A series of electrospun nanofiber mat electrodes with two different commercial Pt/C catalysts and a binder of Nafion and poly(acrylic acid) were fabricated and evaluated. The electrodes were assembled into membrane-electrode-assembly (MEAs) using Nafion 211 as the membrane. Variations in catalyst type, nanofiber composition (the ratio of Pt/C to Nafion), and fiber diameter had little or no impact on hydrogen/air fuel cell power output. 25 cm² nanofiber and sprayed gas diffusion electrode MEAs were compared in terms of beginning of life (BoL) and end of life (EoL) performance after automotive-specific load cycling (Pt dissolution) and start-stop cycling (carbon corrosion) cathode durability protocols. Nanofiber electrode MEAs (0.10 mg/cm² Pt loading for the anode and cathode) were clearly superior to sprayed MEAs; they produced more power at BoL and maintained a higher percentage of their power after the carbon corrosion durability protocol, resulting in much higher EoL fuel cell performance. On the other hand, there was no effect of electrode morphology on MEA durability for the Pt dissolution test. The higher MEA power output after carbon corrosion with electrospun electrodes is attributed to better oxygen and water transport within the nanofiber electrode and a higher electrochemical surface area for the fiber cathode.

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The hydrogen/air proton-exchange membrane fuel cell is a promising candidate for emission-free automotive power plants due to its high power output, efficiency of energy conversion, and quick start-up. The successful integration of a sizable fleet of Electric Vehicles into the transportation sector would greatly diminish local air pollution and alleviate our dependency on depleting oil reserves. Presently, mass commercialization of fuel cell vehicles is challenging due in large part to issues related to the cost and durability of membrane-electrode-assemblies (MEAs).

A principal strategy to reduce the cost of MEAs is to minimize the amount of the platinum catalyst in the electrodes without sacrificing power generation. In this regard, recent R&D efforts have been directed at the investigation of platinum metal alloys, core-shell nanostructures, and the use of platinum-free metal-nitrogen-carbon catalysts. Although these studies have shown some promise in terms of catalytic activity and potential cost savings, they do not currently meet automotive power density and durability targets.

Carbon support corrosion in Pt/C catalysts during fuel cell start-up/shut-down is another ongoing issue that has drawn considerable research attention. In particular, when a hydrogen-air mixture is present in the anode during start-up, the cathode potential spikes as high as 1.5 V vs. SHE, resulting in severe carbon corrosion of the cathode catalyst layer. Researchers have worked to mitigate carbon corrosion at the materials level by investigating catalyst that can better withstand the harsh automotive operating environment. Current efforts are focused on metal oxides and thermally treated carbon supported catalysts.

Another potential strategy to improve the power density and durability of fuel cell electrodes is to alter the catalyst electrode morphology. Researchers have studied various alternatives to the standard catalyst-coated membrane (CCM) and catalyst-coated gas diffusion electrode (GDE) methods of preparing PEM fuel cell MEAs. These new approaches include electrosprayed layers of micron-size catalyst/binder droplets and oriented Pt-coated whisker electrodes. Another promising technique is the electrospinning of particle/polymer (catalyst/ionomer) mixtures into a non-woven nanofiber electrode catalyst mat. Zhang and Pintauro first demonstrated the utility of replacing a conventional MEA cathode with a nanofiber mat where the fibers were composed of Pt/C catalyst with a Nafion/poly(acrylic acid) binder. They found that an MEA with: (i) an electrospun cathode mat (where the average nanofiber diameter was 470 nm), (ii) a Nafion 212 membrane and (iii) a conventional decal anode performed extraordinarily well in a H₂/air fuel cell, producing more than 500 mW/cm² without backpressure at 0.6 V and 80°C with a cathode Pt loading of 0.1 mg/cm². More recently, Brodt et. al. have shown that MEAs with electropun cathodes containing Johnson Matthey Hispec 4000 Pt/Vulcan catalyst produced very high power (up to over 900 mW/cm²) at an ultra-low cathode platinum loading of 0.055 mgPt/cm² in an H₂/air fuel cell at 80°C and 2 atmospheres back pressure. The excellent performance of nanofiber fuel cell electrodes is attributed to facile oxygen and proton transport to catalytic sites and efficient product water removal, which is a direct consequence of the unique nanofiber electrode morphology, with significant inter-fiber and intra-fiber porosity and a well-mixed dispersion of catalyst powder and ionomer binder.

Herein, we report on new results with nanofiber electrodes that were electrosprun with commercially available platinum catalysts supported on either Vulcan carbon (Johnson Matthey catalyst) or high surface area carbon (Tanaka Kikinzoku Kogyo) where the anode and cathode Pt loadings were each fixed at 0.10 mg/cm². Experiments focused on: (i) determining the effects of catalyst type, nanofiber catalyst/binder composition, and nanofiber diameter on initial fuel cell power output and (ii) assessing nanofiber electrode durability, in terms of Pt dissolution and carbon corrosion of the catalyst support. For the durability tests, beginning of life and end of life performance of MEAs with nanofiber catalysts were compared with MEAs with Nissan Technical Center North America (NTCNA)-sprayed GDE cathodes and commercial GDE anodes.

**Experimental**

**Electrospinning electrodes.**—Electrospinning inks were prepared by mixing the following components in an alcohol/water solvent: (a) a commercial Pt/C catalyst powder, either Johnson Matthey Hispec 4000 (40% Pt on Vulcan carbon), henceforth referred to as JM-Pt(Vulcan), or Tanaka Kikinzoku Kogyo TEC10E50E (46.1% Pt on high surface area carbon), henceforth referred to as TKK-Pt(HSAC), (b) 1100 EW Nafion ion exchange resin (20% ionomer in...
lower aliphatic alcohols and water as received from Aldrich), and (c) poly(acrylic acid) (450 kDa molecular weight from Aldrich). Nafion forms a miscellar dispersion in alcohol/water mixtures and will not electrospin into well-formed fibers, unless a suitable carrier polymer is added to the electrospinning solution.16 In the present study, poly(acrylic acid) (abbreviated as PAA) was used as the carrier. An electrospinning ink was prepared by: (i) wetting 0.15 g catalyst with 0.55 g water, (ii) mixing the wet catalyst with 0.26 g Nafion stock solution and 0.45 g isopropanol, (iii) sonicating the catalyst/Nafion suspension for 90 minutes with intermittent mechanical stirring, (iv) adding 0.24 g of a 15 wt% poly(acrylic acid) solution in 2:1 wt ratio isopropanol/water, and (v) stirring the ink mechanically for approximately 48 hours. This ink recipe was used to fabricate dry electrospun mats with 63 wt% Pt/C, 22 wt% Nafion, and 15 wt% PAA. The amount of catalyst and stock Nafion solution was varied for other inks so the Pt/C:Nafion weight ratio of the resulting dry mat contained 55–72 wt% Pt/C and 13–30 wt% Nafion, where the PAA content was held constant at 15 wt%. An ink was drawn into a 3 mL syringe and electrospun using a 22-gauge stainless steel needle spinneter, where the needle tip was polarized to a potential of 10–12 kV relative to a grounded stainless steel rotating drum collector that was operated at a rotation speed of 100 rpm. The spinneret-to-collector distance was fixed at 10 cm and the flow rate of ink was held constant for all experiments at 1.0 mL/h. Nanofibers were collected on an aluminum foil that was attached to the cylindrical collector drum. The drum oscillated horizontally to improve the uniformity of deposited nanofibers. A schematic diagram of the electrospinning apparatus is shown in Figure 1. Electrospinning was performed at room temperature in a custom-built environmental chamber, where the relative humidity was maintained constant at 40%.

Membrane-electrode-assembly (MEA) preparation.— CCMs (Catalyst Coated Membranes) with nanofiber electrodes were fabricated at Vanderbilt University by hot pressing 5 or 25 cm² electrospun electrode mats (anodes and cathodes of identical fiber composition) onto the opposing surfaces of a Nafion 211 membrane (henceforth identified as NR211) at 140°C and 4 MPa for 1 minute, after a 10-minute pre-heating period at 140°C with no applied pressure. The Pt loading of a nanofiber mat was calculated from the total electrode weight and the weight-fraction of Pt/C catalyst used in the electrospinning ink. Carbon paper gas diffusion layers (GDLs) (Sigracet 25 BCH GDL) were physically pressed onto a CCM’s anode and cathode while in the fuel cell test fixture to form an MEA.

Painted gas diffusion electrodes (GDEs) were also fabricated at Vanderbilt University with and without poly(acrylic acid). Pt/C powder was added to the Nafion dispersion (with and without PAA) and stirred mechanically for 48 hours. The inks were painted in multiple layers directly onto a carbon paper gas diffusion layer (Sigracet GDL 25 BCH) and dried at 70°C for 30 minutes after each painted layer. Painted GDEs with 15 wt% PAA were prepared with 72 wt% TPK-Pt(HSAC) and 13 wt% Nafion (the same composition as some electrospun fiber electrodes). GDEs without PAA were prepared with a composition of 67 wt% TPK-Pt(HSAC) and 33 wt% Nafion. All painted GDEs (5 cm² in geometric area) were hot pressed onto NR211 membranes at 140°C and 4 MPa for 1 minute after a 10 minute pre-heating step at 140°C with no applied pressure.

Sprayed GDEs were fabricated at Nissan Technical Center North America (NTCNA). These catalyst inks were made by mixing water, n-propanol, Nafion ionomer dispersion (Ion Power DE2020), and Pt/C powder, either TPK-Pt(HSAC) or JM-Pt(Vulcan) (the same catalysts as the Vanderbilt electrodes). The mass-based ionomer/carbon (I/C) ratio in the ink was kept constant at 0.9. The electrocatalyst cathode layers were formed on gas diffusion layers (GDLs) with microporous layers (SGL Carbon) using an automated robotic spray system. MEAs (25 cm²) were prepared by hot pressing sprayed cathode GDEs (0.1 mg/cm² Pt loading) and commercial Johnson Matthey anode GDEs (with JM-Pt(Vulcan) catalyst at a Pt loading of 0.4 mg/cm²) onto the opposing surfaces of Nafion NR211 membranes. The hot-press conditions were 2 MPa pressure for 10 minutes at 130°C.

Fuel cell tests.— Fuel cell polarization curves were collected at Vanderbilt University and NTCNA. At Vanderbilt, fuel cell tests were performed on 5 cm² MEAs, using a Scriber Series 850 e test station with mass flow, temperature, and manual backpressure control. The fuel cell test fixture accommodated a single MEA and contained single anode and cathode serpentine flow channels. Experiments were performed at 80°C, where the H₂ flow rate was 125 sccm and the airflow rate was 500 sccm. Prior to collecting polarization data, the MEAs were pre-conditioned by operating at 80°C and 1 A/cm² for 8 hours. Polarization curves were generated by measuring the current at a given voltage after waiting 60 seconds for system stabilization. The polarization curves were measured in the anodic (positive voltage) direction.

At NTCNA, fuel cell polarization curves were obtained with 25 cm² MEAs at 100% and 40% relative humidities at 80°C, using hydrogen and air at a gauge pressure of 1 bar. The current was scanned from low current to high current and the system was given 3 minutes to stabilize at each current density before a voltage reading was recorded. MEAs were pre-conditioned by operating at 1 A/cm² at 80°C for 8 hrs. High frequency resistance (HFR) data were recorded in-situ. Performance evaluations were carried out using operating conditions designed to produce meaningful data for automotive applications. The constant gas flow rates used for these evaluations were: 8 normal liters per minute (NLPM) at the cathode and 4 NLPM at the anode, with no/minimal pressure drop across the flow field. Cathode catalyst mass activity data were collected using a current-controlled anodic scan (high current to low current) at 80°C with fully humidified O₂ and H₂ gas feeds and no back pressure, where the system was allowed to stabilize for three minutes at each data point. Mass activities were determined from a plot of IR-free voltage versus the H₂ crossover corrected current density.

Electrochemical surface area (ECA).— In-situ cyclic voltammetry (CV) measurements were performed at NTCNA on 25 cm² MEAs with a sweep rate of 20 mV/s, where a H₂-purged anode served as both the counter and reference electrodes and N₂ was fed to the working cathode. The fuel cell test fixture was operated at 30°C with gas feed streams at a dew point of 30°C (fully humidified). The CV was carried out between +0.02 V and +0.9 V vs. SHE and the electrochemically active surface area was determined from the integrated area above the H₂ gas adsorption portion of a voltammogram (corresponding to a voltage range of approximately +0.1 to +0.4 V), where the charge required to reduce one monolayer of hydrogen atoms on Pt was assumed to be 210 μC/cm².

Durability tests.— MEAs were tested under the Fuel Cell Commercialization Conference of Japan’s (FCCJ) standard start-stop potential cycling and load cycling protocols.19 The goal of these accelerated degradation tests was to generate data for benchmarking and to gain a better understanding of the fundamental mechanisms related to cathode performance loss during fuel cell operation.

Carbon corrosion (start-stop cycling).—This accelerated durability test simulates start-up and shut-down of a stack without the application of any operational controls that may mitigate fuel cell performance losses. During start-up, if the stack has been shut down for some time,
A detailed description of this monitoring system has been reported on CO2 Meter Inc. (Model No. CM-0052-WP), provided an additional method for measuring carbon corrosion during the accelerated potential cycling tests. A desiccant moisture trap upstream to the detector inlet removed moisture from the CO2-containing stream.

The anode and cathode are filled with ambient air and are pinned to the air-air potential; introducing hydrogen gas causes a hydrogen-air front to move through the anode chamber, with a large shift in the cell potential (to a value as high as 1.5 V). The start-stop durability protocol simulates this event many times by cycling from 1.0 V to 1.5 V at a scan rate of 500 mV/s (see Figure 2). In the present study, 1,000 voltage cycles were performed on a single MEA, where the fuel cell was supplied with H2 at the anode and N2 at the cathode (both at 0.5 L/min. and 80°C, with fully humidified feed gases), and the cell potential was cycled using a potentiostat. ECA measurements were made intermittently during a corrosion test and beginning of life (BoL) and end of life (EoL) i-V polarization plots were generated. CO2 monitoring of the cathode air exhaust, using a non-dispersive infrared detector from CO2 Meter Inc. (Model No. CM-0052-WP), provided an additional experimental tool for measuring carbon corrosion during the accelerated potential cycling tests. A desiccant moisture trap upstream to the detector inlet removed moisture from the CO2-containing stream. A detailed description of this monitoring system has been reported elsewhere.

**Pt-Corrosion load cycling**.— This accelerated durability test simulates the high load and no load events that typically occur when a fuel cell vehicle is driven at different speeds. In the present study, the MEA was cycled 10,000 times in steps between 0.60 V and 0.95 V to simulate peak load and OCV/idle (see Figure 3). This square wave voltage regimen represents the largest oscillations that may be encountered during normal operation of a fuel cell vehicle stack. Between 0.6 V and 0.95 V, carbon corrosion is insignificant and the major causes for power loss are Pt dissolution, agglomeration, and migration on the support and through the membrane. The temperature, gas flow rate, and humidity operating conditions were the same as in the carbon corrosion tests. Pt degradation was monitored by periodic measurement of the cathode catalyst ECA and by comparing BoL and EoL i-V hydrogen/air fuel cell polarization curves.

**Results and Discussion**

**Effect of catalyst type**.— JM-Pt(Vulcan) and TKK-Pt(HSAC) catalysts were compared to one another in separate nanofiber anode/cathode MEAs, where each electrode had a Pt loading of 0.10 mg/cm² and the Pt/C:Nafion:PAA wt ratio composition of the fibers was held constant at 63:22:15. As shown in Figure 4, the polarization curves for the two catalysts were essentially the same. The TKK-Pt(HSAC) showed a modest advantage, but the difference was 10% at most, so there was no clear superiority of one catalyst over the other. The Johnson-Matthey MEA results are similar to those previously published by the Pintauro group. Because of the similarity in catalyst performance in Figure 4, JM-Pt(Vulcan) and TKK-Pt(HSAC) were used interchangeably in follow-on electrospinning and MEA experiments.

**Effect of nanofiber composition (catalyst to ionomer ratio).**— The relative amount of catalyst to proton-conducting Nafion ionomer in electrospun nanofiber mats was varied, while the PAA carrier polymer was maintained constant at 15 wt% and the anode and cathode Pt loadings were fixed at 0.10 mg/cm² each. Figure 5 shows the fuel cell performance of TKK-Pt(HSAC) nanofibers for three different catalyst:Nafion:PAA wt ratios: 72:13:15, 63:22:15, and 55:30:15. The fuel cell polarization plots show only marginal differences for the three different MEAs. Unlike a conventional non-structured fuel cell electrode, where binder content has a significant effect on fuel cell performance, the nanofiber cathode power output exhibited only modest variations with changes in Nafion content. We attribute this effect to the robust nanofiber structure, where the morphology remains essentially unaffected by changes in binder content (this was confirmed visually, from SEM images of nanofiber mats). Top-down SEM images of electrospun nanofiber mats (taken before hot pressing) with the least and greatest amount of Nafion are shown in Figure 5b and 5c, respectively.

![Figure 2](image2.png)  
**Figure 2.** Start-stop cycling protocol for accelerated carbon corrosion durability testing.

![Figure 3](image3.png)  
**Figure 3.** Load cycling protocol for accelerated Pt dissolution durability testing.

![Figure 4](image4.png)  
**Figure 4.** Polarization curves for 5 cm² MEAs with a Nafion 211 membrane and electrospun nanofiber electrodes with cathode and anode Pt loading of 0.10 ± 0.005 mg/cm². Fuel cell operating conditions: 80°C, 100% RH feed gases at ambient pressure, 125 sccm H2 and 500 sccm air. (□) TKK-Pt(HSAC), and (●) JM-Pt(Vulcan).
Effect of PAA.—In order to quantify the influence of PAA polymer on cathode performance, two painted MEAs were prepared: one MEA had anode and cathode GDEs with a neat Nafion binder (67 wt% TKK-Pt(HSAC) and 33% Nafion) while the other MEA had GDEs with the same Nafion/PAA binder as a typical nanofiber electrode mat (72 wt% TKK-Pt(HSAC), 13 wt% Nafion, and 15 wt% PAA). The resulting polarization curves, shown in Figure 6, indicate that PAA adversely affects fuel cell performance. In a previous study on electrospinning Nafion polymer nanofibers for membrane applications (where the fibers contained PAA but no catalyst powder), it was found that poly(acrylic acid) lowers the proton conductivity of perfluorosulfonic acid polymer.\textsuperscript{22} The poor performance of the painted MEA with Nafion/PAA binder in Figure 6 is attributed to a similar drop in the ion conductivity of the Nafion.

The results in Figure 6 suggest that more power could be generated in a nanofiber electrode MEA if PAA were removed from the Nafion binder after mat preparation. To further investigate this hypothesis, two methods for removing PAA from nanofiber CCMs were evaluated: (1) boiling a CCM for one hour in 1 M H\textsubscript{2}SO\textsubscript{4} followed by boiling in DI water for one hour and (2) soaking a CCM in 3\% H\textsubscript{2}O\textsubscript{2} for one hour at room temperature and then boiling for one hour in DI water. After soaking, GDLs were attached to the CCMs and the resulting MEAs were tested in a fuel cell. After the fuel cell tests, the GDLs were removed and the nanofiber cathodes were imaged by SEM. The polarization curve and cathode SEM after the peroxide wash procedure (the harsher of the two treatments) are shown in Figure 7a and 7b, respectively. As can be seen, there was no change in MEA performance, as gauged by i-V polarization plots. Additionally, there were no visual differences in the cathode fiber surface morphology, as compared to an untreated cathode. A similar result was found when CCMs were boiled in acid and water. Although this study was unsuccessful in removing PAA, a number of important findings did emerge from the experiments: (a) PAA has a detrimental effect on the performance of painted electrode MEAs in a hydrogen/air fuel cell, (b) at the present time, PAA cannot be removed from the Nafion binder in nanofiber fuel cell electrode mats, (c) the catalyst/Nafion/PAA fibers are chemically and physically robust, and (d) in the future, it might be possible to improve the performance of nanofiber cathodes if a carrier polymer other than PAA were found for Nafion/catalyst electrospinning (such experiments were not part of the present study).

Effect of nanofiber diameter on fuel cell power output.—In these experiments, the average fiber diameter of an electrospun mat was controlled by altering the solvent content in the electrospinning ink recipe. The results of these experiments, in terms of the ink composition, average fiber diameter of an electrode mat, and the performance of the electrodes in a fuel cell MEA are summarized in Table I. TKK-Pt(HSAC) catalyst powder was used in all of the inks and the diameter of electrospun nanofibers was effectively varied from 250 nm to 520 nm. Figure 8 shows two SEM images of an electrode mat surface; Figure 8a is a mat with an average fiber diameter of 250 nm, whereas the average fiber diameter in Figure 8b is 475 nm (for better imaging, the mats were lightly pressed at room temperature onto conductive...
Results from the PAA extraction experiments. (a) Fuel cell polarization curves for 5 cm² MEAs with TKK-Pt(HSAC) catalyst with cathode and anode Pt loadings of 0.10 ± 0.005 mg/cm² and an NR211 membrane operated at 80 °C with fully humidified H₂ (125 sccm) and air (500 sccm) at ambient pressure with or without CCM soaking in 3 wt% hydrogen peroxide and boiling water. (b) Top-down SEM image of an electrospun cathode after soaking in hydrogen peroxide and boiling in water.

Table I. Average Fiber Diameter and MEA Power at 0.65 V for Various Electrospinning Inks (all fibers had a catalyst:Nafion:PAA wt ratio of 63:22:15 and utilized TKK-Pt(HSAC) catalyst).

| Solvents added to Electrospinning Ink | Avg. Diametera (nm) | Power Densitya at 0.65 V (mW/cm²) |
|--------------------------------------|----------------------|-----------------------------------|
| 0.85 g n-propanol, 0.85 g water      | 250                  | 444                               |
| 0.85 g isopropanol, 0.85 g water     | 330                  | 462                               |
| 0.60 g isopropanol, 0.70 g water     | 380                  | 433                               |
| 0.40 g ethanol, 0.50 g water         | 475                  | 475                               |
| 0.30 g ethanol, 0.40 g water         | 485                  | 465                               |
| 0.40 g methanol, 0.50 g water        | 520                  | 489                               |

aThis is the amount and composition of solvent added to an ink after mixing catalyst, Nafion stock solution, and PAA solution, as described in the Experimental Section.

bFiber electrospinning conditions: 10–12 kV for inks containing n-propanol/water and isopropanol/water and 8–10 kV for inks with ethanol/water and methanol/water, ambient temperature air at 40% RH, 10 cm spinneret to collector, 1.0 mL/hr flow rate.

cFuel cell operating conditions: 80 °C, 100% relative humidity feed gases at ambient pressure, 125 sccm H₂ flow rate, and 500 sccm air flow rate. Pt loading was 0.10 mgPt/cm² for cathode and anode.

SEM tape and sputter coated with a thin layer of gold). For both mats, the general shape and surface roughness of the fibers are the same. The fuel cell performance of the different diameter fiber mat MEAs was essentially the same, as quantified by indistinguishable i-V plots, where the measured power density at 0.65 V was 460 mW/cm² ± 7%. This result highlights the superior properties of the nanofiber electrode morphology, where there is sufficient intra-fiber porosity for O₂/Pt-site contact to be independent of fiber diameter and where the binder coating thickness on catalyst particles (the distribution of catalyst and binder in a nanofiber) is independent of fiber size.

Initial FC performance of nanofiber MEAs vs. NTCNA-sprayed MEAs.— MEA tests were performed on 25 cm² MEAs at NTCNA using nanofiber MEAs that were fabricated at Vanderbilt University and sprayed electrode MEAs that were made at NTCNA. All MEAs were prepared with JM-Pt(Vulcan) catalyst or TKK-Pt(HSAC) catalyst cathodes and anodes, where the Pt loading of each electrode was 0.10 ± 0.005 mg/cm². The nanofiber MEAs had a fixed catalyst:Nafion:PAA wt ratio of 72:13:15 and a fixed average fiber diameter of 400 nm (these fiber electrodes produced high power in Vanderbilt University MEA tests). The sprayed cathodes had a catalyst:Nafion wt ratio composition of 67:33.

Figure 9 shows the effect of electrode structure (nanofibers vs. sprayed) on initial fuel cell performance. At 100% RH conditions, the nanofiber MEA produced more power over essentially the entire voltage range, as compared to the spray-coated MEA (Figure 9a). The difference in power densities can be attributed to an increase in the number of active catalyst sites and faster electrode kinetics as shown in Table II, where the nanofiber cathode ECA is 28% higher than the measured values for an MEA with spray-coated Johnson-Matthey catalyst, and the catalytic mass activity of the electrospun fiber cathode is 84% higher than the mass activity of the sprayed MEA. It should be noted that the catalytic activities for the sprayed MEA in Table II, where the nanofiber cathode ECA is 28% higher than the measured values for an MEA with spray-coated Johnson-Matthey catalyst, and the catalytic mass activity of the electrospun fiber cathode is 84% higher than the mass activity of the sprayed MEA. It should be noted that the catalytic activities for the sprayed MEA in Table II, which were measured at ambient pressure, are reasonable but lower than those reported at an elevated oxygen backpressure.23,24

The improved performance of the nanofiber cathode is associated with an improvement in the accessibility of air/oxygen to Pt catalyst sites due to a thinner binder (Nafion + PAA) layer covering the catalyst particles and thus, better reactant mass transfer in the electrospun structure. The high sheer stresses at the spinneret tip during nanofiber electrospinning and the elongation of the fiber as it travels from the spinneret to the collector surface during the electrospinning process thoroughly mixes binder and catalyst on a sub-micron scale and then causes a thinning of the binder coating on catalyst particles. Thus, there is a uniform distribution of binder and catalyst in the nanofibers with little or no catalyst particle agglomeration. There also appears to be better utilization of the catalyst surface area, as the ECA is higher in the electrospun layer, which is associated with more effective electron and/or proton transport to surface Pt sites.

Under low RH conditions, the spray-coated MEA showed significantly better performance than the nanofiber MEA, as shown in Figure 9b. This finding is attributed to nanofiber dehydration at the low RH and high feed gas flow rates used in the experiments (8 NLPM at 207.241.231.81 address. Redistribution subject to ECS terms of use (see ecsdl.org/site/terms_use) unless CC License in place (see abstract).
It is obvious from the results in Figure 9 that the very high gas flow through the entire electrode. The high HFR values support this explanation and are indicative of membrane and catalyst binder drying. The cathode and 4 NLPM at the anode). There appears to be rapid water expulsion from the electrospun cathode due to the combined effects of a small average fiber diameter and significant interfiber porosity associated with a loss in ECA and a substantial thinning/collapse of the cathode layer, causing severe oxygen mass transport and water flooding issues. The cumulative (total) carbon loss for the two MEAs was essentially the same, as shown in Figure 11b (17% for the spray-coated MEA and 18% for the nanofiber electrode MEA), suggesting that the mechanism for carbon corrosion is the same for the two electrode morphologies. Additionally, both MEAs underwent a similar BoL to EoL loss in ECA of ~40%, ending at 29 m²/gPt for the sprayed cathode and 40 m²/gPt for the nanofiber structure. The electrospun electrode started with a higher ECA and maintained its area advantage over the course of the carbon corrosion test.

Start-stop cycling (cathode carbon corrosion test).—It is known that an accelerated start-stop cycling test for carbon corrosion has a much more severe impact on fuel cell power densities than Pt dissolution load cycling. End-of-life and beginning-of-life polarization curves from carbon corrosion tests with JM-Pt(Vulcan) catalyst are shown in Figures 10a and 10b for feed gas relative humidities of 100% and 40%, respectively. The spray-coated MEA showed severe performance losses due to carbon corrosion, significantly more than the nanofiber electrode. It should be noted, in particular, that the EoL performance for the nanofiber electrode MEA was close to the BoL performance of the conventional spray-coated MEA.

The amount of CO₂ detected as a function of time in the air exhaust during the carbon corrosion tests with sprayed and electrospun electrode MEAs is shown in Figures 11a and 11b. For both electrode morphologies, CO₂ generation increased with the number of voltage cycles, illustrating the aggressive nature of this particular accelerated stress test (repeated potential cycling has been found to be more aggressive than fixed potential hold durability tests).

The cumulative (total) carbon loss for the two MEAs was essentially the same, as shown in Figure 11b (17% for the spray-coated MEA and 18% for the nanofiber electrode MEA), suggesting that the mechanism for carbon corrosion is the same for the two electrode morphologies. Additionally, both MEAs underwent a similar BoL to EoL loss in ECA of ~40%, ending at 29 m²/gPt for the sprayed cathode and 40 m²/gPt for the nanofiber structure. The electrospun electrode started with a higher ECA and maintained its area advantage over the course of the carbon corrosion test.

The superior EoL performance of the nanofiber MEA at full humidity is attributed to the combined effects of a higher initial ECA, the retention of the nanofiber structure at EoL, and the inter and intra fiber porosity of the nanofiber cathode mat which allows for the rapid expulsion of product water, thus preventing flooding, even when the carbon support has been oxidized and is more hydrophobic. The drop in performance of the spray-coated MEA, on the other hand, is associated with a loss in ECA and a substantial thinning/collapse of the cathode layer, causing severe oxygen mass transport and water flooding issues. Performance losses for either MEA at 100% RH are not due to an increase in ohmic resistance, as the HFR remained unchanged before vs. after the corrosion test for both the electrospun and sprayed electrode MEAs.

**Table III. ECA Loss and EoL/BoL Power Output after 10,000 Load Cycles (Pt Dissolution Test) for TKK-Pt(HSAC) Catalyst.**

| Electrode Type | ECA Loss (%) | Power at 0.65 V EoL/BoL (100% RH) | Power at 0.65 V EoL/BoL (40% RH) |
|----------------|--------------|----------------------------------|----------------------------------|
| Sprayed        | 42           | 0.95                             | 0.94                             |
| Spray          | 40           | 0.91                             | 0.92                             |

**Figure 9. Effect of electrode morphology on MEA performance with JM-Pt(Vulcan) catalyst using a nanofiber electrode MEA and NTCNA-sprayed MEA. (a) Fuel cell performance with 100% RH feed gases and (b) fuel cell performance with 40% RH feed gases. Data were recorded at a back pressure of 1 bar with 8 NLPM air and 4 NLPM H₂ at 80 °C with a NR211 membrane.**

The effect of electrode morphology on durability under automotive-specific start-stop voltage cycling tests, there was no attempt to find the feed gas flow rate conditions that minimized fiber dehydration.

Effect of load cycling on i-V performance (Pt dissolution test).—The Pt active area/ECA can drop significantly under the load cycle protocol shown in Figure 3 due to Pt dissolution/redistribution/agglomeration, but the effect of these cathode changes on i-V performance is not particularly significant. Nonetheless, to be thorough, load cycling durability tests were performed on MEAs with electrospun nanofiber or NTCNA-sprayed electrodes. Both MEAs used TKK-Pt(HSAC) catalyst for the cathode. As shown in Table III, both MEAs showed a high cathode ECA loss (40–50% after 10,000 cycles), but the resulting power loss was minimal (a 5–10% loss at 0.65 V). These results indicate that the nanofiber electrode architecture does not significantly change the way the fuel cell cathode degrades during load cycling. Thus, it can be concluded that there is no effect of electrode morphology on MEA durability for the accelerated Pt dissolution test.

The Pt dissolution/redistribution/agglomeration test).—It is known that an accelerated start-stop cycling test for carbon corrosion has a much more severe impact on fuel cell power densities than Pt dissolution load cycling. End-of-life and beginning-of-life polarization curves from carbon corrosion tests with JM-Pt(Vulcan) catalyst are shown in Figures 10a and 10b for feed gas relative humidities of 100% and 40%, respectively. The spray-coated MEA showed severe performance losses due to carbon corrosion, significantly more than the nanofiber electrode. It should be noted, in particular, that the EoL performance for the nanofiber electrode MEA was close to the BoL performance of the conventional spray-coated MEA.

The amount of CO₂ detected as a function of time in the air exhaust during the carbon corrosion tests with sprayed and electrospun electrode MEAs is shown in Figures 11a and 11b. For both electrode morphologies, CO₂ generation increased with the number of voltage cycles, illustrating the aggressive nature of this particular accelerated stress test (repeated potential cycling has been found to be more aggressive than fixed potential hold durability tests).

The cumulative (total) carbon loss for the two MEAs was essentially the same, as shown in Figure 11b (17% for the spray-coated MEA and 18% for the nanofiber electrode MEA), suggesting that the mechanism for carbon corrosion is the same for the two electrode morphologies. Additionally, both MEAs underwent a similar BoL to EoL loss in ECA of ~40%, ending at 29 m²/gPt for the sprayed cathode and 40 m²/gPt for the nanofiber structure. The electrospun electrode started with a higher ECA and maintained its area advantage over the course of the carbon corrosion test.

The superior EoL performance of the nanofiber MEA at full humidity is attributed to the combined effects of a higher initial ECA, the retention of the nanofiber structure at EoL, and the inter and intra fiber porosity of the nanofiber cathode mat which allows for the rapid expulsion of product water, thus preventing flooding, even when the carbon support has been oxidized and is more hydrophobic. The drop in performance of the spray-coated MEA, on the other hand, is associated with a loss in ECA and a substantial thinning/collapse of the cathode layer, causing severe oxygen mass transport and water flooding issues. Performance losses for either MEA at 100% RH are not due to an increase in ohmic resistance, as the HFR remained unchanged before vs. after the corrosion test for both the electrospun and sprayed electrode MEAs.

**Table II. Electrochemical Surface Area, Mass Activity, and Specific Current Density for MEAs with Electrospun or Sprayed Electrodes and JM-Pt(Vulcan) Catalyst Cathodes.**

| Electrode Type | ECA (m²/gPt) | Mass Activity* (mA/mgPt) | Specific Current Density (μA/cm²Pt) |
|----------------|--------------|--------------------------|-----------------------------------|
| Electrospun    | 64           | 81                       | 127                               |
| Sprayed        | 50           | 44                       | 89                                |

*measurements taken at 0.90 V in O₂ at ambient pressure and 100% RH.
Figure 10. Carbon corrosion durability test results, where beginning-of-life (BoL) and end-of-life (EoL) MEA polarization plots are compared for electrospun nanofiber and sprayed electrode MEAs at: (a) 100% RH feed gases and (b) 40% RH feed gases. All data was recorded at a back pressure of 1 bar and 80°C with a NR211 membrane, JM-Pt(Vulcan) catalyst was used for all anodes and cathodes. The hydrogen and air flow rates are 4 NLPM and 8 NLPM, respectively.

The performance of the nanofiber MEA is even more impressive after voltage cycling when the power output was measured at 40% RH feed gas conditions. Here, the performance of the electrospun MEA actually improved after the carbon corrosion test. Its EoL performance was significantly better than its BoL performance, even though there was an 18% loss in carbon mass (as measured by the CO2 sensor). After voltage cycling (and carbon support oxidation), the nanofibers were more hydrophilic and less prone to drying during fuel cell operation at low RH with the very high feed gas flow rates that were used during the accelerated tests. As expected, the spray-coated MEA showed a similar drop in EoL performance as was observed in the 100% RH results in Figure 10a. Better catalyst/binder hydration with the nanofiber electrode after carbon corrosion is supported by the observed decrease in HFR at EoL (there was no change in HFR for the sprayed MEA). It should be noted that the unusual nanofiber corrosion test results at low RH were reproducible, as confirmed by repeated tests with identical MEAs.

Durability experiments were also carried with TKK-Pt(HSAC) nanofiber and sprayed electrode MEAs at 0.10 mgPt/cm². The EoL results were qualitatively similar to those found with JM-Pt(Vulcan) catalyst for the electrospun MEAs at both 100% and 40% RH (e.g., the EoL power output was greater than that at BoL when the feed gas RH was 40%), but the sprayed TKK-Pt(HSAC) MEA exhibited a more dramatic loss in EoL power due to more severe water flooding, as compared to the test with JM-Pt(Vulcan) catalyst. A summary of BoL and EoL MEA performance at 100% and 40% RH is presented in Table IV for sprayed and electrospun electrodes JM and TKK catalyst MEAs.

Table IV. EoL/BoL Power Output after 1,000 Start-Stop Cycles (Carbon Corrosion Test).

| Humidity | Catalyst | Electrode Structure | Power at 0.65 V EoL/BoL | Max Power EoL/BoL |
|----------|----------|---------------------|------------------------|------------------|
| 100%     | JM-Pt(Vulcan) | Spun                | 0.53                   | 0.85             |
|          | JM-Pt(Vulcan) | Spray               | 0.28                   | 0.39             |
|          | TKK-Pt(HSAC) | Spun                | 0.58                   | 0.83             |
|          | TKK-Pt(HSAC) | Spray               | 0.29                   | 0.18             |
| 40%      | JM-Pt(Vulcan) | Spun                | 1.71                   | 1.54             |
|          | JM-Pt(Vulcan) | Spray               | 0.51                   | 0.62             |
|          | TKK-Pt(HSAC) | Spun                | 3.14                   | 2.12             |
|          | TKK-Pt(HSAC) | Spray               | 0.27                   | 0.19             |

Conclusions

Experimental results have been presented which show that electrospinning is an effective technique for fabricating robust and high performance nanofiber fuel cell electrodes. TKK TEC10E50E catalyst (Pt on HSAC) and JM catalyst (Pt on Vulcan carbon) performed equally well in nanofiber electrode MEAs. The performance of electrospun nanofiber MEAs with TKK-Pt(HSAC) was insensitive to changes in...
the fiber ionomer content (Nafion 13–30 wt%). Fuel cell performance with TKK-Pt(HSAC) did not change significantly with average fiber diameter, in the range of 250–520 nm. Therefore, precise control of nanofiber electrode composition and fiber diameter is not required for optimum fuel cell power output, which should ease scale up and manufacturing.

Nanofiber electrode MEAs (with anode and cathode loadings of 0.1 mgPt/cm² each) exhibited better performance than NTCNA-sprayed MEAs under 100% RH feed gas conditions. It is believed that the nanofiber structure provides more Pt catalyst active sites and these sites are more accessible to oxygen than traditional spray-coated electrodes, due to a thinner Nafion-PAA binder layer on the Pt catalyst particles. At a very high gas feed flow rate and a low RH feed gas condition (40% RH), the electrosprun MEA showed significantly higher HFR and poor i-V performance, due to fiber dehydration. Load cycling durability tests on both types of MEAs showed that the electrode structure does not have any significant impact on Pt dissolution durability. On the other hand, the nanofiber electrodes showed significantly better durability as compared to a spray-coated MEA in an automotive start-stop potential cycling test for carbon corrosion. Both sprayed and nanofiber MEAs had comparable CO₂ generation rates and overall carbon loss (17–18%), but the spray-coated MEA exhibited a more significant performance decline. For 100% RH feed gases, the end-of-life (EoL) i-V performance of an electrosprun electrode MEA was essentially the same as the beginning-of-life performance of the spray-coated MEA. This result was attributed to the absence of water flooding in the nanofiber electrodes after the carbon support was oxidized and became more hydrophilic (the morphology of a nanofiber mat promotes water removal). The superior electrode characteristics of the nanofiber structure was even more apparent at 40% RH test conditions, where the EoL performance improved and was significantly better than the BoL performance after the harsh start-stop potential cycling test even though the MEA had lost 18% of its carbon mass. This results is associated with a more optimal water content/hydration in the nanofiber electrode mat due to the increased hydrophilic/water retention of the carbon support after start-stop potential cycling. Thus, nanofiber electrode MEAs showed both better initial power output and a less severe performance drop after start-stop durability cycling than sprayed electrode MEAs.

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