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

Peter N. Pintauro

Department of Chemical and Biomolecular Engineering
Vanderbilt University, Nashville, TN 37235

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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
- Project Lead: Peter N. Pintauro, Vanderbilt

Project Relevance and Objectives

Project Relevance:

- The VU/Pajarito 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, LLC.

- 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 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

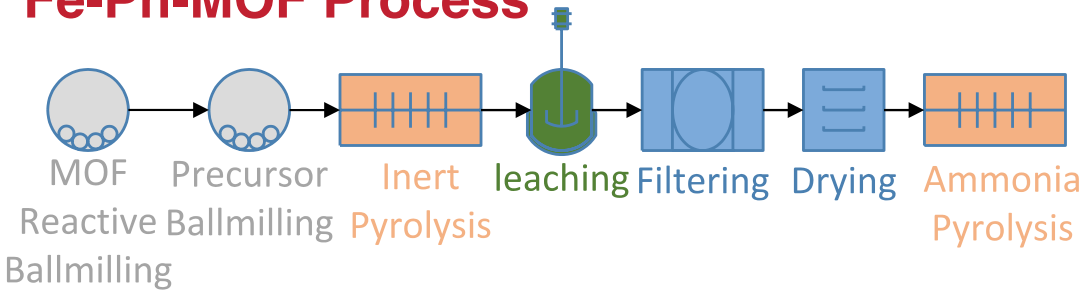
Milestones and Go/No-Go Decision for Year 1

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

Pajarito Fe-Ph-MOF

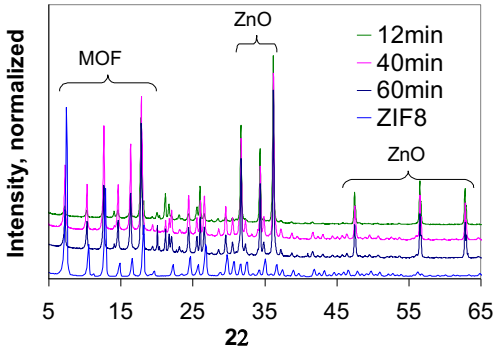
PAJARITO POWDER
FUEL CELL CATALYSTS

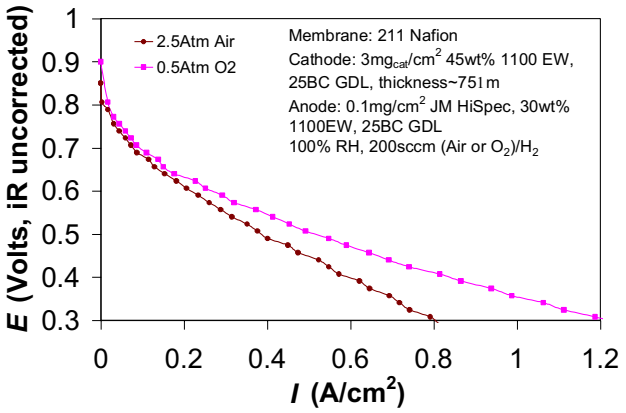
Fe-Ph-MOF Process



- Fe-salt complexes with Phenanthroline AND MOF.
- MOF contents, structure AND size contribute to
  - Catalyst chemical composition and structure
  - Catalyst physical structure shape and size
- Reactive pyrolysis in Ammonia necessary for creating nanoporous active sites
  - Active site exposure
  - Nitrogenation and creation of Fe-N-C site
- Needs:
- Optimization of MOF size and contents
- Optimization of catalyst mixing and treatment

Reactive Milled MOF Synthesis in ~100+ gram/batch

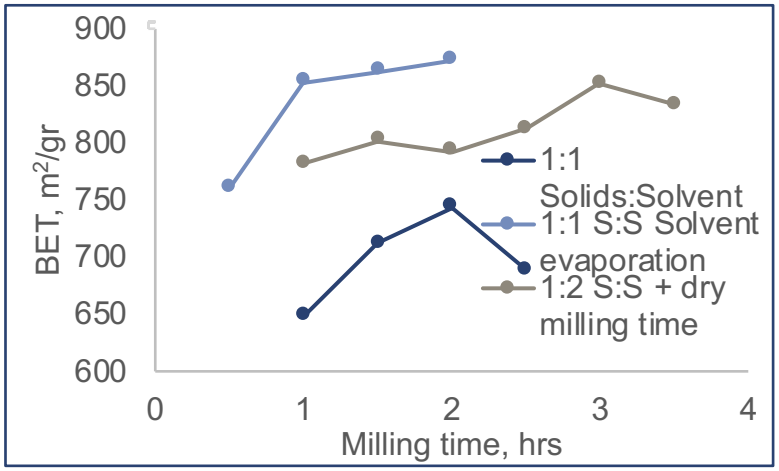




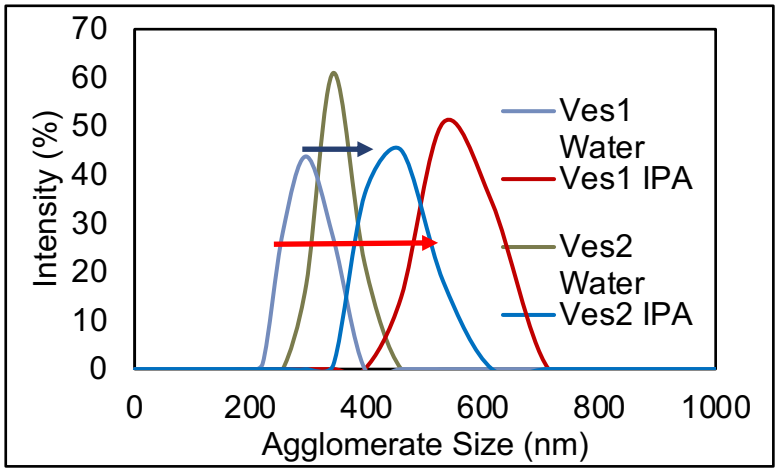
Synthesis Size Effect

PAJARITO POWDER
FUEL CELL CATALYSTS

Zif-8 MOF Surface Area



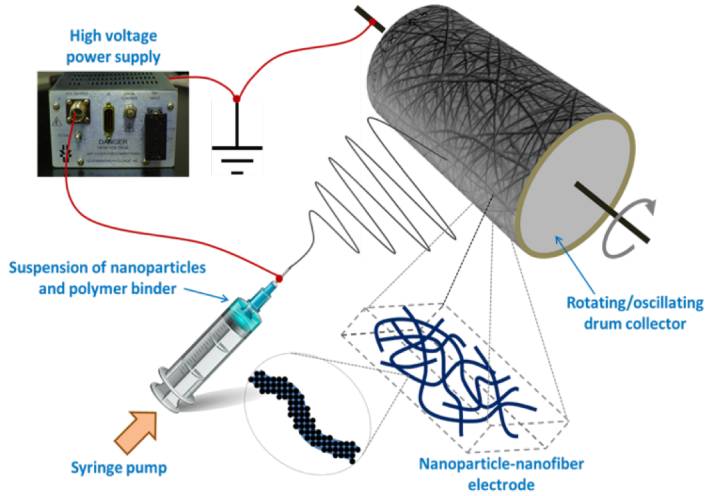
Dynamic Light Scattering



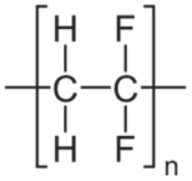
- Zif-8 Synthesis modifications lead to different sized MOF crystallites and agglomeration, apparent by surface area measured.
  - Solvent type, solids/solvent ratio, materials/vessel ratio, milling time effect MOF size
- Bulk measurement of particle agglomeration and sizing via Dynamic Light Scattering of agglomerated particles.
  - Preparation and dispersant effect measured size
  - **Physical structure of different resulting catalysts evident by different rates of change in apparent agglomerate size in different dispersants. Ves2 agglomeration less than Ves1, possibly indicating easier to separate catalysts particles needed for electrospinning.**

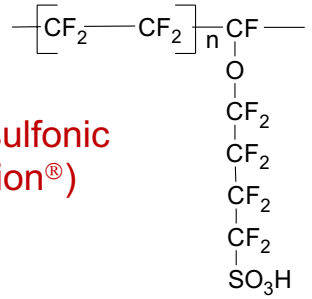
Electrospinning PGM-Free Catalyst into a Nanofiber Electrode

Pajarito PGM-free catalyst: PMF catalyst (hard templating pore former approach) and 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.

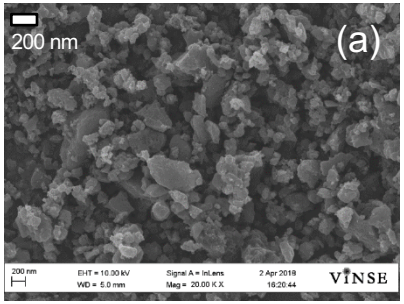


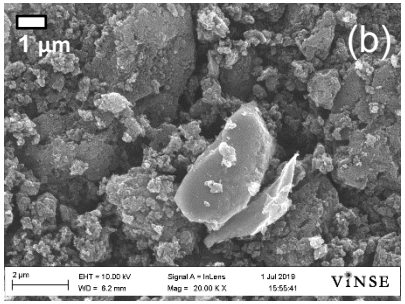
PVDF

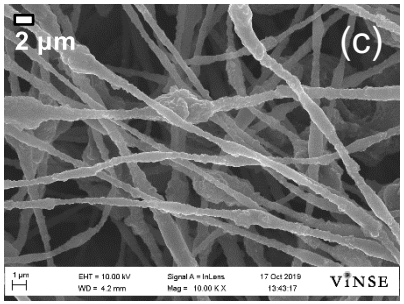


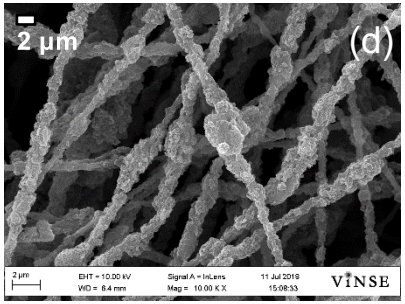


PFSA = Perfluorosulfonic Acid Polymer (Nafion®)









SEM images of

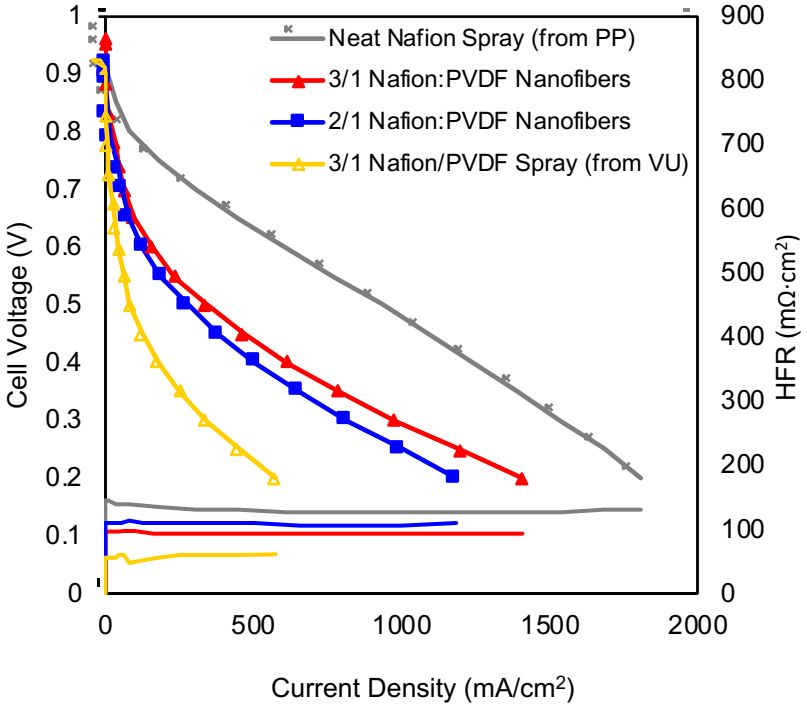
(a) ZIF-8 MOF based PGM-free catalyst particles from PP after ultrasonication (from ChemElectroChem paper)

(b) PMF catalyst from PP (hard templating approach); larger primary particles vs. MOF catalyst.

(c) A nanofiber mat with catalyst (a) and a binder of 3/1 Nafion/PVDF

(d) A nanofiber mat with catalyst (b) and a binder of 3/1 Nafion/PVDF

Accomplishment: H_2/O_2 Fuel Cell Polarization Curves for Nanofiber and Sprayed Cathodes MEAs (**PMF Catalyst**)



	Max. Pow Density (mW/cm^2)	Current density at 0.9 V (mA/cm^2)	OCV (V)
Neat Nafion Spray (from PP)	496	7.8	0.95
3/1 Nafion/PVDF Nanofibers	297	3.2	0.96
2/1 Nafion/PVDF Nanofibers	249	0.2	0.92
3/1 Nafion/PVDF Spray (from VU)	115	0.01	0.90

Current densities are below the project target of 25 mA/cm^2 but max power is reasonably high

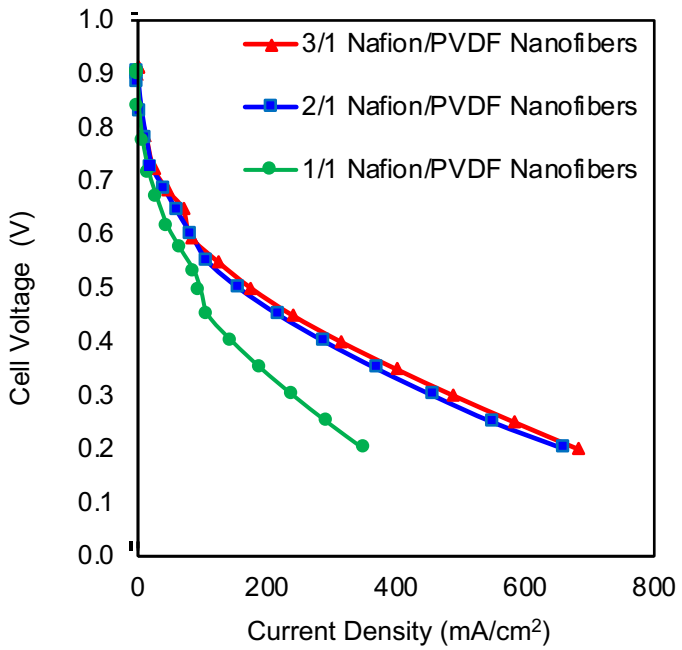
Fuel Cell Operating Conditions:
Feed gases: H_2/O_2 – 250/200 sccm
Temperature: 80 °C
Back Pressure: 200 kPa (absolute)
Relative Humidity: 100%
Cathode catalyst loading: 3.0 mg/cm^2
Anode catalyst (Pt/C) loading: 0.1 mg_{Pt}/cm^2
Hot-pressing conditions:140°C and 10 MPa for 10 minutes.

OCV for nanofiber cathode MEAs is ≥ 0.90 V

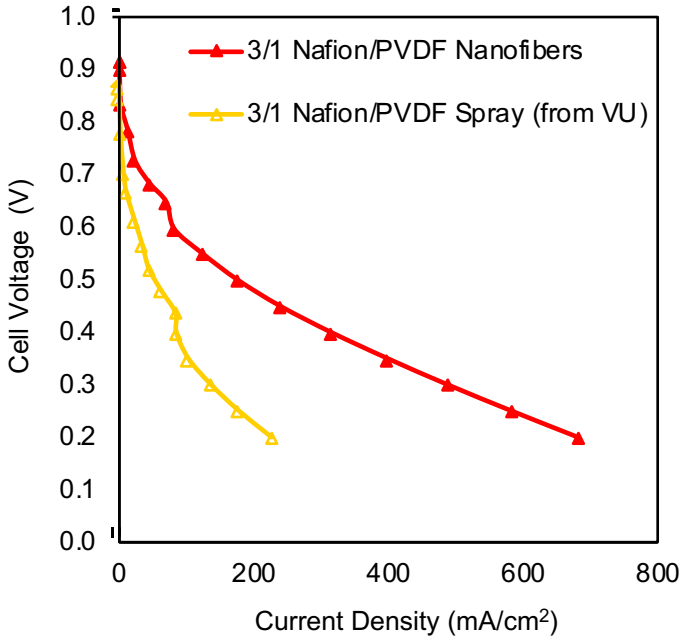
MEA performance does not correlate with HFR (hot pressing conditions are not affecting MEA performance)

*Accomplishment: H_2/Air Fuel Cell Polarization Curves for Nanofiber and Sprayed Cathodes MEAs (**PMF Catalyst**)*

Effect of Nafion/PVDF Wt. Ratio in Nanofibers



Effect of Cathode Morphology (spray vs. nanofibers)



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

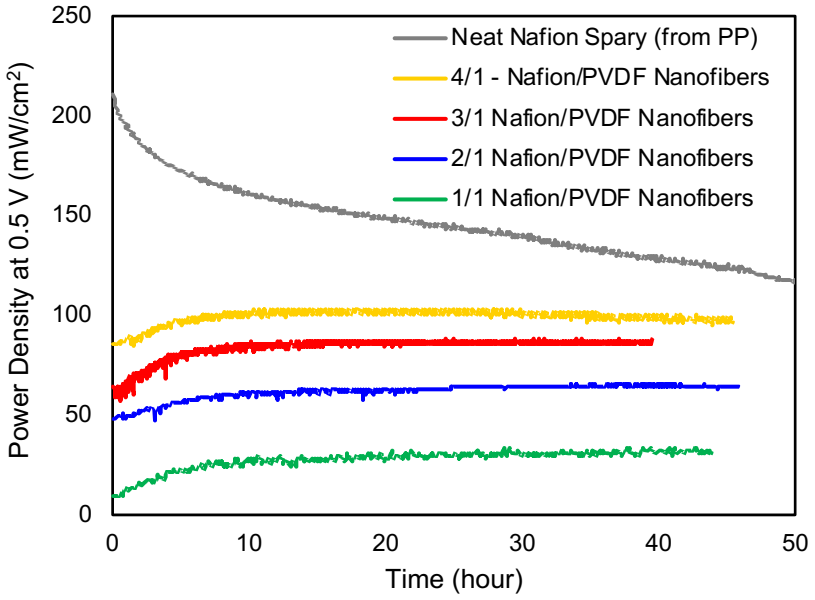
Fuel cell operating conditions: 80 ºC, 100% relative humidity, 200 kPa (abs) backpressure, H_2/air feed gas flow rates of 125/500 sccm. All MEAs have an anode of Johnson Matthew 40% Platinum on carbon with a loading of 0.1mg$_{Pt}$/cm^2.

The performance of nanofiber cathode MEAs and sprayed Nafion/PVDF cathode MEA after 40 hours of constant voltage operation at 0.5 V (with air feed to the cathode). For 2/1 and 3/1 Nafion/PVDF cathode, we obtained 79 mW/cm^2 at 0.5 V after 40 hours of operation.

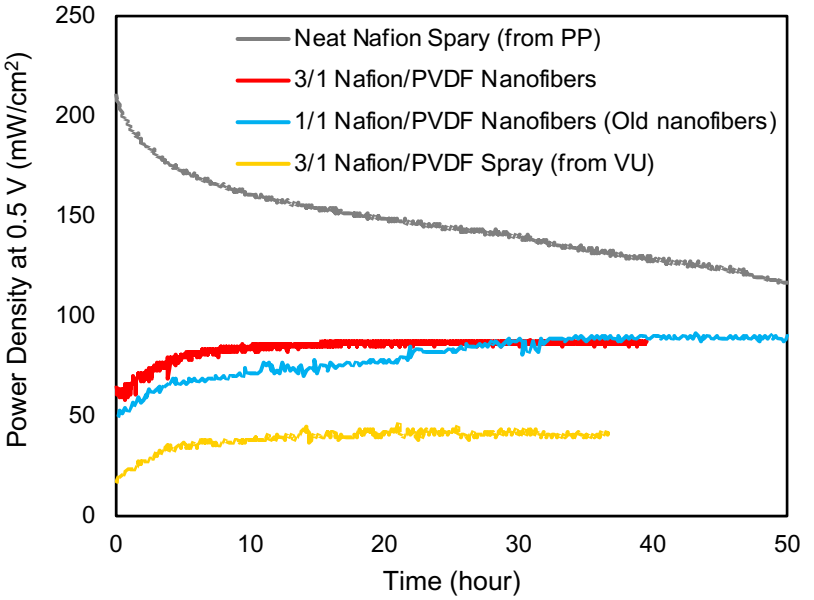
- The nanofiber cathode MEA (3/1 Nafion/PVDF) showed a significant increase in power compared with the sprayed cathode MEA with the same binder.
- A high Nafion/PVDF ratio binder works best in terms of power output

*Accomplishment: H_2/Air Fuel Cell Power Density at 0.5 V vs. Time (**PMF Catalyst**)*

Effect of Nafion/PVDF Wt. Ratio in Nanofibers



Effect of Cathode Morphology
(spray vs. nanofibers; new vs. old nanofibers)

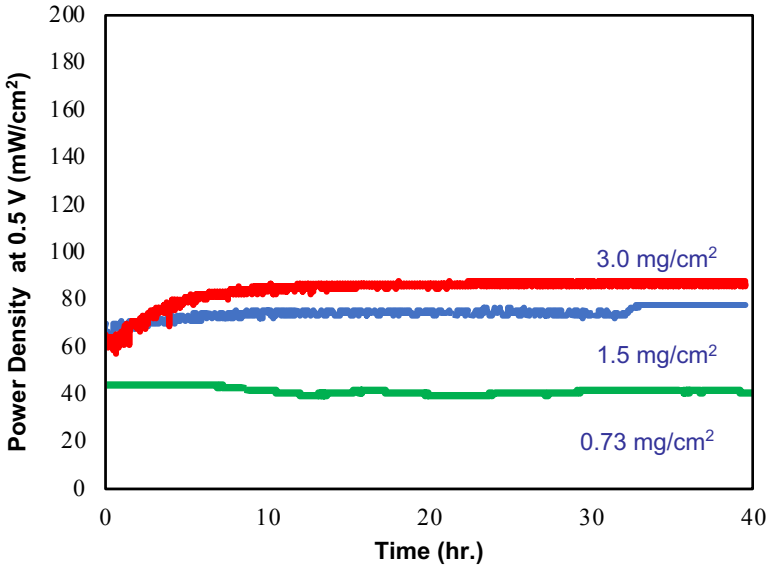


Fuel cell operating conditions: 80ºC, 100% relative humidity, 200 kPa (abs) backpressure, 125 H_2 and 500 air (sccm) feed gas flowrate. All MEAs had a Nafion 211 membrane and a sprayed anode with Nafion binder and Johnson Matthey Pt/C HiSpec 4000 at 0.1mg_{Pt}/cm^2.

- The power output of the cathode MEAs with a Nafion/PVDF binder increased after start-up and reached a constant power density after ca. 10 hours of operation (a break-in period is required for cathodes with a Nafion/PVDF binder).
- Long-term performance is dependent on binder and cathode morphology. The optimum Nafion/PVDF ratio appears to be between 3/1 and 4/1.
- MEA from *ChemElectroChem* paper (old nanofibers) with 1/1 Nafion/PVDF produced the same long-term power as a new MEA with 3/1 Nafion/PVDF (due presumably to a difference in the catalyst from PP)

Accomplishment: Effect of Catalyst Loading on Power Density at 0.5 V (PMF Catalyst)

Nanofiber cathode MEA data with Pajarito **PMF catalyst,** for a 3/1 Nafion/PVDF nanofiber cathode binder



Fuel cell operating conditions:
80ºC, 100% relative humidity, 200 kPa (abs) backpressure, 125 H_2 and 500 air (sccm) feed gas flow rate.

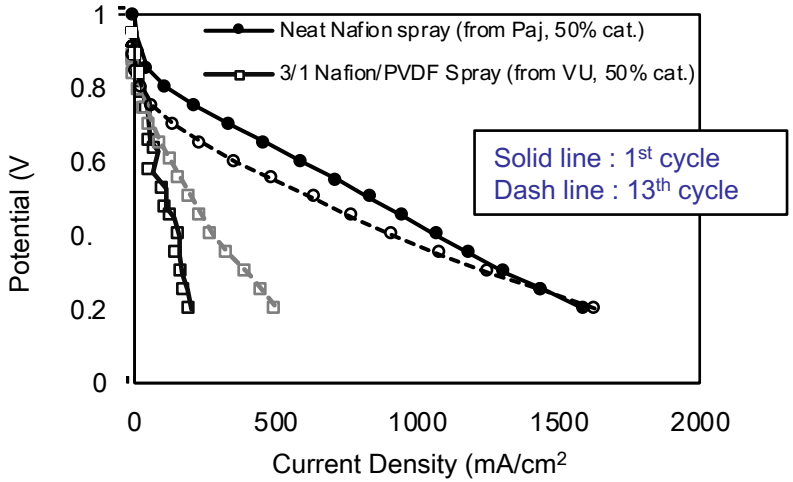
All MEAs had a Nafion 211 membrane and a sprayed anode with Nafion binder and Johnson Matthey HiSpec 4000 Pt/C at 0.1 mg/cm^2 and a PGM-free cathode (3.0 - 3.5 mg/cm^2).

- As loading increases, the constant power output also increases:
- Data suggests that we are not degrading some catalyst while activating other portions of the cathode (unlikely to see constant power vs. time and power that increase with catalyst loading).
- Power doubles from 41 to 78 mW/cm^2 when the loading doubles, from 0.73 to 1.5 mg/cm^2.
- Power increases only 10% when the loading is doubled from 1.5 to 3.0 mg/cm^2.
- We are examining the thickness and porosity of the 0.73 and 1.5 mg/cm^2 PMF fiber mat cathodes.
- Can we get the same thickness at a higher loading by proper compaction?

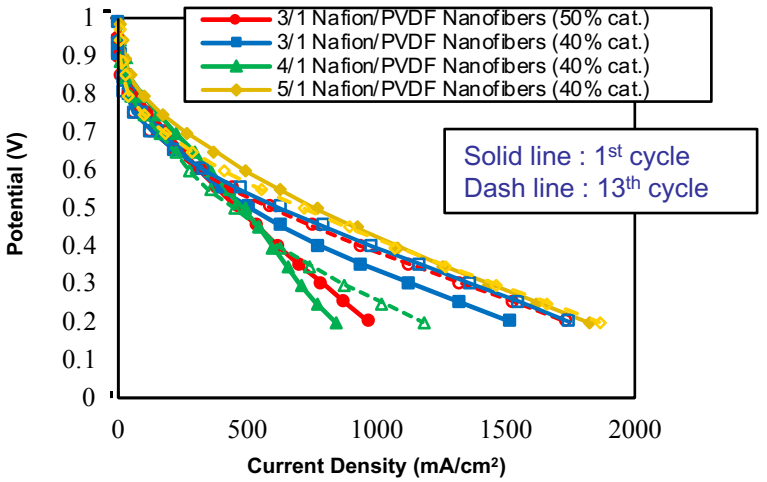
Accomplishment: H_2/O_2 Fuel Cell Polarization Curves for Nanofiber and Sprayed Cathodes MEAs (MOF Catalyst)

NH_3-treated MOF catalyst from Pajarito Powder.

Fuel cell operating conditions: 80ºC, 100% relative humidity, 200 kPa (abs) backpressure, H_2/O_2 feed gas flow rates of 125/500 sccm. cathode (3.0 - 3.5 mg/cm^2), Pt/C sprayed anode (0.1 mg_{Pt}/cm^2).



1St i-V pol curve data

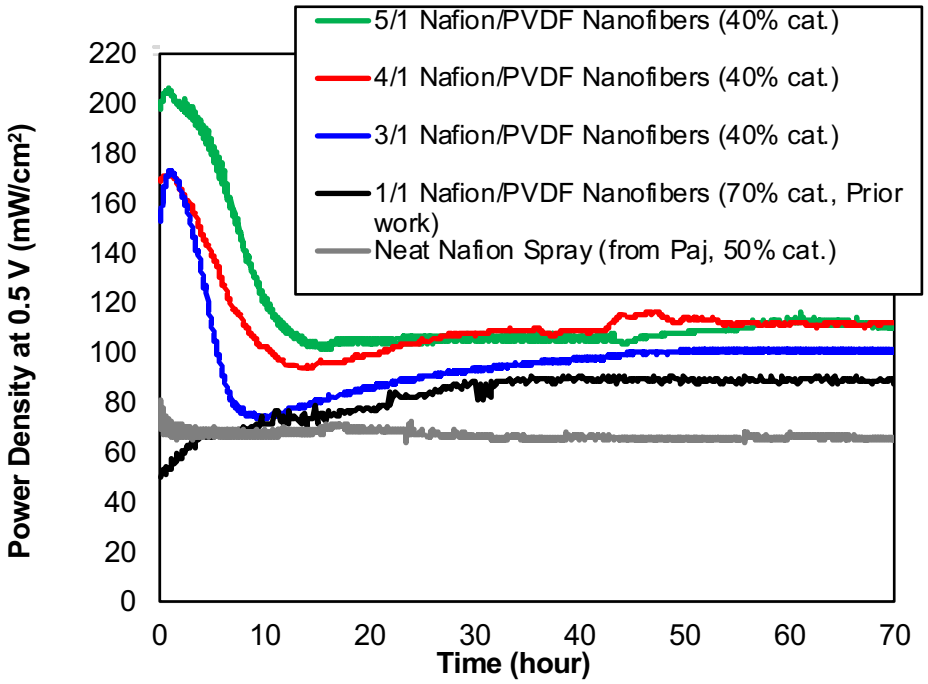


13th i-V pol curve data

	Max. Pow Density (mW/cm^2)	Current Density at 0.9 V (mA/cm^2)	OCV (V)		Max. Pow Density (mW/cm^2)	Current Density at 0.9 V (mA/cm^2)	OCV (V)
Neat Nafion Sprayed (GDE from Paj, 50% cat.)	432	25	0.99		379	0.22	0.90
3:1 Nafion:PVDF Sprayed (50% cat.)	63	9.3	0.94		119	0.03	0.90
3:1 Nafion:PVDF Nanofiber (50% cat.)	248	14	0.98	i-V cycles	397	4.9	0.94
3:1 Nafion:PVDF Nanofiber (40% cat.)	338	16	0.98		409	0.26	0.93
4:1 Nafion:PVDF Nanofiber (40% cat.)	**244**	**28 (Go/No-Go target is 25 mA/cm^2)**	**0.99**		259	4.7	0.94
5:1 Nafion:PVDF Nanofiber (40% cat.)	436	23	0.98		439	8.9	0.97

- With a Nafion/PVDF nanofiber cathode, current densities at high voltage (e.g.,. 0.9 V) decrease after multiple polarization cycles, even when current densities at low voltages are increasing; kinetics is slowing, but transport improves with time due to better hydration of the Nafion/PVDF binder.
- With a Nafion slurry cathode, the current density decreases for all voltages after multiple polarization cycles.

Accomplishment: H_2/Air Fuel Cell Power Density vs. Time at 0.5 V (MOF Catalyst)



Fuel cell operating conditions:
80ºC, 100% relative humidity, 200 kPa (abs) backpressure, 125 H_2 and 500 air (sccm) feed gas flow rate.

All MEAs had a Nafion 211 membrane and a sprayed anode with Nafion binder and Johnson Matthey HiSpec 4000 Pt/C at 0.1 mg/cm² and a PGM-free cathode (3.0 - 3.5 mg/cm²).

The transient behavior of the different MEAs is complex, but all MEAs generated almost the same constant power. Should we be looking at this transient behavior?

- Why is there an initial power decline for an air feed? We also see this in O2 when we are collecting repeated pol curve i-V data.
- The initial performance decline may be due to catalyst degradation (deactivation of Fe-$N_{1,2}$ sites)?
- The increase in power after 20 hours may be due to a slow activation of Fe-N_4 sites or some further changes in the morphology or water content of the Nafion/PVDF binder?
- A Pajarito slurry cathode with neat Nafion binder produced low power, with an initial steep power drop and then a slow power decline.
- From the above data and repeated i-V curves with O_2: Above ~0.5-0.6 V, there is a decrease in power time (catalyst deactivation) and below ~0.5-0.6 V, the power increases with time and then stabilizes.

Accomplishment: PGM-Free Catalysts for This Project (prepared at Pajarito Powder)

Catalyst	Platform	Agglomerate size measured by DLS/SEM	Description
Gen-0	Hard pore formers	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	
Gen-2B	Hard pore formers	40-300 nm	
Gen-2A		30-200 nm	
Gen-2B			

- PMF-type catalysts, made with hard pore formers, proved stable but too large in current format
- Early results showed that MOF-derived catalyst and agglomerate sizes needed to be further reduced for optimal electrospinning
- MOF size reduction was re-prioritized over catalysts with intrinsically higher performance and catalysts modified for improved interaction with the fiber. 300nm agglomerate sized catalysts achieved.

Response to Previous Year Reviewers' Comment

A recommended addition to the project scope includes the development of nanofiber, PGM-free mat electrodes of different thicknesses, with measurement of the catalyst utilization as a function of mat thickness. It could be anticipated that thicker mat electrodes could have lower catalyst utilization, similar to what has been observed with PGM electrodes. This would suggest that with thicker nanofiber PGM-free electrodes would have reduced effectiveness and present limits on increasing the power density of the fuel cell system and, therefore, an inability to achieve performance at a level competitive with PGM fuel cell systems.

Response: The effect of cathode catalyst loading on long-term power output was investigated for nanofiber cathodes with PMF catalyst at 0.73 mg/cm^2, 1.5 mg/cm^2, and 3.0 mg/cm^2, with a binder of 3/1 Nafion/PVDF. A substantial power increase was seen when the loading increase from 0.73 to 1.5 mg/cm^2, with a minimal power increase when the loading was increased further. Over the next year, we will address the reviewer's comment by looking closely at the effect of electrode thickness on power output and catalyst utilization. Our inability to get high power at a high catalyst loading (thick cathodes) is attributed to the low proton conductivity of the binder, where Nafion is diluted with uncharged PVDF. We will examine ways to circumvent this problem, e.g., using cathode mat compaction to make thinner electrodes at 3.0-4.0 mg/cm^2 and/or adding more Nafion binder to a Nafion/PVDF cathode mat.

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

1. Improve the intrinsic activity and use improved Pajarito MOF and PMF catalyst in all experiments.
2. Make better fibers and better MEAs
    a. Examine lower I/C ratios (normally with Pt-based catalysts, we have 60-70 wt.% catalyst in fibers)
    b. Look at shorter electrospinning times, to minimize re-agglomeration of catalyst particles in the needle syringe; add surfactant to get better catalyst dispersion in the electrospinning ink
    c. Look at different solvents (with MOF catalyst, we see that DMAc/THF/acetone is better than DMF/THF/acetone)
    d. Make catalyst surface more hydrophobic with minimal loss in proton conductivity of the ionomer binder (examine catalyst surface coating)
3. Decrease the thickness of the cathode, at a constant loading of 3.0 mg/cm^2
    a. Look at different fiber mat compaction schemes.
    b. What is the effect of cathode porosity and thickness on performance? Is IR drop (electrical or ionic conductivity) or gas/water transport limiting performance?
    c. Select one Nafion/PVDF ratio (5/1) and a low I/C ratio (60-70% catalyst, from 2a)
    d. Measuring electrochemical surface area of our fiber mat cathodes (does power correlate with thickness and/or surface area?
4. If 2 and 3 are successful, go to higher catalyst loading (4 or 5 mg/cm^2).
5. Begin voltage cycling ASTs

ElectroCat Collaborations

1. Measure ionic/electrical resistance as a function of thickness for nanofiber mat cathodes of different interfiber porosity (with MOF and PMF catalyst)
2. Measure GTR in fiber mat cathodes
3. SEM, STEM, and EDS analysis of electrospun mats and sprayed cathode MEAs at ORNL
    - Cross section distribution of catalyst and binder at BOL and EOT
4. Try to spin ElectroCat catalysts into nanofiber mat cathodes

Summary

- 28 mA/cm^2 at 0.9 V was achieved with a nanofiber mat cathode, an O_2 cathode feed, NH_3-treated MOF catalyst from Pajarito Powder, and 4:1 Nafion:PVDF binder in the nanofiber mat, where the fibers contain 40 wt.% catalyst and the cathode catalyst loading was ~ 3.0 mg/cm^2. This current density exceeds the Year 1 Go/No-Go target of 25 mA/cm^2.
- Long-term stable power output: 112 mW/cm^2 at 0.5 V in air at 80^{o}C for ~3.0 mg/cm^2 MOF catalyst loading.
- Long-term power increased with increasing cathode catalyst loading: 41 mW/cm^2 at 0.73 mg/cm^2; 76 mW/cm^2 at 1.5 mg/cm^2; 86 mW/cm^2 at 3.0 mg/cm^2 (PMF catalyst from PP, fuel cell operated with H_2/air at 80^{o}C)
- The highest long-term power output (for stable MEA operation) was achieved with a binder of either 3/1 or 4/1 weight ratio of Nafion/PVDF
- Fiber mat MOF catalyst cathodes that gave the highest current density at 0.9 V in O_2 did not produce the highest maximum power
- After 13 repeated voltage sweeps with O_2, the current density at 0.9 V decreased, but the maximum power density increased for fiber mat MOF catalyst cathodes
- There was an initial decrease and then slow rise and stabilization of fuel cell power output at 0.5 V for fiber mat cathodes with MOF catalyst (H_2 /air fuel cell operation at 80^{o}C).
  - The initial power decline (during the initial 10 hours of operation) may be due to deactivation of Fe-$N_{1,2}$ sites
  - The increase in power after 20 hours may be due to a slow activation of Fe-N_4 sites or some further changes in the morphology or water content of the Nafion/PVDF binder