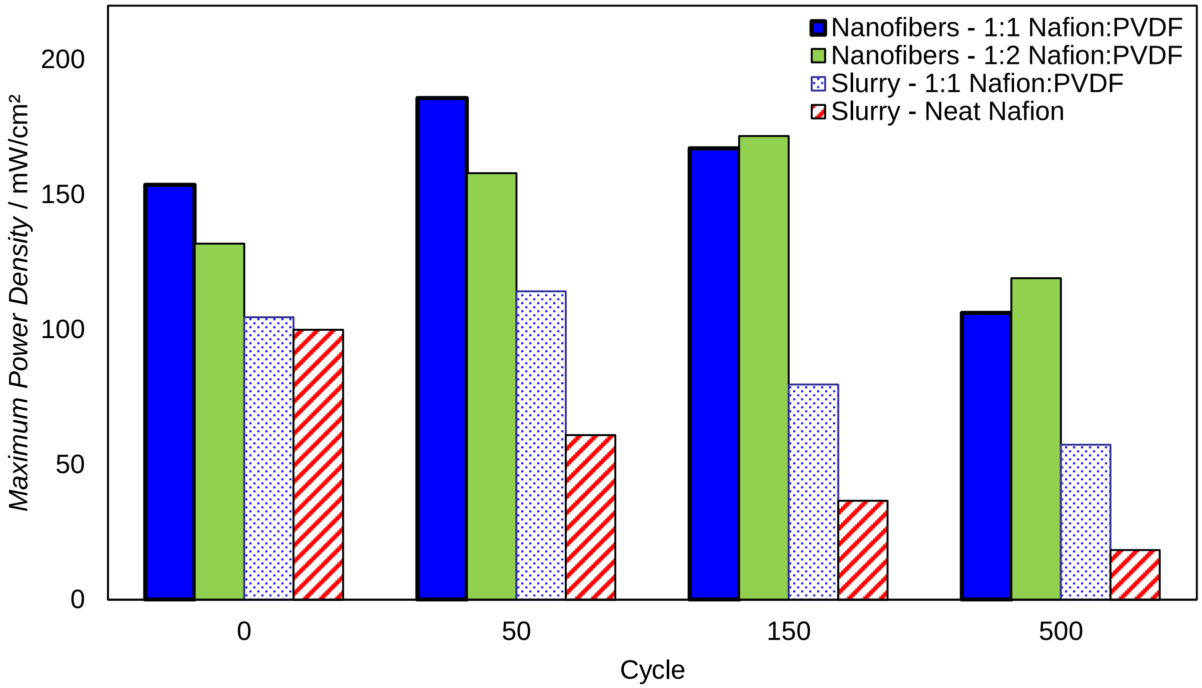






- Power increases for the first 50 cycles (1:1 Nafion:PVDF) or 150 cycles (1:2 Nafion:PVDF) and then decreases with additional voltage cycling.
- Voltage cycling was between 1.0 and 1.5 V in a triangular waveform at 500mV/s.
- Fuel cell operating conditions: 80ºC, 100% relative humidity, 1 atm_g backpressure, H_2/air feed gas flow rates at 125/500 sccm. All MEAs had a Nafion 211 membrane and a sprayed anode with Nafion binder and Johnson Matthey Pt/C HiSpec 4000 at $0.1mg_{Pt}/cm^2$

Prior Results: Comparison of Nanofiber and Sprayed Cathodes During the Carbon Corrosion AST



An increase and then decrease in max power is seen for nanofiber cathode MEAs

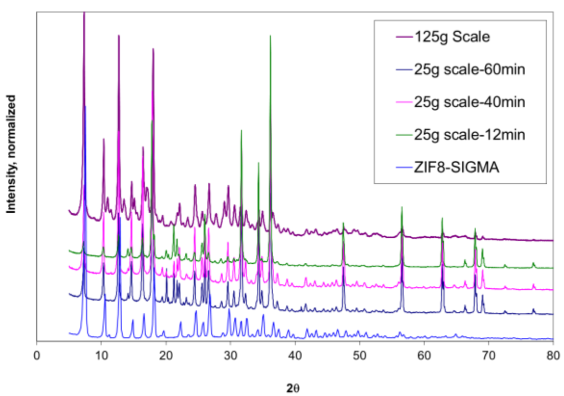
Highest initial power: 1:1 Nafion:PVDF nanofibers
Highest power after 150 cycles: 1:2 Nafion:PVDF
Worst-performing MEA: Sprayed cathode with neat Nafion binder

Voltage cycling was between 1.0 and 1.5 V in a triangular waveform at 500mV/s.

Fuel cell operating conditions: 80ºC, 100% relative humidity, 1 atm_g backpressure, H_2/air feed gas flow rates at 125/500 sccm. All MEAs had a Nafion 211 membrane and a sprayed anode with Nafion binder and Johnson Matthey Pt/C HiSpec 4000 at $0.1mg_{Pt}/cm^2$.

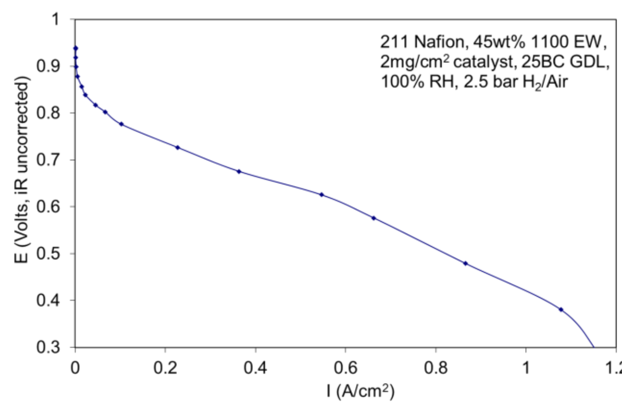
PGM-Free Catalysts for this Project (prepared at Pajarito Powder)

Catalyst	Platform	Agglomorate size measured by DLS/SEM	Description
Gen-0		50-600 nm	
Gen-1	Fe-Ph-MOF	50-600 nm	Baseline
Gen-1A	Fe-Ph-MOF		
Gen-1B	Fe-Ph-MOF		
Gen-2A	Fe-Ph-MOF	40-300 nm	Improved fiber interaction and 300nm size
Gen-2B	Hard pore formers	40-300 nm	
Gen-2A		30-200 nm	Improved fiber interaction and 300 nm size
Gen-2B			



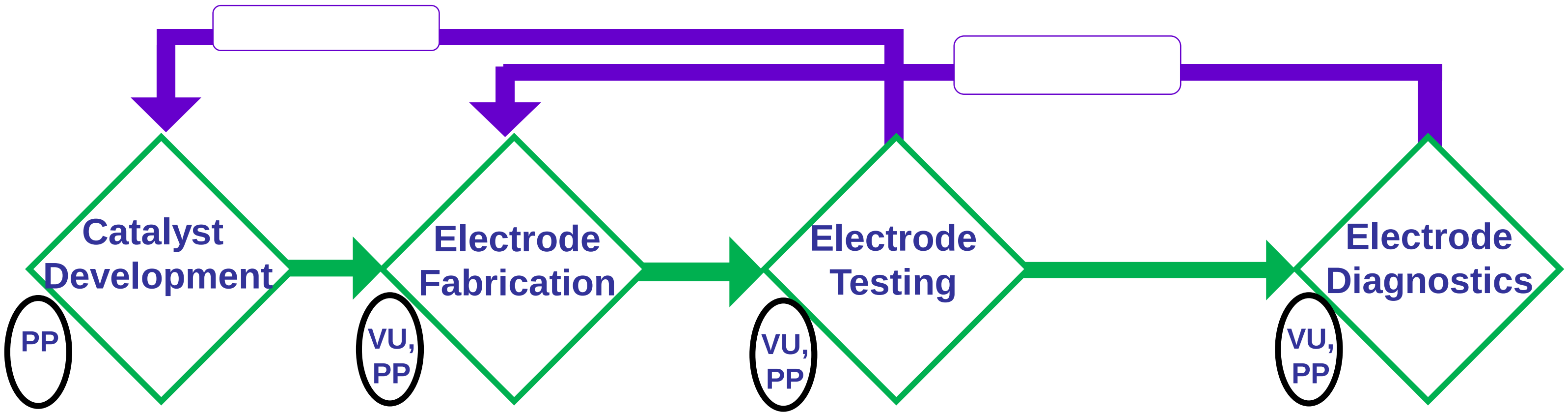
Mechanochemical MOF synthesis
DE-EE0000459

US 8,580,704



Slurry electrode performance:
70 mA @ 0.8 V, 1070 mA @ 0.4 V

Project Integration with ElectroCat



Nodes:
Active sites: Electrochemical analysis; Mossbaur, EXAFS, ACTEM/EELS
Synthesis: Catalyst Hi-throughput synthesis

Nodes:
Electrode structure: SEM, STEM, EELS/EDS

Nodes:
AST development and validation

Nodes:
Electrode Degradation/Failure:
In-situ/Operando catalyst
Post-mortem catalyst
Post-mortem electrode

Response to Previous Year Reviewers' Comments

This project was not reviewed last year.

Collaboration and Coordination

Oak Ridge National Laboratory

- SEM, TEM, cryo-TEM, XCT, and EDS-STEM analyses of nanofibers at beginning-of-life and end-of-life

NREL and Lawrence Berkeley National Laboratory

- PFSA binder effects (water sorption and proton conductivity) and binder coating thickness on PGM-free catalysts
- Assist in the identification of optimized ink recipes to reduce any detrimental impact of ionomer binder on catalyst activity in fiber mat cathodes.

Argonne National Laboratory

- Assist in determining the catalyst/binder distribution and internal porosity of electrospun fibers, to help us better understand and control metal leaching and carbon corrosion in nanofiber cathodes during fuel cell operation.
- Nano and micro-level X-ray computed tomography data will be collected (with ORNL and LBNL) before and after accelerated stress tests to understand inter and intra fiber porosity changes before/after carbon corrosion and metal dissolution with PFSA and PFSA/PVDF catalyst binders.

Lawrence Berkeley National Laboratory

- Modeling beginning-of-life and end-of-life fuel cell operation with nanofiber mat anode/cathode.

Los Alamos National Laboratory

- Verification of nanofiber MEA performance at BoL and after ASTs.

Proposed Future Work

- Pajarito Powder prepares PGM-free Fe-Ph-MOF catalysts of progressively smaller particle size.

	Platform	Target agglomerate size measured by DLS	
Gen-0	Hard pore formers	50-600 nm	Baseline
Gen-1	Fe-Ph-MOF	50-600 nm	Baseline
Gen-1A	Fe-Ph-MOF	50-500 nm	Improved catalyst
Gen-1B	Fe-Ph-MOF	50-500	
Gen-2A	Fe-Ph-MOF	40-300 nm	Improved fiber interaction and 300nm size
Gen-2B	Hard pore formers	40-300 nm	
Gen-2A	Fe-Ph-MOF	30-200 nm	Improved fiber interaction and 300 nm size
Gen-2B	Hard pore formers	30-200 nm	

- Nanofiber mat cathodes will be prepared with the PGM-free catalyst at Vanderbilt.
  - A hydrophilic binder of PFSA + poly(ethylene oxide) (PEO)
  - A hydrophobic mixture of PFSA + polyvinylidene (PVDF)
  - PFSA: 1100 EW Nafion® or 830 EW Aquivion®
  - Cathode catalyst loadings of 3-6 mg/cm^2

- Fuel Cell Testing
  - Screen for initial power density in H_2/O_2 and H_2/air fuel cells.
  - Assess cathode durability in voltage cycling ASTs
  - Compare with sprayed electrode MEAs
  - Optimize on catalyst size and binder

- Prepare Electrodes Using Commercial Electrospinning Equipment at eSpin Technologies, Inc.
  - Test fiber mat cathodes at Vanderbilt

Summary

Maximize MEA power output with PGM-free catalysts. We seek answers to the following questions:

- What is the optimum binder, fiber diameter, and catalyst particle size/loading within a fiber?
- How does power density vary with catalyst loading?
- Can well-formed nanofibers be electrospun with a variety of binders and catalyst materials from Pajarito?

Maximize the long-term durability of MEAs with PGM-free catalysts. We seek answers to the following questions:

- Is it best to control MEA durability by using a hydrophobic binder like PVDF?
- Will low RH operation extend MEA lifetime?
- At the present time, durable PGM-free cathode MEAs produce low power. Are high power densities incompatible with highly durability?
- Is there an optimum binder hydrophobicity/hydrophilicity that will maximize both power and durability?

Fabricate nanofiber electrodes on a commercial electrospinning line at eSpin Technologies, Inc. (Chattanooga, TN)

- Will lab-scale and commercially electrospun electrode MEAs exhibit the same performance and durability?

Continue to investigate the structure and function of particle/polymer nanofiber mat cathodes with PGM-free cathode catalysts

- What is the water distribution in nanofiber MEAs as a function of current density and feed gases RH?
- What is the distribution of PGM-free catalyst and binder in nanofiber cross-sections and along the fiber length?

Technical Back-Up Slides

Electrospinning – Rotating Drum Apparatus