Particle/Polymer Nanofiber Mat Electrodes for Hydrogen/Air Fuel Cells

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ABSTRACT

Considerable efforts have been devoted to identifying new catalyst electrode materials for low Pt-loading fuel cells. One path leads through Pt alloys with non-noble metals and through core-shell nanostructures. An alternative approach to reduce the amount of Pt in a fuel cell without a loss in power output is through improvements in the cathode morphology to maximize catalyst contact with feed gases and enable facile water expulsion while maintaining a sufficient number of pathways for proton and electron conduction. Electrodes with such properties have been created by electrospinning. In this paper, our recent work on the electrospinning of particle/polymer nanofiber Pt/C electrodes is briefly summarized, with a focus on improving the performance of the oxygen cathode in a hydrogen/air PEM fuel cell. The effects of catalyst loading and binder composition (Nafion, Nafion/PVDF blends, and PVDF) on fuel cell power output and durability is discussed.

Keywords: PEM fuel cell, membrane-electrode assembly, electrospinning, nanofiber electrode

1 INTRODUCTION

Among the modern catalytic fuel cell electrode formation methods, electrohydrodynamic deposition (EHDD) has emerged as an atractive competitor enabling not only nanostructuring capability but also commercial vaiability. Its two variants, electrospraying and electrospinning, are gaining popularity within the fuel cell R&D community, as practical tools for the fabrication of ion-conducting membranes and catalytic electrodes.

Electrospraying was employed by Baturina and Wnek [1] for the fabrication of membrane-electrode assembly (MEA) over a decade ago; they reported good initial performance, i.e. 1 A/cm^2 at 0.7V, 80°C and 300 kPa. MEAs prepared by Martin et al. [2] via hotpressing Nafion 212 membrane and electrodes of Pt/C-ionomer ink electrosprayed on a Toray paper GDL, also delivered high power (600-700 mW/cm^2) that corresponded to excellent overall platinum utilizations (30-35 kW/g$_{Pt}$).

The most definitive example of EHDD-based fuel cell electrodes was the successful electrospinning of Pt/C nanofiber mat electrodes by Zhang and Pintauro [3] in 2011. They used Nafion® perfluorosulfonic acid and poly(acyclic acid) (PAA) as the electrode binder and demonstrated that: (i) one can electrospin well-formed cathode nanofiber mats with a fiber diameter of 200-600 nm and a very high Pt/C powder content (60-70 wt%), (ii) electrospun nanofiber cathodes performed very well, e.g., a power density of 524 mW/cm^2 at 0.6 V with 0.1 mg$_{Pt}$/cm^2, and (iii) nanofiber cathodes exhibited superior long-term durability, as compared to a traditional decal cathode.

The electrospun Pt/C fuel cell cathode study summarized in this paper is a continuation of this highly successful work of Zhang and Pintauro; here the focus is on assessing the effects of catalyst loading and polymer binder composition on fuel cell power output and durability.

2 EXPERIMENTAL

Electrospinning Electrodes - Inks were prepared as described in [4-6] and contained Pt/C catalyst (Tanaka Kikinzoku Kogyo TEC10E50E - 46.1% Pt on high surface area carbon or Johnson Matthey HiSpec® 4000 - 40% Pt on Vulcan carbon) with (i) Nafion and PAA in alcohol/water solvent, (ii) PVDF (HSV900, Arkema, Inc.) in DMF/acetone, or (iii) Nafion + PVDF in a solvent of DMF/THF/acetone. Electrospinning was performed at room temperature in a custom-built environmental chamber with relative humidity control (Fig. 1).

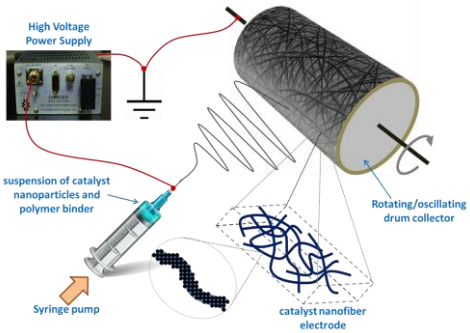

Figure 1: Setup for electrospinning nanofiber electrodes with fibers composed of Pt/C catalyst nanoparticles and a polymer binder.

An ink was drawn into a 3 mL syringe and electrospun using a single 22-gauge needle spinneret polarized to a high positive potential (12-15 kV) relative to a stainless steel rotating drum collector. The spinneret-to-collector distance was fixed at 10 cm and the flow rate of ink was held constant (typically at 1.0 mL/h). Nanofibers were collected on aluminum foil wrapped around the collector drum rotating at a speed of 100 rpm and oscillating horizontally.

Membrane-Electrode-Assembly (MEA) Preparation - Catalyst Coated Membranes (CCMs) with nanofiber electrodes were fabricated by hot pressing (140°C, 5 MPa, 1 min.) electrospun particle/polymer nanofiber mats (5 cm^2) onto either a Nafion 211 or 212 membrane. The CCM was sandwiched between two carbon paper gas diffusion layers (GDLs) (Sigracet 25 BC GDL) and installed in the fuel cell test fixture to form an MEA. Painted gas diffusion electrodes (GDEs) were also fabricated as described elsewhere [4-6]. All MEAs contained a nanofiber anode with Nafion/PAA binder and a Pt loading of 0.10 mg/cm^2.

Fuel Cell Testing - Fuel cell tests were performedusing a Scribner Series 850e test station. Experiments with fully humidified H_2 and air at atmospheric (ambient) pressure were carried out at 80°C where the H_2 flow rate was 125 sccm and the airflow rate was 500 sccm. Prior to collecting polarization data, MEAs were pre-conditioned by alternating every 2 minutes between operation at consant current (150 mA/cm^2) and constant voltage (0.2 V). 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) – In-situ cyclic voltammetry (CV) measurements were performed on 5 cm^2 MEAs, with a sweep rate of 20 mV/s, where a H_2-purged anode served as both the counter and reference electrodes and N_2 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 (+0.1 to +0.4 V).

Durability Tests - For a carbon corrosion accelerated durability test [6], the voltage at the cathode was cycled between 1.0 and 1.5 V at a scan rate 500 mV/s with a triangular voltage wave. 1,000 total voltage cycles were performed on a single MEA, where the fuel cell was supplied with 125 sccm H_2 at the anode and 250 sccm N_2 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.

3 RESULTS AND DISCUSSION

In order to successfully electrospin a polymer solution or suspension into well formed fiber mats, the solute(s) and solvent(s) components need to meet certain criteria, among which, polymer chain entanglement appears to be the most important. Typical PEM fuel cell electrode inks contain Nafion ionomer as the catalyst binder but Nafion lacks the necessary chain entanglements and will not electrospin into well-formed fibers unless a suitable carrier polymer is present [7]. In the present study, either PAA or PVDF was used as the carriers.

3.1 Electrospun Pt/C Cathodes with Nafion-PAA Binders

In the present study, both cathodes and anodes have been fabricated by electrospinning an alcohol/water suspension of Pt/C catalyst powder (HiSpec™ 4000) with a binder composed of Nafion® ionomer and poly(acrylic acid) (PAA).The fuel cell power output was then correlated with the Pt loading of a fibrous electrospun cathode.

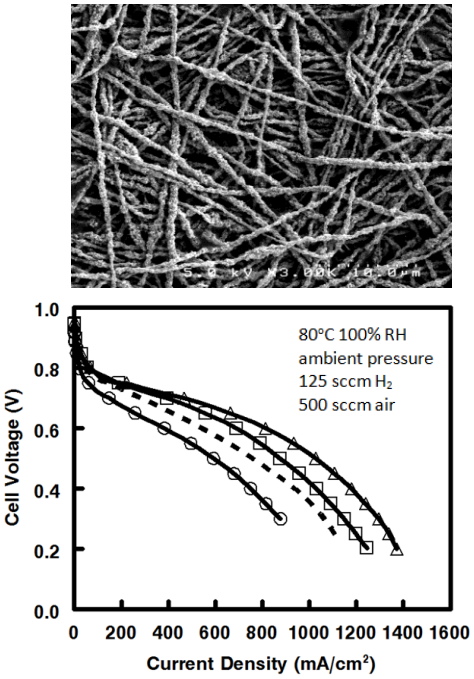

Figure 2: (a) SEM micrograph of an electrospun catalyst nanofiber mat with a Pt loading of 0.065 mg/cm^2; (b) Polarization curves for 5 cm^2 MEAs with a Nafion 212 membrane and electrospun HiSpec™ 4000 cathodes and anodes. The Pt/C:Nafion:PAA weight ratio was fixed at 65:23:12. The anode Pt loading was 0.10 mg/cm^2. The cathode Pt loading was: (Δ) 0.107 mg/cm^2 (□), 0.065 mg/cm^2, and (○) 0.029 mg/cm^2. Performance of a decal MEA with cathode and anode Pt loadings of 0.104 mg/cm^2 and 0.40 mg/cm^2, respectively is also shown (---). Adapted *with permission from J. Electrochem. Soc., 160, F744 (2013), Copyright 2013, The Electrochemical Society.*

An SEM image of the surface of a cathode nanofiber mat with a Pt loading of 0.065 mg/cm^2 and an average fiber diameter of 589 nm is shown in Fig. 2a. Under higher magnification, porous fibers with a highly roughened surface can be observed, offering high Pt surface area exposure to the feed gas, with a uniform distribution of catalyst and ionomer over the fiber length. Hydrogen/air fuel cell polarization data were collected at 80^{o}C, 100% RH, and ambient pressure (Fig. 2b). For nanofiber MEAs, the anode Pt loading was fixed at 0.1 mg/cm^2 and the cathode Pt loading was either 0.107, 0.065, or 0.029 mg/cm^2. The perofmance of nanofiber MEAs was excellent, with only a modest drop in power output when the cathode loading was reduced from 0.107 to 0.065 mg/cm^2 (the maximum power density decreased only 15%, from 513 to 437 mW/cm^2 when the Pt loading was reduced by about 40%). It should be noted that the performance of the 0.065 mg$_{Pt}$/cm^2 nanofiber cathode was superior to that of a decal cathode at a Pt loading of 0.104 mg/cm^2.

The electrochemical surface area and mass activity of nanofiber cathodes and a reference decal cathode are shown in Table 1. The active area of electrospun cathodes is about 30% higher than a conventional decal cathode (39-41 m^2/g for electrospun cathode vs. 30 m^2/g for a decal electrode). ECA is a measure of the quality and extent of contact between active catalyst sites, reactants, and both electron and proton conducting pathways; isolated catalyst does not contribute to the electrochemical reaction and is not accounted for during a CV scan. The higher measured area for the electrospun morphology suggests an improved distribution of carbon-supported Pt powder and binder. Interestingly, the ECA of nanofiber mats was found to be independent of cathode Pt loading. The Pt mass activity of all nanofiber cathodes was also greater than that of an MEA with a decal cathode (0.16-0.17 A/mg$_{Pt}$ vs. 0.11 A/mg$_{Pt}$) and was independent of cathode fiber Pt loading.

Electrode Type	Cathode Pt Loading (mg/cm^2)	ECA (m^2/g)	Mass Activity at 0.9 V (A/mg$_{Pt}$)
Decal	0.104	30	0.11
Electrospun	0.107	41	0.16
Electrospun	0.065	41	0.16
Electrospun	0.029	39	0.17

Table 1: Electrochemical Surface Areas (ECA) and Mass Activities at 0.9 V, 150 kPa$_{abs}$. *Adapted with permission from J. Electrochem. Soc., 160, F744 (2013), Copyright 2013, The Electrochemical Society.*

3.2 Electrospun Pt/C Cathodes with Nafion-PVDF Binders

These experiments assessed the durability of electrospun cathodes by means of accelerated carbon corrosion tests where the cathode was cycled between 1.0 and 1.5 V. Here polyvinylidene fluoride (PVDF) was investigated as both a carrier for Nafion/cataylst fiber electrospinning (an alternative to PAA) and as a co-binder with Nafion that was expected to increase the hydrophobicity of the cathode, thus reducing the extent of carbon corrosion on fuel cell performance declines. Initial MEA fuel cell tests were performed with two limiting case cathode binders: (1) neat PVDF and (2) 80/20 weight ratio for Nafion/PVDF, which represented 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 was 70 wt% Pt/C and 30 wt% PVDF for the neat PVDF mat and 70 wt% Pt/C, 24 wt% Nafion, and 6 wt% PVDF for the 80/20 Nafion/PVDF mat. Inspection of SEM images of the electrospun catalyst mat surface with PVDF and Nafion/PVDF binders revealed highly porous structures with strongly roughened fiber surface. The mat with a neat PVDF binder had an average fiber diameter of 620 nm , whereasthe average fiber diameter for the 80/20 Nafion/PVDF mat was 450 nm (Fig. 3a).

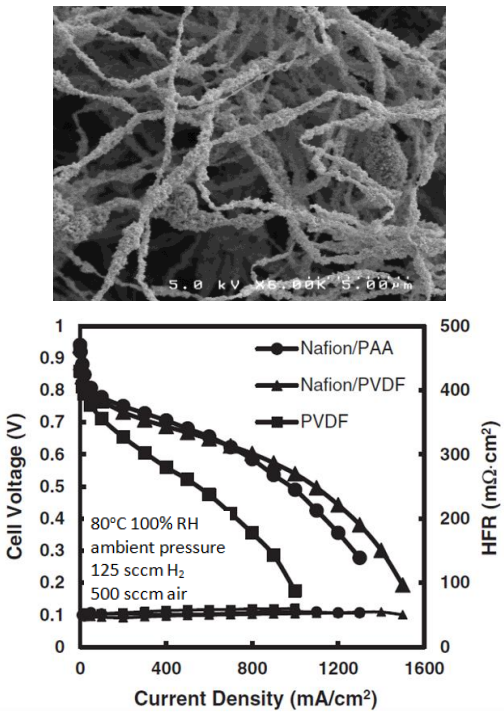

Figure 3: (a) SEM micrograph of an electrospun Pt/C nanofiber mat with a binder of 80/20 Nafion/PVDF; (b) Beginning-of-life polarization curves for 5 cm^2 MEAs with a Nafion 211 membrane, a 0.10 mg$_{Pt}$/cm^2 electrospun cathode and a 0.10 mg$_{Pt}$/cm^2 electrospun anode. The cathode binder (w/w) was: (●) Nafion/PAA (67/33), (▲) Nafion/PVDF (80/20), or (■) PVDF. *Reproduced with permission from J. Electrochem. Soc., 163, F401 (2016). Copyright 2016, The Electrochemical Society.*

Hydrogen/air fuel cell polarization curves for MEAs with cathodes containing Nafion/PVDF (80/20 wt ratio) and neat PVDF binders at a cathode Pt loading of 0.10 mg/cm^2 are shown in Fig. 3b. For comparison, data are also

presented for a 0.10 mg/cm^2 nanofiber cathode with a binder of Nafion/PAA where the fiber composition is 64 wt% Pt/C, 24 wt% Nafion, and 12 wt% PAA. Data were collected at 80°C with air and hydrogen at ambient pressure and 100% relative humidity (RH). 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 and slightly smaller current densities at voltages > 0.65 V. The neat PVDF cathode MEA, with no proton conducting ionomer in the cathode binder, worked surprisingly well (max. current density >1 A/cm^2), but at lower performance level compared to the MEAs with Nafion/PVDF or Nafion/PAA binder.

Finally, the effect of binder composition was studied by changing a PVDF content between 20 and 100%, i.e., nanofiber cathode MEAs were fabricated with Nafion/PVDF ratios of 67/33, 50/50, 33/67, and 20/80, and their initial fuel cell performance and cathode durability after an accelerated carbon corrosion test were tested and compared to a conventional painted GDE cathode MEA with a Nafion binder. The Pt loading was fixed at 0.10 mg/cm^2 and the total binder content was constant relative to the amount of catalyst at 30 wt% binder. With fully humidified feed gases, cathodes with a Nafion/PVDF binders of 80/20 and 67/33 (i.e., where the major binder component was Nafion) generated less power at EoL vs. BoL, while cathodes with a Nafion/PVDF binder of 20/80 and 33/67 (i.e., where the major binder component was PVDF) generated more power at EoL vs. BoL. With 40% RH feed gases, all Nafion/PVDF nanofiber cathode MEAs showed an increase in EoL power (at 0.65 V) as compared to their BoL power densities.

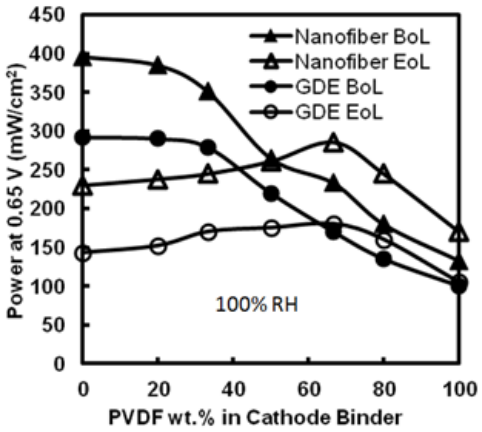

Figure 4: Power densities at 0.65 V at BoL (solid symbols) and EoL (open symbols) of MEAs as a function of PVDF wt% in the cathode binder. The cathodes had a Pt loading of 0.10 mg/cm^2 and the nanofiber 0.10 mg/cm^2 anodes were used with a 67 wt% Nafion and 33 wt% PAA binder. *Reproduced with permission from J. Electrochem. Soc., 163, F401 (2016). Copyright 2016, The Electrochemical Society.*

At EoL, the MEA that produced the highest power at 100% RH had a binder composition of 33/67 Nafion/PVDF (Fig. 4). Surprisingly, there was an increase in power at EoL for those nanofiber MEAs with a PVDF binder content greater than 50 wt%. After 1,000 voltage cycles, all Nafion/PVDF electrospun cathode MEAs generated more power than the conventional Nafion-based GDE MEA. At EoL, the power output for a conventional electrode MEA was essentially identical to that for the nanoifber MEA with a neat PVDF cathode binder, another surprising and unanticipated result.

4 SUMMARY

Nanofiber electrode mats for a hydrogen/air fuel cell were fabricated by electrospinning particle/polymer mixtures containing commercial Pt/C catalyst and one of the following binders: Nafion/poly(acrylikc acid) (PAA), Nafion/poly(vinylidene fluoride) (PVDF) with different Nafion/PVDF wt ratios, or neat PVDF. High magnification scanning electron microscope images of electrospun nanofibers showed porous fibers with a highly roughened surface and a uniform distribution of catalyst and polymer over the fiber length. MEAs with a nanofiber cathode performed very well in a hydrogen/air fuel cell, generating high power at low Pt loadings, outperforming conventional MEAs with a decal or gas diffusion electrode (GDE) cathode. Increasing the hydrophobicity of the cathode binder by replacing PAA with PVDF and decreasing the Nafion/PVDF ratio slowed catalyst carbon support corrosion in the cathode, presumably by reducing the amount of water near the catalyst surface.

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5 ACKNOWLEDGMENTS

The work at Vanderbilt University was supported by grants from Nissan Technical Center North America, Merck KGaA and the National Science Foundation, TN-SCORE program (NSF EPS-1004083) under Thrust 2.

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