Power Output and Durability of Electrosprun Fuel Cell Fiber Cathodes with PVDF and Nafion/PVDF Binders
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Membrane-electrode-assemblies (MEAs) with electrosprun nanofiber mat electrodes (0.10 mg/cm² Pt loading) and a Nafion 211 membrane were prepared and tested in a H₂/air fuel cell at 100% and 40% relative humidity. The cathode binder was either neat poly(vinylidene fluoride) (PVDF) or a Nafion/PVDF blend (20 to 80 wt% Nafion) and the anode binder was Nafion with poly(acrylic acid). Polarization curves were recorded at 80°C and ambient pressure before, intermittently, and after a carbon corrosion voltage cycling experiment. The Nafion/PVDF cathode MEA with the smallest amount of PVDF (80/20 Nafion/PVDF weight ratio) produced the highest maximum power at beginning-of-life (BoL), 545 mW/cm² at 100% RH, which was 35% greater than that for a conventional MEA with a neat Nafion binder. Carbon corrosion scaled inversely with cathode PVDF content, with a 33/67 Nafion/PVDF cathode binder MEA producing the highest end-of-life (EoL) power (330 mW/cm²). MEAs with < 50 wt% PVDF in the cathode binder exhibited a power density decline during carbon corrosion, whereas the power increased during/after carbon corrosion for nanofiber cathodes with binders containing > 50 wt% PVDF due to favorable increases in the hydrophilicity of the carbon support and Pt mass activity, coupled with a lower carbon loss.

The limited wettability of the catalyst carbon surface is critically important for increasing its corrosion resistance in an MEA, since water is directly involved in the electrochemical oxidation of the carbon support material of a fuel cell cathode (via Equation 1). It is expected that the introduction of a hydrophobic polymer, such as poly(vinylidene fluoride) (henceforth abbreviated as PVDF) into the cathode catalyst binder will slow carbon corrosion rates.

C + 2H₂O → CO₂ + 4H⁺ + 4e⁻ [1]

The use of a PVDF electrode binder, however, is challenging because it does not conduct protons and its oxygen permeability is low. Nevertheless, PVDF has been employed with the cathode binder in PBI-based hydrogen/air fuel cell electrodes. The limited power and carbon corrosion durability of nanofiber MEAs with a cathode binder of neat poly(vinylidene fluoride) (PVDF) or various Nafion/PVDF blends, where the binder composition effects the concentration of water at the surface of Pt/C particles. Methods for electrosprining high Pt/C content nanofibers with these new binders were identified and MEAs were fabricated with the resulting nanofiber non-woven mat cathodes. Fuel cell tests were carried out to compare beginning-of-life (BoL) and end-of-life (EoL) fuel cell power output after a carbon corrosion voltage cycling experiment for nanofiber

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The hydrogen/air proton-exchange membrane fuel cell is a promising candidate for emission-free automotive power plants, but issues remain regarding the high cost and durability of membrane-electrode-assemblies (MEAs). For commercialization, the Pt loading of fuel cell MEAs (particularly the cathode) must be reduced while maintaining high power output and the catalytic activity of the cathode for electrochemical oxygen reduction must be maintained during long-term operation with various power cycles and numerous stack start-ups and shut-down events.

In a series of recent papers, Pintauro and coworkers have shown that an electrosprun nanofiber cathode, composed of Pt/C particles and a binder of Nafion + poly(acrylic acid) (abbreviated as PAA) performs remarkably well in a hydrogen/air proton exchange membrane fuel cell. For example, a nanofiber electrode MEA with 0.055 mg/cm² at the cathode and 0.059 mg/cm² at the anode (Johnson Matthey Pt/C catalyst) produced more than 900 mW/cm² at maximum power in a H₂/air fuel cell at 80°C, 100% RH, and high feed gas flow rates at 2 atm backpressure. In a recent collaborative study between Vanderbilt University and Nissan Technical Center North America, Brodt et al. showed that MEAs with an electrosprun polymer/catalyst cathode generated high beginning-of-life power and also exhibited excellent durability, as determined from end-of-life polarization curves after an accelerated start-stop voltage cycling (carbon corrosion) test. Thus, after 1,000 simulated start-stop cycles, a nanofiber MEA with Johnson Matthey Pt/C catalyst and a binder of Nafion + PAA maintained 53% of its initial power at 0.65 V and 85% of its maximum power, as compared to a 28% power retention at 0.65 V and 58% retention at maximum power for a conventional sprayed electrode MEA. The excellent initial performance of nanofiber fuel cell electrodes was attributed to the unique nanofiber electrode morphology, with inter- and intra-fiber porosity which results in better accessibility of oxygen to Pt catalyst sites and the efficient removal of product water. The superior end-of-life performance of the nanofiber MEA after a carbon corrosion test was associated with the combined effects of a high initial electrochemical cathode surface area, the mechanical robustness of the nanofiber structure, and the rapid/effective expulsion of product water from the cathode which minimizes/eliminates flooding.
and conventional painted GDE cathode MEAs of the same binder composition and Pt loading.

It is generally known that Nafion and PVDF are incompatible/immiscible polymers which phase-separate when solution cast into thin film membranes. We have found that well-mixed PVDF/Nafion blends with nanometer-size domains can be prepared by electrospinning Nafion + PVDF mixtures. The present paper does not deal with the chemistry/morphology of Nafion/PVDF blends, (this topic will be addressed in separate publications), but only with the use of these blends as binders in hydrogen/air fuel cell cathodes.

Experimental

Materials.—Johnson Matthey HiSpec 4000 (40% Pt on Vulcan carbon) catalyst was used for all electrodes. 450 kDa molecular weight poly(acrylic acid) (PAA) was purchased from Sigma Aldrich, from which a 15 wt% stock solution was created in 2:1 (w:w) isopropanol (IPA):water solvent. Kynar HSV 900 polyvinylidene fluoride (Arkema, Inc.) was used to prepare a 10 wt% stock solution in 7:3 (w:w) dimethylformamide (DMF):acetone. 1100 EW Nafion ion exchange resin (purchased from Ion Power) was dried to solid crystals and used to make two different stock solutions: (1) a 20 wt% Nafion solution in 2:1 (w:w) n-propanol:water and (2) a 20 wt% Nafion solution in 7:3 (w:w) DMF:acetone.

Electrospinning electrodes.—Table I lists the compositions for each cathode electrospinning ink and final dry nanofiber cathode. Inks were prepared using the following sequence: (i) wetting catalyst with water (ink 1 in Table I) or DMF (inks 2–7), (ii) adding the appropriate amount of isopropanol (IPA) (ink 1), tetrahydrofuran (THF) (inks 2–6), or acetone (ink 7), (iii) adding the appropriate weight of Nafion via stock solutions A or B (defined in Table I), (iv) sonicating the suspension for 90 minutes with intermittent mechanical stirring, (v) adding PAA (stock solution C for ink 1) or PVDF (stock solution D) to make two different stock solutions: (1) a 20 wt% Nafion solution in 2:1 (w:w) n-propanol:water and (2) a 20 wt% Nafion solution in 7:3 (w:w) DMF:acetone for inks made with PVDF.

Table I. Electrospinning Ink Composition and Final Dry Nanofiber Composition of Electrospun Cathodes.

| Ink | Ink Composition (g) | Dry Electrode Composition Wt.% |
|-----|---------------------|-------------------------------|
| 1   | 0.20 g catalyst, 0.80 g water, 0.53 g IPA, 0.37 g stock solution A\(^1\), 0.25 g stock solution C\(^2\) | 24 catalyst, 12 Nafion, 66 PAA |
| 2   | 0.20 g catalyst, 0.27 g DMF, 0.80 g THF, 0.34 g stock solution B\(^3\), 0.17 g stock solution D\(^4\) | 24 catalyst, 6 Nafion, 64 PVDF |
| 3   | 0.20 g catalyst, 0.67 g DMF, 0.60 g THF, 0.29 g stock solution B, 0.29 g stock solution D | 20 catalyst, 10 Nafion, 70 PVDF |
| 4   | 0.20 g catalyst, 0.52 g DMF, 0.52 g THF, 0.214 g stock solution B, 0.43 g stock solution D | 15 catalyst, 15 Nafion, 70 PVDF |
| 5   | 0.20 g catalyst, 0.78 g DMF, 0.68 g THF, 0.145 g stock solution B, 0.57 g stock solution D | 10 catalyst, 20 Nafion, 70 PVDF |
| 6   | 0.20 g catalyst, 0.68 g DMF, 0.57 g THF, 0.09 g stock solution B, 0.70 g stock solution D | 6 catalyst, 6 Nafion, 24 PVDF |
| 7   | 0.20 g catalyst, 0.30 g DMF, 1.6 g acetone, 0.87 g stock solution D | 30 catalyst, 30 PVDF |

\(^1\)Stock Solution A: 20 wt% Nafion in 2:1 n-propanol:water w:w
\(^2\)Stock Solution B: 20 wt% Nafion, in 7:3 DMF:acetone w:w
\(^3\)Stock Solution C: 15 wt% PAA in 2:1 IPA:water w:w
\(^4\)Stock Solution D: 10 wt% PVDF in 7:3 DMF:acetone w:w

SEM imaging of nanofiber mats.—Top-down SEM images of electrospun nanofiber mats were taken with a Hitachi S4200 Scanning Electron Microscope with a 5.0 kV electron beam. Prior to imaging, the mats were lightly pressed at room temperature onto conductive SEM tape and then sputter coated with a thin layer of gold to improve contrast. Digitized images of the SEM micrographs, using ImageJ software, were used to determine the average fiber diameter of an electrode mat.

Membrane-electrode-assembly (MEA) preparation.—CCMs (Catalyst Coated Membranes) with nanofiber electrodes were fabricated by hot pressing 5 cm\(^2\) electrospun particle/polymer nanofiber mats onto a Nafion 211 membrane at 140°C and 4 MPa for 2 minutes, after a 10-minute pre-heating period at 140°C with no applied pressure. The Pt loading of a nanofiber electrode 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 BC 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. Catalyst/PVDF or catalyst/Nafion/PVDF inks were painted in multiple layers directly onto a carbon paper gas diffusion layer (Sigracet GDL 25 BC) and dried at 70°C for 30 minutes after depositing each layer. The same Nafion/PVDF ink recipes (inks 2–7 in Table I) were used for the painted GDEs, except an additional 1.0 g of DMF and 1.0 g of acetone was added to each ink, in order to decrease the ink viscosity so that thin layers could be easily spread onto the carbon paper. Conventional cathode GDEs were also prepared with a composition of 70 wt% catalyst and 30% Nafion, using n-propanol/water as the solvent. All painted GDEs (5 cm\(^2\) in geometric area) were hot pressed onto Nafion 211 membranes at 140°C and 4 MPa for 2 minutes after a 10 minute pre-heating step at 140°C with no applied pressure (same conditions as the nanofiber electrodes).

The Pt loading of both nanofiber and GDE cathodes was fixed at 0.10 mg/cm\(^2\). All nanofiber and GDE cathode MEAs contained a nanofiber anode with Nafion/PAA binder (electrospinning ink 1 from Table I) at a Pt loading of 0.10 mg/cm\(^2\).

Fuel cell tests.—Fuel cell tests were performed on 5 cm\(^2\) MEAs, using a Scribner Series 850e 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 with fully humidified H\(_2\) and air at atmospheric (ambient) pressure were performed at 80°C where the H\(_2\) flow rate was 125 scm and the air flow rate was 501 cm\(^3\)/min. Prior to collecting polarization data, MEAs were pre-conditioned at 80°C with fully humidified air and hydrogen by switching every 2 minutes between galvanostatic and potentiostatic operation (at 150 mA/cm\(^2\) and 0.2 V, respectively). The Pt loading of both cathodes was fixed at 0.10 mg/cm\(^2\). All nanofiber and GDE cathode MEAs contained a nanofiber anode with Nafion/PAA binder (electrospinning ink 1 from Table I) at a Pt loading of 0.10 mg/cm\(^2\).
respectively). This break-in process was continued until steady-state was achieved (typically ~4 hours, but as long as 12 hours for cathodes with a neat PVDF binder). Polarization curves were generated by measuring the voltage at a given current in the anodic (positive voltage) direction after waiting two minutes for system stabilization. High frequency resistance (HFR) data were collected at 6000 Hz.

Electrochemical surface area (ECA) and mass activity.—In-situ cyclic voltammetry (CV) measurements were performed on 5 cm² MEAs, with a sweep rate of 20 mV/s, where a H₂-purged anode served as both 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). A cyclic voltammogram was generated between +0.04 V and +0.9 V vs. SHE and the electrochemically active surface area was determined from the integrated area above the hydrogen adsorption portion of the curve (corresponding to a voltage range of approximately +0.1 to +0.4 V), after correction for double layer charging, where the charge required to reduce one monolayer of hydrogen atoms on Pt was assumed to be 210 μC/cm². Pt cathode mass activity measurement data was collected with a current-controlled anodic scan (high current to low current) at 80°C with fully humidified O₂ and H₂ gas feeds at 100 sccm and 1.5 atm (150 kPaabs). The system was given 3 minutes to stabilize at each current density before a voltage reading was taken. Mass activities were determined at 0.90 V from a plot of IR-free voltage vs. current density corrected for hydrogen-crossover. BoL and EoL mass activities were based on an initial Pt loading of 0.10 mgPt/cm².

Cathode durability tests.—MEAs were tested under the Fuel Cell Commercialization Conference of Japan’s (FCCJ) standard start-stop potential cycling protocol. For a carbon corrosion accelerated durability test, the voltage at the cathode was cycled between 1.0 and 1.5 V at a scan rate 500 mV/s with a triangular wave. 1,000 total voltage cycles were performed on a single MEA, where the fuel cell was supplied with 125 sccm H₂ at the anode and 250 sccm N₂ at the cathode (both feed gases were fully humidified at ambient pressure). Beginning-of-life (BoL) and end-of-life (EoL) polarization curves were collected at each current density before a voltage reading was taken. Mass activities were determined at 0.90 V from a plot of IR-free voltage vs. current density corrected for hydrogen-crossover. BoL and EoL mass activities were based on an initial Pt loading of 0.10 mgPt/cm².

Results and Discussion

Analysis of nanofiber cathodes with Nafion/PAA, Nafion/PVDF or neat PVDF binder.—It has already been shown by the present authors that MEAs with nanofiber mat cathodes composed of Pt/C powder and a catalyst binder of Nafion + poly(acrylic acid) (abbreviated as PAA) produce higher power at beginning-of-life (BoL) and have better durability after an accelerated carbon corrosion test, as compared to MEAs with a conventional GDE slurry or sprayed cathode. In the present study, polyvinylidene fluoride (PVDF) was investigated as: (1) a carrier polymer for Nafion fiber electrospinning (an alternative to PAA) and (2) the sole binder or a blending agent with Nafion to increase the hydrophobicity and carbon corrosion resistance of the cathode. Initial MEA fuel cell tests were performed with two limiting case PVDF-containing binders: (1) neat PVDF and (2) 80/20 wt% Nafion/PVDF, which represents the minimum PVDF content required to electrospin well-formed electrode fibers with Nafion and Pt/C powder. The final (dry) cathode fiber composition for these two cases is 70 wt% Pt/C + 30 wt% PVDF for the neat PVDF mat case and 70 wt% Pt/C + 24 wt% Nafion + 6 wt% PVDF for the 80/20 Nafion/PVDF mat. As shown by the SEM images in Figure 1, electrospun Pt/C catalyst fibers with PVDF and Nafion/PVDF binders appear to be highly porous with a roughened surface. The overall fiber/mat morphology is nearly identical to catalyst fibers electrospun with Nafion/PAA binder, although there was some variability in fiber diameter and catalyst content along the 80/20 Nafion/PVDF fibers. The mat with a neat PVDF binder had an average fiber diameter of 620 nm, whereas the average fiber diameter for the 80/20 Nafion/PVDF mat was 450 nm; for cathodes with a Nafion/PAA binder, such differences in fiber diameter had no detectable effect on fuel cell performance, and a similar insensitivity was assumed in the present study. The observed fiber structure is a direct consequence of the electrospinning process, where catalyst and binder are well mixed due to high shear stresses within the catalyst ink at the spinneret tip followed by fiber elongation as the filament travels to the collector surface and rapid solvent evaporation which “freezes in” a well-dispersed particle/polymer morphology with significant intra-fiber voids and a very thin coating of binder on all catalyst particles. Differences in fiber diameter with binder composition are statistically significant. Inks without Nafion were more viscous than inks containing both Nafion and PVDF. The increase in fiber diameter with ink viscosity is due to a reduction in the extent of jet elongation during electrospinning (i.e., there is more resistance

Figure 1. Top-down 6,000 x SEM images of: (a) an electrospun Pt/C-PVDF nanofiber mat (fiber composition: 70 wt% Pt/C powder and 30 wt% PVDF) and (b) an electrospun Pt/C-Nafion/PVDF nanofiber mat with a binder of 80/20 Nafion/PVDF w/w (fiber composition: 70 wt% Pt/C powder, 24 wt% Nafion, and 6 wt% PVDF).
to charge-induced bending instabilities of the filament as it emerges from the spinneret tip).

In Figure 2, beginning-of-life (BoL) hydrogen/air fuel cell polarization curves are shown for MEAs with cathodes containing 80/20 Nafion/PVDF and neat PVDF binders at a cathode Pt loading of 0.10 mg/cm². For comparison, V-i data are also presented for a 0.10 mg/cm² nanofiber cathode with a binder of Nafion/PAA (ink 1 in Table I) where the fiber composition is 64 wt% Pt/C + 24 wt% Nafion + 12 wt% PAA (similar to that in Reference 5). Data were collected at 80 °C with air and hydrogen at ambient pressure and 100% relative humidity (RH). The HFR for all three MEAs was essentially the same, indicating good electrode/membrane adhesion and minimal contact resistance and all MEAs utilized the same kind of nanofiber anode (binder and Pt loading), so any changes in MEA power output were attributed to the functioning of the cathode. The Nafion/PVDF and Nafion/PAA cathode MEAs generated similar polarization curves, with the Nafion/PVDF cathode MEA having slightly higher current densities at voltages < 0.65 V (associated with better water expulsion at high current densities) and slightly smaller current densities at voltages > 0.65 V (insufficient water at the catalyst surface sites for fast ORR). With regards to the former observation, an improvement in cathode mass transfer due to an increase in binder hydrophobicity has been reported previously by Song et al. who found that an MEA with a cathode binder composed of 5 wt% polytetrafluoroethylene (PTFE) and 95% Nafion had lower ORR catalytic activity, but produced more power at low voltages (e.g. ~20% more power at 0.4 V, as compared to a standard Nafion binder MEA). Consequently, the maximum power density for the Nafion/PVDF cathode MEA was 13% higher than that for a nanofiber cathode MEA with a Nafion/PAA binder cathode (545 vs. 484 mW/cm²). The neat PVDF cathode MEA, with no proton conducting ionomer in the cathode binder, worked surprisingly well (current densities > 1 A/cm² were achieved), but not at the same performance level as MEAs with Nafion as a binder component. Low power was associated with minimal water content at the surface of catalyst particles and restricted proton migration, which adversely affect ORR kinetics, in combination with the low oxygen permeability of PVDF at 0.09 Barrers, the oxygen permeability of PVDF is about two orders of magnitude lower than that in wet Nafion. Current flow and some level of proton transport in ionomer-free fuel cell cathodes has been observed previously and associated with the presence of Pt oxide/hydroxide layers and water, but the general phenomenon is not well understood and it is not known if such surface oxide species were affecting PVDF cathode performance in the present study.

The effect of Nafion/PVDF weight ratio on nanofiber cathode performance.—The effect of cathode binder composition on initial fuel cell performance and cathode durability after an accelerated carbon corrosion test was assessed for a range of Nafion/PVDF weight ratios (80/20, 67/33, 50/50, 33/67, 20/80, and 0/100). Power generation was compared to a MEA with a conventional (painted) GDE cathode with a neat Nafion binder. For all cathodes, the Pt loading was fixed at 0.10 mg/cm² and the total binder content was constant relative to the amount of catalyst at 30 wt%.

The beginning-of-life (BoL) polarization curves in Figure 3a contrast the differences between MEAs with Nafion/PVDF nanofiber and neat Nafion GDE cathodes. As the PVDF content of the nanofiber cathode binder was increased from 20 to 100 wt%, less power was generated for all voltages. Nafion/PVDF nanofiber cathode MEAs with a PVDF content ≤ 50 wt% performed well at high and low current densities, due to the combined effects of: (i) the nanofiber mat architecture, with inter-fiber and intra-fiber porosity, (ii) adequate binder hydrophilicity for fast ORR currents in the high voltage region of a polarization curve, and (iii) a sufficient amount of hydrophobic PVDF for facile water expulsion from the fibers at high current densities, without adversely affecting conductivity. There also may be a structural aspect (i.e., nano and micro roughness of a fiber mat electrode) to the observed enhancement in electrode hydrophobicity.

Figure 2. Beginning-of-life polarization curves for 5 cm² MEAs with a Nafion 211 membrane, a 0.10 mg/cm² electrospray cathode and a 0.10 mg/cm² electrosprayed anode. Fuel cell operating conditions: 80 °C, 125 sccm H₂ and 500 sccm air at ambient pressure and 100% RH. The cathode binder (w/w) is: (●) Nafion/PAA (67/33), (■) Nafion/PVDF (80/20), or (■) PVDF.

Figure 3. Polarization curves for MEAs with electrosprayed Nafion/PVDF cathodes (unbroken lines) and an MEA with a conventional painted GDE cathode with 70 wt% Pt/C and 30 wt% Nafion (dashed line). The electrosprayed cathode Nafion/PVDF w/w are: (1) 80/20, (2) 67/33, (3) 50/50, (4) 33/67, (5) 20/80, and (6) 0/100. All MEAs are 5 cm² and contain a Nafion 211 membrane and 0.10 mgps/cm² at the cathode and anode. Fuel cell operating conditions are 80 °C, 125 sccm H₂ and 500 sccm air at ambient pressure and 100% RH. (a) BoL data, (b) EoL data.
for fibers with a significant PVDF content versus those with Nafion + PAA. The poor BoL power generation of electrospun mat cathode MEAs where the binder was predominantly PVDF was not entirely surprising, given the poor results for the neat PVDF nanofiber MEA in Figure 2.

At EoL, after the voltage cycling carbon corrosion tests, there was a much smaller difference in power output among the Nafion/PVDF nanofiber cathode MEAs where the binder was predominantly PVDF was not entirely surprising, given the poor results for the neat PVDF nanofiber MEA in Figure 2.

Comparison of nanofiber and painted GDE MEAs with Nafion/PVDF cathode binders.—In an effort to decouple the effects of nanofiber morphology and Nafion/PVDF binder compositions on MEA performance, painted GDEs were created and tested with the same cathode binders as the fibers in Figure 3. Fuel cell BoL and EoL results are shown in Figures 4a–4f. The measured HFR (not shown in Figure 4) was constant at 50 ± 5 mΩ · cm² for nanofiber and electrospun cathode MEAs generated more power than the conventional neat Nafion GDE MEA. At EoL, the polarization curve for the conventional MEA was essentially identical to that for the neat PVDF nanofiber cathode MEA, another surprising and unanticipated result.
painted/conventional cathode MEAs for all cathode binder compositions at both BoL and EoL. Overall, the Nafion/PVDF and neat PVDF electrospun fiber MEAs produced higher power than their painted GDE MEA analogues at both BoL and EoL. The improvement in MEA performance at BoL was associated with the nanofiber mat morphology, with inter and intra fiber porosity and a thin and uniform coating of binder on all catalyst particles which enhance oxygen access to Pt surface sites and facilitate water removal. At EoL, the Nafion/PVDF electrospun and painted GDE cathode MEAs showed three similar trends: (1) Nafion/PVDF binder MEAs with > 50 wt% Nafion lost power after the corrosion test, (2) MEAs with > 50 wt% PVDF generated more power after carbon corrosion, i.e., the EoL/BoL power density ratio was > 1.0, and (3) the power densities at BoL and EoL were essentially the same with a 50/50 Nafion/PVDF binder. Thus, the relative changes in EoL vs. BoL power appear to be controlled by cathode binder composition and not by cathode morphology. At the same time, there were differences in MEA behavior due to cathode structure. EoL power losses for nanofiber cathode MEAs with low PVDF content were always smaller than those for GDE cathode MEAs at the same Nafion/PVDF binder composition, e.g., for 80/20 Nafion/PVDF cathode binder, the painted cathode MEA lost 48% of its initial power at 0.65 V and 26% of its maximum power, as compared to a 38% power loss at 0.65 V and 20% power loss at maximum power for the nanofiber cathode MEA. Similarly, power increases after carbon corrosion (EoL relative to BoL) were always greater for electrospun cathodes, where, for example, the largest relative improvement in fuel cell performance was seen with a 20/80 Nafion/PVDF MEA, i.e., the blended polymer binder with the least amount of Nafion, where the EoL power increased by 36% at 0.65 V for a nanofiber cathode but only a 20% increase for the painted GDE cathode.

Similarities and differences between nanofiber and painted GDE cathodes are further revealed by the measured cathode carbon loss during a voltage cycling experiment and by the measured electrochemically active cathode area and cathode kinetic parameters at BoL and EoL. Figures 5a and 5b show typical CO2 concentration vs. time plots during a voltage cycling accelerated carbon corrosion experiment. The shape of these curves is similar to that reported previously, where the spikes in CO2 are attributed to the rapid decomposition of accumulated surface oxide species on the Pt carbon support material.31,32 The cumulative carbon loss for all nanofiber and GDE cathodes after 1,000 voltage cycles is presented in Figure 6 for Nafion/PVDF binders of different PVDF content. The extent of carbon support corrosion was strongly dependent on the amount of PVDF in the cathode binder, but not on cathode morphology (nanofiber vs. painted). The decrease
in carbon corrosion with increasing PVDF content is attributed to the binder hydrophobicity, with less water at the Pt/C cathode surface.\textsuperscript{33,34}

Measured nanofiber and GDE cathode electrochemical surface areas (ECAs) and kinetic parameters for ORR (mass activity and Tafel slope) at BoL and EoL are listed in Table II for the different cathode binders. The BoL ECAs for electrospun and GDE MEAs are essentially independent of the Nafion/PVDF binder ratio with an ECA of 44–45 m\textsuperscript{2}/g for nanofibers (the same ECA as a nanofiber mat cathode with Nafion + PAA binder) vs. 34–36 m\textsuperscript{2}/g for the GDE cathodes (the same ECA as a painted or decal GDE with neat Nafion binder\textsuperscript{2,35}).

So, the addition of PVDF to Nafion does not change the number of active Pt sites for proton reduction (H generation) in a given fuel cell cathode structure, but nanofibers provide substantially better access to catalyst sites as compared to a GDE, presumably due to a more favorable distribution of catalyst and binder, coupled with the presence of intrafiber voids. At EoL, there is a substantial loss in ECA for all cathodes, with slightly less ECA loss for binders of high PVDF content. As was the case at BoL, the nanofiber morphology provides for more electrochemical surface area after carbon corrosion (i.e., the initially high ECA of nanofibers does not promote excessive carbon corrosion). A plot of % ECA loss vs. % carbon loss (shown in Figure 7) reaffirms what was already seen in Figure 6, that the relative deterioration of the cathode after a voltage cycling experiment is binder-composition-dependent and not a function of cathode structure (electrospun nanofibers vs. GDE). The absolute values of ECA, mass activity, and power density at both BoL and EoL, however, are greater for the nanofiber cathode case. Thus, cathode morphology and binder composition contribute to the observed performance of nanofiber cathode MEAs at BoL and EoL during a carbon corrosion experiment. Measured cathodic Tafel slopes were essentially the same for all MEAs, between 70–84 mV/dec, and showed no correlation with composition or structure, indicating no change in the ORR reaction mechanism for nanofiber vs. GDE cathodes.

Table II. BoL and EoL Electrochemical Surface Area, Mass Activity Data, and Tafel Slopes for MEAs with Electrospun or Painted GDE Cathodes.

| Cathode Pt/C Binder (w/w) | Electrospun Cathodes | Painted GDE Cathodes |
|--------------------------|----------------------|----------------------|
|                          | ECA (m\textsuperscript{2}/gPt) | Mass Act\textsuperscript{\circ} (A/mgPt) | Tafel Slope (mV/decade) | ECA (m\textsuperscript{2}/gPt) | Mass Act\textsuperscript{\circ} (A/mgPt) | Tafel Slope (mV/decade) |
| Neat PVDF                | 29                   | 0.051                | 82                   | 36                   | 0.035                | 72                   |
| 20 Nafion/80 PVDF        | 44                   | 0.067                | 77                   | 45                   | 0.044                | 75                   |
| 33 Nafion/67 PVDF        | 45                   | 0.071                | 82                   | 36                   | 0.053                | 79                   |
| 50 Nafion/50 PVDF        | 44                   | 0.093                | 75                   | 36                   | 0.067                | 81                   |
| 67 Nafion/33 PVDF        | 45                   | 0.11                 | 75                   | 36                   | 0.081                | 84                   |
| 80 Nafion/20 PVDF        | 45                   | 0.12                 | 80                   | 36                   | 0.083                | 82                   |
| 67 Nafion/33 PAA         | 45                   | 0.16                 | 70                   | 36                   | 0.083                | 79                   |

*measurements taken at 0.90 V in O\textsubscript{2} at 7 psig, 80 °C, and 100% RH.
In contrast to the ECA data, the mass activity of Nafion/PVDF binder cathodes at BoL was strongly influenced by both the binder composition and cathode structures, with nanofiber activities >40% greater than those for a GDE at the same Nafion/PVDF weight ratio. The measured decrease in mass activity with increasing PVDF content for GDE and nanofibers at BoL (for binders with a high PVDF content) is attributed to a loss of water at the cathode surface, which adversely affects ORR kinetics. The low O2 permeability of PVDF content) is attributed to less water at the cathode surface, which adversely affects ORR kinetics. Normally, this inversely affects ORR kinetics. For all electrospun cathodes, this mass-corrected activity is equal to the EoL activity in Table II multiplied by ECAEoL/ECABoL. It is shown in Table II. If one assumes that the EoL/BoL ECA ratio is representative of the relative Pt mass loss after a carbon corrosion experiment, then the measured mass-corrected EoL activity of Pt in Nafion/PVDF nanofibers is equal to the EoL activity in Table II multiplied by ECAEoL/ECABoL. For all electrospun cathodes, this mass-corrected activity is ∼0.165 A/mgPt, which is close to the BoL mass activity of a nanofiber cathode with a hydrophilic Nafion/PAA binder. A similar approach holds for the GDE MEAs with Nafion/PVDF binders (the Pt mass-adjusted EoL activity is ∼0.11 A/mgPt, i.e., the same as that for a GDE cathode with a hydrophilic neat Nafion binder). This increase in EoL mass-corrected activity is most pronounced for high PVDF content binders, where the mass activity at BoL is very low and the root-cause for the increase in power densities after the accelerated carbon corrosion test for some Nafion/PVDF binders shown in Figure 4. The Nafion/PVDF nanofibers cathodes of high PVDF content also have the requisite binder hydrophobicity to extract any excessive water that might be present near the catalyst, thus minimizing the usual flooding issues that accompany carbon corrosion. This point is best illustrated by examining the Nafion/PAA electrospun cathode MEA results in Table II. Here, the EoL mass activity is much higher than that for any Nafion/PVDF binder, but the EoL power is lower. This is due to the combined effects of a smaller EoL ECA and the hydrophilicity of the binder which cannot stop flooding after carbon corrosion and the formation of surface oxide species on the catalyst support.

As expected, the BoL and EoL ECAs and mass activities of MEAs with a neat PVDF cathode binder were quite low, but the measured ECAs (before and after carbon corrosion) were surprisingly similar for both nanofiber and GDE cathode structures. In both cathode structures, the available electrochemical area is limited by proton access to Pt sites. The results indicate that a nanofiber morphology cannot completely counterbalance the deleterious effects of a poorly functioning binder cathode. While the ECAs of electrospun fibers and GDEs suffer equally from PVDF’s lack of conductivity, the nanofiber morphology does produce a higher mass activity (at both BoL and EoL), due presumably to better oxygen transport in a fiber, i.e. intrafiber porosity and a thin and uniform coating of PVDF on catalyst particles.

Intermittent polarization curves at 100% RH were collected during the corrosion tests to track how power density varied with cycle number. The resulting power densities at 0.65 V for nanofiber and GDE cathode MEAs are shown in Figures 8a and 8b, respectively.
and are either electrospun (triangles) or painted GDEs (circles). For all MEAs, a nanofiber 0.10 mgPt/cm² anode was used with a 67 wt% Nafion and 33 wt% PAA cathode binder. The cathodes have a Pt loading of 0.10 mg/cm².

The rate at which MEA power density changed with cycle number was affected by both binder composition and cathode morphology. Most of the power losses or gains occurred during the first 500 voltage cycles. Power densities vs. cycle number curves for the painted and electrospun cathode MEAs were qualitatively similar for a given cathode binder composition, with the painted MEAs producing much less power. Nanofiber cathode MEAs with 50/50 Nafion/PVDF binder showed essentially no change in power density for 1,000 voltage cycles. This flat power density vs. cycle number curve may have important benefits when using inexpensive non-PGM cathode catalysts, where one can compensate for a low power density (due to the presence of PVDF) by increasing the cathode catalyst loading.

Low humidity fuel cell operation.—BoL and EoL polarization data with Nafion/PVDF MEAs were collected at 40% RH feed gas condition, where the carbon corrosion test was performed under standard conditions with fully humidified feed gases. The results are shown in Figure 9. The performance of the Nafion/PVDF cathode binder MEAs was inversely proportional to the binder PVDF content, i.e., less current (less power) was generated over the entire voltage range as the PVDF content increased (see Figure 9a). At BoL and 40% RH, only the Nafion/PVDF electrospun fiber cathode with the smallest amount of PVDF (20 wt% of the cathode binder) worked better than a conventional Nafion GDE. This same trend was seen with fully humidified feed gases, although the activation/kinetic and ohmic losses are more severe at low humidity. Not surprisingly, the deleterious effects of cathode drying at low feed gas RH are exacerbated as the cathode binder becomes more hydrophobic. The performance of MEAs with little or no Nafion in the cathode (0 and 20 wt% Nafion) were particularly poor, e.g., the neat PVDF MEA produced only 7 mW/cm² at 0.65 V and 76 mW/cm² at maximum power at 40% RH and H₂/air at ambient pressure. These results were not unexpected and are qualitatively similar to that observed with 3M Company’s NSTF platinum whisker cathodes, e.g., a power loss of ∼70% at 0.8 V when the H₂/O₂ feed gas RH is decreased from 100% RH to 50% RH.

One would expect that power losses could be partially mitigated if the hydrophilicity of the cathode was increased and this appears to be the case in the present study, as shown by the EoL data in Figure 9b. Indeed, after a voltage cycling carbon corrosion test, the nanofiber Nafion/PVDF polarization curves shift upward, due presumably to the presence of surface carbon oxidation species on the catalyst support which makes the cathode more hydrophilic.

Power output results at 0.65 V and 100% RH and 40% RH are summarized in Figure 10 for all electrospun and GDE cathode MEAs. The plotted results represent average power densities from duplicate MEAs (variations in experimental polarization curves were typically...
±5%), to ensure that the reported trends are reproducible and statistically significant. These data highlight the benefit of a nanofiber morphology with Nafion/PVDF binders, i.e., at the same binder composition, BoL power densities with nanofiber PVDF/Nafion MEAs are higher than those with a GDE MEA. Furthermore, at EoL with fully humidified feed gases, all nanofiber cathode MEAs worked better than all GDE cathode MEAs, regardless of binder type (i.e., electrode morphology dominated over the Nafion/PVDF binder composition). At BoL, the best nanofiber cathode contained a binder of either 67/33 Nafion/PAA or 80/20 Nafion/PVDF. The best binder at EoL was 33/67 Nafion/PVDF (at EoL, this nanofiber cathode MEA produced 79% more power at 0.65 V than the best GDE cathode MEA). With 40% RH feed gases, only the Nafion/PAA and 80/20 Nafion/PVDF binders worked well at EoL.

Conclusions

The effects of cathode morphology (nanofiber vs. painted GDE) and cathode binder composition (various Nafion/PVDF blends and neat PVDF) on beginning-of-life (BoL) and end-of-life (EoL) MEA power output was assessed at 80 °C with ambient pressure H2 and air. The intended goal of this work was to increase the hydrophobicity of the cathode, thereby reducing the water content at the catalyst surface and decreasing the extent of carbon corrosion after an accelerated voltage cycling experiment. Electrospun nanofiber mats were fabricated with 70% Pt/C catalyst (Johnson-Matthey) and 30% Nafion/PVDF binder, where the PVDF content was varied from 20% to 80 wt.%; a neat 30 wt% PVDF binder was also examined. The anode and cathode Pt loading were each 0.10 mg/cm², where the anode for all MEAs was an electrospun fiber anode with a binder of Nafion and poly(acrylic acid).

For both nanofiber and painted GDE cathodes, BoL power output decreased with increasing PVDF content due to poor proton conductivity in the electrode, less water at the catalyst surface (which adversely affected ORR kinetics), and/or the low O2 permeability of PVDF as compared to wet Nafion. Nanofiber cathode MEAs, however, always produced higher power densities for all voltages both before and after carbon corrosion at a given binder composition, due to a larger ECA and higher mass activity. The unique morphology of a nanofiber cathode is clearly beneficial, where there is interfiber and intrafiber porosity and a very thin and uniform coating of binder on all catalyst sites for facile transport of reactants and products. After 1,000 voltage cycles (1.0 to 1.5 V), the % cathode carbon loss was identical for the two cathode structures, where carbon loss decreased linearly with increasing PVDF content, but the impact of carbon corrosion on power output was less severe with nanofibers.

An 80/20 Nafion/PVDF binder electrospun cathode morphology MEA generated the highest maximum power at BoL: 545 mW/cm² at 80 °C, 100% RH and ambient pressure. Nanofiber cathode power densities at EoL for binders with < 50% PVDF decreased vs. BoL due to a decrease in ECA which overwhelmed a small increase in the mass activity of Pt material remaining after carbon corrosion. EoL power densities increased for binders with > 50% PVDF due to the combined effects of less carbon corrosion and ECA loss, a dramatic increase in the Pt mass activity due to the formation of hydrophilic chemical oxidation species on the carbon support, and the presence of hydrophobic binder which in combination with the nanofiber morphology continuously facilitated water extraction from the catalyst surface, thereby minimizing the deleterious effects of flooding. The highest power at EoL (286 mW/cm² at 0.65 V) was generated with a nanofiber MEA with a 33/67 Nafion/PVDF cathode binder. For a 50/50 Nafion/PVDF cathode binder MEA, the power output was constant (260 mW/cm² at 0.65 V) throughout a voltage cycling experiment.

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