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

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Subcontractors:
- Nissan Technical Center North America, Farmington Hills, MI
- Georgia Institute of Technology, Atlanta, GA
- 3M Company, St. Paul, MN

Project Start Date: January 1, 2017
Project End Date: December 31, 2020

Overall Objectives

- Fabricate, characterize, and evaluate membrane electrode assemblies (MEAs) with nanofiber mat cathodes containing highly active oxygen reduction reaction (ORR) catalysts for H_2/air fuel cells.
- Generate useful correlations and insightful understandings regarding nanofiber electrode electrospinning.
- Develop collaborations with Fuel Cell Performance and Durability Consortium (FC-PAD) researchers at national laboratories.

Fiscal Year (FY) 2018 Objectives

- Synthesize and evaluate shape-controlled platinum-alloy catalyst (at Georgia Tech).
- Evaluate/characterize nanofiber anode and cathode MEAs with new binders, TKK (Tanaka Kikinzoku Kogyo) PtCo/C and PtNi/C cathode catalysts, and Pt/C anode catalyst (Vanderbilt and Nissan Technical Center North America.
- Begin to electrospin nanofiber electrodes on commercial equipment at eSpin Technologies, Inc.

Technical Barriers

This project addresses the following technical barriers from the Fuel Cells section of the Fuel Cell Technologies Office Multi-Year Research, Development, and Demonstration Plan[1]:

(A) Durability (aging and degradation of fuel cell electrodes).

(B) Cost (reducing the material and manufacturing costs of high-performance electrodes and MEAs).

(C) Performance (fabricating MEAs that generate higher power at lower precious-metal loading, with special emphasis on the cathode).

Technical Targets

The 2020 DOE technical targets and project status are shown in Table 1.

FY 2018 Accomplishments

- MEAs were fabricated with electrospun particle/polymer nanofiber mat cathodes (0.1 mg_{Pt}/cm^2 PtCo/C or PtNi/C) and anodes (0.1 mg_{Pt}/cm^2 Pt/C), where the binder was a mixture of Nafion and poly(acrylic acid) or neat Nafion (for the latter, a new carrier polymer was utilized that could be easily removed from the fibers after electrospinning).
- MEA performance was verified at Nissan and at an FC-PAD lab (Los Alamos National Laboratory).

[1] https://energy.gov/eere/fuelcells/downloads/fuel-cell-technologies-office-multi-year-research-development-and-22

- A 5 cm^2 MEA with a PtCo/C nanofiber cathode performed very well and produced 906 mW/cm^2 at rated power (95°C, 200 kPa_{abs}, and 0.20 mg/cm^2 total Pt loading) and 809 mW/cm^2 at rated power (95°C, 200 kPa_{abs}, and 0.115 mg/cm^2 total Pt loading).
- There was a modest power loss after a metal dissolution, load-cycling accelerated stress test (AST) (30,000 voltage cycles); power loss was within the DOE target of 20%–30% loss in max power, and only a 12% loss in power when a recovery protocol was used. This power loss is significantly less than that in a conventional slurry electrode MEA.
- Energy dispersive X-ray spectroscopy experiments found that there was greater retention of Co in a PtCo/C nanofiber cathode after a metal dissolution load-cycling AST, as compared to the retention in a conventional sprayed cathode (61% versus 49% Co retention). High Co retention is an indicator of improved durability.
- A nanofiber MEA with a PtCo/C cathode and Pt/C anode (each at 0.1 mg/cm^2 Pt loading) produced high power at high- and low-relative humidity (RH) conditions: 1.1 W/cm^2 at 100% RH and 0.967 W/cm^2 at 40% RH (all data collected at 80°C and 200 kPa_{abs} pressure).
- Preliminary fiber characterization work was carried out at Oak Ridge National Laboratory, Los Alamos National Laboratory, and the Nissan Technical Center North America. Results from scanning transmission electron microscopy experiments show that fibers are ~30% porous with a uniform distribution of catalyst and binder (minimal agglomerates of catalyst or binder); the O_2 mass-transfer resistance is low in a nanofiber cathode (35 versus 52 s/m for a sprayed cathode); the ionomer resistance of a nanofiber cathode was substantially less than that of a sprayed particle/Nafion electrode.
- Shape-controlled $Pt_{2.6}Co$ catalyst was prepared at Georgia Tech and showed good mass activity in a slurry cathode MEA after four recovery cycles (0.384 A/mg_{Pt}) with high fuel cell power densities (e.g., a maximum power of 0.73 W/cm^2 after recovery).
- The following Year 2 go/no-go milestones were met: (1) nanofiber MEA with >280 mA/cm^2 at 0.8V (see Figure 3); (2) rated power >900 mW/cm^2; and (3) <40% drop in ORR mass activity after load cycling (see Table 4). Milestones associated with start up–shut down and drive cycle durability were not met (<10% drop in voltage at 1.2 A/cm^2 after start up–shut down and <20% loss in rated power after drive cycle durability) because these tests were not performed; they were not deemed to be of critical importance given the other technical accomplishments in 2018.

Table 1. Progress Toward Meeting Technical Targets for Electrocatalysts and MEAs for Transportation Applications

Characteristic	Units	DOE 2020 Electrocatalyst and MEA Targets	Project Status
Mass activity	A/mg_{PGM} @ 0.90 $V_{iR\text{-}free}$	0.44	0.464[a]
PGM total loading (both electrodes)	$mg\text{-}PGM/cm^2_{geo}$	0.125	0.20
Loss in performance @ 0.80 A/cm^2 after a load-cycling AST (30,000 voltage cycles)	mV	<30	68[b]
Loss in performance @ 1.5 A/cm^2 after a load-cycling AST (30,000 voltage cycles)	mV	<30	32[b]
MEA performance @ 0.80 V	mA/cm^2_{geo}	300	402[b]
MEA performance @ rated power (150 kPa_{abs})	mW/cm^2_{geo}	1,000	945[c]

[a] Measured at Los Alamos National Laboratory.
[b] 5 cm^2 MEA, TKK PtCo/C cathode catalyst, Pt/C anode catalyst, Nafion + poly(acrylic aid) binder, Nafion 211 membrane, T = 80°C, 200 kPa_{abs}, 100% RH.
[c] 10 cm^2 MEA, TKK PtCo/C cathode catalyst, TKK Pt/C anode catalyst, Nafion binder, Nafion 211 membrane, T=95°C, 200 kPa_{abs}, 100% RH.

INTRODUCTION

Despite widespread literature demonstration of excellent oxygen reduction reaction activity of some new catalysts in rotating disk electrode experiments, almost none of them have shown promising performance in fuel cell MEAs. This is because MEA fabrication remains centered on decal, catalyst-coated membrane, and catalyst-coated gas diffusion electrode methodologies, with little or no control over the macro-scale organization of catalyst particles and polymer binder. Features such as electrode macroporosity, microporosity, and particle and binder interconnectivity become more critical when high-performance nanomaterials are used in electrodes. Consequently, new electrode fabrication techniques are needed for next-generation MEAs, which accommodate and control the multi-scale arrangement of catalyst and binder for improved power output and durability.

Building from strong initial data showing electrospinning as a viable approach to the design and fabrication of fuel cell electrodes [1–3], this project seeks to fabricate MEAs with electrospun nanofiber electrodes containing Pt and Pt-alloy catalyst powders and selected perfluorosulfonic acid ionomer binders with the capability of meeting the DOE 2020 performance and durability targets for MEAs and catalyst layers.

APPROACH

The research approach for this project directly addresses three critical issues: (1) the use of high-activity PtNi/C and PtCo/C catalysts in hydrogen/air fuel cell MEA cathodes; (2) the organization of Pt-alloy catalytic nanoparticles into intelligently designed nanofiber mat electrodes via particle/polymer electrospinning, in which the fiber volume fraction, nanoparticle loading, binder type, fiber diameter, and mat thickness are independently controlled; and (3) the identification of the optimum composition and structure of nanofiber electrode MEAs which meet the DOE 2020 performance, Pt-loading, and durability targets.

The project has five major tasks: (1) prepare and evaluate MEAs with commercial Pt-alloy cathodes at ultra-low Pt loading with various perfluorinated ionomer-based binders; (2) synthesize Pt-alloy octahedra catalysts with high oxygen reduction activity; (3) incorporate the octahedra Pt-alloy catalysts into nanofiber and sprayed electrode MEAs; (4) optimize the nanofiber cathode mat composition and mat morphology to maximize fuel cell performance and durability at high and low relative humidity conditions; and (5) provide catalyst powder, electrospun cathode mats, MEAs, experimental skills, and the team's electrospinning knowledgebase to our FC-PAD collaborators.

RESULTS

H_2/air fuel cell polarization curves for nanofiber electrode MEAs at 80°C with different cathode catalysts are shown in Figure 1. The Pt cathode and anode loadings were each 0.1 mg/cm^2, and the electrode binder was a mixture of Nafion and poly(acrylic acid) (PAA). The PtCo (I/C = 1.08) and PtNi (I/C = 1.08) catalysts were from TKK (TEC36E52 and TECNiE52) and the Pt/C catalyst (I/C = 0.90) was from Johnson-Matthey (HiSPEC 4000). As expected, the Pt-alloy cathodes worked best with a maximum power density >1.0 W/cm^2. The performance of the three different MEAs is summarized in Table 2; a higher power output for the alloy catalysts is associated with a higher mass activity.

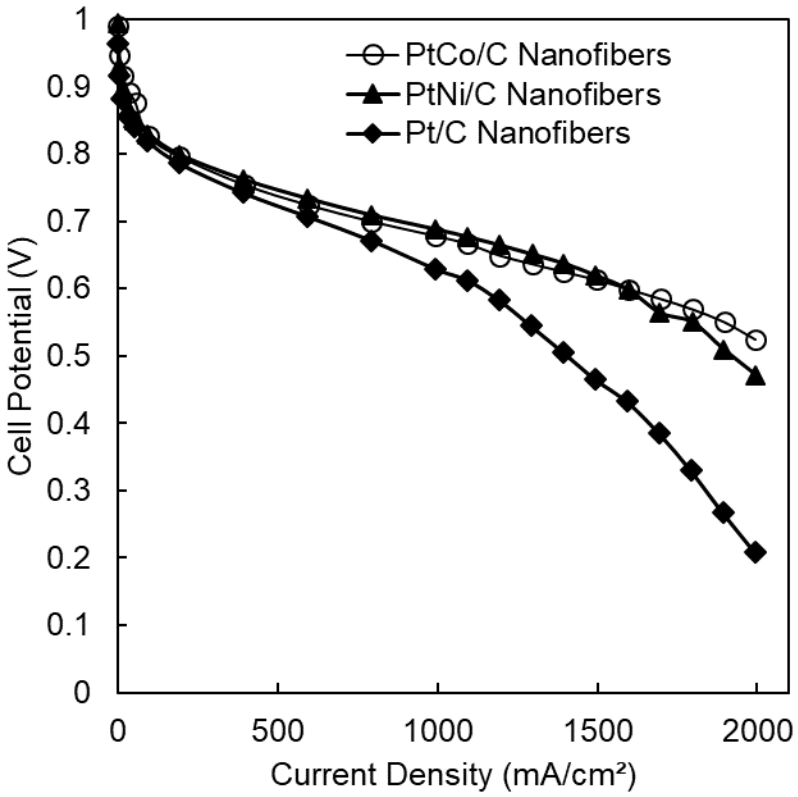

Figure 1. H_2/air fuel cell polarization curves for nanofiber MEAs with different cathode catalysts and with a catalyst binder of Nafion + PAA. All cathodes are 0.1 mg_{Pt}/cm^2 (TKK PtCo/C and PtNi/C and J-M Pt/C, as listed in Table 2); 80°C; 200 kPa_{abs}; 90% RH; Nafion 211 membrane; and 4/8 L/min H_2/air flow rates.

Table 2. Cathode Electrochemical Surface Area (ECSA) and Mass Activity and Fuel Cell Power Results for Nanofiber Electrode MEAs with Different Cathode Catalysts (0.1 mg_{Pt}/cm^2) and an Anode of Pt/C (J-M HiSPEC 4000 at 0.1 mg_{Pt}/cm^2). Fuel Cell Operating Conditions Are Listed in the Caption for Figure 1.

Cathode Catalyst	ECSA (m^2/g_{Pt})	Mass Activity (mA/mg_{Pt})	Power Density at 0.65 V (mW/cm^2)	Max Power Density (mW/cm^2)
Pt/C (J-M HiSPEC 4000)	45	160	579	704
PtNi/C (TKK TECNiE52)	46	266	840	988
PtCo/C (TKK TEC36E52)	48	270	803	1,034

Nanofiber electrode MEAs with a TKK PtCo/C cathode, a TKK Pt/C anode, and a Nafion binder performed exceptionally well at both high- and low-relative-humidity fuel cell conditions, as shown in Figure 2. Power output was high over a wide range of feed gas relative humidities, where the fuel cell temperature was 80°C, the pressure was 200 kPa_{abs}, and the total MEA Pt loading was either 0.20 mg/cm^2 or 0.115 mg/cm^2.

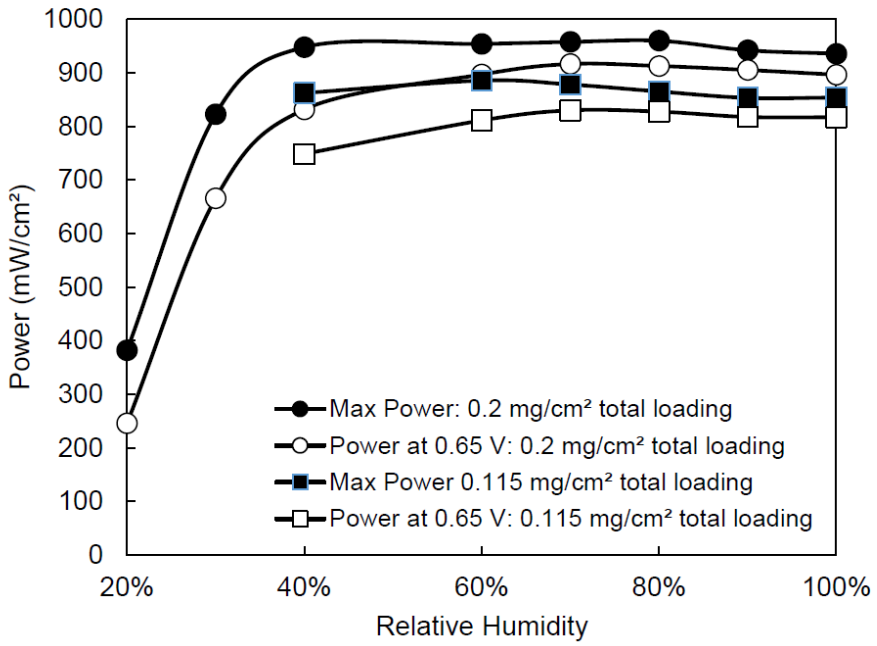

Figure 2. H_2/air fuel cell power output for nanofiber MEAs operating at different feed gas relative humidities, with a PtCo/C cathode (TKK TEC36E52) and a Pt/C anode (TKK TEC10F50E). MEA with 0.2 mg_{Pt}/cm^2 loading: 0.098 mg_{Pt}/cm^2 cathode and 0.102 mg_{Pt}/cm^2 anode. MEA with 0.115 mg_{Pt}/cm^2 loading: 0.096 mg_{Pt}/cm^2 cathode and 0.019 mg_{Pt}/cm^2 anode. 80°C; 200 kPa_{abs}; Nafion 211 membrane; 125/500 standard cubic centimeters per minute H_2/air flow rates.

Rated power was found from fuel cell polarization data, at a voltage given by Equation 1, where the stack power was selected to be 90 kW, Q/ΔT was fixed at 1.45 kW/°C, the fuel cell operating temperature was set at 95°C, the pressure was 200 kPa_{abs}, and the ambient temperature was 40°C. At rated power (0.663 V, according to Equation 1), the power density of a nanofiber MEA with a Nafion binder and a total Pt loading of 0.117 mg/cm^2 (TKK TEC36E52 PtCo/C cathode at 0.095 mg_{Pt}/cm^2 and TKK TEC10F50E Pt/C anode at 0.022 mg_{Pt}/cm^2) was 945 mW/cm^2, which exceeds the project's 2018 go/no-go target.

$$Q/\Delta T = \frac{\left[Stack\ Power\ (kW) \times (1.25 - V\ @\ rated\ power) \Big/ V\ @\ rated\ power\right]}{Cell\ Operating\ Temperature\ (^oC) - Ambient\ Temperature\ (^oC)} \quad (1)$$

Voltage cycling metal dissolution ASTs were performed with nanofiber electrode MEAs, where the nanofiber cathode/anode was a mixture of Nafion + PAA or neat Nafion. H_2/air fuel cell polarization curves before and after 30,000 voltage cycles between 0.6 V to 0.95 V are shown in Figure 3. The fuel cell operating pressure during collection of polarization data was 200 kPa_{abs}, the feed gas flow rates were 500 cm^3/min for H_2 and 2,000 cm^3/min for air, the temperature was 80°C, and the RH was fixed at 100%. Both the anode and cathode Pt loadings were 0.1 mg/cm^2. Beginning-of-life (BoL) and end-of-life (EoL) fuel cell performance data are summarized in Table 3.

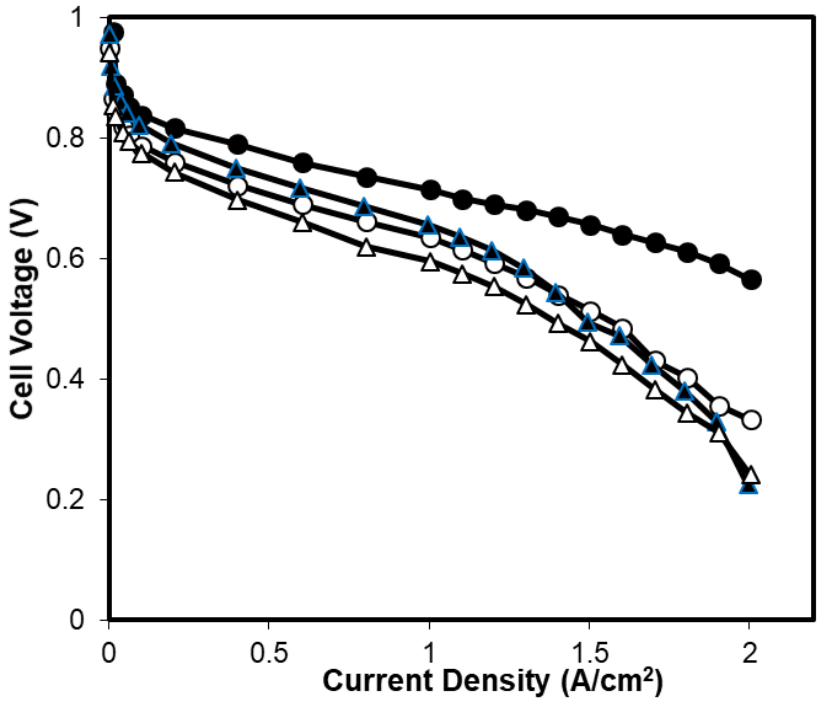

Figure 3. Fuel cell polarization results before and after a metal dissolution AST (end-of-life after 30,000 voltage cycles, 0.6 V to 0.95 V) for nanofiber electrode MEAs with a PtCo/C cathode (0.1 mg_{Pt}/cm^2 TKK TEC36E52) and a Pt/C anode (0.1 mg_{Pt}/cm^2 Johnson-Matthey HiSPEC 4000). Nafion + PAA binder: ▲ (BoL) and Δ (EoL); Nafion binder: ● (BoL) and ○ (EoL). 80°C; 200 kP_{abs}; 100% RH; Nafion 211 membrane; 0.5/2.0 L/min H_2/air flow rates.

Table 3. Nanofiber Fuel Cell Performance Before and After a Metal Dissolution Voltage Cycling AST for Two Different Binders. Summary of Result from Figure 3.

	Beginning of Life (BoL)		End of Life (EoL)	
Nanofiber Binder	Max Power (mW/cm^2)	Power at 0.65 V (mW/cm^2)	Max Power (mW/cm^2)	Power at 0.65 V (mW/cm^2)
Nafion + PAA	759	661	695	419
Nafion	1,132	998	777	575

The durability of the nanofiber MEAs was excellent, with EoL maximum power losses of 8.4% (for a Nafion + PAA binder) and 31% (for Nafion binder). When a recovery step (a low-temperature hydrogen pump) was added to the AST, the deleterious effects of metal dissolution were mitigated, as shown in Table 4. Thus, after 15,000 voltage cycles and a single recovery step, the MEA was restored to its original condition in terms of cathode mass activity and power output. After 30,000 voltage cycles with a recovery, the drop in power density as compared to that at BoL was small (only 12%). Overall, it can be concluded that recovery has little effect on cathode ECSA but it does partially/totally restore the cathode mass activity for ORR and the MEA power density.

Table 4. The Use of a Recovery Step to Improve the Power Output of a Nanofiber Electrode MEA After a Metal Dissolution Voltage Cycling Accelerated Stress Test

	ECSA (m^2/g_{Pt})	Mass Activity (A/mg_{Pt})	Max Power Density (W/cm^2)
BoL	40	0.464	0.900
After 15,000 cycles	27	0.236	0.740
15,000 cycles + recovery	31	0.496	0.905
After 30,000 cycles	26	0.202	0.734
30,000 cycles + recovery	22	0.296	0.793

CONCLUSIONS AND UPCOMING ACTIVITIES

Nanofiber electrode MEAs produce high power at low platinum loadings, over a wide range of feed gas relative humidities and after a metal dissolution voltage cycling accelerated stress test. Power densities at or above 1.0 W/cm^2 were measured for an MEA with a total Pt loading of 0.2 mg/cm^2. Rated power at 95°C, 200 kPa_{abs} pressure, and a total MEA Pt loading of 0.115 mg/cm^2 was >900 mW/cm^2. High power with improved durability after a metal dissolution AST is associated with a more uniform distribution of binder and catalyst particles throughout the fiber mat electrode (no agglomerates), which results in higher catalytic activity for the ORR, low gas-transport resistance for O_2, and low ionic resistance in the catalyst layer. Additionally, fibers with neat Nafion binder appear to hold water at low feed-gas humidity conditions, resulting in high power at 40% RH.

Future work will focus on the following.

- Working with FC-PAD collaborators at national labs to probe the structure of electrospun particle/polymer nanofiber electrodes with Nafion/PAA and neat Nafion binder to better understand why fiber electrodes work well in a fuel cell.
- Optimizing the nanofiber anode and cathode composition and MEA hot pressing conditions for optimal power and durability at a total Pt loading of 0.125 mg/cm^2.
- Preparing and evaluating nanofiber cathodes and anodes that are electrospun on commercial equipment at eSpin Technologies, Inc.

FY 2018 PUBLICATIONS/PRESENTATIONS

1. P.N. Pintauro, “Recent Progress on Improving the Performance of Nanofiber Electrodes in a Hydrogen/Air Fuel Cell” (invited talk), 8th International Fuel Cell Workshop, Yamanasihi University, August 2018.
2. John Slack, Krysta Waldrop, Ryszard Wycisk, Cenk Gumeci, Nilesh Dale, and Peter N. Pintauro, “Electrospun Fiber Mat Electrode MEAs for Hydrogen/Air Fuel Cells,” Electrochemical Society Fall Meeting, Cancun, Mexico, October 2018.
3. Krysta Waldrop, John Slack, Peter N. Pintauro, and Ryszard Wycisk, “Electrospun Particle/Polymer Fiber Mats as Hydrogen/Air Fuel Cell Electrodes,” American Institute of Chemical Engineers Annual Meeting, Pittsburgh, PA, November 2018.

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1. W. Zhang, and P.N. Pintauro, “High Performance Nanofiber Fuel Cell Electrodes,” *Chem. Sus. Chem.* 4 (2011): 1753–1757.
2. M. Brodt, R. Wycisk, and P.N. Pintauro, “Nanofiber Electrodes with Low Platinum Loading for High Power Hydrogen/Air PEM Fuel Cells,” *J. Electrochem. Soc*. 160 (2013): F744–F749.
3. M. Brodt, T. Han, N. Dale, E. Niangar, R. Wycisk, and P. Pintauro, “Fabrication, In-Situ Performance, and Durability of Nanofiber Fuel Cell Electrodes,” *J. Electrochem. Soc.* 162 (2015): F84–F91.