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

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Subcontractors:
• Nissan Technical Center North America, Farmington Hills, MI
• eSpin Technologies, Inc. (eSpin), Chattanooga, TN

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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 catalysts for H₂/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) 2019 Objectives

• Fabricate and evaluate nanofiber electrode MEAs with PtCo/C, PtNi/C, and Pt/C cathode catalyst and two different perfluorosulfonic acid (PFSA) binders (Vanderbilt and Nissan Technical Center North America).

• Investigate different carrier polymers for electrospinning nanofiber mat cathodes with Nafion binder.

• Probe the structure of electrospun cathode catalyst nanofibers and nanofiber mat cathodes.

• Contrast the water content profile in operating MEAs with nanofiber and slurry electrodes.

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 Plan1:

• (A) Durability (aging 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).

Technical Targets

The DOE 2020 technical targets and our current project status are listed in Table 1 for comparison.

FY 2019 Accomplishments

• MEAs were fabricated with electrospun particle/polymer nanofiber mat cathodes (0.1 mgPt/cm² Pt/C or PtNi/C) and anodes (0.1 mg/cm² Pt/C), where the binder was a mixture of the acid form of Nafion (H⁺-Nafion) and PAA or the sodium form of Nafion (Na⁺-Nafion), where the carrier polymer (either PAA or PEO) was removed from the fibers after electrospinning.

• Electrospun electrodes were prepared with Pt/C catalyst and a Na⁺-Nafion and PEO carrier polymer using the multi-spinneret industrial electrospinning equipment at eSpin.

Technologies. The electrodes were then evaluated in a hydrogen/air fuel cell at Vanderbilt University. MEAs using eSpin electrodes performed very well at beginning of life, with power densities comparable to Vanderbilt fiber electrodes, but the maximum power decreased by 45% after 30,000 catalyst AST cycles versus a 25% power loss for a Vanderbilt electrode MEA.

- Fiber electrodes were prepared with Pt/C catalyst, Na\(^+\)-Nafion, and either PAA or PEO as the carrier polymer. MEAs prepared with Na\(^+\)-Nafion performed similarly to each other, exhibiting a marked improvement in power density, especially at low RH, as compared to a nanofiber cathode MEA with a binder of H\(^+\)-Nafion and PAA (PAA cannot be extracted from the cathode fiber mat and lowers the proton conductivity of the binder).

- Water content in a Pt/C fiber electrode MEA was compared to that in conventional spray electrode MEAs during fuel cell operation via neutron imaging experiments at the National Institute of Standards and Technology. Under fully humidified conditions and high-current-density operation, there was less water within fiber electrode MEAs when the binder was H\(^+\)-Nafion + PAA.

- Fiber electrode MEAs with a neat Nafion binder (prepared from Na\(^+\)-Nafion + PEO or PAA) exhibited a 25% loss in maximum power after 30,000 catalyst AST cycles, as compared to a 12% loss when the cathode binder was H\(^+\)-Nafion + PAA.

- Scanning transmission electron microscopy with energy-dispersive X-ray spectroscopy (STEM-EDX) imaging of electrospun fiber cross sections at Oak Ridge National Laboratory and Vanderbilt revealed that fiber electrodes (using a Pt/C or PtCo/C catalyst) prepared with H\(^+\)-Nafion + PAA binder had a Na\(^+\)-Nafion + either PAA or PEO showed an ionomer-rich surface and a catalyst-rich fiber interior. A similar segregated morphology was observed with PtNi/C catalyst where the binder was either H\(^+\)-Nafion + PAA or Na\(^+\)-Nafion + PEO.

- PtNi/C fiber cathode MEAs prepared with either H\(^+\)-Nafion + PAA or Na\(^+\)-Nafion + PEO exhibited high maximum power at low RH (40%), at 750 mW/cm\(^2\) and 820 mW/cm\(^2\), respectively.

- An all-electrospun MEA was prepared using 725 equivalent weight (EW) PFSA (provided by 3M) for the membrane and electrode binder and Pt/C catalyst at the anode and cathode. The 725 EW MEA generated high and near-constant power over a wide feed gas RH range (20%–100%). At 20% RH the 725 EW MEA generated a maximum power of 815 mW/cm\(^2\).

- Rated power targets were achieved at 250 kPa\(_{abs}\) for low-loading Pt (0.117 mgPt/cm\(^2\)) with PtCo/C -PEO cathode, Pt/C-PEO anode MEA.
Table 1. Progress toward Meeting Technical Targets for Electrocatalysts and MEAs for Transportation Applications

<table>
<thead>
<tr>
<th>Characteristic</th>
<th>Units</th>
<th>DOE 2020 Electrocatalyst and MEA Targets</th>
<th>Project Status</th>
</tr>
</thead>
<tbody>
<tr>
<td>Mass activity</td>
<td>A/mg_{PGM} @ 0.90 V_{irr-free}</td>
<td>0.44</td>
<td>0.464&lt;sup&gt;a&lt;/sup&gt;</td>
</tr>
<tr>
<td>PGM total loading (both electrodes)</td>
<td>mg PGM/cm&lt;sup&gt;2&lt;/sup&gt;_geo</td>
<td>0.125</td>
<td>0.117</td>
</tr>
<tr>
<td>Loss in performance at 0.80 A/cm&lt;sup&gt;2&lt;/sup&gt; after a load cycling AST (30,000 voltage cycles)</td>
<td>mV</td>
<td>&lt;30</td>
<td>68&lt;sup&gt;b&lt;/sup&gt;</td>
</tr>
<tr>
<td>Loss in performance at 1.5 A/cm&lt;sup&gt;2&lt;/sup&gt; after a load cycling AST (30,000 voltage cycles)</td>
<td>mV</td>
<td>&lt;30</td>
<td>32&lt;sup&gt;b&lt;/sup&gt;</td>
</tr>
<tr>
<td>MEA performance @ 0.80 V</td>
<td>mA/cm&lt;sup&gt;2&lt;/sup&gt;_geo</td>
<td>300</td>
<td>424&lt;sup&gt;c&lt;/sup&gt;</td>
</tr>
<tr>
<td>MEA performance @ rated power (150 kPa_{abs})</td>
<td>mW/cm&lt;sup&gt;2&lt;/sup&gt;_geo</td>
<td>1,000</td>
<td>803&lt;sup&gt;d&lt;/sup&gt;</td>
</tr>
</tbody>
</table>

PGM – platinum group metal; AST – accelerated stress test; TKK – Tanaka Kikinzoku; PAA – poly(acrylic acid); PEO – poly(ethylene oxide)

<sup>a</sup> Measured at Los Alamos National Laboratory; Nafion-PAA cathode with PtCo/C at 0.2 mg_{Pt/cm<sup>2</sup>} total loading.

<sup>b</sup> 5-cm<sup>2</sup> MEA, TKK PtCo/C cathode catalyst (0.1 mg_{Pt/cm<sup>2</sup>}), Pt/C anode catalyst (0.1 mg_{Pt/cm<sup>2</sup>}), Nafion + PAA binder, Nafion 211 membrane, T = 80°C, 200 kPa_{abs}, 100% RH.

<sup>c</sup> 5-cm<sup>2</sup> MEA, TKK PtCo/C cathode catalyst (0.1 mg_{Pt/cm<sup>2</sup>}), Pt/C anode catalyst (0.1 mg_{Pt/cm<sup>2</sup>}), Nafion + PEO binder, Nafion 211 membrane, T = 80°C, 200 kPa_{abs}, 100% RH.

<sup>d</sup> 10-cm<sup>2</sup> MEA, TKK PtCo/C cathode catalyst (0.1 mg_{Pt/cm<sup>2</sup>}), TKK Pt/C anode catalyst (0.1 mg_{Pt/cm<sup>2</sup>}), Nafion + PEO binder, Nafion 211 membrane, T = 95°C, 150 kPa_{abs}, 100% RH.

<sup>e</sup> 10-cm<sup>2</sup> MEA, TKK PtCo/C cathode catalyst (0.11 mg_{Pt/cm<sup>2</sup>}), TKK Pt/C anode catalyst (0.013 mg_{Pt/cm<sup>2</sup>}), Nafion binder, Nafion 211 membrane, T = 95°C, 150 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/or catalyst-coated gas diffusion electrode methodologies, with little or no control over the macroscale 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 PFSA 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, 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 that 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 (completed last year), (3) incorporate commercial Pt and Pt-alloy catalysts
into nanofiber and sprayed electrode MEAs, (4) optimize the electrospun nanofiber composition and
morphology and nanofiber cathode mat morphology to maximize fuel cell performance and durability at high
and low RH conditions, and (5) provide catalyst powder, electrospun cathode mats, MEAs, experimental skills,
and the team’s electrospinning knowledge base to our FC-PAD collaborators.

RESULTS

One attractive characteristic of nanofiber mat electrode MEAs is their ability to expel product water from the
cathode with little or no flooding at high current densities. This was investigated further by viewing the water
profile in an operating fuel cell MEA directly via neutron imaging. Data were collected on a nanofiber
electrode MEA (0.10 mg/cm² Pt/C anode and cathode with an H⁺-Nafion + PAA binder) and a sprayed
electrode MEA (Pt/C and a neat Nafion binder). Water profiles are shown in Figure 1 for various operating
current densities during H₂/air fuel cell operation at 80°C, 200 kPa abs, and 100% RH. As can be seen, there is
less water in the nanofiber electrode MEA (more water in the outer portions of the anode and cathode gas
diffusion layers) as compared to the sprayed electrode MEA due to intrafiber and interfiber porosity of the
fiber mat cathode.

Structure/composition of fiber and sprayed cathode cross sections were analyzed for Pt (catalyst) and fluorine
(Nafion ionomer) via STEM-EDX, as shown in Figure 2. Figure 2a shows a Pt/C fiber with a binder of H⁺-
Nafion + PAA, where there is a uniform distribution of catalyst and ionomer in the radial fiber direction. In
Figures 2b and 2c, the Pt and F profiles across a fiber are shown for a fiber containing Pt/C catalyst and a
binder of Na⁺-Nafion with either PAA (2b) or PEO (2c) carrier. Fibers with Na⁺-Nafion have an ionomer-rich
surface and catalyst-rich interior. This unusual morphology is unique to electrospun fibers; no such segregation
is observed in sprayed electrodes with Pt/C and Na⁺-Nafion (2d).

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Figure 1. Water profiles in a sprayed electrode MEA and a nanofiber MEA at different fuel cell operating voltages and
current densities. MEAs had Pt/C anode and cathode loadings of 0.1 mgPt/cm², Nafion 211 membrane, with neat Nafion
binder for the sprayed gas diffusion electrodes and H⁺-Nafion + PAA binder for the nanofiber MEA. Data were collected in
H₂/air at 80°C, 200 kPa abs, and 100% RH.
Figure 2. STEM-EDX cross-sectional elemental maps: (a) a single fiber with a binder of H\textsuperscript+-Nafion + PAA and PtCo/C catalyst, (b) a single fiber with a binder of Na\textsuperscript+-Nafion + PAA and PtCo/C catalyst, (c) a single fiber with a binder of Na\textsuperscript+-Nafion + PEO and PtCo/C catalyst, and (d) a sprayed electrode with a binder of Na\textsuperscript+-Nafion and PtCo/C catalyst

An all-electrospun MEA (nanofiber composite membrane and particle/polymer nanofiber electrodes) with 725 EW PFSA ionomer as the membrane and electrode binder was prepared and tested in an H\textsubscript{2}/air fuel cell. The membrane was 20 µm thick, with a Pt/C fiber mat cathode and anode (each electrode had a catalyst loading of 0.10 mgPt/cm\textsuperscript{2} and a binder of the Na\textsuperscript+-form of 725 EW PFSA + PEO). Maximum power density was recorded between 20% and 100% RH and contrasted to a Nafion-based nanofiber electrode MEA using PtCo/C as seen in Figure 3. The two MEAs produced similar power down to 30% RH. At 20% RH the Nafion-based PtCo/C MEA generated approximately half the power that was observed for the 725 EW PFSA-based MEA. All anodes and cathodes had a Pt loading of 0.1 mg/cm\textsuperscript{2} and data were collected at 80°C and 200 kPa\textsubscript{abs}.

Figure 3. H\textsubscript{2}/air fuel cell performance of an all-electrospun MEA with a nanofiber composite 725 EW PFSA (20 µm thick) membrane, nanofiber anode and cathode containing Pt/C catalyst (each at 0.1 mgPt/cm\textsuperscript{2}), and 725 EW PFSA binder. (a) Effect of feed gas RH on polarization plots and (b) maximum power density vs. feed gas relative humidity for the 725 EW MEA and a nanofiber electrode MEA with Nafion binder and a Nafion 211 membrane. All data were collected at 80°C, 200 kPa\textsubscript{abs}, and H\textsubscript{2}/air flow rates of 125/500 sccm.
Rated power results at 95°C (0.663 V) and 100% RH are summarized in Table 2 for nanofiber MEAs at two total anode + cathode loadings and three different backpressures. The MEAs had a total Pt loading of 0.2 mg/cm² (0.1 mgPtf/cm² anode and 0.1 mgPtc/cm² cathode) or 0.017 mg/cm² (0.095 mgPtc/cm² at the cathode and 0.022 mgPtf/cm² at the anode). Hydrogen and air flow rates of 4 L/min and 8 L/min were used at the anode and cathode, respectively. The membrane was Nafion 211. At an elevated backpressure of 250 kPaabs, both nanofiber MEAs meet the 2020 DOE performance target.

<table>
<thead>
<tr>
<th>Total Nanofiber MEA Loading</th>
<th>Rated Power at 150 kPaabs (mW/cm²)</th>
<th>Rated Power at 200 kPaabs (mW/cm²)</th>
<th>Rated Power at 250 kPaabs (mW/cm²)</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.2 mgPtf/cm²</td>
<td>803</td>
<td>961</td>
<td>1,033</td>
</tr>
<tr>
<td>0.117 mgPtf/cm²</td>
<td>702</td>
<td>945</td>
<td>1,018</td>
</tr>
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</table>

To demonstrate that nanofiber electrodes can be made on a commercial electrospinning line, particle/polymer fiber mats were prepared at eSpin Technologies and then the electrodes were tested in MEAs at Vanderbilt University. Electrodes were made with Pt/C (TEC10F50E), Na⁺-Nafion, and PEO carrier polymer, with a catalyst loading of 0.1 mgPtc/cm². A summary of a Vanderbilt fiber electrode MEA and an eSpin fiber MEA before and after 30,000 catalyst durability AST cycles is shown in Table 3. Beginning of life power density and cathodic oxygen reduction mass activity are similar between the two electrodes (within 10%). After the catalyst durability AST, the Vanderbilt MEA lost 25% in maximum power whereas the eSpin MEA lost considerably more power (45%).

<table>
<thead>
<tr>
<th></th>
<th>Mass Activity (mA/mgPtc)</th>
<th>Maximum Power Density (mW/cm²)</th>
<th>Power Density at 0.65 V (mW/cm²)</th>
</tr>
</thead>
<tbody>
<tr>
<td>VU</td>
<td>Beginning of life</td>
<td>138</td>
<td>961</td>
</tr>
<tr>
<td>30,000 cycles</td>
<td>105</td>
<td>729</td>
<td>585</td>
</tr>
<tr>
<td>eSpin</td>
<td>Beginning of life</td>
<td>146</td>
<td>890</td>
</tr>
<tr>
<td>30,000 cycles</td>
<td>103</td>
<td>493</td>
<td>407</td>
</tr>
</tbody>
</table>

The fiber mats were made at Vanderbilt University (VU) or eSpin Technologies, Inc. Power density data were collected at 80°C, 100% RH, H₂/air gas flow rates of 125/500 sccm, and 200 kPaabs. Anode and cathode catalyst loadings were 0.1 mgPtc/cm². The membrane was Nafion 211.

**CONCLUSIONS AND UPCOMING ACTIVITIES**

Nanofiber electrode MEAs produced high power at low Pt loadings, over a wide range of feed gas RH conditions, and after a catalyst durability voltage cycling AST. Power densities approaching 1.0 W/cm² were measured for a Pt/C MEA with a total loading of 0.2 mgPtf/cm². Fiber mat electrodes retain less water than spray electrodes during fuel cell operation at high humidity and high current density, which in part explains the improved durability and transport properties of fiber cathodes. Fibers prepared with Na⁺-Nafion have a different radial distribution of ionomer and catalyst vs. fibers made with H⁺-Nafion. An all-electrospun MEA with 725 EW PFSA (nanofibers with neat PFSA binder and a 20-μm-thick PFSA membrane that was reinforced with polyvinylidene fluoride [PVDF] fibers) generated high power (a maximum power of 800–900 mW/cm²) over a wide feed gas RH range (20%–100% RH). MEAs with fiber mat cathodes prepared on commercial electrospinning equipment at eSpin Technologies, Inc. generated high power at beginning of life (a maximum power of 890 mW/cm² at 100% RH).

Future work will focus on:

- 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, choice of PFSA binder, and MEA hot pressing conditions for optimal power and durability at a total Pt loading of 0.125 mg/cm² and at higher Pt loadings (0.25 and 0.35 mg/cm²).

FY 2019 PUBLICATIONS/PRESENTATIONS


REFERENCES
