Recent Advances in Electrospun Fiber Mat Electrode MEAs for Hydrogen/Air Fuel Cells

Krysta Waldrop[*], Xiaozong Fan[*], Narae Kang[*], Ryszard Wycisk[*], Cenk Gumeci[**], Nilesh Dale[**], and Peter N. Pintauro[**]

[*]Department of Chemical and Biomolecular Engineering
Vanderbilt University, Nashville, TN 37235
[**]Zero Emission - Research, Fuel Cell & Battery Laboratory
Nissan Technical Center North America, Farmington Hills, MI 48331

ABSTRACT

The hydrogen/air proton-exchange membrane fuel cell is a promising candidate for automotive power plants, but Pt/C catalyst electrode cost and durability are still issues that require further study. Recently, there has been considerable work on identifying new catalyst electrode materials for low Pt-loading fuel cell operation, including metal alloys and core-shell nanostructures. Another way to reduce the amount of Pt in a fuel cell without a loss in power output is to improve the cathode morphology in order to maximize catalyst contact with feed gases and to enable facile water expulsion from the cathode while maintaining a sufficient number of pathways for proton and electron conduction. Electrodes with such properties can be created by nanofiber electrospinning. This paper presents representative result which show the superior performance of nanofiber mat electrode MEAs for H_2/air fuel cells.

Keywords: fuel cells, nanofibers, electrospinning, membrane-electrode-assembly, power density.

1 INTRODUCTION

Membrane-Electrode-asemblies (MEAs) for proton-exchange membrane H_2/air fuel cells are made by a decal, catalyst-coated-membrane, or catalyst-coated GDL (gas diffusion layer) method,. With these methods, there is little or no control over the macro-scale organization of the catalyst and binder. Thus, the high oxygen reduction reaction catalytic activity of Pt-based catalysts seen in rotating disk experiments is rarely observed in an operating fuel cell MEA. Features such as particle and binder interconnectivity, macroporosity, and microporosity become more critical when high-performance nanomaterial catalysts are employed in fuel cell electrodes. Consequently, new electrode fabrication techniques are needed for next-generation MEAs. Nanofiber electrospinning is just such a method, which can address fuel cell electrode manufacturing and structure/performance issues. As a fabrication method, electrospinning is scalable, robust, and cost-effective, especially for the creation of non-woven mats of sub-micron diameter polymer fibers. Although not as well studied, the method can also be used to prepare particle/polymer fiber networks with high particle loading and high intra- and inter-fiber porosity. Mats from such fibrous materials have been used as electrodes in fuel cells [1-5] and batteries [6,7] where high interfacial electrode area is of prime importance.

In this paper, recent experimental work on nanofiber mat electrode MEAs for hydrogen/air fuel cells is described. Procedures for fabricating high particle-loaded nanofibers containing various Platinum and Platinum-alloy catalysts are presented. The effects of catalyst type and fuel cell operating conditions on MEA power output and durability are discussed.

2 EXPERIMENTAL

Nanofiber electrodes were electrospun from a polymer/particle ink composed of catalyst powder Nafion®, and polyethylene oxide or poly(acrylic acid) carrier polymer in an alcohol/water solvent. The cathode catalyst was either Tanaka Kikinzoku Kogyo Group (TKK) TEC36E52 PtCo/C, TKK TECNiE52 PtNi/C or Johnson-Matthey Hispec 400 Pt/C. The anode was Pt/C powder from TKK or Johnson-Matthey. Electrospinning was carried out using a single needle syringe as the spinneret, with a rotating and horizontally oscillating drum collector, as described elsewhere [5]. The final platinum loading of the electrode was controlled by the duration of the electrospinning process. The conditions to electrospin catalyst/Nafion nanofibers with polyehtylene oxide carrier were: 9 kV, 0.75 mL/hr, 20% RH, and 21 cm from tip to collector. Dried fiber mats had a mass ratio composition of 52:37:11 for catalyst:Nafion:PEO. The electrospinning conditoins for fibers with catalyst, Nafion and poly(acryli aid) can be found in References 4 and 5.

A series of different nanofiber MEAs (5 cm^2) were prepared with fiber mat anodes and cathodes. All MEAs used a Nafion 211 membrane and Sigracet carbon paper gas diffusion layers.

Hydrogen/air fuel cell polarization data were collected at 80^{o}C and H_2/air feed flow rates of 125/500 sccm. Oxygen reduction reaction mass activities were obtained using

methodologies in the literature at 80°C and 0.9V at 150 kPa absolute pressure with 100 sccm H_2 and 100 sccm O_2 at the anode and cathode, respectively [8]. The electrochemical surface area (ECSA) of cathodes was determined from cyclic voltammograms of H_2 generation/stripping with no gas flow at ambient pressure and 30°C [9].

3 RESULTS AND DISCUSSION

An ultra-low Pt-loading MEA was prepared with a cathode mat at 0.096 mg_{Pt}/cm^2 and an anode at 0.019 mg_{Pt}/cm^2, i.e., a toal MEA loading of 0.115 mg_{Pt}/cm^2 (Pt loading was determined by XRF at Nissan Technical Center North America). Fuel celll polarization plots for this MEA at 80°C, 100% RH and backpressures of 100, 150, and 200 kPa (abs) are shown in Figure 1. The maximum power density and the power density at 0.65 V are listed in Table 1. Very high power was achieved with this MEA. If this MEA were used in an 80 KW fuel cell stack, operating at 200 kPa and 0.65 V, the total Pt content of the MEAs in the stack would be only 11.3 grams.

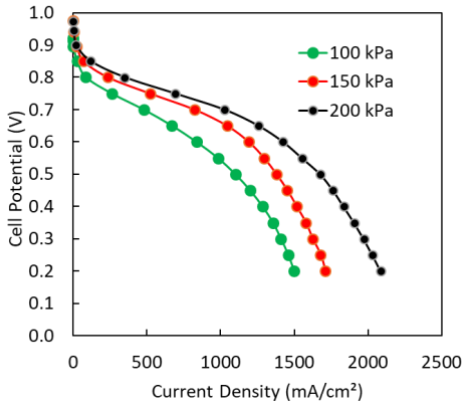

Figure 1. Fuel Cell polarization curves for a PtCo/C fiber cathode (0.096 mg_{Pt}/cm^2) and a Pt/C fiber anode (0.019 mg_{Pt}/cm^2). Data were collected at 80 °C and 100% RH with hydrogen and air flowrates of 125 sccm and 500 sccm, respectively.

Table 1. Power Densities at Three Different Backpressures from the Polarization Curves Shown in Figure 1.

Back Pressure (absolute)	Power at 0.65V (mW/cm²)	Max Power (mW/cm²)
100 kPa	435	550
150 kPa	677	713
200 kPa	817	854

Another example of a fiber mat electrode is shown in Figure 2. Here, the nanofiber cathode was TKK PtCo/C at 0.1 mg_{Pt}/cm^2 and the nanofiber anode was Johnson-Matthey HiSpec 40% Pt/C at 0.1 mg_{Pt}/cm^2. H_2/air fuel cell tests were carried out at 95°C and 70% RH at a backpressure of either 150, 200, or 250 kPa (abs). From the pol curves, rated power was determined for this MEA. Rated power is defined by the following equation

$$Q/\Delta T = \frac{\left[Stack\ Power(90kW) \times (1.25 - V@rated\ power)/V@rated\ power\right]}{Stack\ coolant\ outlet\ temperature - ambient\ temperature(40°C)}$$

where Q/ΔT is fixed at 1.45. According to the above equation, the rated power at 95°C is the measured power density at a cell voltage of 0.663 V. Values of rated power at 95°C and 100, 200, and 250 kPa backpressure are listed in Table 2 for the MEA with a PtCo/C fiber cathode and Pt/C fiber anode.

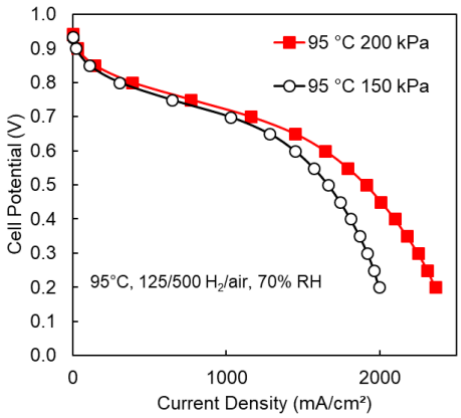

Figure 2. H_2/air fuel cell polarization curves for a nanofiber mat MEA with a PtCo/C cathode and a Pt/C anode.

Table 2. Values of Rated Power at 95°C for the MEA from Figure 2.

Rated Power at 95°C and 0.663V	
Backpressure	**Power Density (mW/cm²)**
150 kPa	802
200 kPa	906
250 kPa	1072

In Tables 3 and 4, performance data is given for three different nanofiber mat electrode MEAs, where the cathode catalyst was either Johndon-Matthey Pt/C, TKK PtNi/C, or TKK PtCo/C. The power density results were collected from H_2/air polarization curves at 80°C, 200 kPa_{abs} pressure, and 90% RH feed gases. The MEA was made with a Nafion 211 membrane. Gas flow rates were 4/8 L/min for H_2/air. The cathode binder was a mixture of

Nafion + poly(acrylic acid). All cathodes and anodes had a Pt loading of 0.1 mg_{Pt}/cm^2. As can be see, the two Pt-alloy cathodes worked best, in terms of highest power density.

Table 3. Power Densities for Nanofiber Mat Electrode MEAs at at 80 °C, 200 kPa_{abs} pressure, and 90% RH.

Cathode Catalyst	Power density at 0.65 V (mW/cm^2)	Max Power Density (mW/cm^2)
Pt/C (J-M HiSPEC 400)	579	704
PtNi/C (TKK TECNiE52)	840	988
PtCo/C (TKK36E52)	803	1,034

Table 4. Electrochemical Surface Area and Oxygen Reduction Reaction Mass Activity for the Fiber Mat MEAs in Table 3.

Cathode Catalyst	ECSA (m^2/g)	Mass Activity (mA/mg_{Pt})
Pt/C (J-MHiSPEC 400)	45	160
PtNi/C (TKK TECNiE52)	46	266
PtCo/C (TKK36E52)	48	270

Fuel cell polarization results before (beginning-of-life) and after (end-of-test) a metal dissolution accelerated stress test are shown in Table 5. To assess cathode durability, the MEA was subjecgted 30,000 square-waverf voltage cycles from 0.6 V to 0.95 V. Nanofiber electrode MEAs with a PtCo/C cathode (0.1 mg_{Pt}/cm^2 TKK TEC36E52) and a Pt/C anode (0.1 mg_{Pt}/cm^2 Johnson-Matthey HiSPEC 400) were tested where the cathode fiber bibnder was either neat Nafion (made from Nafion + polyethylene oxide fibers) or Nafion + poly(acrylic aid). Although the initial (beginning-of -ife) power was higer with the neat Nafion binder, the percent power loss was much less when the cathode binder wa a mixture of Nafion and poly(acrylic acid).

Table 5. Initial (beginning-of-life) and end-of-test power density results for a metal dissolution accelerate stress test (30,000 square wave voltage cycles from 0.6 to 0.95 V).

	Beginning-of Life	End-of-Test
% Nanofiber Binder	Max Power (mW/cm^2)	Max Power (mW/cm^2)
Nafion + Poly(acrylic acid)	759	695
Nafion	1132	777

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