V.B.7 Fuel Cell Membrane Electrode Assemblies with Ultra-Low Pt Nanofiber Electrodes

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Overall Objectives

- Improve performance and local transport properties in fuel cell electrodes through development of elctrospun electrode structures.
- Fabricate, characterize, and evaluate membrane electrode assemblies (MEAs) with nanofiber mat cathodes containing highly active oxygen reduction reaction catalysts for hydrogen–air fuel cells.
- Generate useful correlations and insightful understandings regarding nanofiber electrode electrospinning.
- Develop collaborations with The Fuel Cell Consortium for Performance and Durability researchers at national laboratories.

Fiscal Year (FY) 2017 Objectives

- Synthesize PtNi/C shape-controlled catalyst (at Georgia Tech).
- Identify and optimize conditions for electrospinning particle/polymer nanofiber mats with TKK (Tanaka Kikinzoku Kogyo) PtCo/C and PtNi/C catalysts and with Georgia Tech PtNi/C catalyst, where the catalyst binder is a perfluorsulfonic acid or perfluoroimide acid ionomer.
- Fabricate and evaluate the performance of nanofiber and sprayed cathode MEAs.

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.

(A) Durability (ageing and degradation of fuel cell electrodes)

(B) Cost (lowering 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)

Table 1 shows the progress towards meeting the technical targets for electrocatalysts and MEAs for transportation applications.

FY 2017 Accomplishments

- Electrospun particle/polymer nanofiber mat cathodes were prepared at 0.1 mg_{Pt}/cm^2 with commercial PtCo/C and PtNi/C catalysts, where the binder was a mixture of Nafion and PAA.
- A 5 cm^2 MEA with a PtNi/C nanofiber cathode (0.1 mg_{Pt}/cm^2) produced 68% more power at 0.65 V, 80°C, 100% relative humidity, and 200 kPa_{abs} vs. a conventional sprayed cathode MEA at the same conditions.
- In 5 cm^2 MEAs with a Nafion 211 membrane, PtCo/C nanofiber cathodes performed very well, with a rated power of 784 mW/cm^2 at 95°C and 150 kPa_{abs} (which is approaching the DOE 2020 target of 1 W/cm^2).
- Nanofiber cathode MEAs exhibited excellent durability in a load cycling accelerated stress test, with a power loss of 30% at 0.65 V after 30,000 voltage cycles from 0.60 V to 0.95 V. This power loss is significantly less than that in a conventional slurry electrode MEA.
- Batches of shape-controlled PtNi/C catalyst were prepared at Georgia Tech and sent to Vanderbilt for initial electrospinning studies.

TABLE 1. Progress towards Meeting Technical Targets for Electrocatalysts and MEAs for Transportation Applications

Characteristic	Units	DOE 2020 Electrocatalyst and MEA Targets	Project Status[a]
Mass activity	A/mg_{PGM}@0.90 $mV_{iR\text{-}free}$	0.44	0.29[b]
PGM total loading (both electrodes)	$mg\text{-}PGM/cm^2_{geo}$	0.125	0.20
Loss in performance at 0.80 A/cm^2 after a load cycling AST (30,000 voltage cycles)	mV	<30	59
Loss in performance at 1.5 A/cm^2 after a load cycling AST (30,000 voltage cycles)	mV	<30	95
MEA performance @ 0.80 V	mA/cm^2_{geo}	300	347
MEA performance @ rated power (150 kPa_{abs})	mW/cm^2_{geo}	1,000	784

[a] 5 cm^2 MEA, TKK PtCo/C cathode catalyst, Pt/C anode catalyst, Nafion® + poly(acrylic acid) (PAA) binder, Nafion 211 membrane, temperature = 80°C, 200 $kPa_{abs,}$ 100% relative humidity.
[b] measured at 150 kPa_{abs}
PGM – platinum group metal; AST – accelerated stress test

- 5 cm^2 nanofiber cathode MEAs were prepared and sent to Los Alamos National Laboratory for preliminary testing.

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/or 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], the present project seeks to fabricate MEAs containing nanostructured Pt-alloy catalyst powders and selected perfluorosulfonic acid ionomer and blended polymer 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 new 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, where 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 compare nanofiber and sprayed electrode MEAs with commercial Pt-alloy cathodes at ultra-low Pt loading with various perfluorinated ionomer-based binders; (2) synthesize Pt-Ni octahedra catalysts with high oxygen reduction activity; (3) incorporate the octahedra Pt-Ni 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 knowledge base to our Fuel Cell Consortium for Performance and Durability collaborators.

RESULTS

Figure 1 shows a top-down scanning electron microscope image of an electrospun mat composed of commercial TKK PtCo/C catalyst powder with a binder of Nafion perfluorosulfonic acid and PAA. The catalyst/Nafion/PAA weight ratio of the fibers is 55/30/15 and the average fiber diameter is approximately 600 nm. Representative examples of hydrogen–air fuel cell polarization data from nanofiber and slurry PtCo/C cathode MEAs (both made at Vanderbilt University) are shown in Figure 2. The nanofiber MEA power density at 0.65 V was 40% higher than that for the slurry electrode MEA (where the latter utilized a neat Nafion binder), i.e., 784 mW/cm^2 vs 559 mW/cm^2. At

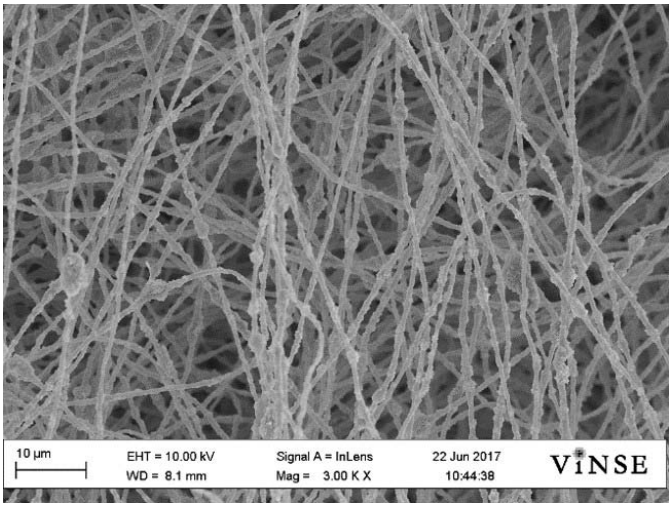

FIGURE 1. Scanning electron microscope image of a nanofiber mat with TKK PtCo/C catalyst and a binder of Nafion and PAA

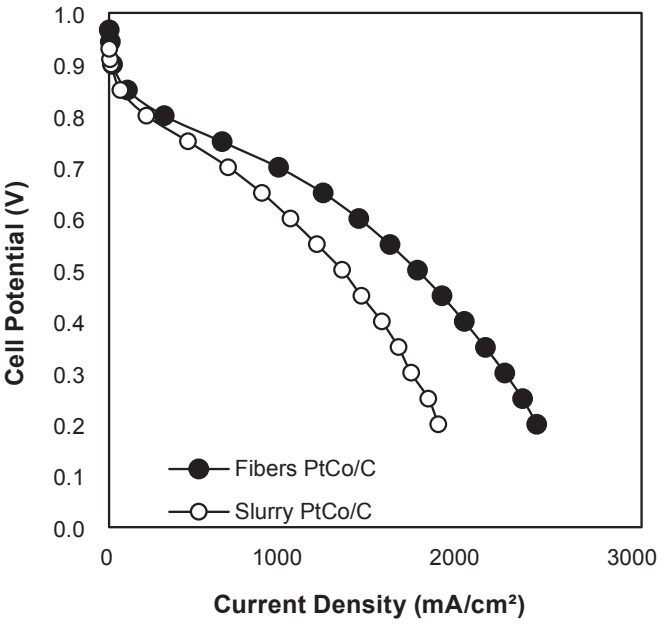

FIGURE 2. Hydrogen–air fuel cell polarization data for a nanofiber cathode MEA vs. a slurry cathode MEA using PtCo/C at 80°C and 200 kPa_{abs} pressure

maximum power, the improvement was 32%. Higher power densities are attributed to (1) a more uniform distribution of binder and catalyst particles throughout the fiber, resulting in a significantly higher electrochemically active surface area for the nanofiber cathode (60 vs. 34 m^2/g) and (2) rapid removal of product water due to inter- and intra-fiber porosity, which is particularly important at maximum power where the current density is high.

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 1.4 kW/°C, the fuel cell operating temperature was set at 95°C, the pressure was 150 kPa_{abs}, and the ambient temperature was 40°C. At rated power (0.674 V, according to Equation 1), the power density of a PtCo/C nanofiber cathode MEA at 0.1 mg_{Pt}/cm^2 was 784 mW/cm^2, which is approaching the DOE 2020 target of 1,000 mW/cm^2.

Catalyst support (carbon corrosion) and electrocatalyst (metal dissolution) voltage cycling ASTs were performed with nanofiber electrode and painted slurry electrode MEAs, where the nanofiber cathode had a binder of Nafion + PAA and where the slurry MEA used a neat Nafion binder. The catalyst support AST protocol involved triangular wave potential cycling from 1.0 V to 1.5 V for 1,000 cycles. For the electrocatalyst AST, the voltage was cycled 30,000 times from 0.6 V to 0.95 V. 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 hydrogen and 2,000 cm^3/min for air, the temperature was 80°C, and the relative humidity was fixed at 100%. Both the anode and cathode Pt loadings were 0.1 mg/cm². Beginning of life and end of life fuel cell polarization curves for the catalyst support AST are shown in Figure 3. The slurry electrode lost 41% of its maximum power during the test, as compared to a 27% power loss for the nanofiber cathode (where the latter is closely approaching the 2020 DOE target). The results of the electrocatalyst AST are shown in Figure 4. As was the case for the catalyst support AST, the durability of the nanofiber electrode MEA in the electrocatalyst AST is excellent (only a 32% power loss at 0.65 V), with an end of life polarization curve that is at or above the beginning of life curve for the slurry electrode.

CONCLUSIONS AND UPCOMING ACTIVITIES

The use of nanofiber electrode MEAs significantly improved the fuel cell performance with a commercial TKK PtCo/C catalyst at 0.10 mg_{Pt}/cm^2, with a 32% boost in the maximum power and 40% higher power at 0.65 V vs. a slurry cathode MEA. The rated power at 95°C and 150 kPa_{abs} pressure was promising at 784 mW/cm^2. The nanofiber MEA also exhibited improved durability vs. a non-optimized slurry cathode MEA, with higher power densities at end of life, after catalyst support and electrocatalyst ASTs.

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

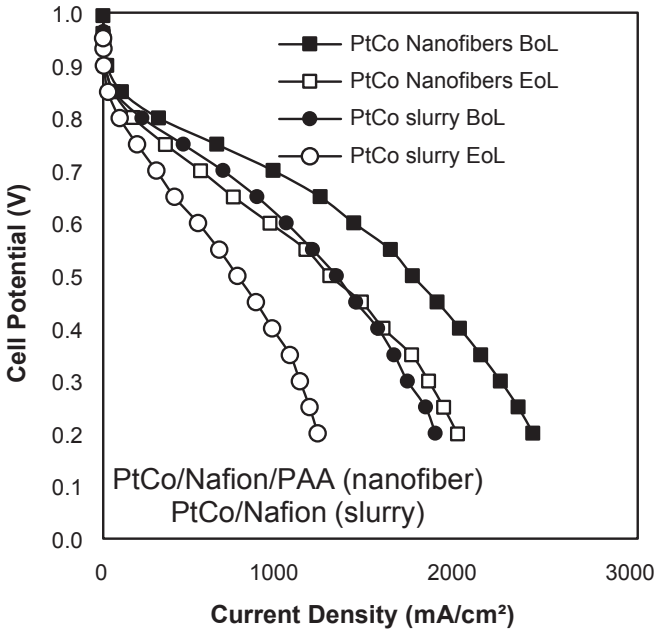

FIGURE 3. Carbon corrosion AST (1,000 voltage cycles at end of life) results for nanofiber and slurry cathode MEAs with PtCo/C and a binder of Nafion + PAA

Upcoming activities will focus on:

- Preparing, characterizing, and testing nanofiber mat cathodes with (1) TKK PtCo/C catalyst and different binders, (2) TKK PtNi/C catalyst and Nafion/PAA binder, and (3) Georgia Tech shape-controlled PtNi/C catalyst and Nafion/PAA binder.
- Measuring oxygen limiting current in nanofiber cathode MEAs.
- Preparing 5 cm^2 and 25 cm^2 nanofiber MEAs for initial performance assessment and durability testing at Nissan Technical Center North America and at Los Alamos National Laboratory.

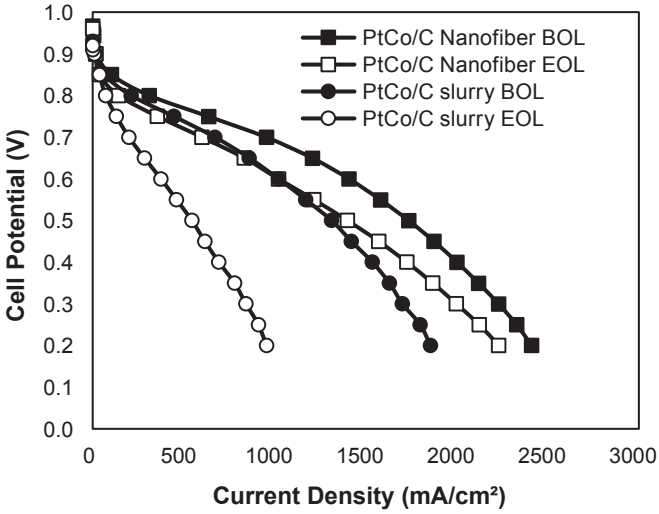

FIGURE 4. Fuel cell polarization results before and after a metal dissolution AST (end of life after 30,000 voltage cycles, 0.6 V to 0.95 V) for nanofiber and slurry cathode MEAs with PtCo/C and a binder of Nafion + PAA

FY 2017 PUBLICATIONS/PRESENTATIONS

1. J.J. Slack, R. Wycisk, N. Dale, A. Kumar, and P.N. Pintauro, "Electrospun Nanofiber Fuel Cell MEA Cathodes with PtCo/C Catalyst" *ECS Transactions* (2017).

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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**, F744–F749 (2013).

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**, F84–F91 (2015).