Fuel Cell Membrane-Electrode-Assemblies with Ultra-Low Pt Nanofiber Electrodes

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Project ID: # FC158

Overview

Timeline and Budget

- Project Start Date: 1/1/2017
- Project End Date: 12/31/2019
- Percent complete: 72%

- Total Project Budget: $3,173,854
- Total Recipient Share: $640,291
- Total Federal Share: $2,533,563
- Total Funds Spent:
  - $1,869,536 = $1,509,154 (DOE) + $360,382 (recipient)

Barriers and Targets

- Barrier Addressed:
  - High current density performance of MEAs is low for low cathode Pt-loading
- Targets: DOE 2020 performance targets for MEAs
  - Anode + Cathode Pt loading ≤ 0.125 mg_{Pt}/cm^2
  - 65% peak efficiency
  - 5,000 hour durability
  - > 1W/cm^2 at rated power

Partners

- Nissan Technical Center North America (NTCNA)
- Georgia Institute of Technology
- eSpin Technologies, Inc.
- FC-PAD Consortium Labs (LANL, ORNL, LBNL, ANL)
- Project Lead: Peter N. Pintauro, Vanderbilt

Project Relevance and Objectives

Project Relevance:

- The VU/GaTech/NTCNA/eSpin team seeks to better understand and further improve the performance and durability of low Pt loaded nanofiber mat fuel cell electrodes and MEAs.
- This project was selected to address the EERE/FCTO mission to advance PEMFC technology for automotive applications and is part of the FC-PAD consortium.

Project Objectives:

- Fabricate, characterize, and evaluate nanofiber mat electrode MEAs with highly active ORR catalysts for hydrogen/air fuel cells
- Focus on nanofiber cathodes with commercial Pt-alloy catalysts and Pt-Ni octahedra catalysts prepared at GaTech, with various ionomer and blended polymer binders.
- The nanofiber mat cathode/anode composition and morphology will be identified for MEAs that meet the DOE's 2020 performance and durability targets:

  Pt loading: $\leq$ 0.10 mg/cm^2 cathode and $\leq$ 0.025 mg/cm^2 anode; > 1 W/cm^2 at rated power for T = 80-95^{o}C; <40% drop in ORR mass activity after load cycling, <5% drop in voltage at 1.2 A/cm^2 after unmitigated start up-shut down and < 10% loss in rated power after drive cycle durability.

- Improved power output at low relative humidity (40% RH), especially at high current density
- Generate insightful understanding regarding the structure and function of electrospun nanofiber electrodes to guide future nanofiber electrode R&D

Project Go/No-Go Decisions and 2019 Milestones

Go/No-Go Description	Date	Status
• Nanofiber MEA with >240 mA/cm^2 at 0.8V • >800 mW/cm^2 at rated power • <50% drop in ORR mass activity after load cycling • <20% drop in voltage at 1.2 A/cm^2 after start up-shut down • <30% loss in rated power after drive cycle durability.	12/2017	All targets met
• Nanofiber MEA with >280 mA/cm^2 at 0.8V, • >900 mW/cm^2 at rated power, • < 40% drop in ORR mass activity after load cycling, • <10% drop in voltage at 1.2 A/cm^2 after start up-shut down • <20% loss in rated power after drive cycle durability	12/2018	All targets met (except drive cycle durability)
Deliver to NTCNA or FC-PAD Labs at least 10 nanofiber MEAs with: • 300 mA/cm^2 at 0.8V and >1000 mW/cm^2 at rated power • <40% drop in ORR mass activity after load cycling, • <5% drop in voltage at 1.2 A/cm^2 after unmitigated start up-shut down	12/2019	On track
2019 Milestone Description		
eSpin delivers nanofiber electrode mat material to Vanderbilt (~0.5 m^2 per month for 4 months), then 2 anode mats and 2 cathode mats per month. Vanderbilt tests the eSpin electrode material in MEAs.	Jan.-Dec 2019	On going
Vanderbilt continues to prepare and evaluate fiber electrode MEAs and identify samples that meet/exceed the 12/2019 performance targets.	Jan.-Dec. 2019	On going
Better understanding of water management and low RH operation for nanofiber electrode MEAs (focus on inter and intra-fiber porosity). • Adjust binder composition/structure accordingly to improve performance and durability. • Identify a recommended operating protocol for optimal fuel cell performance with nanofiber electrode MEAs.	Feb.-Dec. 2019	On going
Demonstrate fuel cell performance of eSpin electrodes that matches the performance of nanofiber mat electrodes prepared at VU.	Sept.-Nov. 2019	planned

Approach

1. Prepare nanofiber and sprayed electrode MEAs with commercial PtCo/C cathodes with various binders (VU for nanofibers and painted cathodes; NTCNA for sprayed cathodes).
2. Evaluate MEA performance and durability. Optimize the nanofiber cathode mat composition and mat morphology to maximize fuel cell power output and durability at high and low relative humidity conditions (VU and NTCNA).
3. Collaborate with FC-PAD researchers at National Labs to: (1) verify MEA performance, (2) assess durability, (3) perform diagnostic tests.
4. Perform structural characterization of fibers and begin linking structure to function (VU, NTCNA, and FC-PAD labs).
5. Prepare and test nanofiber mat electrodes using the commercial electrospinning equipment at eSpin Technologies, Inc.

Electrospun Pt/C Gen-1 Fibers and PtCo/C Gen-2 Fibers

- High molecular weight polymers with sufficient chain entanglements will form fiber structures that dry-deposit on a grounded collector
- Nafion does not dissolve in alcohol/water solvents; it forms a micellar dispersion.
- A carrier polymer is required to spin Nafion fibers.

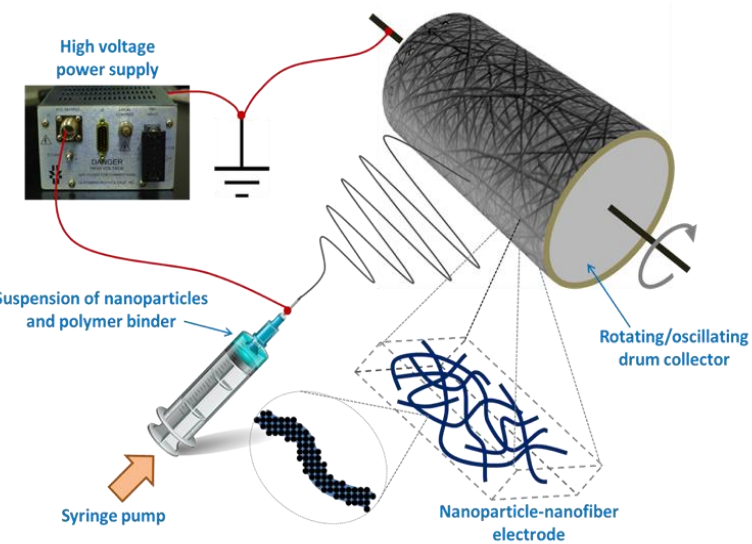
Ink: Catalyst+PFSA/PAA + solvent

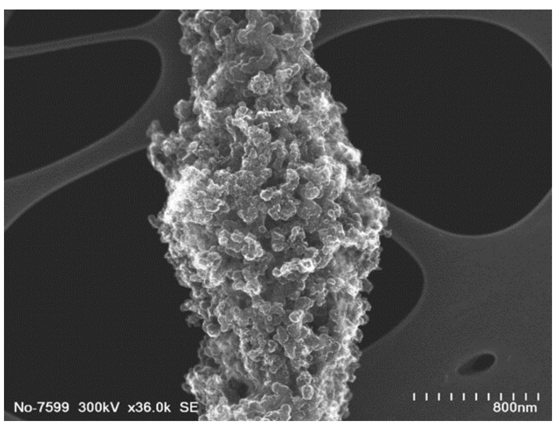
↓

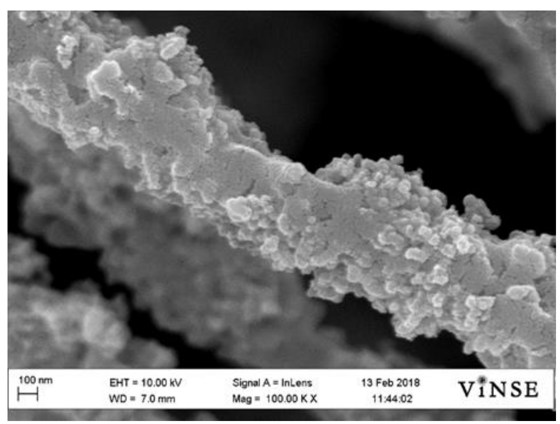
Electrospinning on Aluminum Foil or GDL or membrane

↓

Hot Press to make MEA







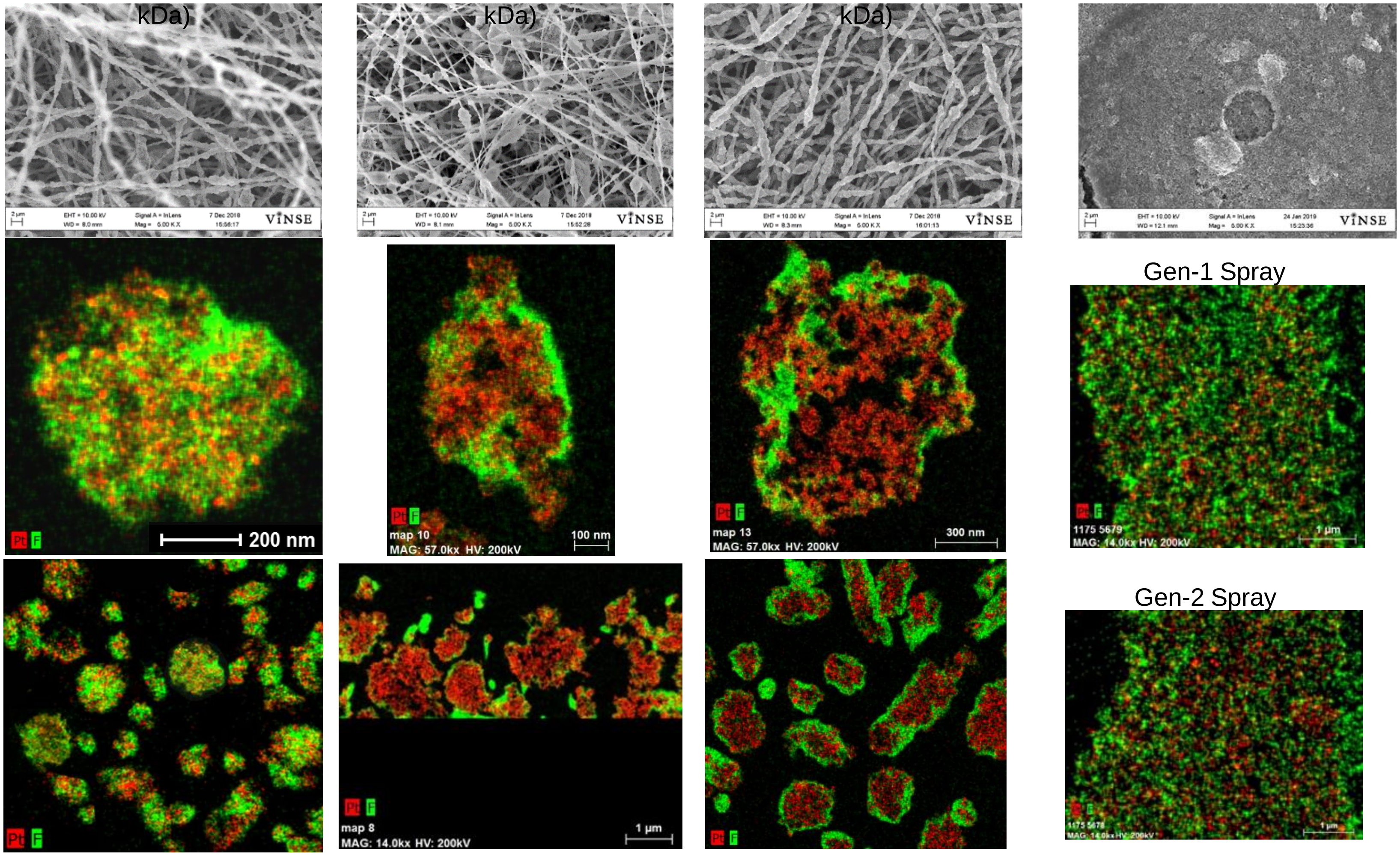
Gen-1 and Gen-2 fibers are similar in appearance and are characterized by:

- A very high catalyst particle content (> 50 wt.%)
- A fiber diameter of 400-800 nm.
- A highly roughened surface where individual 50 nm catalyst particles can be seen.
- A thin coating of binder covering all catalyst particles.
- Fibers are porous.
- No agglomerates of catalyst or binder.

- **Gen-1 fiber mat electrodes:** catalyst + Nafion(acid form) + poly(acrylic acid) (PAA)
- **Gen-2 fiber mat electrodes:** catalyst + Nafion(salt form) + either PAA or polyethylene oxide (PEO)

Accomplishment: SEM and STEM-EDX of Gen-1 and Gen-2 Pt/C Electrodes

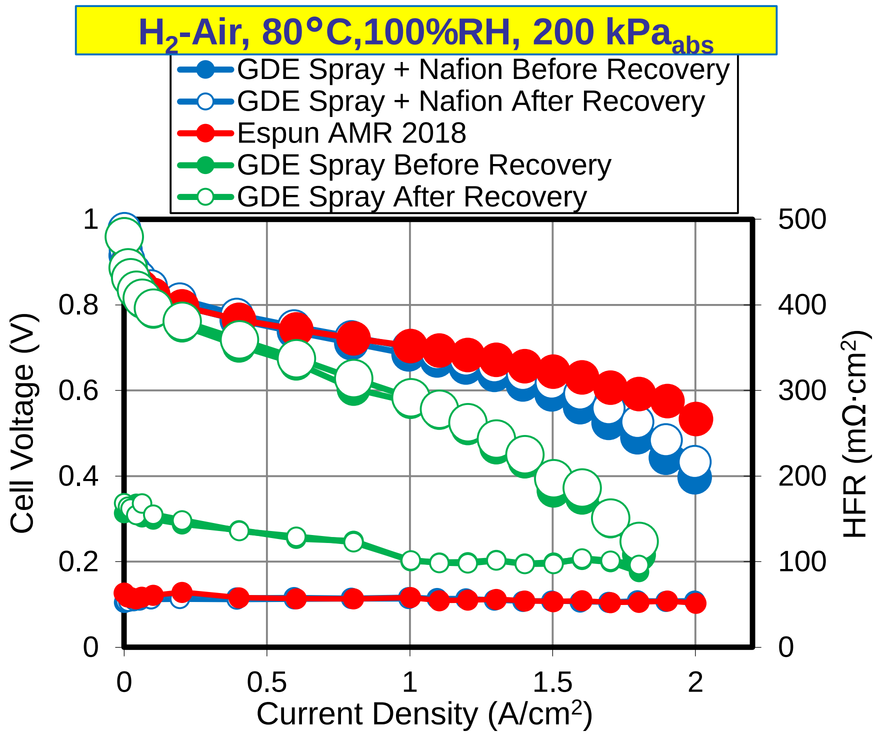
Nafion (H^+): PAA (450 kDa) | Nafion (Na^+): PAA (450 kDa) | Nafion (Na^+): PEO (600 kDa) | NTCNA Sprayed Electrode

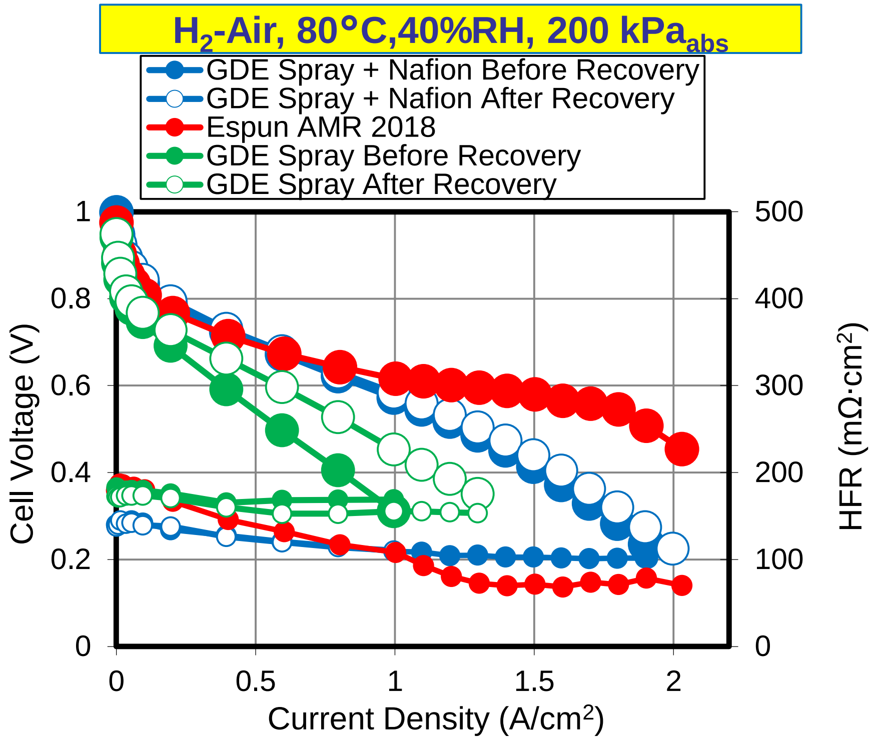


Conclusions:

- I/C of Gen-2 fibers based on composition: 1.15 → Average I/C from EDX analysis of fiber cross-sections: 1.07 ± 0.07
- Fiber core: 60% of the catalyst; Average I/C (from EDX) = 0.46 ± 0.1
- Fiber shell: 40% of the catalyst; Average I/C (from EDX): 1.93 ± 0.12

Accomplishment: Comparing Nanofiber (Gen-2 binder) and Sprayed Electrode (Nafion binder) MEAs at High and Low RH



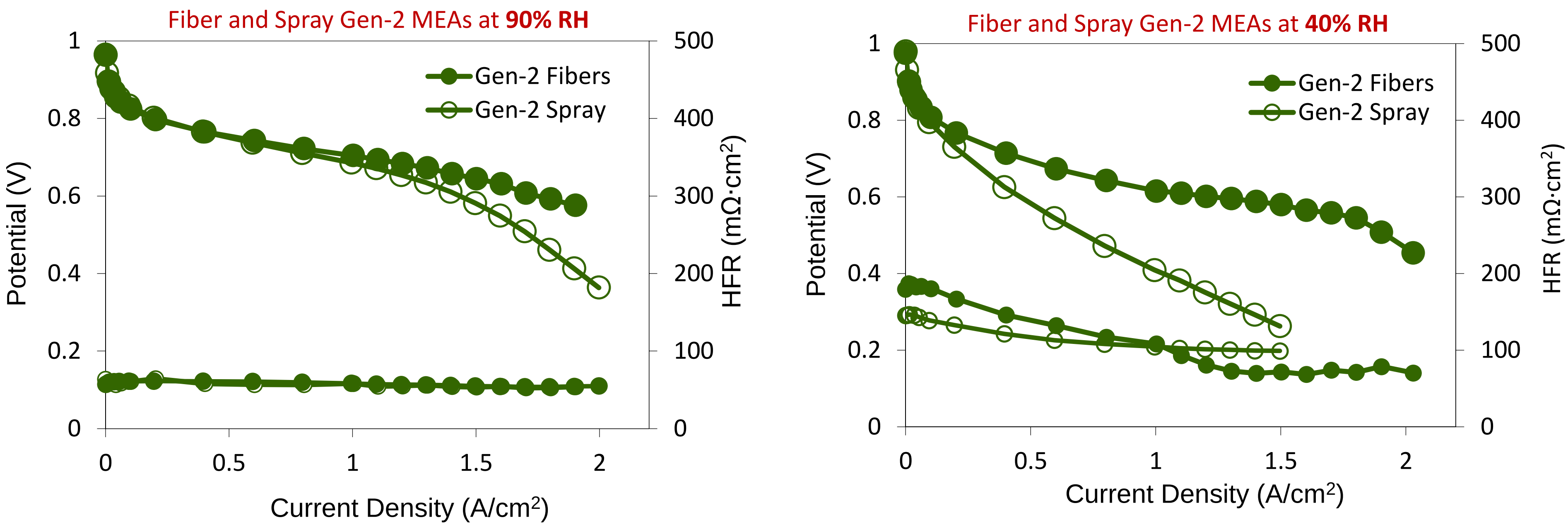


- **Anode**: 0.1 m_{Pt}/cm^2 (TEC10E30E)
- **Cathode**: PtCo/C : 0.1 mg_{Pt}/cm^2 (TEC36E52)
- **Espun:** Espun electrodes with PtCo/C- PEO cathode, Pt/C-PEO Anode
- **GDE Spray:** PtCo/C sprayed (I/C:0.9)
- **GDE Spray+ Nafion**: 0.5 mg/cm^2 Nafion coating on GDE Spray. The Nafion coating is on both anode and cathode sides.
- **Recovery**: Based on LANL protocol

Conclusions:

- Nanofiber MEA (Gen-2 binder) produces ~10% higher power vs. a sprayed electrode MEA (Nafion binder) at 100% RH: 1,040 vs. 900 mW/cm^2 at 0.60 V.
- Nanofiber MEA produces significantly more power at 40% RH: 770 vs. 540 mW/cm^2 at 0.60 V

Accomplishment: Gen-2 Binder In Nanofiber and Sprayed Cathode MEAs



Operating Conditions:

80 ° C, 200 kPa_{abs}, 4000 sccm H_2, 8000 sccm air

All MEAs had an active area of 10 cm^2,

Nafion 211 membrane and Sigracet 29 BC gas diffusion layers

Cathode Loading was 0.1 mg_{Pt}/cm^2

Gen-2 Fiber and Spray Cathodes :

PtCo/C (TEC36E52): Nafion (Na^+ form): PEO (600 kDa)

Gen-2 Fiber Anodes:

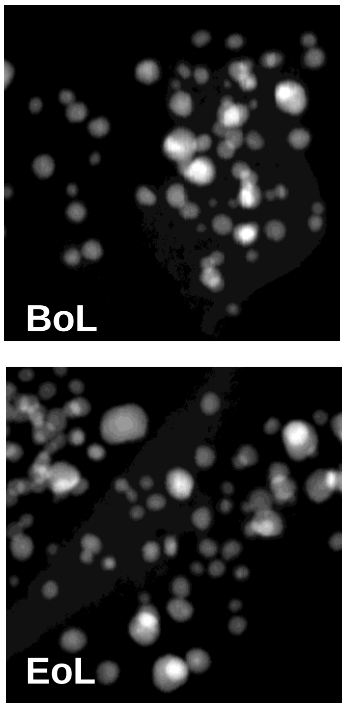
TKK Pt/C: Nafion (Na^+ form): PEO (600 kDa)

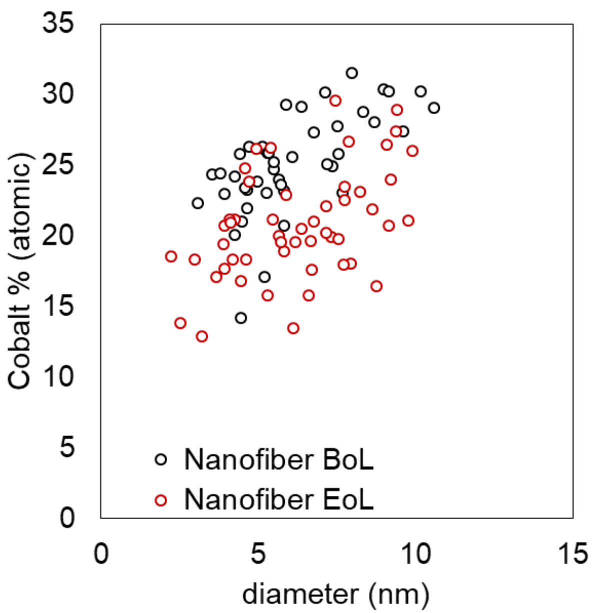
Conclusions:

- At 100% RH: the Gen-2 fiber and sprayed cathode MEAs perform in same (except at high current densities)
- At 40% RH: the Gen-2 fibers generated more power than the Gen-2 sprayed cathode MEA.

Accomplishment: Retention of Cobalt after 30,000 Metal Dissolution Voltage Cycles (TKK PtCo/C cathode, Gen-1 binder)

Cobalt content in catalyst particles vs. particle size at BoL and EoL(for Gen-1 Nanofibers with TKK PtCo/C)

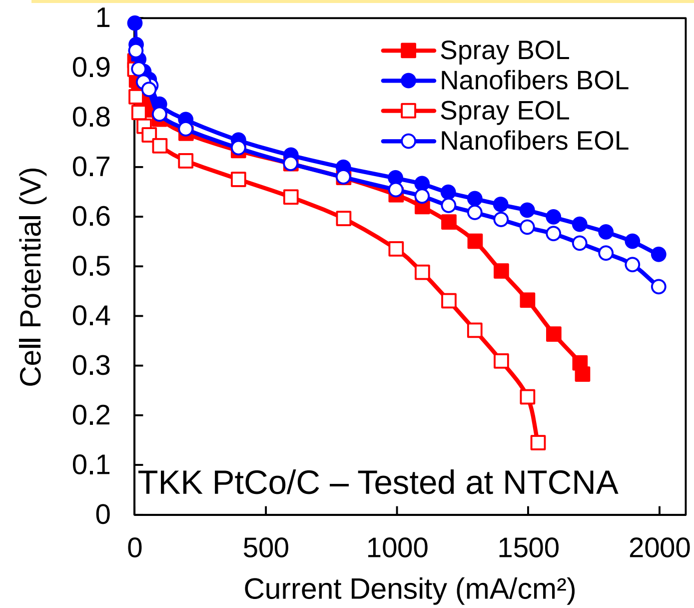




Max Power (fiber vs. spray): 1045 vs 869 mW/cm^2

Power at 0.65 V (fiber vs. spray): 751 vs. 715 mW/cm^2

Max Power loss at EoL: 8% (fibers) vs. 32% (spray)



Operating conditions:
80°C, 200 kPa, 4/8 L/min H_2/air
0.1 mg/cm^2 for both cathode and anode

The same EDX Co% analysis is repeated for the sprayed electrode at BoL and EoL.

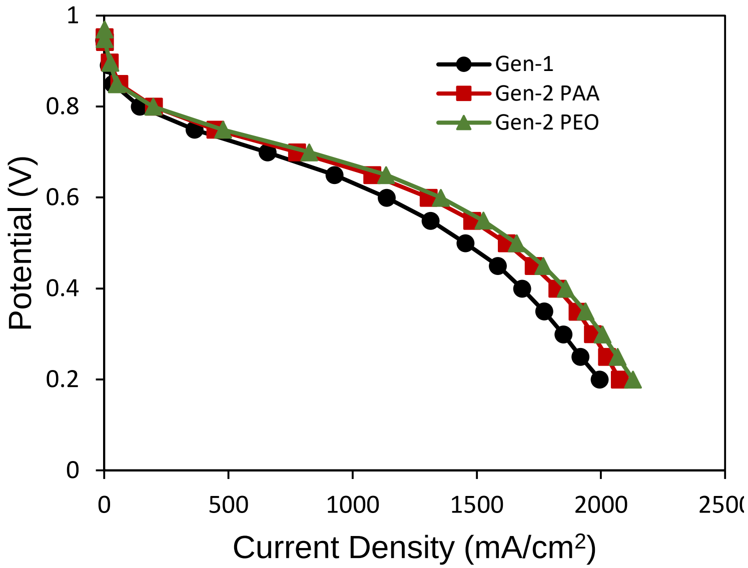
$$Co\ retention = 1 - \left(\frac{\left[\frac{Co\%}{Size}\right]_{EOL}}{\left[\frac{Co\%}{Size}\right]_{BOL}} \right)$$

Conclusion:

- Cobalt Retention (slurry)= 49%
- Cobalt Retention (nanofibers)= 61%

Accomplishment: Comparing Gen-1 and Gen-2 Binders in Nanofiber Cathodes

Pt/C anode and cathode at BoL: Fiber Electrode MEAs at 80°C, 200 kPa_{abs}, 100% RH



Operating Conditions:

125 sccm H_2, 500 sccm air

All MEAs had an active area of 5 cm^2, anode and cathode, and utilized TKK Pt/C (TEC10F50E), Nafion 211, and Sigracet 29 BC gas diffusion layers.

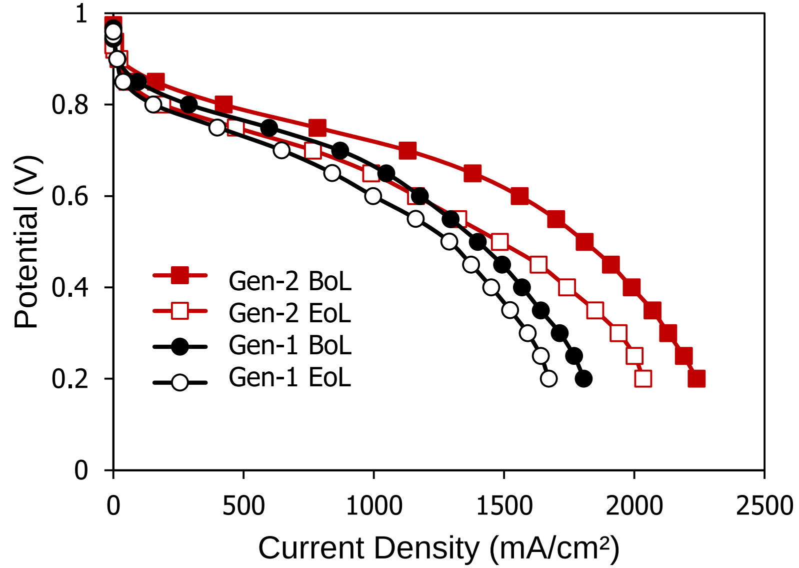
Electrode Loading was 0.1 mg_{Pt}/cm^2

Gen-1 : Nafion (H^+ form): PAA (450 kDa)

Gen-2 PAA: Nafion (Na^+ form): PAA (450 kDa)

Gen-2 PEO: Nafion (Na^+ form): PEO (600 kDa)

Gen-1 and Gen-2 Fiber MEAs before and after 30,000 Load Cycles (0.6-0.95 V) at 100% RH



Operating Conditions:

80 ° C, 200 kPa_{abs}, 125 sccm H_2, 500 sccm air

All MEAs had an active area of 5 cm^2 and utilized Nafion 211, and Sigracet 29 BC gas diffusion layers.

Gen-1 : Nafion (H^+ form): PAA (450 kDa)

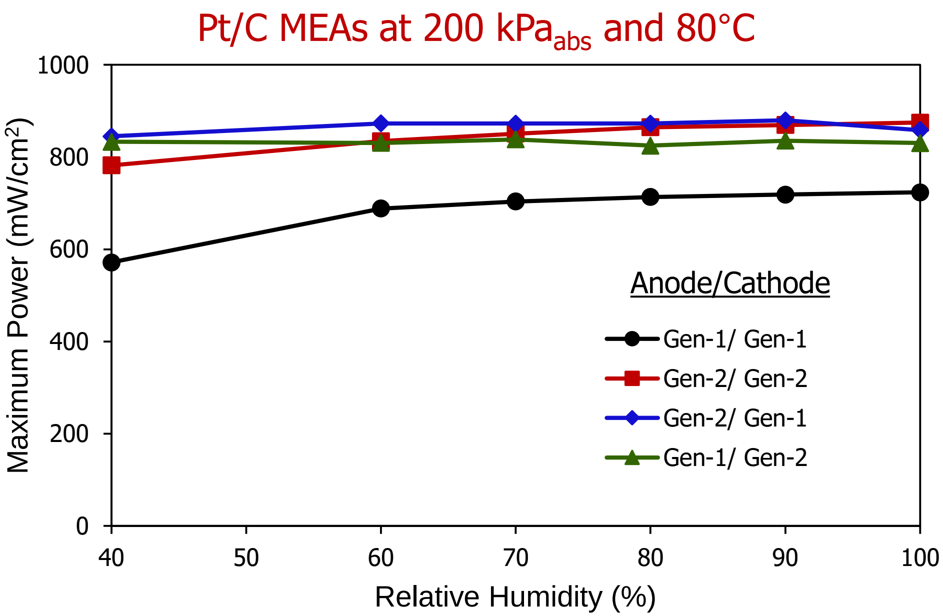
Gen-2 : Nafion (Na^+ form): PEO (600 kDa)

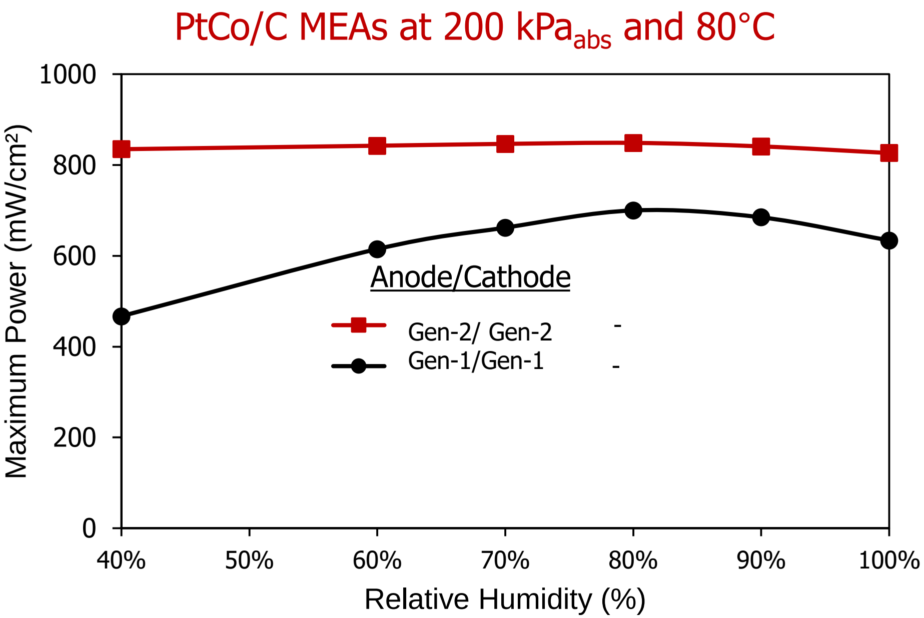
Anodes used Pt/C (TEC10F50E) and cathodes used PtCo/C (TEC36E52); each 0.1 mg_{Pt}/cm^2

Conclusions:

- Under fully humidified conditions, Gen-2 (PAA or PEO carrier) MEAs perform similarly (better than Gen-1).
- Gen-2 cathode lost more power after AST, but had higher EoL power as compared to Gen-1.

Accomplishment: Comparing Gen-1 and Gen-2 Fiber Cathodes: RH Effect





Operating Conditions:

80 ° C, 200 kPa$_{abs}$, 125 sccm H_2, 500 sccm air

All MEAs had an active area of 5 cm^2 and utilized a Nafion 211 membrane, and Sigracet 29 BC gas diffusion layers.

Electrode Loading was 0.1 mg$_{Pt}$/cm^2

Pt/C (TEC10F50E_ MEAs:

PtCo/C (TEC36E52) cathode MEAs:

Anodes used Pt/C (TEC10F50E) and cathodes used

Conclusions:

- The presence of a Gen-2 binder at the anode or cathode improves power output at low RH.
- Maximum power is essentially independent of feed gas RH with Gen-2 binder.
- A similar effect seen for Pt/C and PtCo/C cathodes.

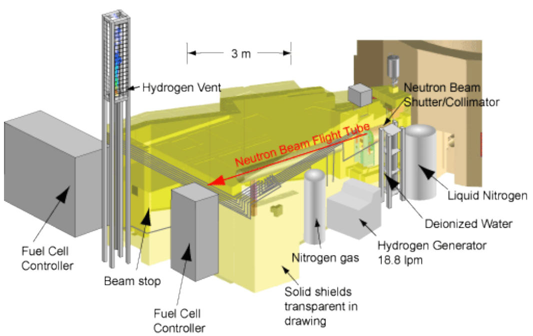
Accomplishment: Neutron Imaging of Vanderbilt MEAs

Andrew M. Baker, Kavitha Chintam, Rod Borup, Rangachary Mukundan (Los Alamos National Laboratory) and Jacob LaManna, Dan Hussey, David Jacobson (NIST Center for Neutron Research)

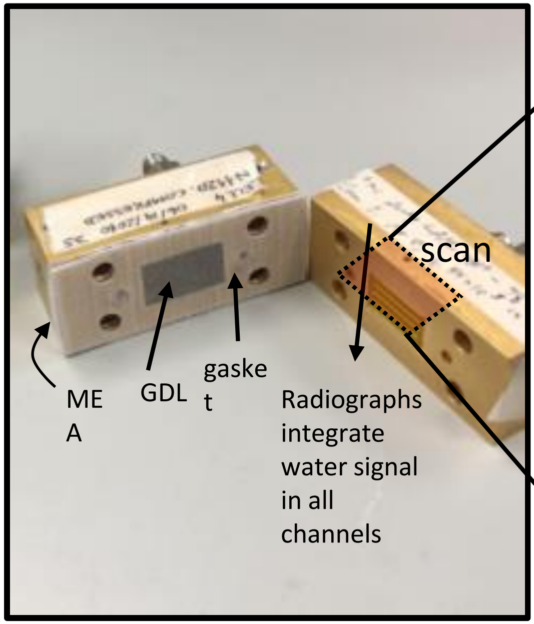
Samples

- GDE = 0.1/0.1 mg/cm^2 spray-coated GDEs
- NF = electrospun 0.1/0.1 mg/cm^2 Pt/C (Nafion/PAA binder) CCM
- *NR-211 PEMs*
- *29BC GDLs*
- *PTFE gaskets*

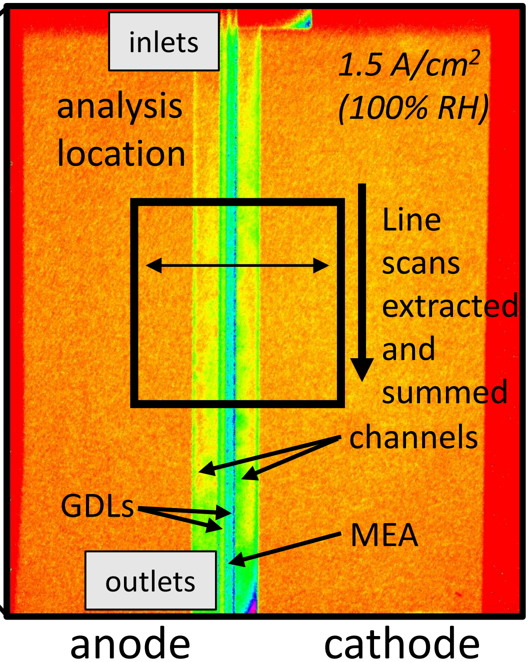
NIST Neutron Imaging Facility



Hardware and scan location



Typical neutron radiograph



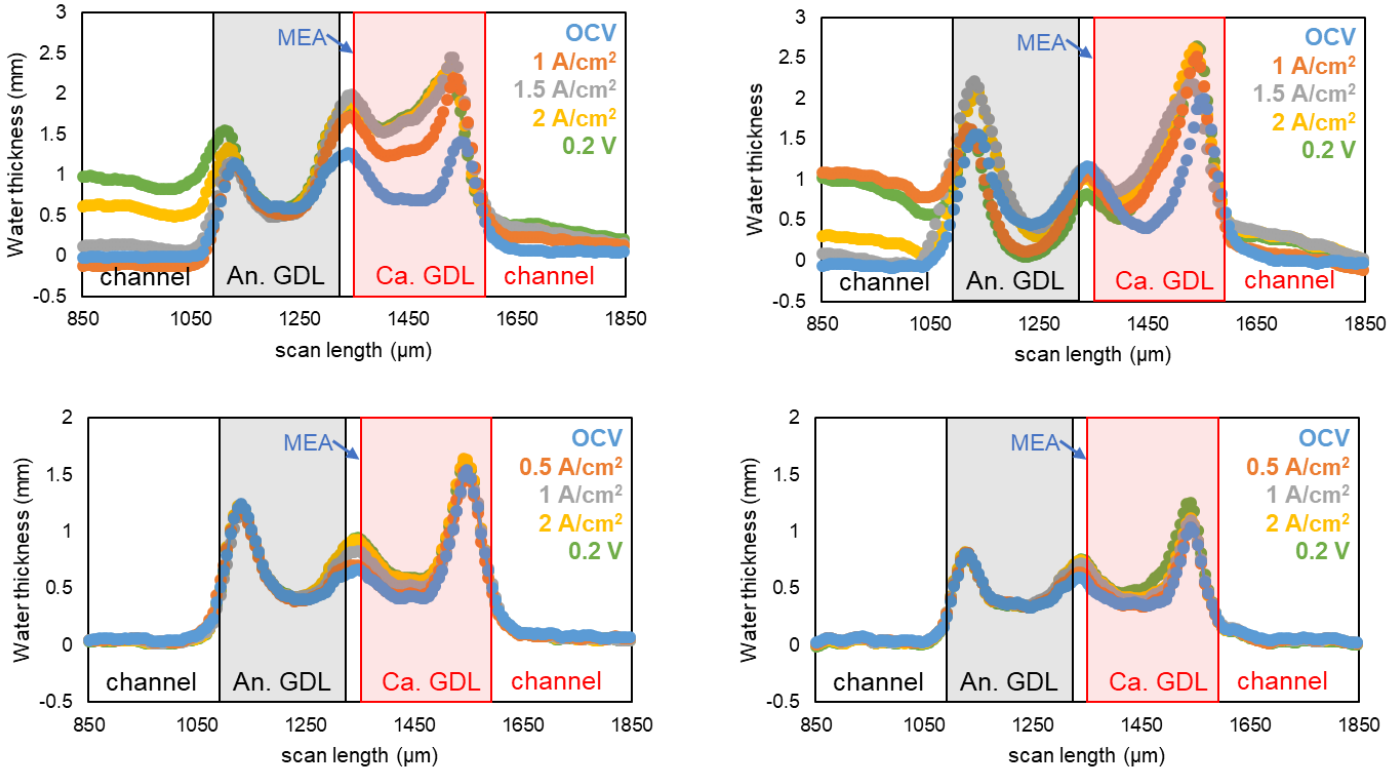
- 2 cm^2 differential cell hardware
- Test conditions: 80˚C, 200/200 sccm H_2/air, variable RH and outlet pressure

Accomplishment: MEA Water Profiles at Different Load Conditions

Sprayed GDE | $P_{outlets}$ = 200 kPa_{abs} | Nanofiber

100% RH

40% RH



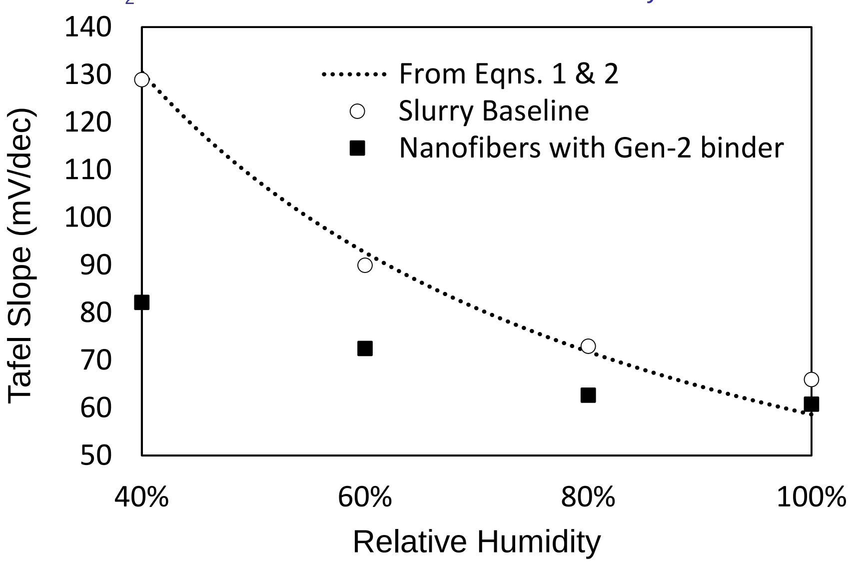
Conclusions:

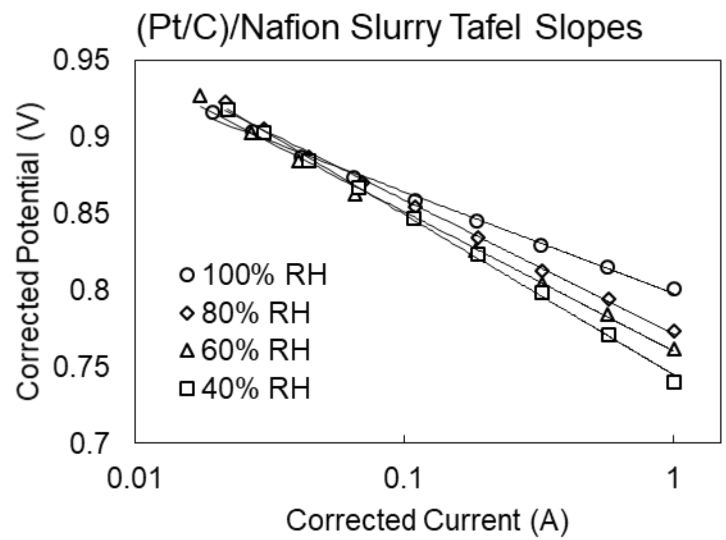
- Significantly less water in the nanofiber MEA and cathode MPL/GDL at high current densities at 100% RH.
- Little difference in MEA performance and water content between nanofiber and sprayed GDE at 40%RH.

FCPAD FUEL CELL PERFORMANCE AND DURABILITY

Accomplishment: Relative Humidity Effect on ORR Kinetics for Pt/C Slurry and Nanofiber Cathode (with Gen-2 Binder)

O_2 concentration was maintained at unit activity for each RH

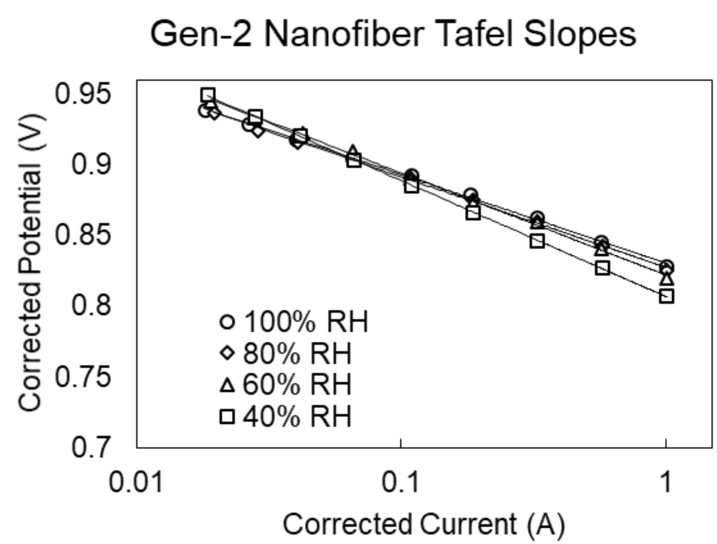




$$Tafel\ Slope = \frac{2.303RT}{\alpha_o n_{\alpha o} F} \quad [1]$$

Transfer coefficient:

$$\alpha_o = (0.0011552RH + 0.000139)T \quad [2]$$



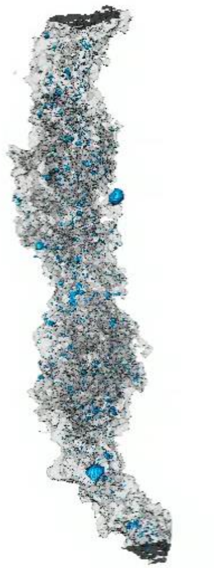
Conclusions:

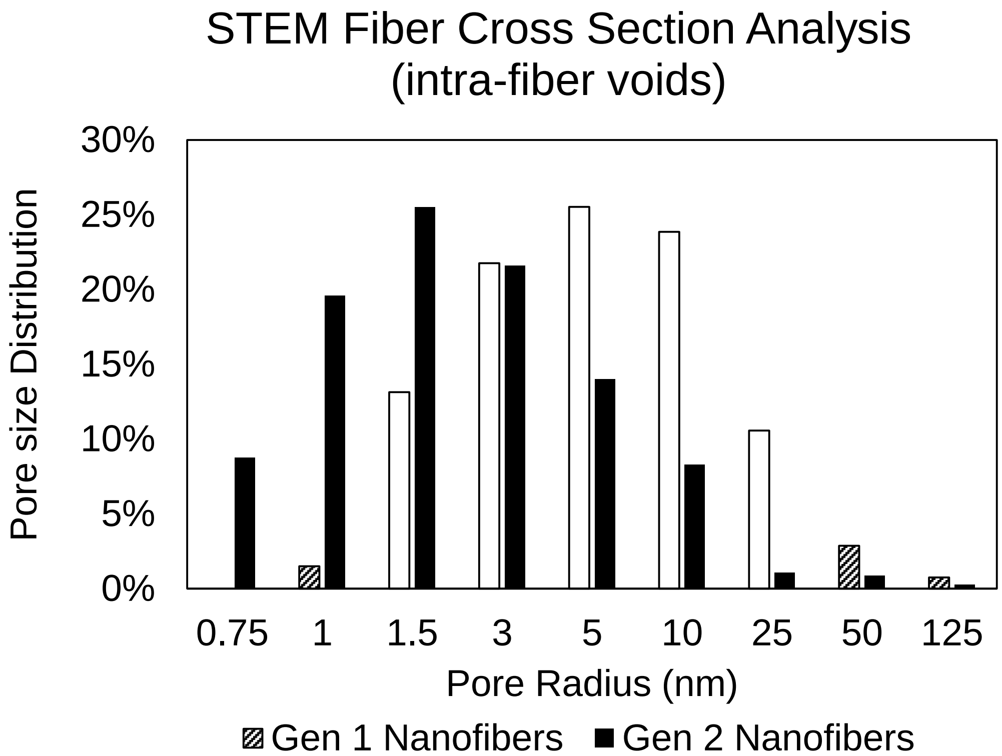
- ORR kinetics is faster with Gen-2 binder at low RH. We also know that ohmic resistance is lower at low RH with Gen-2 binder.
- Results suggest better water retention at low RH for fibers with Gen-2 binder.

References

1. Song C., Zhang J. (2008) Electrocatalytic Oxygen Reduction Reaction. In: Zhang J. (eds) PEM Fuel Cell Electrocatalysts and Catalyst Layers. Springer, London
2. J. Zhang, Y. Tang, C. Song, Z. Xia, H. Li, H. Wang, J. Zhang. (2008), Electrochimica Acta. 53, 16. 5315-5321

Accomplishment: Pore Size Distribution in Gen-1 and Gen-2 Nanofibers (with PtCo/C catalysts)





Kelvin Equation

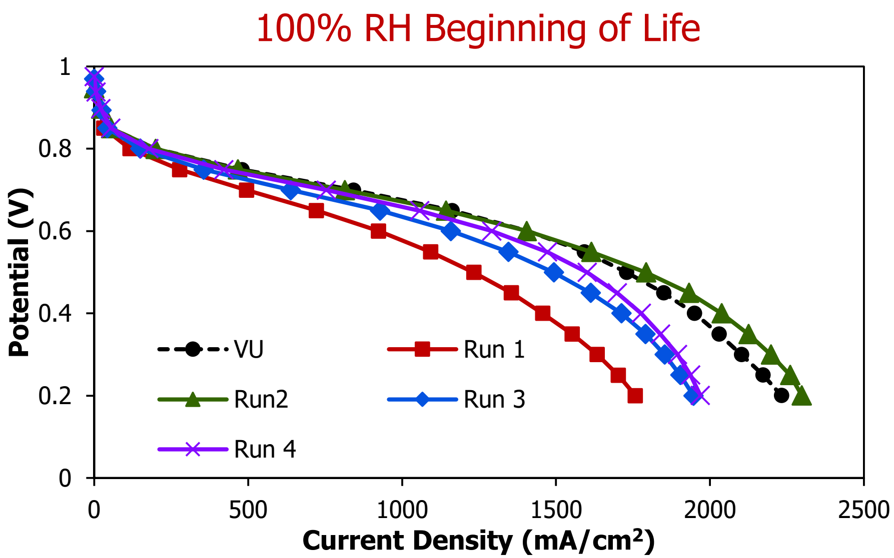
$$\ln \frac{p}{p_0} = \frac{2\gamma V_{\mathrm{m}}}{rRT}$$

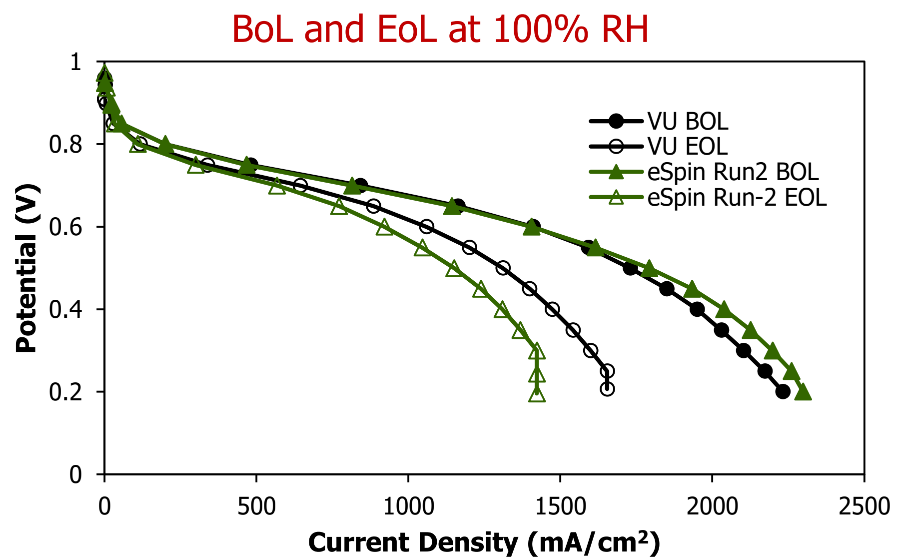
p = pressure
p_o = saturation vapor pressure
γ = surface tension
R = pore radius
V_m = partial molar volume

Conclusions:

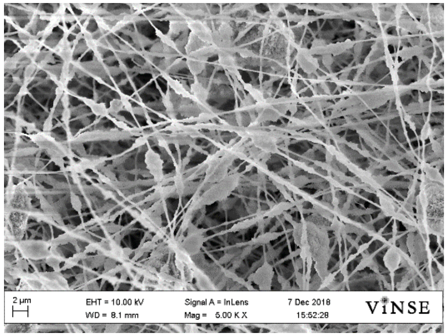
- According to the Kelvin Equation, water will condense at 40% RH and 80^{o}C in pores with a radius < ~0.6 nm.
- Fibers with Gen-2 binder have smaller pores, some may be small enough for capillary condensation of water.

Accomplishment: eSpin Technologies Gen-2 Electrode MEAs with Pt/C Catalyst

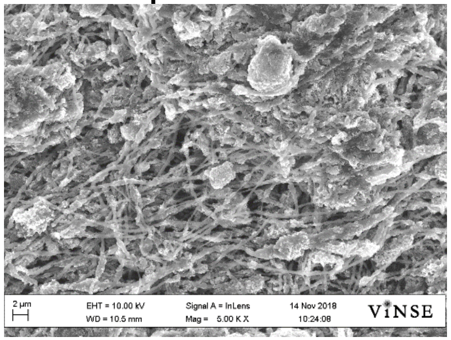




VU



eSpin Run 2



EoL: 30,000 square wave load cycles from 0.60 to 0.95 V (3s at each voltage)

Operating Conditions:

80 ° C, 200 kPa_{abs}, 125 sccm H_2, 500 sccm air

All MEAs had an active area of 5 cm^2, with a Nafion 211 membrane, TKK Pt/C (TEC10F50E) for the anode and cathode, and Sigracet 29 BC gas diffusion layers.

Electrode Loading was ~0.1 mg_{Pt}/cm^2

Conclusions:

- eSpin fiber mat electrodes have some large droplet defects (> 5 μm in diameter).
- eSpin mats perform well at BOL and100% RH, but they do not exhibit the same durability as Vanderbilt electrodes.
- eSpin is working on improving fiber mat quality, performance, and reproducibility.

Response to Previous Year Reviewers' Comments

The elimination of catalyst work at Georgia Tech is recommended.

Response: The Georgia Tech catalyst work ended at the end of Year 2. They are not part of the project in Year 3.

It is suggested the team increase focus on systematic parameterization (perhaps using a design of experiment) and optimization of the process variables (such as I/C, percentage of PGM, electrode thickness, ionomer, carrier, electrospinning process variables, etc.), complete with characterization and testing. It is also recommended the team include multiple samples where needed.

Response: It is difficult to perform a systematic study of process variables such as I/C ratio, fiber diameter, electrode thickness, fiber porosity, ionomer/carrier ratio, etc. because we must first create a mat of well-formed fibers before any fuel cell tests are carried out. This requirement, which is not encountered in normal electrode/MEA development, complicates the examination of one process variable at a time. For example, the range of I/C ratios that give good fibers may be limited and might require changes in the binder/carrier ratio, solvent composition, and electrospinning conditions (where the latter conditions may also change the fiber diameter and porosity).

The team should focus more on gas diffusion media/water management. The use of alternative catalysts should be considered. The team should focus on using different ionomers. Also, the characterization of the pore size distribution in the catalyst layer is likely critical to better performance.

Response: Characterization experiments have been initiated with FC-PAD collaborators. We have begun to examine binder/catalyst and pore size distribution in Gen-1 and Gen-2 fibers (with ORNL). We have begun to examine water management (neutron imaging with LANL and NIST). The use of different ionomer binders will be addressed in Year 3.

The baseline (sprayed) performance is also sub-par.

Response: NTCNA has modified its MEA hot-pressing procedure and their sprayed electrode MEAs are now working well with high BoL power densities.

FC-PAD Collaboration and Coordination

Oak Ridge National Laboratory

- Analysis of nanofiber electrode MEAs by high resolution STEM imaging.
- Mapping of ionomer and Pt in nanofiber mat cathode MEAs at beginning of life (BoL) and end of life (EoL).
- Mapping of Co at BoL and EoL

Lawrence Berkeley National Laboratory

- Measure water vapor uptake in nanofiber electrodes and MEAs as a function of RH.
- Investigate Nafion/carrier polymer interaction; how does a carrier polymer interact with Nafion.
- Possible modeling of nanofiber MEA operation with different RH for the anode/cathode feed gases.

Argonne National Laboratory

- Possible modeling of metal dissolution and carbon corrosion in agglomerate-free nanofiber cathodes.

Los Alamos National Laboratory

- Verification of nanofiber MEA performance at BoL and after ASTs.
- Neutron water imaging with NIST to understand better Gen-2 MEA performance at low RH

Proposed Future Work

Prepare nanofibers and characterize MEAs made with low EW PFSA ionomers in the acid form and salt form.

Continue the neutron scattering studies with fibers made with salt-form and acid-form Nafion binders (and low EW ionomer binders).

Continue to evaluate electrospun Pt/C and PtCo/C nanofiber mat electrodes made at eSpin.

Continue to optimize the composition and post-electrospinning processing of Gen-2 nanofiber electrode MEAs. Include a recovery protocol when evaluated performance.

- Perform load cycle and start-stop cycle durability tests on 0.125 mg/cm^2 Pt-loaded MEAs (total anode+cathode loading).

Continue to probe the structure of Gen-1 and Gen-2 binder MEAs and correlate results with fuel cell performance.

- What is the hydrophobicity/hydrophilicity of the fiber interior and fiber surface?
- Why do we see high power at low RH with Gen-2 MEAs at either the anode or cathode? Can modeling studies help here?
- What is the structure and EDX Pt and binder distributions in Gen-1 and Gen-2 fibers after load cycling and carbon corrosion ASTs?

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

Summary

- Well-formed fiber mats with no sprayed droplets, made with salt-form Nafion binder, worked exceptionally well in a MEA, with high BoL power, high power at low RH, and minimal power loss after a load cycling AST.
  - 349 mA/cm^2 at 0.8 V and 200 kPa backpressure, for a PtCo/C cathode with a total anode + cathode loading of 0.115 mg_{pt}/cm^2.
  - Rated power of 945 mW/cm^2 for a PtCo/C cathode, 0.117 mg_{Pt}/cm2 total anode + cathode loading, 95^{o}C,
    100% RH, and 200 kPa, (power at 0.663 V).
  - 19% drop in mass activity after a load cycling AST.
  - An 18% drop in voltage at 1.2 A/cm^2 after a start/stop voltage cycling AST.
- Fiber mats containing droplets (micron-size agglomerates) produce high BoL power, but have poor durability and a power loss at low RH.
- Fibers made with salt-form Nafion binder:
  - Have an unusual morphology with high binder on the fiber surface and a low I/C ratio in the fiber interior (a core-shell structure).
  - Hold water at low RH. Ne possible explanation is capillary condensation of pores within ta fiber.
  - Salt-form Nafion has no benefit in a sprayed electrode MEA.
- Fibers made with acid-form Nafion and PtCo/C catalyst exhibit high power after a load cycling AST, as compared to a sprayed electrode MEA, due to better Co retention.
- Fibers made with acid-form Nafion expel water better during fuel cell operation at 100% RH (due to inter-fiber porosity) and hold water at low RH (due to intra-fiber pores).

Technical Back-Up Slides

Electrospinning – Rotating Drum Apparatus