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
- (subcontracts and NDAs were not signed until early 2017)
- Project End Date: 12/31/2020
- Percent complete: 77%

- Total Project Budget: $3,173,854
- Total Recipient Share: $640,291
- Total Federal Share: $2,533,563
- Total Funds Spent:
  - $1,942,488 (DOE) + $485,622 (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)
- eSpin Technologies, Inc.
- Project Lead: Peter N. Pintauro, Vanderbilt

Project Relevance and Objectives

Project Relevance:

- The VU/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 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: ≤ 0.10 mg/cm^2 cathode and ≤ 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

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. Begin preparing and testing 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

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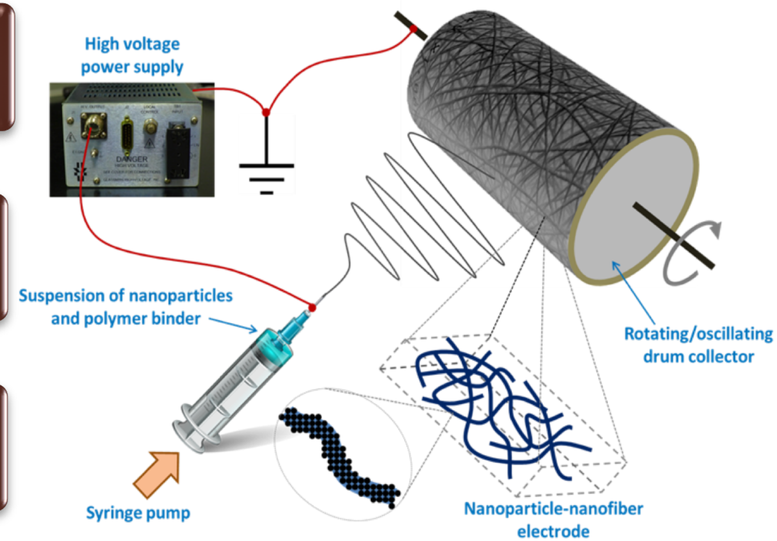
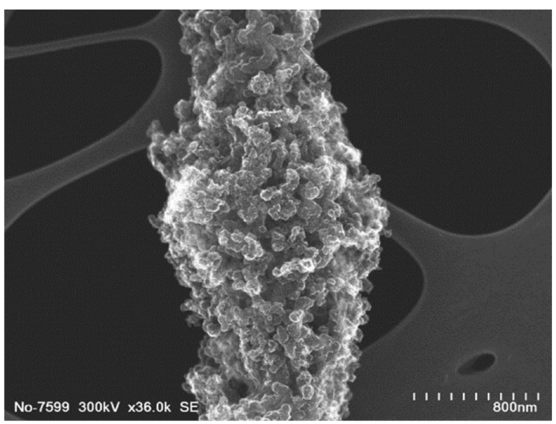
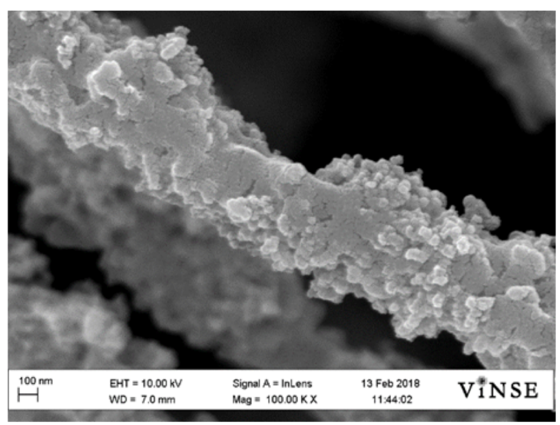
Electrospinning on Aluminum Foil or GDL or membrane

↓

Hot Press to make MEA





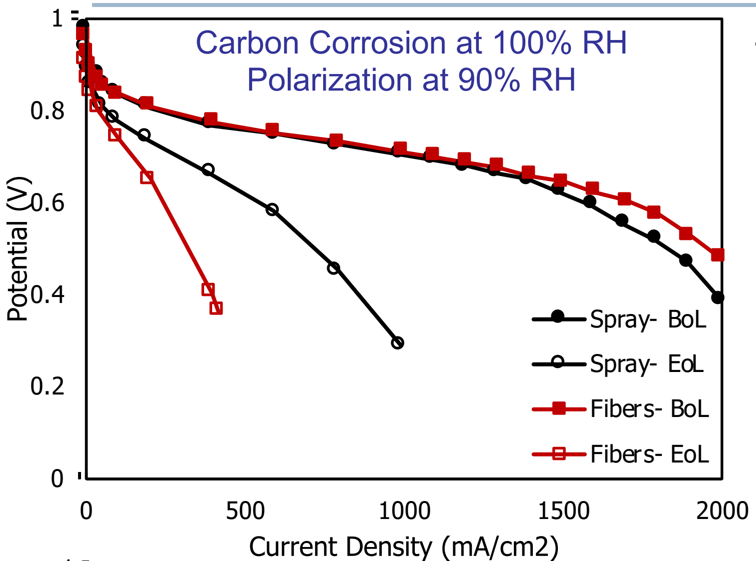


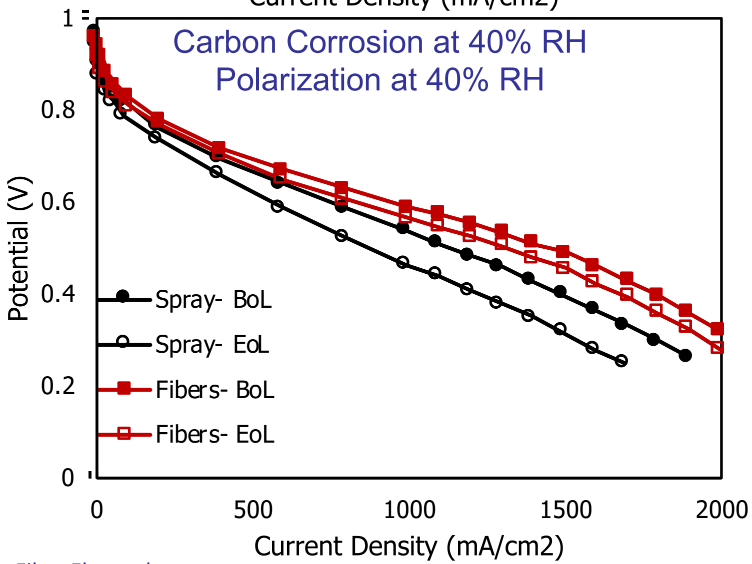
Gen-1 and Gen-2 fibers are similar in appearance and are characterized by:

- 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: Improved Gen-2 PtNi/C Fiber Electrode MEA: Carbon Corrosion Durability at High/Low Humidity





100% RH Corrosion			40% RH Corrosion		
Electrode	Spray	Fibers	Electrode	Spray	Fibers
Power at 0.65 V 90% RH EoL/BoL (mW/cm^2)	290/720	100/810	Power at 0.65 V 40% RH EoL/BoL (mW/cm^2)	290/380	400/450
ECSA EoL/BoL (m^2/g_{Pt})	37/78	63/68	ECSA EoL/BoL (m^2/g_{Pt})	65/68	49/47
Mass Activity EoL/BoL (mA/mg_{Pt})	133/256	76/245	Mass Activity EoL/BoL (mA/mg_{Pt})	132/240	184/238
Carbon Loss (%)	26	18	Carbon Loss (%)	13	15

Conclusions

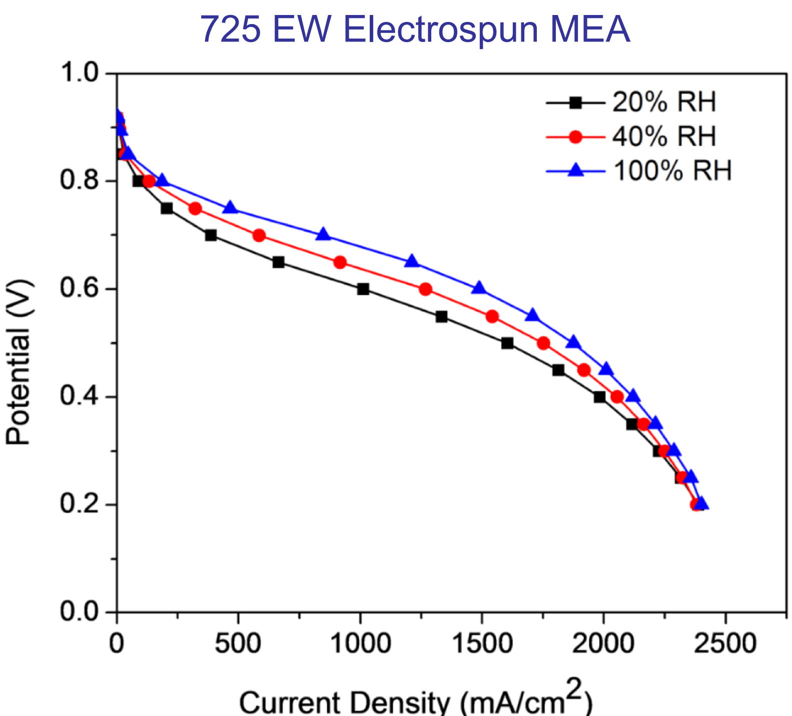
- PtNi/C fiber MEAs undergo significant power loss after carbon corrosion at 100% RH as compared to PtNi/C spray electrodes.
- Conducting carbon corrosion voltage cycling at low humidity drastically improves EoT performance for both fiber and spray electrodes.
- The effect of low humidity corrosion was more pronounced in fiber electrodes.

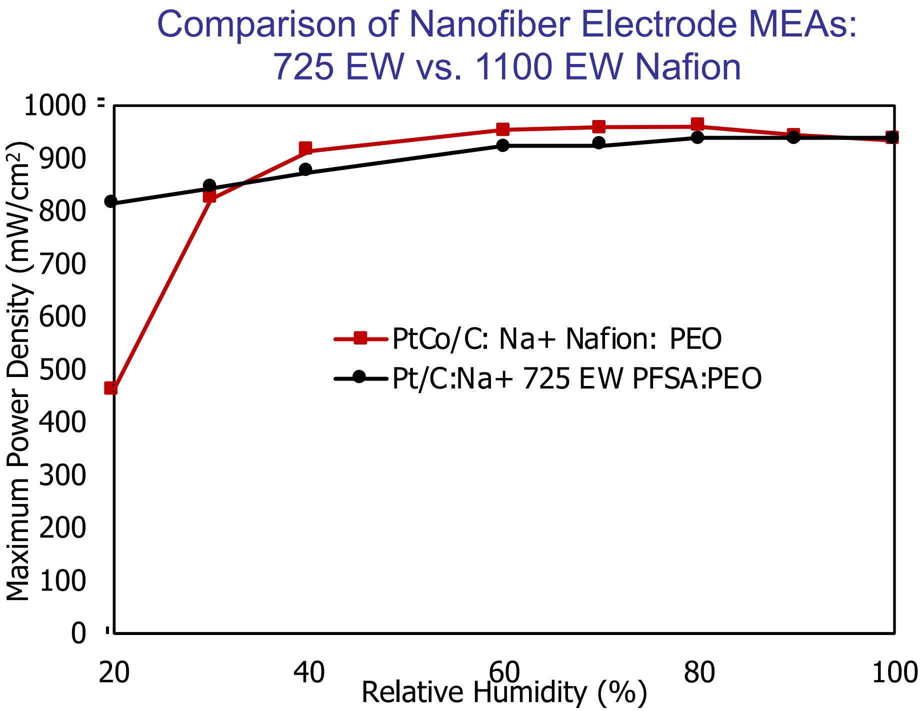
Fiber Electrodes
Anode: Pt/C (TKK):Na^+ Nafion:PEO
Cathode: PtNi/C (TKK):Na^+ Nafion:PEO
Spray Electrodes
Anode: Pt/C (TKK):H^+ Nafion
Cathode: PtNi/C (TKK):H^+ Nafion

Anode/Cathode: 0.1 mgPt/cm^2
Nafion 211 membrane
Sigracet 29 BC GDLs 10 cm^2 area and parallel flow fields
Polarization data collected at 80 °C, 200 kPa_{abs}, H_2/air 4000/8000 sccm
Carbon Corrosion EoT: 1000 triangular wave cycles from 1-1.5 V

Spray electrodes prepared by NTCNA
Testing conducted at NTCNA

Accomplishment: An All-electrospun Gen-2 MEA with 725 EW PFSA from 3M Co. (electrodes and membrane)





Conclusions

- An all-electrospun 725 EW PFSA MEA exhibited excellent performance at very low humidity, where maximum power dropped by only 15% when going from 100% RH to 20% RH operation.
- A Nafion MEA produced high power down to 30% RH, but power dropped by 50% when operating at 20% RH.

725 EW PFSA MEA

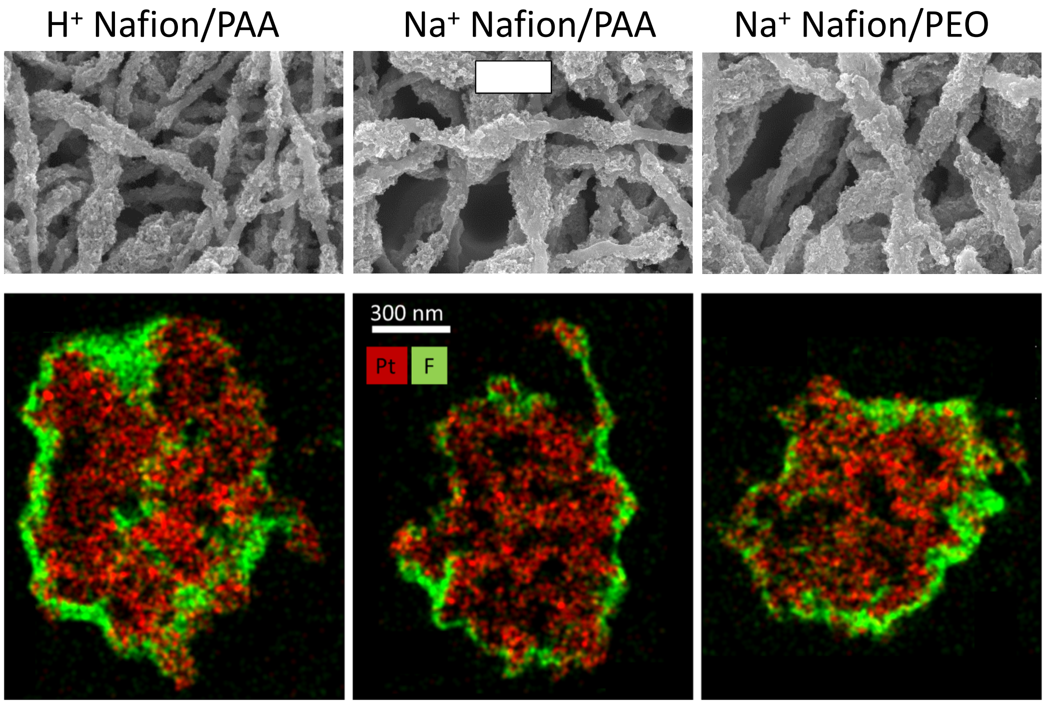
- Cathode/Anode: Nanofiber Pt/C (TEC10F50E):Na^+ 725 EW PFSA:PEO
- Membrane: Nanofiber 80:20 wt. ratio 725 EW PFSA:PVDF) (Dual fiber) 20 μm thickness

Nafion MEA

- Cathode: Nanofiber PtCo/C (TEC36E52):Na^+ Nafion:PEO
- Membrane: Nafion 211 - 25 μm thickness
- Anode: Nanofiber Pt/C (TEC10F50E):Na^+ Nafion:PEO

Electrodes: 0.1 mg_{Pt}/cm^2 ± 0.005
52:37:11 wt. ratio of catalyst:ionomer:carrier
Sigracet 29 BC GDLs 5 cm^2 single serpentine flowfields
Polarization data collected at 80 °C, 200 kPa_{abs}, 125/500 sccm H_2/air

Accomplishment: The Effect of Electrode Binder on Fiber Morphology (data collected at ORNL)

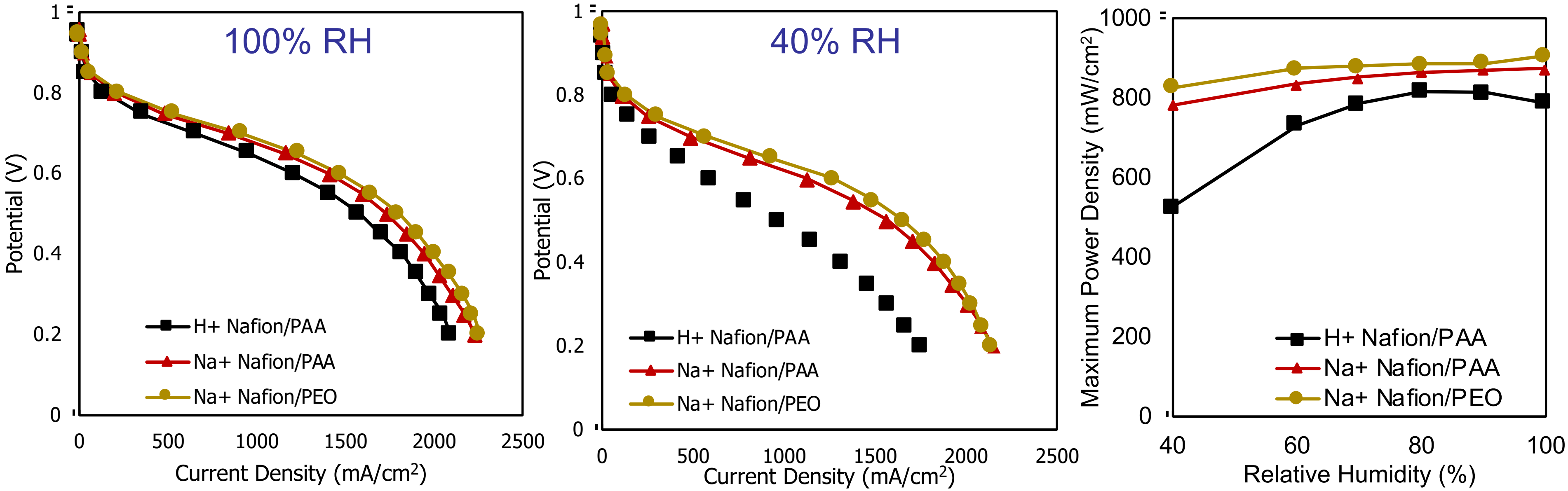


Conclusions

- All three binder types resulted in well-formed fibers with a uniform distribution of catalyst along the length of the fiber and no spray defects.
- Regardless of binder type, all fibers exhibited a catalyst enriched interior and an ionomer enriched surface.

Fiber weight ratios
Pt/C:H^+ Nafion/PAA 58:28:14
Pt/C:Na^+ Nafion:PAA 58:28:14
Pt/C:Na^+ Nafion:PEO 52:37:11
STEM/EDS samples prepared at Oak Ridge

Accomplishment: Electrospinning Nafion in the Salt Form for High Power at Low RH



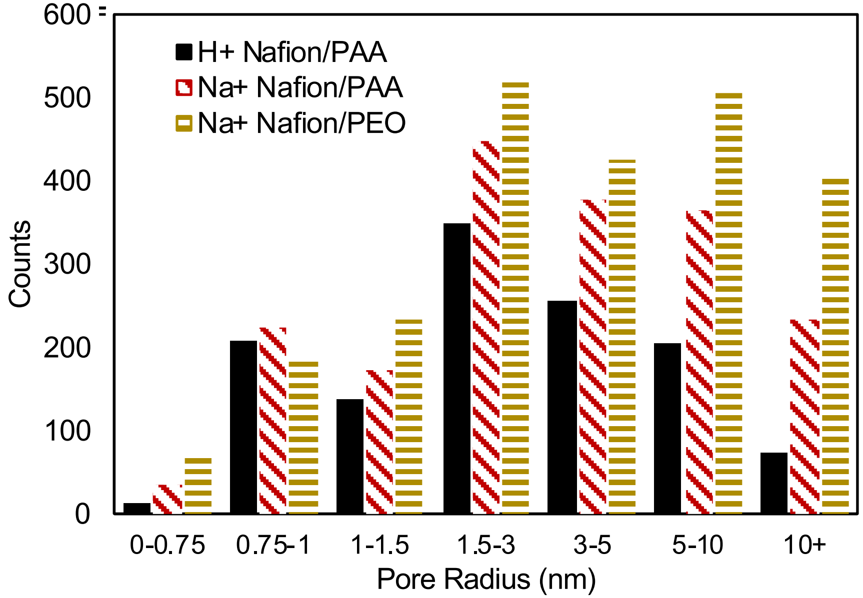
Conclusion

- Use of Na^+ Nafion and either PEO or PAA carrier polymer results in a modest improvement in power under fully humidified conditions and loses only 10% maximum power when operating at 40% RH with respect to power at 100% RH.

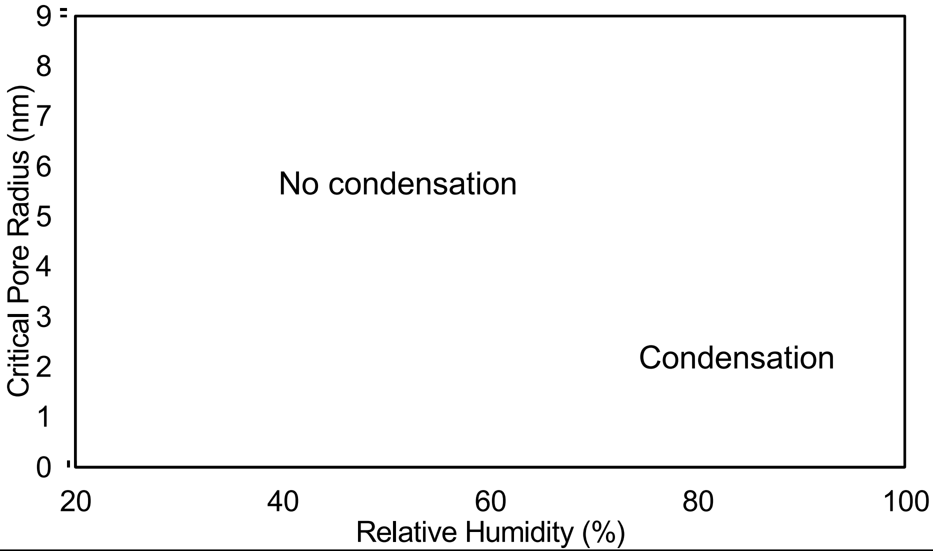
Anode/Cathode: 0.1 mg_{Pt}/cm^2
Polarization data collected at 80 °C, 200 kPa_{abs}, 125/500 sccm H_2/air
Nafion 211 membrane, Sigracet 29 BC
PAA electrodes: 58:28:14 weight composition 50 wt.% Pt/C (TEC10F50E):Nafion (H+ or Na+):PAA
PEO electrodes: 52:37:11 weight composition 50 wt.% Pt/C (TEC10F50E):Na+ Nafion:PEO

Accomplishment: Intrafiber Porosity and Pore-Size Distribution Affect Low Humidity Performance

Pore-size distribution after 1-hour water soak at 80 °C



Critical Pore Radius for Capillary Condensation



Intrafiber porosity before and after a 1-hour soak in 80 °C water

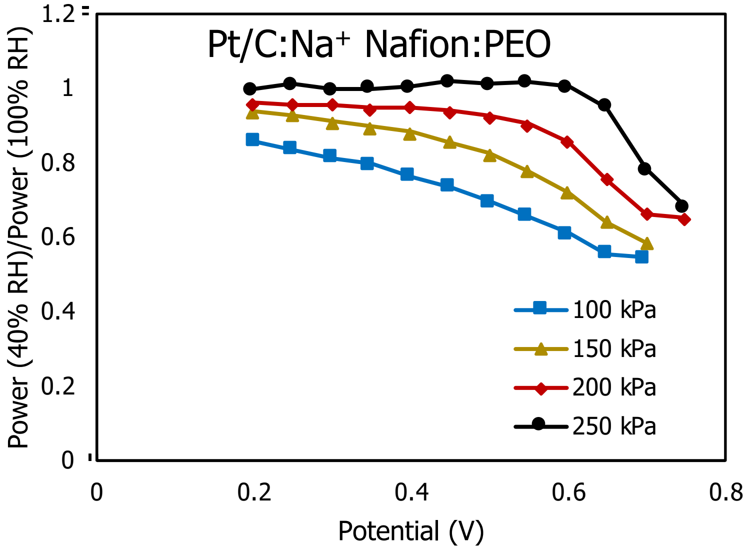
Binder	Before water soak	After water soak
H^+ Nafion/PAA	N/A	6%
Na^+ Nafion/PAA	7%	15%
Na^+ Nafion/PEO	13%	17%

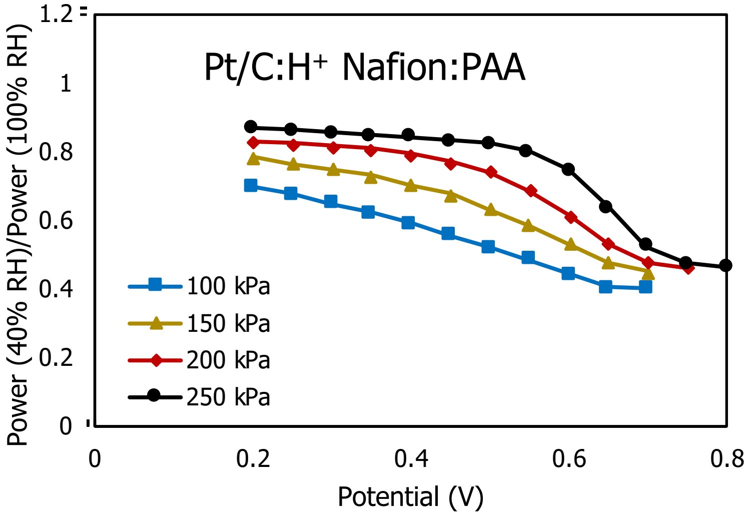
Conclusions

- Fiber electrodes with both H^+ Nafion and Na^+ Nafion binder have pores which should condense water at low RH
- At 40% RH, the Na^+ Nafion/PEO fibers have 25% more pores which can condense water than H^+ Nafion/PAA fibers
- For fibers with Na^+ Nafion, an increased number of small pores allows for retention of water at low RH, while an increased number of large pores facilitates removal of excess water

PAA electrodes: 58:28:14 weight composition 50 wt.% Pt/C (TEC10F50E):Nafion (H+ or Na+):PAA
PEO electrodes: 52:37:11 weight composition 50 wt.% Pt/C (TEC10F50E):Na+ Nafion:PEO

Accomplishment: Increasing Operating Pressure Improves Power at Low Humidity





Conclusions

- The ratio of power at 40% RH to 100% RH is closer to 1, and the ratio stays flat at higher voltages for Na^+ Nafion/PEO binder fibers than those prepared with H^+ Nafion/PAA.
- Higher back-pressure increased the ratio of power at 40% RH/100% RH, especially at higher voltages
- A ratio of 0.9 can be achieved at or below 0.55 V for Na^+ Nafion/PEO fibers at 200 kPa_{abs} and 80 °C.

Anode/Cathode: Pt/C (TKK):Na^+ Nafion:PEO fiber or Pt/C (TKK):H^+ Nafion:PAA fiber electrodes

Anode/Cathode Loading: 0.1 mg_{Pt}/cm^2

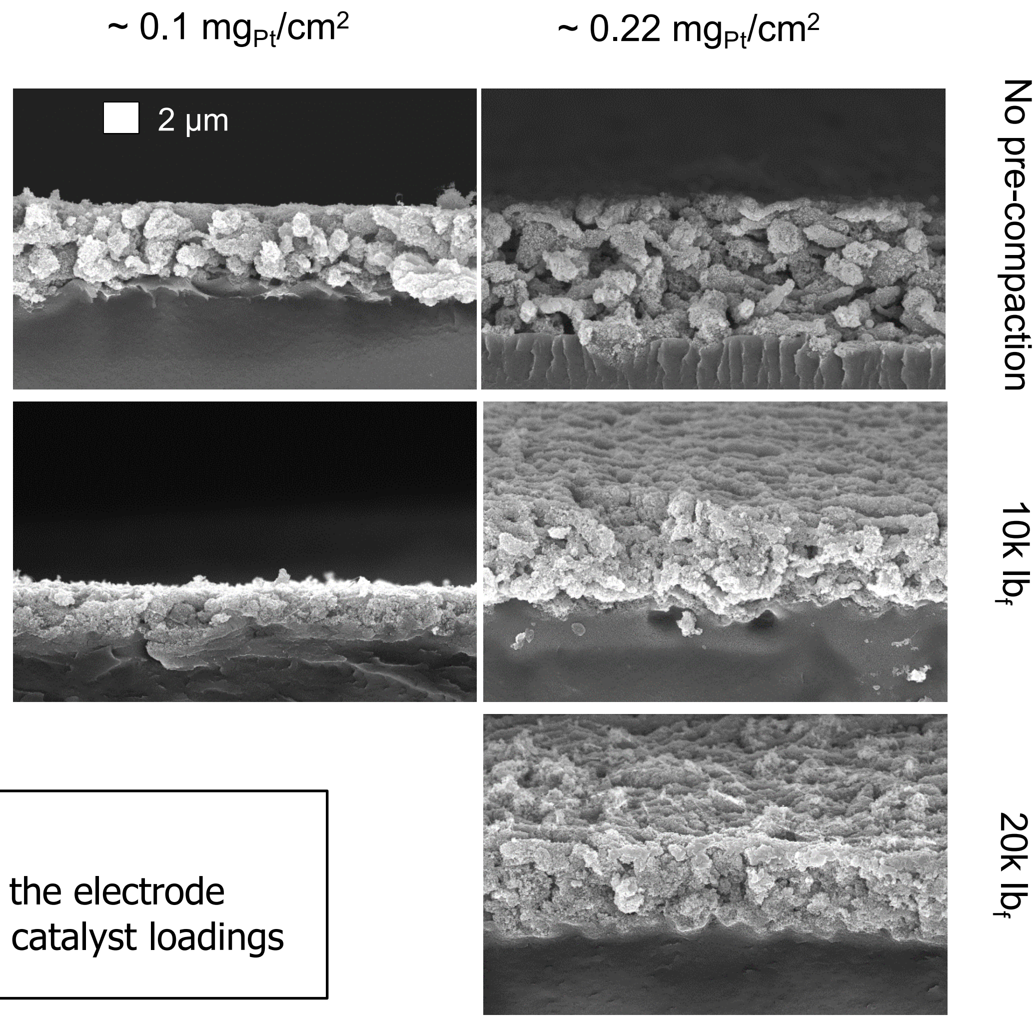
Nafion 211 membrane and Sigracet 29 BC GDLs 5 cm^2 area and single serpentine flow fields

Polarization data collected ay 80 °C, H_2/air 125/500 sccm

Accomplishment: Decreasing Gen-2 Cathode Thickness at High Cathode Catalyst Loadings

Fiber cathodes were pre-compacted with Nafion 211 membrane at 140 °C before addition of fiber anode

Cathode Loading mg_{Pt}/cm^2	Cathode Pre-Compaction	Cathode Thickness µm
0.10	None	4.3
0.11	10k lb_f Press	2.9
0.22	None	10
0.22	10k lb_f Press	5.6
0.25	20k lb_f Press	5.2

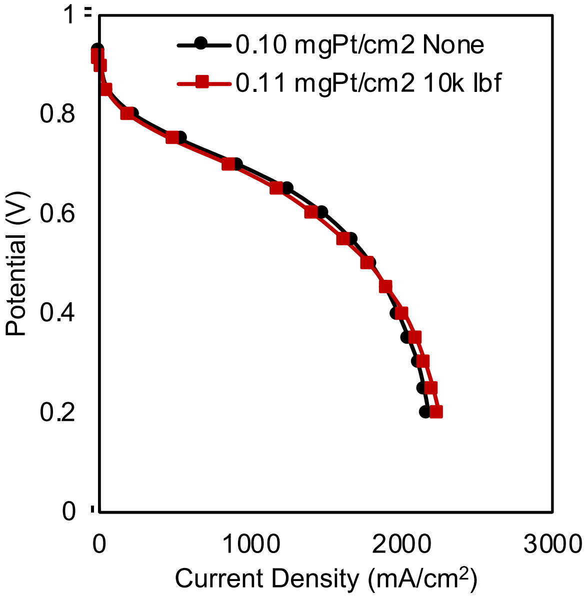


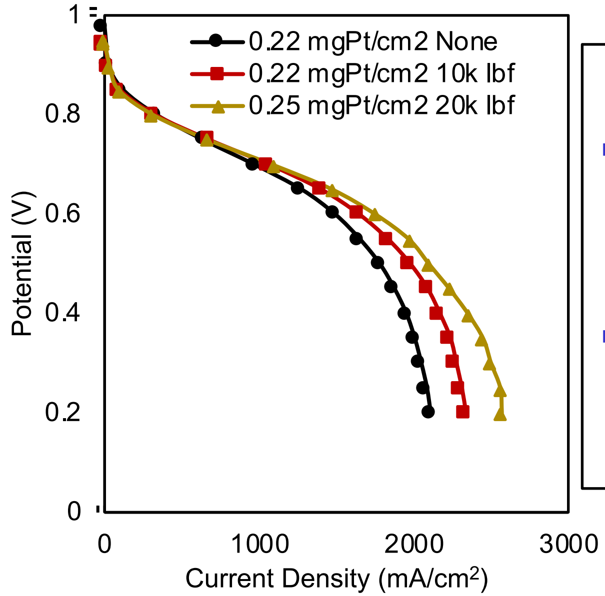
Conclusion

- Pre-compaction of cathodes nearly halved the electrode thickness for electrodes with high and low catalyst loadings

Electrodes were 52:37:11 weight composition 50 wt.% Pt/C (TEC10F50E):Na^+ Nafion:PEO
Compaction was completed before removal of PEO

Accomplishment: Fiber Mat Compaction Improves MEA Performance for Gen-2 Cathodes at High Pt Loading





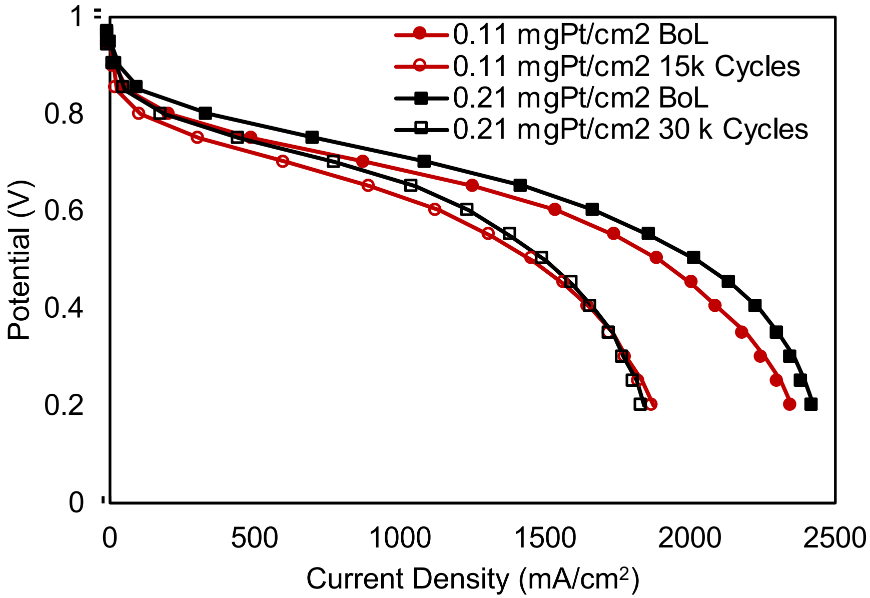
Conclusions

- Pre-compaction of a 0.1 mg_{Pt}/cm^2 cathode resulted in a thinner electrode but did not affect fuel cell performance
- Pre-compaction of ~0.22 mg_{Pt}/cm^2 cathodes resulted in thinner electrodes, and improved fuel cell performance in the ohmic region

Cathode Loading mg_{Pt}/cm^2	Cathode Pre-Compaction	Cathode Thickness µm	Maximum Power mW/cm^2	Mass Activity mA/mg_{Pt}	ECSA m^2/g_{Pt}
0.10	None	4.3	917	164	88
0.11	10k lb_f Press	2.9	893	151	90
0.22	None	10	908	188	72
0.22	10k lb_f Press	5.6	1008	215	72
0.25	20k lb_f Press	5.2	1082	165	58

Anode/Cathodes were 52:37:11 weight composition 50 wt.% Pt/C (TEC10F50E):Na^+ Nafion:PEO
Compaction was completed before removal of PEO
Anode Loading: 0.1 mg_{Pt}/cm^2
Nafion 211 membrane and Sigracet 29 BC GDLs 5 cm^2 area and single serpentine flow fields
Polarization data collected at 80 °C, 200 kPa_{abs}, 100% RH, and H_2/air 125/500 sccm

Accomplishment: Improved Metal Dissolution Durability of a Gen-2 Electrode MEA at High Cathode Catalyst Loading



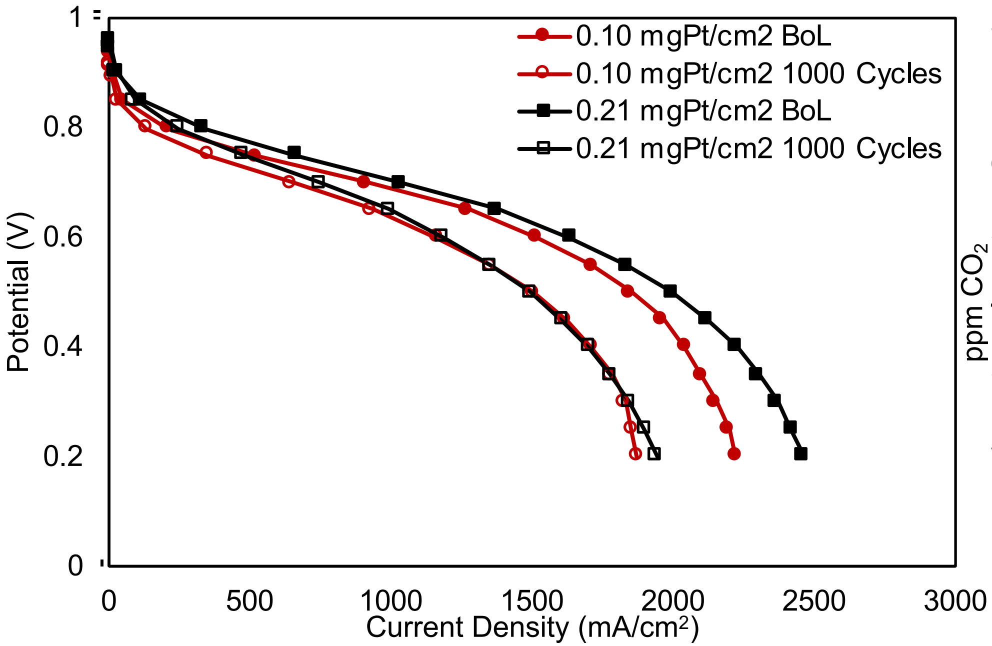
	0.11 mg_{Pt}/cm^2 15000 Cycles	0.21 mg_{Pt}/cm^2 30000 Cycles
Mass Activity EoT/BoL mA/mg_{Pt}	129/138	111/126
ECSA EoT/BoL m^2/g^{Pt}	35/86	34/60
EoT/BoL Power at 0.65 V (%)	76	74
EoT/BoL Maximum Power (%)	71	73

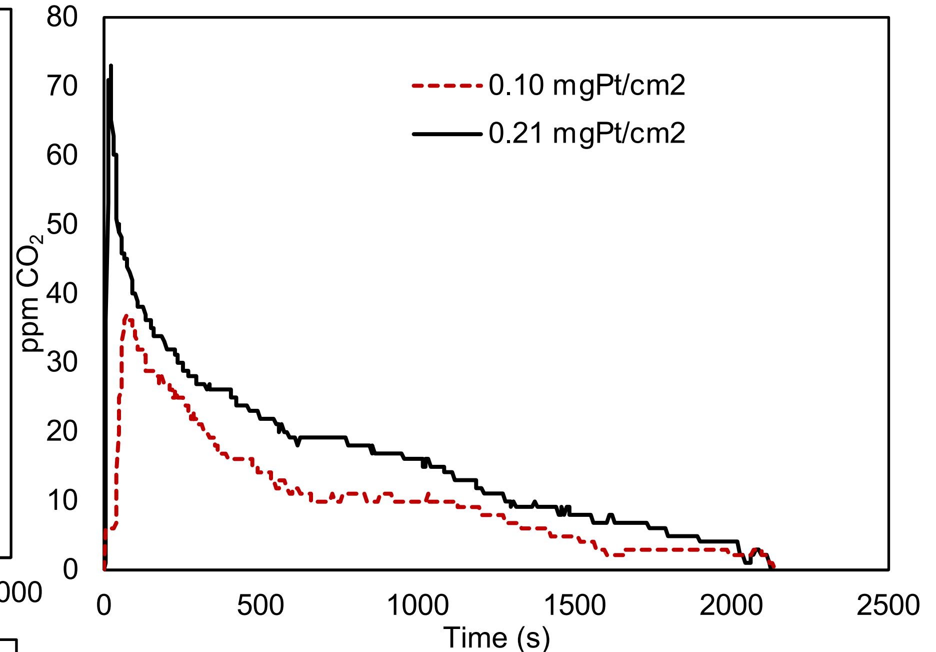
Conclusions

- Power loss for a 0.21 mg_{Pt}/cm^2 cathode MEA after 30,000 metal dissolution voltage cycles is the same as that for a 0.106 mg_{Pt}/cm^2 cathode MEA after only 15,000 cycles.
- At 0.65V and 100%, the power loss was 26%
- Mass activity loss was 12% (< the FC-PAD target of 40%).

Anode/Cathode: **Pt/C (TKK)**:Na^+ Nafion:PEO fiber electrodes
Anode: 0.1 mg_{Pt}/cm^2
Cathode: 0.21 mg_{Pt}/cm^2 prepared by pressing at 10k lb_f or 0.11 mg_{Pt}/cm^2
Nafion 211 membrane and Sigracet 29 BC GDLs 5 cm^2 area and single serpentine flow fields
Polarization data collected at 200 kPa_{abs}, H_2/air 125/500 sccm
Metal Dissolution: 0.6 V to 0.95 V square wave cycles at 100% RH

Accomplishment: Carbon Corrosion Durability of a Gen-2 Electrode MEA with a High Cathode Catalyst Loading





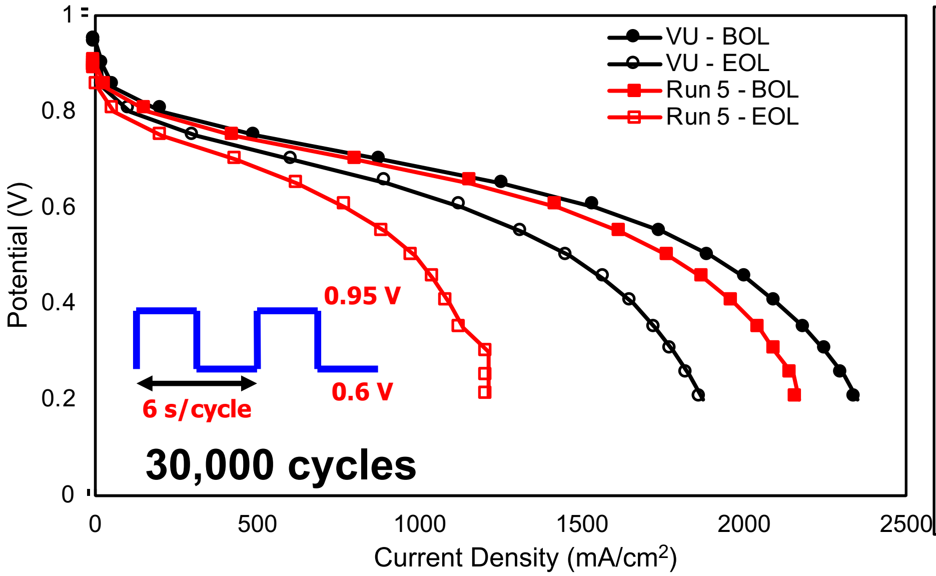
Conclusions

- Power loss in a 0.21 mg_{Pt}/cm^2 cathode MEA was similar to what was observed in a 0.1 mg_{Pt}/cm^2 cathode MEA at potentials greater than 0.6 V
- At 0.65V and 100%, the power loss was 26%
- The effect of carbon corrosion of the high loading MEA was most severe in the ohmic region, indicative of delamination

	0.10 mg_{Pt}/cm^2	0.21 mg_{Pt}/cm^2
Mass Activity (mA/cm^2) BoL/1,000 Cycles	194/148	146/146
ECSA (m^2/g_{Pt}) BoL/1,000 Cycles	77/51	70/45
Power at 0.65 V (mW/cm^2) BoL/1,000 Cycles	826/606	894/646
Maximum Power (mW/cm^2) BoL/1,000 Cycles	939/751	1009/747
Carbon Loss (wt. %)	14	10

Anode/Cathode: **Pt/C (TKK)**:Na^+ Nafion:PEO fiber electrodes
Anode: 0.1 mg_{Pt}/cm^2
Cathode: 0.21 mg_{Pt}/cm^2 prepared by pressing at 23k lb_f or 0.10 mg_{Pt}/cm^2
Nafion 211 membrane and Sigracet 29 BC GDLs 5 cm^2 area and single serpentine flow fields
Polarization data collected at 200 kPa_{abs}, H_2/air 125/500 sccm
Carbon Corrosion: 1.0 V to 1.5 V triangular wave cycles at 100% RH

Accomplishment: Gen-2 Fiber Mat Electrodes Made at eSpin Technologies, Inc.



Conclusions

- eSpin electrodes exhibited poor durability.
- eSpin anode/cathode MEA: 46% current density loss at 0.65 V after the metal dissolution AST.
- VU nanofiber MEA: 28% power loss at 0.65 V after the metal dissolution AST.
- eSpin does not appear to have the necessary electrospinning equipment to make particle/polymer electrode mats (no further experiments are planned at eSpin)

		Maximum Power Density (mW/cm^2)	Power Density at 0.65 V (mW/cm^2)
VU	BOL	961	818
	30000 Cycles	729	585
Run 5 (eSpin)	BOL	889	754
	30000 Cycles	493	407

Anode and Cathode: 52:37:11 TKK Pt/C (TEC10F50E): Nafion(Na^+ form)/PEO. Nafion 211 membrane and Sigracet 29 BC gas diffusion layers

Cathode catalyst loading was 0.106 mg_{Pt}/cm^2 for the VU fiber electrode MEA and 0.074 mg_{Pt}/cm^2 for the eSpin Run 5 MEA.

Data were collected at 80°C, 200 kPa_{abs}, with fully humidified H_2 and air fed at 125 and 500 sccm, respectively.

Response to Previous Year Reviewers' Comments

It would be interesting to see the project use the better 3M ionomers

Response: An all-electrospun MEA utilizing 725 EW PFSA from 3M in the anode, cathode, and the membrane was studied and exhibited excellent performance down to 20% RH.

One major problem with the work is the very high flow rates that are used in the test conditions for the CCMs. The project uses 80°C, 200 kPa (abs), 125 sccm H2, and 500 sccm air for 5 cm2 cells, while 4000 sccm H2 and 8000 sccm air are used with all MEAs for cells with an active area of 10 cm2.

Response: The Nissan Technical Center of North America (NTCNA) has studied the effect of flowrate on fuel cell performance and determined that at 90% RH, polarization performance is comparable when testing at hydrogen/air flowrates of 1000/2000 sccm and 4000/8000 sccm. Below 1000/2000 sccm, the performance of their MEAs suffers due to flooding. At 40% RH, polarization data were unaffected by hydrogen/air flowrates between 500/1000 and 4000/8000 sccm.

The project team should add more characterization and modeling to understand the performance differences between these systems and cast systems.

Response: Porosity and pore-size were more thoroughly studied this year through collaboration with ORNL. These data in combination with a model based on a modified Kelvin equation helped to expand understanding of the high power observed at low humidity.

The I/C ratios that were targeted for making MEAs are also not very clear.

Response: Studying I/C ratios in fiber electrodes is difficult, as variations in ink composition are limited based on our ability to spin well-formed fibers. Changing the I/C ratio may require a change in solvent system or electrospinning conditions, which complicates the ability to study solely the effect of I/C ratio on MEA performance and durability. For some I/C ratios, fibers cannot be spun.

Collaboration and Coordination

Oak Ridge National Laboratory

- Preparation of fiber electrode samples for STEM imaging
- 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).

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

Remaining Challenges and Barriers

Show that a nanofiber mat can be made on a multi-needle commercial electrospinner.

Optimize the thickness and maximize the power output of 0.1 and 0.2 mg_{Pt}/cm^2 fiber mat cathodes.

Better understand why nanofiber mat cathodes generate higher power at low and high RH and exhibit better durability. Obtain more EIS and GTR data as a function of binder and cathode thickness.

Proposed Future Work

Continue to investigate the performance and durability of fiber mat cathodes at a Pt loading of 0.2 mg/cm^2 with compression of electrode thickness, where

- The cathode catalyst is PtCo/C or PtNi/C
- The binder is low EW PFSA.
- The binder is either Gen-1 (acid-form PFSA) and Gen-2 (salt-form PFSA)

Prepare of fiber mat electrodes on a pilot-scale electrospinner at Vanderbilt (to replace eSpin tasks)

Carry out neutron scattering studies to compare the water content in fiber mat and conventional electrode MEAs

Continue to improve our understanding of the performance and durability of fiber MEAs with Gen-1 and Gen-2 binders at 0.1 and 0.2 mg/cm^2 through collaboration with LANL, Nissan, and ORNL by:

- Ionic resistance measurements
- GTR measurements
- SEM/STEM/EDX analyses

Characterize Gen-2 fiber mat MEAs after metal dissolution and carbon corrosion (SEM/STEM of electrodes, EIS, GTR)

Summary

- Fiber electrodes prepared at eSpin exhibited similar power to those prepared at Vanderbilt but suffered from poor metal dissolution durability due to the presence of spray droplets.
- The carbon corrosion durability of a Gen-2 fiber electrode MEA with PtNi/C catalyst was greatly improved when the AST was conducted at 40% RH as compared to 100% RH. The effect of low humidity AST was more pronounced in the fiber electrode MEA than a spray.
  - 90% power loss in fiber electrode MEAs at 0.65 V after 1000 carbon corrosion cycles at 100% RH and 60% loss for a spray
  - 12% power loss in fiber electrode MEAs at 0.65 V after 1000 carbon corrosion cycles at 40% RH and 25% loss for a spray
- An all electrospun Gen-2 MEA was prepared using 725 EW PFSA from 3M exhibited exceptionally high power at low humidity
  - Maximum power of 815 mW/cm^2 at 20% RH compared to 463 mW/cm^2 at 20% RH for a Nafion based MEA
- Fiber electrode MEAs prepared with salt-form Nafion binder worked exceptionally well in an MEA at low humidity and had a higher intrafiber porosity and an increased number of pores small enough to condense water at low humidity as compared to MEAs with acid-form Nafion.
- Pre-compaction of cathodes resulted in thinner electrodes and improved fuel cell performance for cathodes with a loading of ~0.22 mg_{Pt}/cm^2
- Increased cathode catalyst loading improved metal dissolution durability.
  - After 30,000 metal dissolution cycles, a 0.2 mg_{Pt}/cm^2 fiber cathode MEA lost 26% of power at 0.65 V. A 0.1 mg_{Pt}/cm^2 fiber cathode MEA lost the same power after only 15,000 cycles.
- Increased cathode catalyst loading led to similar power loss after carbon corrosion AST compared to a 0.1 mgPt/cm2 cathode
  - 26% loss in power at 0.65 V after 1000 carbon corrosion cycles