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

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Overview

Timeline and Budget

- Project Start Date: 11/1/2016 (subcontracts and NDAs were not signed until early 2017)
- Project End Date: 12/31/2019
- Percent complete: 47%

- Total Project Budget: \$3,173,854
- Total Recipient Share: \$640,291
- Total Federal Share: \$2,533,563
- Total Funds Spent: \$794,319
 = \$652,395 (DOE)+\$141,924 (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
 - $_{\circ}$ Anode + Cathode Pt loading ≤ 0.125 mg_{Pt}/cm²
 - \circ 65% peak efficiency
 - \circ 5,000 hour durability
 - \circ > 1W/cm² at rated power



- Nissan Technical Center North America (NTCNA)
- Georgia Institute of Technology (GaTech)
- Project Lead: Peter N. Pintauro, Vanderbilt University (VU)

Project Relevance and Objectives

Project Relevance:

- The VU/GaTech/NTCNA 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: $\leq 0.10 \text{ mg/cm}^2$ cathode and $\leq 0.025 \text{ mg/cm}^2$ anode; $> 1 \text{ W/cm}^2$ at rated power for T = 80-95°C; <40% drop in ORR mass activity after load cycling, <5% drop in voltage at 1.2 A/cm² 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

- Prepare nanofiber and sprayed electrode MEAs with commercial PtCo/C and PtNi/C cathodes with various binders (VU for nanofibers and painted cathodes; Nissan 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 Nissan).
- 3. Synthesize Pt-Ni octahedra catalysts with high ORR activity; Type-1 with no Pt coating and Type-2 with a Pt nanolayer coating (GaTech).
- 4. Incorporate the octahedra Pt-Ni catalysts into nanofiber and sprayed electrode MEAs with selected ionomer binders (VU and Nissan).
- 5. Collaborate with FC-PAD researchers at National Labs to: (1) verify MEA performance, (2) assess durability, (3) perform diagnostic tests, and (4) begin structural characterization of fibers.

Collaborations – Team Members

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

- Electrospins nanofiber mat electrodes with different catalysts and binders (identifies ink composition and electrospinning conditions)
- Fabricates MEAs with nanofiber mat electrodes and performs preliminary screening fuel cell screening tests, including start-stop cycling and load cycling ASTs.

Nissan Technical Center North America (NTCNA) (Sub) led by Dr. Nilesh Dale (project co-PI) and Dr. Cenk Gumeci (technical contact)

- Prepares and tests sprayed electrode MEAs
- Evaluates/validates the performance of nanofiber electrode MEAs
- Performs O₂ mass transfer resistance experiments on sprayed and nanofiber electrode MEA
- Evaluates GaTech shape-controlled catalyst in sprayed electrode MEAs

Georgia Institute of Technology (Sub) led Professor Younan Xia (project co-PI) and Dr. D. Qin (technical contact)

The GaTech team prepares batches of Pt-Ni/C octahedra catalyst for initial screening at NTCNA

Milestones and Go/No-Go Decision for 2017-18

Milestone Description	Date	Status as of April 17, 2018	
Prepare/deliver nanofiber MEAs to NTCNA and FC-PAD team at LANL	On going during 2017	Prior targets met; future targets on track	
Test nanofiber and sprayed MEAs at NTCNA	and 2018		
Go/No-Go Description			
 Nanofiber MEA with >240 mA/cm² at 0.8V >800 mW/cm² at rated power <50% drop in ORR mass activity after load cycling <20% drop in voltage at 1.2 A/cm² after start up-shut down <30% loss in rated power after drive cycle durability Measurements at NTCNA and VU; verification at LANL 	Dec. 31, 2017	Targets met (drive cycle durability test was not performed)	
 Nanofiber MEA with >280 mA/cm² at 0.8V, >900 mW/cm² at rated power, < 40% drop in ORR mass activity after load cycling, <10% drop in voltage at 1.2 A/cm² after start up-shut down <20% loss in rated power after drive cycle durability 	Dec. 31, 2018	On track	

Accomplishment: Electrospun Pt/C Gen-1 Fiber and PtCo/C Gen-2 Fiber

- 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.





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 + poly(acrylic acid) (PAA)
- Gen-2 fiber mat electrodes: catalyst + proprietary blend of ionomer and carrier (with carrier removal after electrospinning)

Accomplishment: STEM Imaging of an Electrospun Nanofiber with PtCo/C and Nafion/PAA Binder (FC-PAD Collaboration)

Data collected at Oak Ridge National Laboratory by John Slack (VU grad student) and Karren More's group

- Gen-1 Fibers (TKK PtCo/C + Nafion + PAA)
- A series of STEM images were obtained on a single fiber at various tilt angles.
- These images were combined using a computer software package at ORNL to obtain a 3D reconstructed image of the fiber (to identify the location of PtCo/C, carbon, binder, and void space).
- Blue visualization is PtCo metal.
- Grey area is Carbon, Nafion & Poly(acrylic acid).
- White is void space.
- 30% of the total fiber surface area comes from internal porosity.
- Outer fiber roughness accounts for additional ~20% of the surface area.
- EDX results of Pt and F mapping in Gen-1 Fibers show that there is good mixing of binder and Pt in the fiber interior with a thin Nafion coating (~20 nm) on the outside of the nanofiber (from an average of the EDX signal over a single fiber)



Accomplishment: A Comparison of PtCo Spray and Electrospun Electrode MEAs at 80°C and 200 kPa (NTCNA Results)



Relative Humidity (%)

MEA details:

Cathode: 0.1 mg_{Pt}/cm² Anode: 0.1 mg_{Pt}/cm² (Espun), J-M 0.4 mg_{Pt}/cm² (Spray) Membrane: NR 211 GDL: SGL 29 BC

	100% RH		40% RH			
Sample	Max Power (mW/cm²)	Power at 0.65 V (mW/cm ²)	HFR (mΩ-cm²)	Max Power (mW/cm²)	Power at 0.65 V (mW/cm ²)	HFR (mΩ-cm²)
PtCo Spray	652	544	70	315	85	208
Gen-1 PtCo Espun	759	661	76	590	250	219
Gen-2 PtCo Espun	1132	998	56	967	488	120

- Nanofiber MEAs displays improved performance, as compared to a spray electrode MEA, possibly due to the porous fiber structure which allows better reactants transport to the catalyst surface and fast removal of water.
- Gen-2 displays much better performance and its power density is less sensitive to RH.

Accomplishment: PtCo/C Spray and Electrospun Electrode MEAs: Transport/Ionomer Resistance/Polarization (NTCNA Results)



Accomplishment: Metal Dissolution Load Cycle ASTs for PtCo/C Sprayed and Fiber Electrode MEAs (NTCNA Results)



	Beginning of Life (BoL)			End of Life (EoL)		
Sample	Max Power (mW/cm²)	Power at 0.65 V (mW/cm ²)	O ₂ GTR (s/m)	Max Power (mW/cm²)	Power at 0.65 V (mW/cm ²)	O ₂ GTR (s/m)
PtCo Spray	652	544	52	534	339	69
Gen-1 PtCo	759	661	35	695	419	43
Gen-2 PtCo	1132	998	42	777	575	46

MEA details: Cathode: 0.1 mg_{Pt}/cm² Anode: 0.1 mg_{Pt}/cm² (Espun), J-M 0.4 mg_{Pt}/cm² (Spray) Membrane: NR 211, GDL: SGL 29 BC



• At the end of life after Pt dissolution, Espun electrodes outperform the spray electrode MEA.

- This is most likely due to their unique, porous nanofiber structure.
- Gen-2 Espun electrode shows better performance than that of Gen-1 Espun.
- A comprehensive analysis including neutron imaging is underway with the help of FC-PAD members for Gen-2 Espun electrode.
- EoL power at 0.65 V for Gen-2 > BoL power density for PtCo sprayed electrode MEA.

Accomplishment: Rated Power at 95 °C and 70% RH with a Gen-2 MEA(PtCo/C)/Nafion Cathode; (Pt/C)/Nafion Anode



$$Q/\Delta T = \frac{\left[\frac{Stack Power(90kW) \times (1.25 - V @ rated power)}{V @ rated power}\right]}{Stack coolant outlet temperature - ambient temperature(40°C)}$$

Calculations made with $Q/\Delta T=1.45$

Accomplishment: Gen-2 and Gen-1 MEA Performance with Repeated Recovery Protocols (LANL Collaboration)



- Recovery: Low T, high RH, hydrogen pump to clean cathode catalyst.
- 1 recovery step improves nanofiber MEA power density
- Power density is high after recovery; 1 W/cm² at 0.6 V and 150 kPa; 1.2 W/cm² at 0.6 V and 200 kPa
- % power loss at EOL is less than that seen at Vanderbilt (before recovery 82% vs. 72% at Vanderbilt)

Accomplishment: Performance of a Nanofiber Cathode/Anode MEA at 0.115 mg_{Pt}/cm^2 Loading



Loadings measured by XRF at Nissan: 0.096 mg_{Pt}/cm^2 cathode 0.019 mg_{Pt}/cm^2 anode

MEA Composition Gen-2 Nanofiber Cathode: TKK TEC36E52 PtCo/C Membrane: Nafion 211 Gen-2 Nanofiber Anode: TKK 20% Pt/C

Back Pressure (absolute)	Power at 0.65V (mW/cm²)	Max Power (mW/cm²)
100 kPa	435	550
150 kPa	677	713
200 kPa	817	854

- Rated power at 95°C and 200 kPa (at 0.663 V) is 809 mW/cm² vs. 906 mW/cm² at 0.20 mg/cm² Pt loading.
 - An 11% decrease in rated power for a 42.5% drop in overall Pt loading.

Accomplishment: Comparison of TKK PtNi/C vs. GaTech Shape-Controlled PtNi/C in Sprayed Electrode MEAs



	Beginning of Life (BoL)			
Sample	Mass Activity (mA/mg _{Pt})	ECSA (m²/g _{Pt})	lonomer Resistance (Ω-cm²)	O ₂ GTR (s/m)
TKK PtNi	220	48	0.277	65
GaTech PtNi	150	34	0.339	81

Response to Previous Year Reviewers' Comments

It is NOT clear the long term durability of these electrodes due to the presence of 20 to 30 weight % of hydrocarbon carrier polymer. This is an important issue to keep aware of when developing this technology. This may be a top priority of FC PAD and Nissan.

<u>Response</u>: Gen-2 nanofiber MEAs do not use Poly(acrylic acid) as the carrier polymer. The new carrier polymer is easily removed from the fibers after electrospinning, by a short water soak.

The cost of nanofiber based electrode and MEA for the proposed process needs to be justified for competitive cost - yields are very important.

<u>Response</u>: The materials and fabrication costs of electrospun fiber mat electrode MEAs is comparable to MEAs with slot die coating slurry electrodes at high production rates, as per a recent economic analysis by Strategic Analysis, Inc.

The PI will fabricate nanofiber electrode MEAs next year on commercial electrospinning equipment at eSpin Technologies, Chattanooga, TN. Based on this work, a better estimate of processing costs will be made.

The proposed future research is reasonable. But the PI should to some degree focus on the nanofiber MEA characterizations to elucidate the microstructures using in-situ and ex-situ approach. Why does the nanofiber MEA show superior performance to the conventional MEA?

<u>Response</u>: Characterization experiments have been initiated with FC-PAD collaborators; ORNL is examining nanofiber structure at BoL and EoL (STEM and XPS) and with LANL/Nissan (O_2 mass transfer resistance). Next year additional nanofiber mat electrode characterization experiments are planned, including STEM, water vapor uptake, SAXS, and nano-CT (with ORNL, LANL, LBNL, and ANL)

FC-PAD National Lab Collaborations

Oak Ridge National Laboratory

- Analysis of nanofiber electrode MEAs by high resolution STEM imaging
- Mapping of ionomer and Pt catalyst 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.

Argonne National Laboratory

• Tomography analysis of Gen-2 inks

Los Alamos National Laboratory

- Verification of nanofiber MEA performance at BoL and after ASTs.
- Structural analysis of fibers before/after removing carrier polymer.
- Neutron water imaging with NIST to understand better Gen-2 MEA performance at low RH

Remaining Challenges and Barriers

Continue to optimize the materials and fabrication conditions for nanofiber electrode MEAs , to achieve the highest power and best durability at a total anode + cathode Pt loading of $\leq 0.125 \text{ mg/cm}^2$)

- Optimize on the ionomer/carrier/catalyst wt.. ratio in the ink and the electrospinning conditions.
- Examine new Pt-alloy catalysts and high surface area carbon support catalysts.
- Optimize on the post-electrospinning steps in creating a MEA (hot-pressing, removing carrier polymer, etc.)
- Performance Targets:
- 1000 mW/cm² at rated power while meeting the Q/ Δ T target requirement
- <40% drop in ORR mass activity after load cycling
- <5% drop in voltage at 1.2 A/cm² after unmitigated start up-shut down
- < 10% loss in rated power after drive cycle durability

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

• Compare lab-scale and commercially electrospun electrode MEAs.

Continue to investigate the structure and function of particle/polymer nanofiber mat cathodes and anodes and then correlate data to MEA performance.

- Why do nanofiber cathodes exhibit:
 - higher power
 - less power loss after ASTs
 - less power loss at low RH operation
 - Lower O₂ mass transfer resistance
- What is the difference in structure/function between Gen-1 and Gen-2 fiber electrode MEAs

Proposed Future Work for April 2018 – April 2019

Assess performance of commercial Pt-alloy catalysts and shape-controlled Pt-Ni catalysts in nanofiber electrode MEAs that are made in the lab and on commercial electrospinning equipment.

- 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/cm²Pt-loaded MEAs (total anode+cathode loading).
- Evaluate new shape-controlled catalyst(s) from GaTech.
- Begin pilot-scale nanofiber MEA fabrication and evaluation.

Probe the structure of Gen-1 and Gen-2 MEAs and correlate results with fuel cell performance

- Where is carrier polymer during/after fiber electrospinning for Gen-1 and Gen-2 MEAs?
- Why do nanofibers work well? Are there agglomerates? What is the binder distribution/coating on catalyst particles in nanofibers? What is the internal porosity?
- 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?
- What is the structure of fibers (binder distribution, % loss in Co or C, etc.) after ASTs?

Milestones:

- 1. <u>Sample delivery</u>: Gen-2 nanofiber MEAs (5 cm² and 25 cm²) to NTCNA, LANL, and LBNL for testing/analysis.
- <u>Technical Targets</u>: MEAs with 300 mA/cm² at 0.8V and >1000 mW/cm² at rated power while meeting the Q/∆T target requirement; <40% drop in ORR mass activity after load cycling, <5% drop in voltage at 1.2 A/cm² after unmitigated start up-shut down.

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

Technology Transfer Activities

Patents have been filed/issued on nanofiber-based particle/polymer fuel cell electrodes.

- P. N. Pintauro and W. Zhang, "Nanofiber Fuel Cell Electrode and Method of Forming Same" U.S. patent 9905870, issued February 2018.
- Non-U.S. patents are in the prosecution stage.
- Provisional patents on Gen-2 fuel cell electrodes and the ink composition used to prepare Gen-2 electrodes and MEAs.

Arrangements have been made to commercially produce fuel cell electrodes and MEAs at eSpin Technologies, Inc., Chattanooga, TN.

- MEA performance will be tested at Vanderbilt, NTCNA, and LANL (performance should be the same as MEA made in Pintauro's lab at Vanderbilt).
- MEAs are available to OEMs for purchase.
- Today, the working width of electrodes is up to 24 inches.
- Orders for large MEAs orders will be considered soon. Trials are planned for large-scale production (≥ 20,000 linear feet per trial).





Summary

- Last year focused on preparing and evaluating nanofiber cathode/anode MEAs. High performance MEAs were prepared. There was a significant improvement in performance of Gen-2 MEAs as compared to Gen-1 MEAs.
 - MEA performance was verified at Nissan and an FC-PAD lab (LANL).
 - Gen-2 fuel cell results with a Pt/C nanofiber anode and PtCo/C nanofiber cathode are encouraging:
 - 906 mW/cm² at rated power, 95°C and 200 kPa_{abs} at 0.20 mg/cm²
 - 809 mW/cm² at rated power, 95°C and 200 kPa_{abs} at 0.115 mg/cm²
 - 20-30% power loss after a load cycling durability test (30,000 voltage cycles)
 - High power at low RH
- Preliminary fiber characterization work has been carried out at ORN, LANL, and NTCNA.
 - Fibers are ~30% porous with a uniform distribution of catalyst and binder (minimal agglomerates of catalyst or binder)
 - O₂ mass transfer resistance is low
 - Loss of Co during a load cycling is less than the loss in a sprayed cathode MEA
- Particle/polymer nanofiber mat electrodes are a promising alternative to conventional fuel cell electrode structures
 - Electrospinning is a versatile and scalable nano/micro-fabrication method for preparing MEAs
 - The method can exploit new catalysts and binders, as they are developed/discovered, such as GaTech's shape controlled PtNi catalyst

Technical Back-Up Slides

Electrospinning – Rotating Drum Apparatus



Rated Power and $Q/\Delta T$ Constraint

- \Box Q/ Δ T is a measure of radiator size
- \Box Rated Power is Power at which Q/ ΔT is met
- **<u>Target Q/ΔT<1.45 kW/°C heat loss constraint based on car radiator's Q/</u>ΔT**

$$Q/\Delta T = \frac{\begin{bmatrix} Stack Power(90kW) \times (1.25 - V @ rated power) \\ V @ rated power \end{bmatrix}}{Stack coolant outlet temperature - ambient temperature(40°C)}$$

- To meet this constraint
 - When T_{coolant stack} is high → Operate FC stack at higher Temp (limited by current membrane technologies)
 - When V@ rated power is high → <u>Operate FC stack at higher Pressure and/or</u>



Gas Transport Losses in the Cathode Catalyst Layer at low Pt Loading – Analysis Performed at NTCNA

- O₂ transport resistance measurements, including limiting current experiments developed by Nissan, were completed at 80°C, 90% RH.
- Gas transport loss in CL is inversely proportional to Pt loading, indicating local gas transport dominates gas transport in CLs.
- O₂ GTR measurements are a valuable diagnostic technique for new electrode structures (e.g., electrospun electrodes) with low Pt loading (0.1 mg_{Pt}/cm2) MEAs.



T. Mashio et al., *ECS Trans.* 11, 529, (2007).
K. Sakai et al., *ECS Trans.* 25, 1193 (2009).
Y. Fukuyama et al., *Electrochim. Acta*, 117, 367 (2014).

Polarization Loss Analysis – Performed at NTCNA

- Polarization Loss Analysis was performed using a model developed by Nissan to deconvolute various losses in fuel cell performance using H₂/O₂ and H₂/Air iV data.
- The model uses theoretical values of resistances losses to identify the relative importance of each loss (such as activation loss, ohmic loss, mass transfer loss etc.).
- For mass transfer loss: the iV curve obtained with O₂ is assumed to have no mass transfer loss. It is calculated by subtracting the air iV plot and the internal ohmic loss from the O₂ iV curve.



Representative H_2/O_2 and H_2/Air Performance and Polarization Losses