

# Electrospun Fiber Mat Cathode with Platinum-Group-Metal-Free Catalyst Powder and Nafion/PVDF Binder

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Electrospun nanofiber cathode mats were prepared with a metal-organic framework (MOF)-derived Fe–N–C catalyst and a blended binder of Nafion and polyvinylidene fluoride (PVDF). The electrodes were incorporated into H<sub>2</sub>/air fuel cell membrane-electrode assemblies (MEAs) and compared with conventional sprayed-cathode MEAs, in terms of power output and durability. The addition of hydrophobic PVDF into the electrode binder of nanofiber and sprayed cathodes produced a stable power output for 300 hours, whereas the sprayed-electrode MEA with neat Nafion binder exhibited a 63% power loss. The steady-state maximum power density output of a PGM-free nanofiber-cathode MEA with a 1:1 Nafion:PVDF cathode binder at 80 °C and 1 atm backpressure was 154 mW/cm<sup>2</sup>. MEAs with a nanofiber cathode generated significantly more power than a sprayed cathode and the nanofiber cathodes continued to produce power throughout a carbon-corrosion voltage cycling accelerated-stress test. After 50 carbon corrosion-voltage cycles, the maximum power density rose from 154 to 186 mW/cm<sup>2</sup> and then decreased to 106 mW/cm<sup>2</sup> at 500 cycles.

A variety of strategies are being pursued to lower the platinum content in proton exchange membrane fuel cells. These include the use of Pt-alloy, core-shell and shape-controlled platinum catalysts which exhibit very high oxygen reduction reaction (ORR) activity. Another approach is focused on inexpensive platinum-group-metal-free (PGM-free) powders as the cathode catalyst. PGM-free catalysts are typically carbon-based powders with metal/nitrogen/carbon (Me/N<sub>x</sub>/C<sub>y</sub>) catalytic surface sites, where the metal ion is often cobalt, or iron.<sup>[1–3]</sup> The ORR activity of these catalysts is lower than that of Pt, but they can be used at higher loadings to compensate for slower oxygen reduction kinetics. Additionally, prior studies have reported poor durability of MEAs with non-PGM catalysts in hydrogen/air fuel cells

due to several effects including loss of the carbon support material, loss of metal ions from the catalyst which lowers catalytic activity and binder conductivity, water flooding which impedes oxygen transport, and the generation of peroxide species which degrades the catalyst and binder.<sup>[4–6]</sup>

The present study was initiated to obtain preliminary fuel cell performance and durability data on one type of PGM-free catalyst powder in particle/polymer nanofiber mat cathodes. The catalyst used in this study was a MOF-derived Fe–N–C catalyst with 0.5 wt% Fe, a BET surface area of 1362 m<sup>2</sup>/g, and a reported RDE mass based kinetic current density of 7.78 A/g<sub>cat</sub> at 0.8 V.<sup>[7]</sup> MEAs with electrospun and conventional sprayed cathodes were examined and their performance compared. Pintauro and co-workers<sup>[8–10]</sup> have shown that an electrospun nanofiber cathode with a conventional Pt/C catalyst performs well in a hydrogen/air proton exchange membrane fuel cell with high power at low Pt loadings and good performance after accelerated carbon corrosion and Pt dissolution tests. Carbon corrosion was significantly suppressed by using a Nafion:PVDF mixture, with some degree of hydrophobicity depending on the Nafion:PVDF weight ratio, as the binder in cathode mat nanofibers.<sup>[10]</sup>

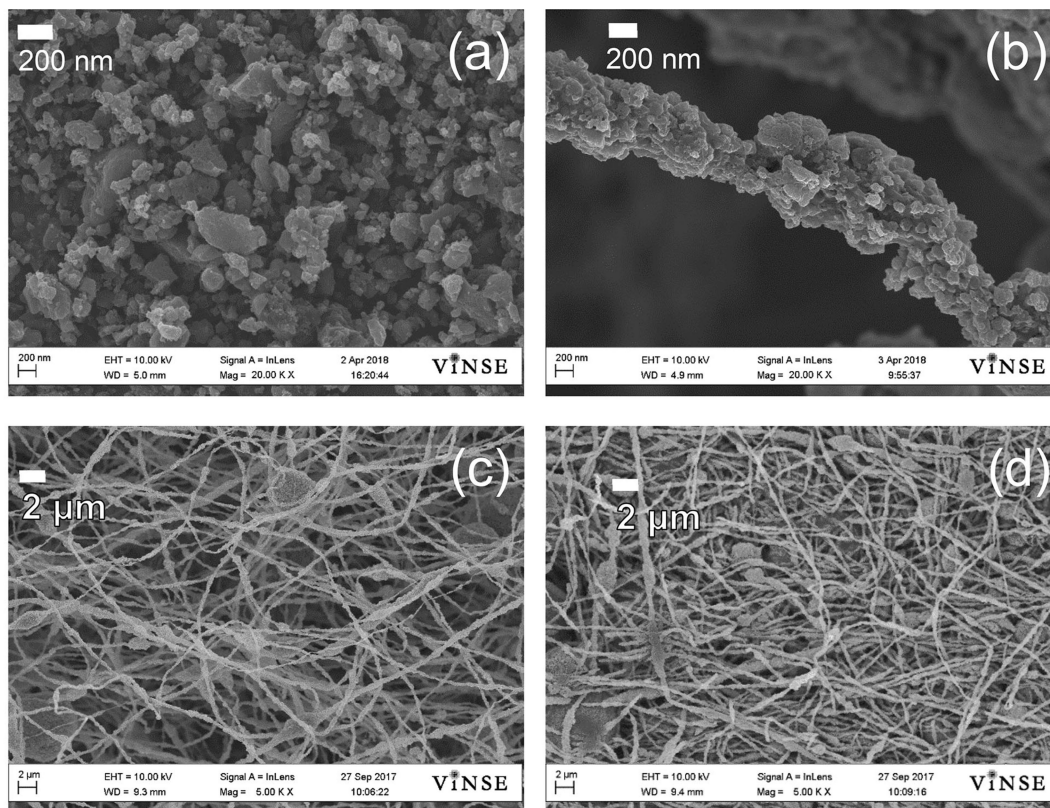
An SEM image of the PGM-free catalyst particles after ultrasonic agitation are shown in Figure 1a. The particles range in size from 50 to 500 nm. Figure 1b shows an SEM of a single catalyst-loaded fiber, with well-distributed catalyst particles through the fiber length. Large particles are not seen in the fiber, suggesting that shearing/mixing events during electrospinning are breaking-up large catalyst agglomerates. Top-down low-magnification SEM images of an electrospun nanofiber mat before and after hot-pressing at 4 MPa and 140 °C are shown in Figures 1c and 1d. Most of the catalyst was contained in fibers, with a few droplet defects. The average fiber diameter, as determined by mapping digitized SEM images using ImageJ software, is ~750 nm. The porosity of the hot-pressed fiber mat was estimated to be ~50%, as determined by comparing the measured density of the compressed mat (0.86 g/cm<sup>3</sup> from the fiber mat mass and volume) to the theoretical density based on the fiber composition and the known densities of catalyst and binder (1.75 g/cm<sup>3</sup>).

Figures 2a and 2b show polarization curves taken immediately upon loading an MEA into the fuel cell test fixture and after 50 hours of operation at a constant voltage of 0.5 V, for one nanofiber and two sprayed cathodes with humidified hydrogen and air feeds. The nanofiber cathode binder was a 1:1 weight ratio blend of Nafion:PVDF (a catalyst:Nafion:PVDF

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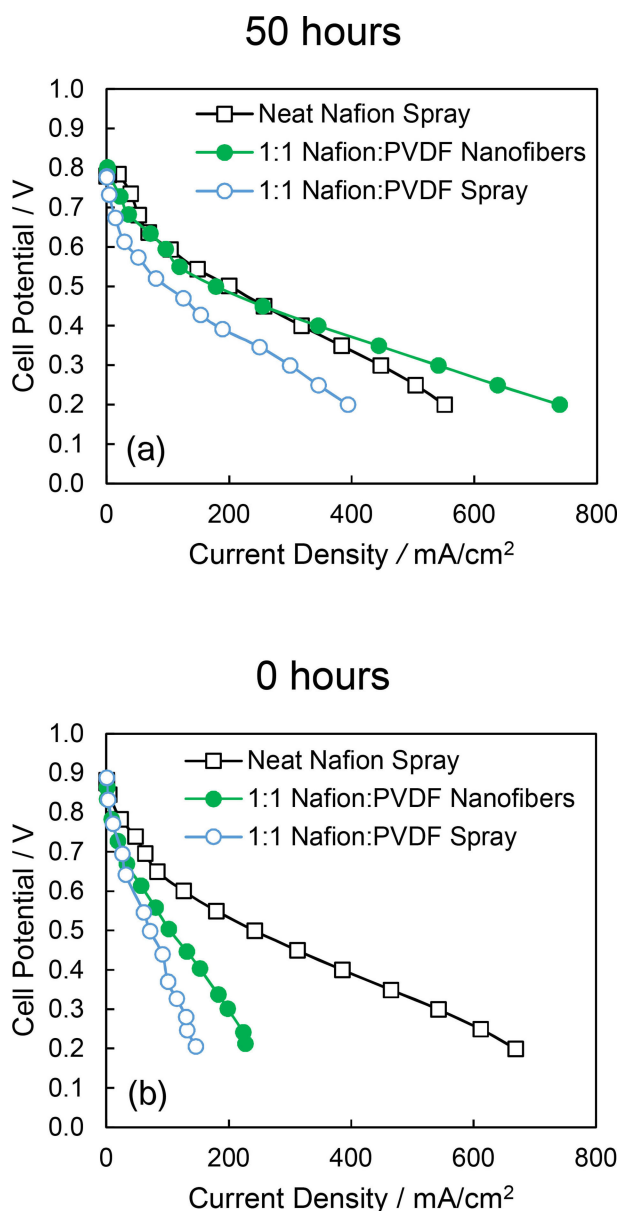


**Figure 1.** Top-down SEM images of (a) the PGM-free catalyst particles after ultrasonication to break up agglomerates, (b) a nanofiber composed of PGM-free catalyst:Nafion:PVDF (70:10:20 weight ratio), (c) an electrospun mat of the same composition at 5,000x magnification, (d) an electrospun mat of the same composition after hot pressing at 140 °C and 4 MPa.

weight ratio of 70:15:15) and the sprayed cathodes employed either a neat Nafion binder or a 1:1 weight ratio Nafion:PVDF blend. The initial time data was collected with no MEA break-in protocol. The neat Nafion sprayed GDE initially outperformed the nanofiber MEA, with power densities that are comparable to data in the literature, e.g., 120 mW/cm<sup>2</sup> at 0.5 V in Figure 2a vs 100 mW/cm<sup>2</sup> at 0.5 V from reference 5 and 150 mW/cm<sup>2</sup> at 0.5 V in references 1, and 11. After 50 hours, the power output of the neat Nafion sprayed cathode decreased (as observed by others),<sup>[5,12]</sup> whereas the performance of the nanofiber cathode MEA increased. The initial power output of the sprayed cathode MEA with a 1:1 Nafion/PVDF binder was very low, with a modest improvement in performance after 50 hours of constant voltage operation. Thus, the observed (unexpected) increase in power over 50 hours of operation for the two Nafion:PVDF binder MEAs is due to binder composition effects (a slow break in period for a Nafion:PVDF binder), whereas the high power of the nanofiber cathode MEA after 50 hours is attributed to the fiber morphology.

The transient behavior of two nanofiber cathode MEAs (with 1:1 and 1:2 Nafion:PVDF weight ratio binders) and two slurry cathode MEAs (neat Nafion and 1:1 Nafion:PVDF binders) during 300 hours of fuel cell operation is summarized in Figure 3, where the power density at 0.5 V is plotted vs. time. The results clearly show the beneficial effects of both binder composition and electrode morphology on MEA performance.

As expected, based on data in the literature,<sup>[5]</sup> the initial high performance from a slurry electrode MEA degraded over time, with a 63% decrease in power density at 0.5 V after 300 hours, due presumably to catalyst degradation.<sup>[4]</sup> The power output of the slurry electrode MEA with a 1:1 weight ratio Nafion:PVDF binder increased after start-up, reached a maximum power density at approximately 150 hours of operation, and then slowly declined for the remainder of the test, with a final power density of only 47 mW/cm<sup>2</sup>. The low but stable power is associated with the hydrophobicity of the binder. Initially, there is insufficient water at the catalyst surface for fast oxygen reduction kinetics. During fuel cell operation the catalyst surface becomes more hydrated due to the generation of water during oxygen reduction and the power rises and then stabilizes. There is a slow increase in binder conductivity as the electrode becomes more hydrated. This is evidenced by a decrease in high frequency resistance (from an initial value of 225 mΩ cm<sup>2</sup> to 115 mΩ cm<sup>2</sup> after 150 hours) throughout the voltage hold. The water content in the Nafion:PVDF binder remains lower than that in a Nafion cathode, which allows for better catalyst stability and constant power operation between 150 and 300 hours. The benefits of a nanofiber cathode morphology are clearly seen in Figure 3, for the two Nafion:PVDF binder MEAs. Power output was essentially constant from 150–300 hours for the 1:1 Nafion:PVDF binder with a 72% improvement in power density at 0.5 V after 300 hours



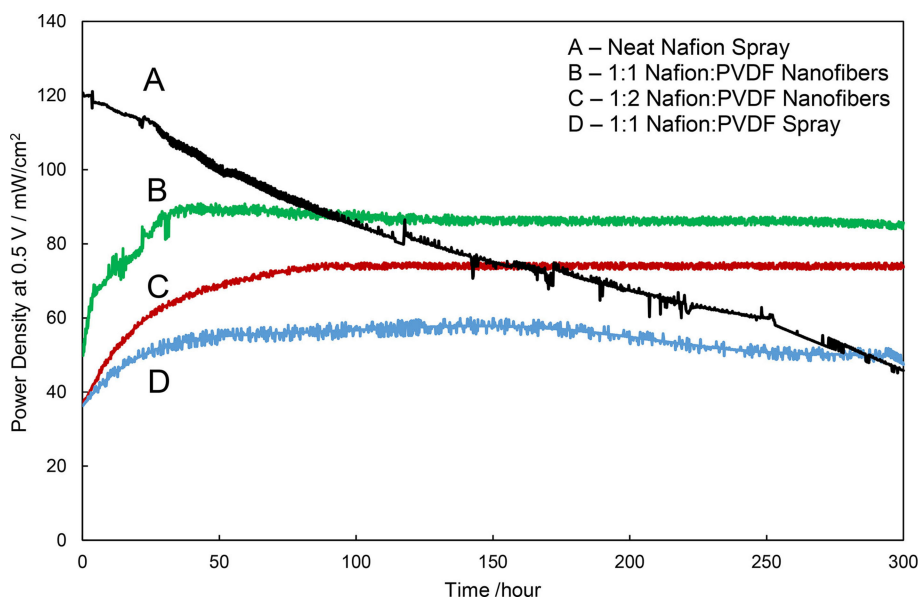
**Figure 2.** H<sub>2</sub>/air fuel cell polarization curves for nanofiber and sprayed cathodes MEAs with a PGM-free cathode catalyst (3.0 mg/cm<sup>2</sup>), a Nafion 211 membrane, and a Pt/C sprayed anode (0.1 mg/cm<sup>2</sup> with a neat Nafion binder). (a) Initial fuel cell performance and (b) fuel cell performance after 50 hours of constant voltage operation at 0.5 V. Fuel cell operating conditions: 80 °C, 100% relative humidity, 1 atm<sub>g</sub> backpressure, and 125/500 sccm H<sub>2</sub>/air feed gas flow rates. All MEAs have an anode of Johnson Matthey 40% Platinum on carbon with a loading of 0.1 mg<sub>Pt</sub>/cm<sup>2</sup>.

(86 mW/cm<sup>2</sup> vs. 50 mW/cm<sup>2</sup> comparing the nanofiber and slurry cathode MEAs with a 1:1 Nafion:PVDF binder). A similar power density improvement for a nanofiber vs. sprayed cathode MEA was seen previously with a Pt/C catalyst,<sup>[8–10]</sup> which was attributed to intrafiber and/or interfiber voids in a fiber mat and good mixing of catalyst and binder with a thin and uniform coating of binder on all catalyst particles (which allows for facile O<sub>2</sub> access to catalyst sites and water removal from the electrode). When the nanofiber cathode binder was made more hydrophobic by using a 1:2 Nafion:PVDF binder, there was a

slower rise in power during the initial stages of the test (the power did not stabilize until 100 hours of constant voltage operation) and a 15% decrease in the long-term power density (73 mW/cm<sup>2</sup> vs. 86 mW/cm<sup>2</sup> at 300 hours). This result suggests that there may be an optimum PVDF binder content ( $\leq 50$  wt.% PVDF), where the beneficial effects of PVDF regarding catalyst stability are balanced by its adverse effects on power output (decreasing the concentration of water at the catalyst surface and lowering the proton conductivity of the binder). Clearly, further work is needed to optimize the Nafion:PVDF weight ratio of the binder for PGM-free ORR catalysts; such experiments were not part of the present study but they are being planned and will be the subject of a future publication.

Carbon corrosion voltage cycling (from 1.0–1.5 V vs. SHE) accelerated stress tests (ASTs) were performed on all MEAs after 300 hours of operation at 0.5 V. It is well known that exposing cathodes with PGM-free-based catalysts to potentials above 1.2 V vs. SHE results in extreme degradation.<sup>[13–14]</sup> The results of these experiments are shown in Figure 4a, which presents the maximum H<sub>2</sub>/air fuel cell power output at 80 °C, 1 atm backpressure, and 100% relative humidity, measured intermittently over the course of 500 carbon corrosion voltage cycles. The fuel cell polarization plots used to calculate the maximum power for the two-nanofiber cathode MEAs are shown in Figures 4b and 4c. The power density at any point on the curve is calculated by taking the product of voltage and current density. The results are significant in that all three PGM-free cathodes with PVDF survived the AST. I.e., each retained greater power after 500 voltage cycles compared to the neat Nafion sprayed cathode. For the neat Nafion sprayed cathode MEA, there was a sharp decline in maximum power with voltage cycling. In contrast, both nanofiber MEAs exhibited an increase in power output after 150 voltage cycles, followed by a gradual decrease in MEA performance for the duration of the test. The difference in results between the two binder compositions demonstrates the effect of hydrophilicity at the beginning of life (BoL) and end of life (EoL). At BoL, the MEA with more PVDF produces lower power compared to the 1:1 Nafion:PVDF and at EoL, the MEA with more PVDF produces higher power. The increase in power during the initial stages of the carbon corrosion AST is consistent with prior studies on the carbon corrosion durability of Pt/C-containing nanofiber cathodes, when the Nafion:PVDF binder weight ratio was  $< 0.5$ . As explained in reference 10, the presence of hydrophobic PVDF in a cathode binder with Nafion limits water contact with the catalyst surface, resulting in less carbon corrosion but poor/slow kinetics for the oxygen reduction reaction (a low ORR catalytic mass activity). With continued voltage cycling, hydrophilic carbon oxidation species (e.g., C=O and C-OH) are formed on the catalyst and result in an improvement in power output. Normally, for a conventional cathode structure, this increase in hydrophilicity results in cathode flooding and a loss in power which is observed in Figure 4a for the sprayed electrode with a 1:1 weight ratio Nafion:PVDF binder. The nanofiber cathode mat morphology with the same composition, however, allows for the rapid expulsion of water from the sub-micron diameter fibers, so that power losses by cathode flooding are less significant. After 150





**Figure 3.** H<sub>2</sub>/air fuel cell power density at 0.5 V vs time for 300 hours with MEAs using PGM-free catalyst at 3.0 mg/cm<sup>2</sup> and either a nanofiber cathode (with a 1:1 or 1:2 Nafion:PVDF binder) or a sprayed cathode (with neat Nafion or a 1:1 Nafion:PVDF binder). All MEAs had a Nafion 211 membrane and a sprayed anode with Nafion binder and Johnson Matthey Pt/C HiSpec 4000 at 0.1 mg<sub>Pt</sub>/cm<sup>2</sup>. Fuel cell operating conditions: 80 °C, 100% relative humidity, 1 atm<sub>g</sub> backpressure, and 125/500 sccm H<sub>2</sub>/air feed-gas flow rates.

voltage cycles, the benefits of further increasing cathode hydrophilicity and water content at the catalyst surface are overwhelmed by carbon losses/oxidation and water flooding. This explanation of the sprayed and nanofiber cathode behavior in Figure 4a is further substantiated by the measured carbon loss from the cathode during the AST (as determined from the measured CO<sub>2</sub> concentration and flow rate in the air exhaust). Carbon corrosion was affected by binder composition (less carbon loss for a binder with more PVDF) and not by cathode morphology. Nanofiber vs sprayed cathodes with the same composition had nearly the same percent carbon loss after 500 voltage cycles (9% for the sprayed electrode with a 1:1 Nafion:PVDF binder and 8% for the nanofiber cathode with a 1:1 Nafion:PVDF binder). The nanofiber morphology, however, does play an important role in that it minimizes the deleterious effect of catalyst surface hydrophilicity on cathode flooding.

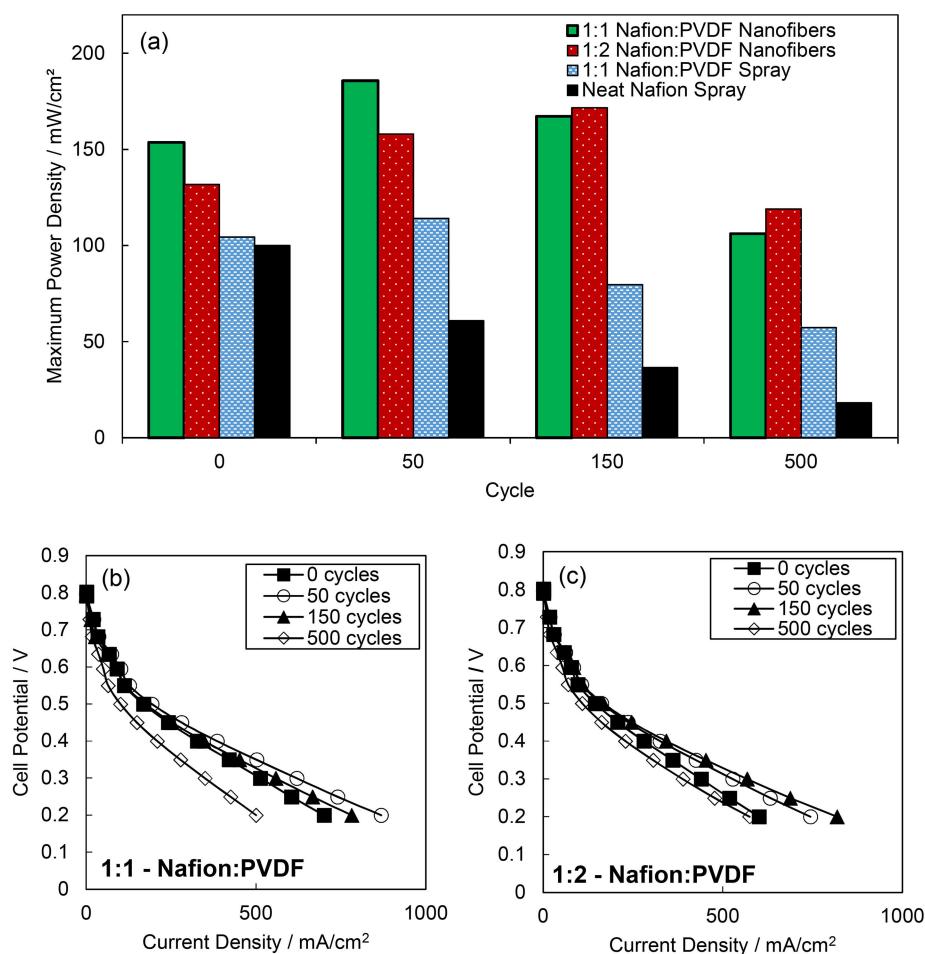
Sprayed and nanofiber cathode MEAs with a MOF-derived Fe–N–C PGM-free cathode catalyst (at 3.0 mg/cm<sup>2</sup>) were investigated in an H<sub>2</sub>/air fuel cell. The use of a Nafion:PVDF binder allowed for stable long-term (300 hour) power output for both nanofiber and sprayed cathode MEAs; this result is much different from that observed for a neat Nafion binder (sprayed cathode morphology) where there was a sharp decline in power. Thus, a particle/polymer nanofiber mat cathode with PGM-free catalyst and a 1:1 weight ratio Nafion:PVDF binder exhibited a stable power density of 80 mW/cm<sup>2</sup> at 0.50 V and a stable maximum power density of 154 mW/cm<sup>2</sup> at 0.30 V, 80 °C and 1 atm backpressure for 300 hours. The nanofiber MEA cathode also exhibited excellent resistance to the deleterious effects of carbon corrosion, with a maximum power density increase from 150 to 186 mW/cm<sup>2</sup> after 50 voltage cycles (from 1.0 to 1.5 V) followed by a slow but steady power loss to

106 mW/cm<sup>2</sup> after 500 cycles. The 1:1 weight ratio Nafion:PVDF binder produced more power after 300 hours of operation, but the power density decreased more rapidly during a carbon corrosion accelerated stress test, as compared to a nanofiber cathode with a binder of 1:2 Nafion:PVDF. The excellent performance of the nanofiber cathode was attributed to the combined effects of the somewhat hydrophobic Nafion:PVDF binder, which minimized catalyst degradation, and the nanofiber morphology which allows for facile oxygen access to catalyst sites and the efficient expulsion of water, where the latter allowed for reasonable power output after a carbon corrosion test.

## Experimental Section

Non-PGM catalyst was synthesized at Pajarito Powder, LLC, using a method developed by Mukerjee and Dodelet.<sup>[7,15]</sup> Specifically, zinc oxide (calcinated 400 °C), 2-methylimidazole, and ammonium sulfate were ball milled for one hour in the presence of isopropyl alcohol, water, and surfactant to form the metal organic framework (ZIF-8). The addition of (NH<sub>4</sub>)<sub>2</sub>SO<sub>4</sub> promotes the reaction between ZnO and 2-methylimidazole (the ligand which forms the ZIF-8 structure) via protonation of imidazolium groups. Further addition of iron sulfate and 1,10-phenanthroline monohydrate was followed by two hours of ball mixing. The resulting powder (FePhenMOF) was then pyrolyzed under flowing nitrogen at 1035 °C for 60 minutes, where the final temperature was attained using a ramping rate of 15 °C per minute. The pyrolyzed powder was ball milled, heat treated in ammonia at 950 °C for 30 minutes, and then allowed to cool down to room temperature before obtaining the final powder (FePhenMOF-ArNH<sub>3</sub>).

All anodes were prepared by spraying gas diffusion electrodes with an ink composed of 35 wt.% Nafion and 65 wt.% Johnson Matthey Pt/C powder (HiSpec4000) in a 2:1 (w/w) water:isopropanol



**Figure 4.** Results from the start/stop carbon-corrosion voltage cycling accelerated-stress test for MEAs with a nanofiber cathode (3.0 mg/cm<sup>2</sup> with 1:1 or 1:2 Nafion:PVDF binders) a sprayed cathode (3.0 mg/cm<sup>2</sup> with a 1:2 Nafion:PVDF binder), and a neat Nafion-sprayed cathode with 3.0 mg/cm<sup>2</sup> cathode loading. (a) Change in the maximum power density with voltage cycle number. (b) Fuel cell polarization curves during the stress test for the nanofiber cathode MEA with a 1:1 Nafion:PVDF binder. (c) Fuel cell polarization curves during stress test for the nanofiber cathode MEA with a 1:2 Nafion:PVDF binder. Voltage cycling was between 1.0 and 1.5 V in a triangular waveform at 500 mV/s. Fuel cell operating conditions: 80 °C, 100% relative humidity, 1 atm<sub>g</sub> backpressure, and 125/500 sccm H<sub>2</sub>/air feed-gas flow rates. All MEAs had a Nafion 211 membrane and a sprayed anode with Nafion binder and Johnson Matthey Pt/C HiSpec 4000 at 0.1 mg<sub>Pt</sub>/cm<sup>2</sup>.

mixture. For electrospun fiber cathodes, two inks were prepared with a catalyst:Nafion:PVDF wt.% composition of 70:15:15 and 70:10:20, where the solvent was a 7:3 (w/w) mixture of dimethylformamide (DMF) and acetone and the solvent content of the ink was 85 wt.%. Electrospinning inks were prepared by the following three-step procedure: (1) a dispersion of PGM-free catalyst powder in a mixed solvent of 7:3 (w/w) DMF:acetone was mixed by ultrasonic agitation for 30 minutes (Sonics & Materials Inc. VibraCell ultrasonicator), (2) a Nafion/solvent dispersion (20 wt.% 1100 EW Nafion resin, obtained by drying an Ion Power Liquion 115 solution, in 7:3 (w/w) DMF:acetone solvent) was added to the catalyst solution followed by an additional 30 minutes of sonication, and (3) a 10 wt.% PVDF solution was added to the ink mixture (Kynar HSV 900 PVDF from Arkema, Inc. in 7:3 (w/w) DMF:acetone) followed by 12 hours of mechanical stirring.

Two electrode inks for conventional sprayed cathodes were also prepared, with either 70:15:15 wt.% catalyst:Nafion:PVDF (same composition used in a nanofiber cathode) or 65:35 catalyst:Nafion in a 2:1 (w/w) water:isopropanol solvent. These inks were prepared in a similar way to the nanofiber inks, but the sprayed inks were much more dilute (97.5 wt.% solvent) to facilitate spraying. Conventional sprayed cathodes were made by airbrush spraying ink

directly onto a Sigracet 29 BC series carbon paper gas diffusion layer (GDL), where the catalyst loading was fixed at 3.0 mg/cm<sup>2</sup>.

The apparatus and general procedure for electrospinning cathode mats with PGM-free catalyst are similar to those reported previously for Pt/C catalyst powders.<sup>[8–10]</sup> Fiber mats were electrospun under controlled humidity conditions using a single needle syringe as the spinneret (22 gauge needle) and a rotating and laterally oscillating drum fiber collector. Electrospinning conditions for producing well-formed particle/polymer fibers with PGM-free catalyst and Nafion:PVDF binder were: 75% relative humidity air at 23 °C, a syringe pump flow rate of 0.2 mL/h, an applied voltage of 12 kV, and a spinneret-to-collector distance of 8 cm. Fibers were electrospun on aluminum foil. Sufficient ink was used to generate a fiber mat with a catalyst loading of 1.5 mg/cm<sup>2</sup>.

Electrospun nanofiber mats were cut into 5 cm<sup>2</sup> free-standing cathodes. Two electrospun fiber mats (each at 1.5 mg/cm<sup>2</sup>) were stacked and pressed together during MEA fabrication to achieve a catalyst loading of 3.0 mg/cm<sup>2</sup>. Fiber cathodes were then hot-pressed together with a Nafion 211 membrane, an anode (0.1 mg<sub>Pt</sub>/cm<sup>2</sup>), and two Sigracet 29 BC Series carbon paper GDLs at 140 °C at

4 MPa for 10 minutes. The same membrane and hot-pressing conditions were used for the sprayed cathode MEAs.

Fuel cell tests were performed using a Scribner Series 850e test station with mass flow, temperature, and backpressure control. The fuel cell test fixture housed a single MEA and contained a single serpentine flow channel for both the anode and cathode. Polarization curves in H<sub>2</sub>/air were collected at 80 °C, 100% relative humidity, 1 atm backpressure, and feed gas flow rates of 125 sccm for H<sub>2</sub> and 500 sccm for air. The durability of MEAs was evaluated in a sequence of two experiments: (1) measuring the H<sub>2</sub>/air fuel cell output current over a time of 300 hours for a constant voltage of 0.5 V and then immediately thereafter (2) performing a carbon corrosion accelerated stress test using the DOE's start-stop potential cycling protocol (triangular wave voltage cycles between 1.0 and 1.5 V vs. SHE at a scan rate 500 mV/s). During the carbon corrosion cathode cycling test, the fuel cell test fixture was supplied with 100 sccm H<sub>2</sub> at the anode and 100 sccm N<sub>2</sub> at the cathode (both feed gases were fully humidified at ambient pressure). During the carbon corrosion test, CO<sub>2</sub> in the air exhaust was monitored to gauge carbon loss. A non-dispersive infrared CO<sub>2</sub> detector (CO<sub>2</sub> Meter Inc. – Model No. CM-0152) in the air exhaust generated CO<sub>2</sub> (ppm) vs. time data, which was then integrated to yield the total carbon loss from the cathode.

## Acknowledgements

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## Conflict of Interest

The authors declare no conflict of interest.

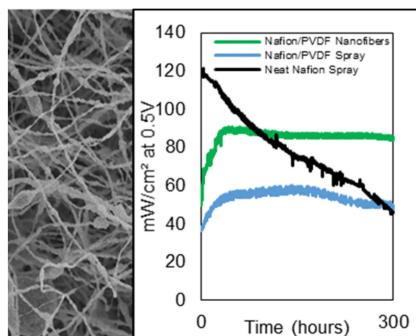
**Keywords:** energy Conversion · fuel Cells · nanofibers · pgm-free catalyst · polymers

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## COMMUNICATIONS

**Pt-free catalyst nanofibers:** Nanofibers with a Nafion/PVDF binder significantly improve the durability of proton-exchange membrane fuel cells with platinum-group-metal-free catalyst cathodes. This improvement is attributed to the increased hydrophobicity imparted by the PVDF and porosity of the nanofibers.



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