

V.F.19 Engineered Low-Pt Catalyst Layers

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Project End Date: September 30, 2015

Overall Objectives

- Overcome the “unaccounted” low-Pt loading loss in fuel cell performance by tailoring the topology of the ionomer within an otherwise conventional catalyst layer
- Establish through modeling the theoretical underpinnings and validity of the approach

Fiscal Year (FY) 2015 Objectives

- Develop the techniques necessary to achieve the desired ionomer topologies in catalyst layers formed by conventional ink processing
- Demonstrate recovery of the “unaccounted” performance loss in 0.05 mg Pt/cm² 50 cm² membrane electrode assemblies (MEAs) by comparison with commercial low-Pt MEAs using side-by-side testing

Technical Barriers

This project addresses the following technical barriers from the Fuel Cells section of the Fuel Cell Technologies Office Multi-Year Research, Development, and Demonstration Plan:

- (B) Cost
- (C) Performance

Technical Targets

The technical target that reflects the catalyst layer development effort is shown in Table 1.

TABLE 1. Technical Targets for Transportation Applications Relevant to this Project

Metric	Units	DOE 2020 Target	Project Status
PGM Total Loading	mg PGM/cm ²	0.125	0.05 (cathode only)

PGM—Precious Group Metals

FY 2015 Accomplishments

- The project team modeled the idealized catalyst layer configuration of ionomer nanofibers with thin ionomer films coating catalyst agglomerates. The modeling predicts that incorporating ionomer nanofibers significantly increases fuel cell performance.
- Two separate high-temperature processes for post-processing of electrospun Nafion[®] nanofibers for increased durability and insolubility were developed.
- Nafion[®] coated multi-walled carbon nano-tubes (MWCNTs) as a surrogate for ionomer nanofibers were used to prepare 50 cm² MEAs with high and low thin film ionomer compositions. The unoptimized latter showed performance approaching that of commercial low-Pt MEAs.



INTRODUCTION

When conventional fuel cell MEA cathode Pt loadings are below about 0.1 mg Pt/cm², a drop-off in performance occurs, substantially more so than can be ascribed to simple kinetic losses. This negatively impacts efforts to lower Pt loadings to, say, 0.05 mg Pt/cm² and still maintain high fuel cell performance. While the reasons are not entirely clear [1], this “unaccounted” loss appears to be primarily manifested as an elevated oxygen transport resistance. One explanation is that the oxygen flux through any ionomer film overlying the catalyst must increase as the amount of catalyst is decreased, resulting in the greater mass transfer barrier. As such, decreasing the ionomer content in conventional-style catalyst layers such that only a very thin film coats the catalyst could alleviate the difficulty by minimizing the transport barrier. However, simply decreasing the amount of Nafion[®] in the ink formulation is not sufficient as any improvement in reactant transport is negated by the decrease

in ionic conductivity through the catalyst layer. Further, a minimum of ionomer is needed to provide sufficient robustness for conventional catalyst layer ink processing and cell assembly. Consequently, the intention of this project is to engineer the topology of the catalyst layer ionomer to provide low-Pt catalyst layers with low oxygen transport resistance, high bulk conductivity, and structural integrity.

APPROACH

The general approach in this project is to configure the distribution of the ionomer in the catalyst layer to provide the desired combination of properties described above. It is proposed that the optimal configuration consists of two separate “phases” of ionomer in the catalyst layer, a very thin first one coating the catalyst surfaces to provide local conductivity with a minimal oxygen transport barrier, and a second phase of a solid ionomer network to provide bulk ionic conductivity and structural integrity (Figure 1a). Modeling explores the validity of the approach and provides insight into the effects of the relative amounts of the two phases.

To a certain extent, realizing the very thin first ionomer “phase” (light blue in Figure 1a) can be accomplished by adding only enough ionomer to the ink formulation to form a thin film over the catalyst surface area, but the dispersion of this limited amount of ionomer becomes critical for maximizing the electrochemical surface area (ECSA). Consequently, a subsidiary effort in the project is to investigate the synthesis of carbon supports doped with heteroatoms beyond nitrogen to provide greater wettability and corrosion resistance.

The very thin ionomer films will not alone provide sufficient bulk ionic conductivity to the catalyst layer, nor a dried ink layer that will remain intact during processing and assembly. A separate second phase of ionomer in the form of a stable highway network is included to provide

ionic connectivity to catalyst agglomerates and throughout the catalyst layer, shown as medium blue fibers in Figure 1a. Ideally, this solid ionomer addition would have a high-aspect ratio to help with connectivity and binding the catalyst layer together; possibilities include nanofibrillated fibers, fibers formed in the nanopores of sacrificial scaffolds, or electrospun nanofibers. The first two result in discrete fiber “powders” that can be added directly to the catalyst ink, whereas the continuous electrospun fibers formed as a mat need to be milled for ink processing. However, fibers formed by low-temperature recasting such as electrospinning are fragile. Consequently, durability and insolubility, necessary for processing and withstanding the catalyst layer operating environment, will be need to be improved significantly. Otherwise, dissolution, deformation, and compaction result in a low-porosity and densified catalyst layer with poor reactant transport. For conventional catalyst layer ink processing, the toughened electrospun nanofibers are powdered to form small fiber networks for inclusion into the ink (though the formation of uniform dispersions is not without challenges). If successful, a sturdy and durable catalyst layer with high bulk ionic conductivity and low oxygen transport resistance is formed by conventional ink processing. MEAs fabricated in this manner are combined with commercial gas diffusion layers (GDLs) specifically designed for low-Pt loadings for fuel cell testing and side-by-side comparisons with baseline commercial MEAs using similar catalysts, GDL's and hardware.

RESULTS

A multiscale model of the approach has been developed to investigate the effect of ionomer nanofiber-thin film distribution on fuel cell performance. Figure 1b depicts the model configuration of the cathode catalyst layer (CL) with the components situated between the membrane and the GDL. H^+ is transported from the membrane through ionomer nanofibers (blue) to ionomer films (red), ultimately arriving at Pt sites around agglomerate cores. Oxygen diffuses through the red thin films in Figure 1b to reach catalyst sites. The volume fractions of catalysts, ionomers, and pores in the CL are 0.36, 0.34, and 0.30, respectively. The GDL porosity is 30% and the CL and GDL thicknesses are 10 μm and 50 μm , respectively. The fraction of ionomer in the nanofiber phase is varied from 0% (thin film only) to 90%. The radius of agglomerate cores is 50 nm and the thin film is 5 nm in thickness when no nanofiber phase is present. Assuming the ionomer-wetted surface area of the carbon phase is constant, the thin film thickness, and hence oxygen transport barrier, varies proportionally with the total volume fraction of ionomer film in the CL. The H^+ conductivities employed here are ionomer-film = 10^{-3} S/cm and nanofiber = 10^{-1} S/cm, reflecting the lower value observed in thin ionomer films [2]. Lastly, the O_2 diffusion coefficient through the thin film

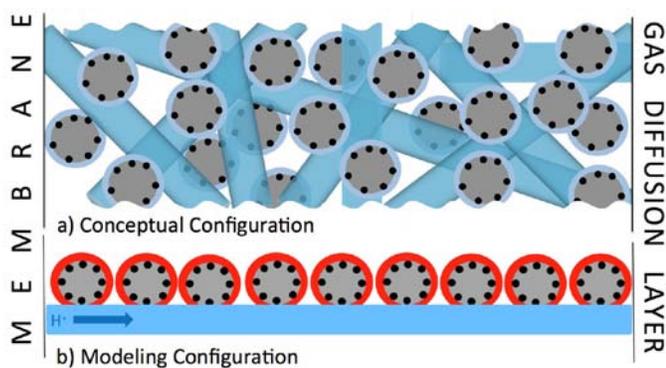


FIGURE 1. (a) The conceptual catalyst layer configuration of thin ionomer film coated agglomerates covering ionomer nanofibers, (b) configuration used for modeling, here the thin-film ionomer is in red

= $9.7 \times 10^{-6} \text{ cm}^2/\text{s}$ and the bulk O_2 concentration in the CL macropores is $0.005 \text{ mol}/\text{m}^3$.

Figure 2 shows the color-graded distributions of ionic potential of the CL ionomer for scenarios with 10%, 70%, and 90% nanofiber (with the balance comprising the thin film) with the ionic potential fixed at 0.4 V at the membrane interface. With high fiber contents, the drop in fiber ionic potential further away from the membrane is relatively minor, but this benefit is counteracted by increased potential drops in the ionomer films around the (unseen) agglomerates as the films become thinner (variations in film thicknesses not depicted). Since the film ionic potential is a reasonable proxy for the oxygen reduction reaction rate, the far sides of the agglomerates from the fiber are relatively inactive in the 90% case. In the 10% case, the entire periphery of each individual agglomerate contributes fairly equally, but those further away from the membrane less so. The 70% case is a compromise of the two extremes; each agglomerate contributes roughly equally and the potential drop around the agglomerate periphery is not severe.

Figure 3 depicts a series of fuel cell polarization curve simulations with the nanofiber content varied from 0 to 90% of total ionomer. Increasing the second phase nanofiber ionomer content significantly improves performance, with the maximum current densities at 0.6 V occurring with 50–60% nanofiber ionomer contents (Figure 3 inset). At 50% content and below, the oxygen diffusion tangentially through the ionomer thin film is the rate-limiting transport mechanism. At 60% and above, H^+ conduction through the thin film is rate-limiting, consequently, the maximum

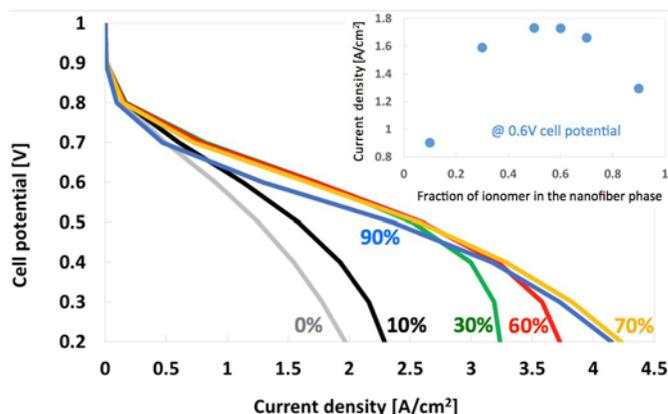


FIGURE 3. Polarization curve simulations for catalyst layers with nanofibers ranging from 0 to 90% of the total ionomer content. Inset depicts the current densities at 0.6 V as a function of nanofiber content.

current density occurs where the two limitations are about equal. While the modeling reflects an idealized structure (e.g., all nanofibers in the z-direction, all agglomerates immediately adjacent a nanofiber, etc.), it clearly indicates the potential for substantially increasing CL performance. The nanofibrillation of Nafion® did not produce high-aspect ratio structures, consequently efforts focused on electrospinning to produce precursor mats for subsequent milling to provide a powder for the catalyst layer inks. Nafion® was readily electrospun provided the solution contained $\leq 0.1\%$ PEO, unfortunate but necessary to provide phase continuity for the electrostatically induced drawing of the fibers. A more severe hindrance was that the essentially low-temperature recast

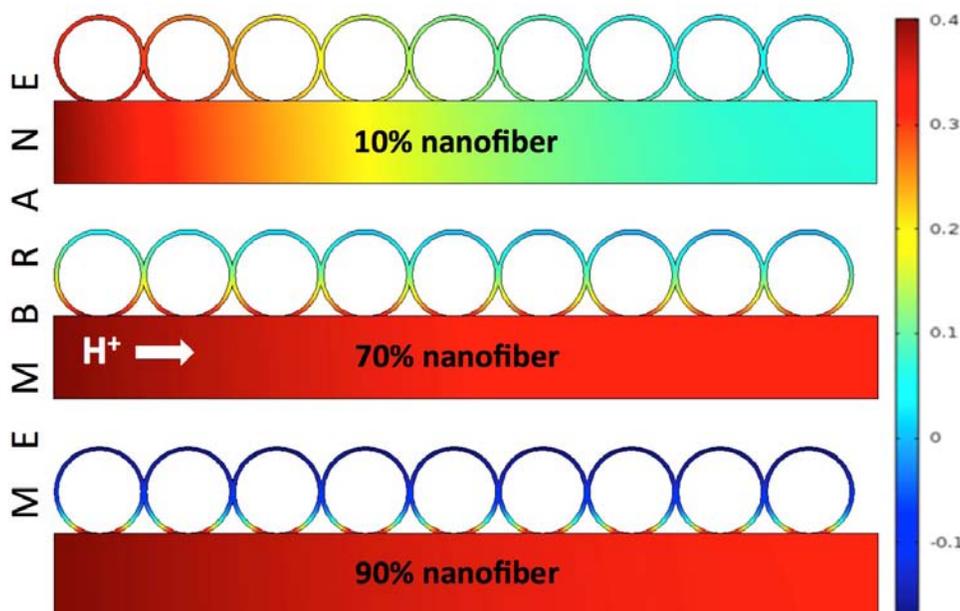


FIGURE 2. Ionomer ionic potential distributions within the thin films surrounding the (unseen) agglomerates and the bulk phase nanofibers for 10%, 70%, and 90% nanofiber ionomer content

electrospun ionomer fibers were both physically fragile and easily redissolved, of concern for withstanding the rigors of ink processing and the operating catalyst layer. The as-spun Nafion[®] quickly dissolved in solutions typically used for catalyst inks and even fibers annealed at 120°C succumbed.

The initial lack of durable and insoluble fibers stimulated an alternate attempt to demonstrate the proposed ionomer topology. MWCNTs coated with high-temperature recast Nafion[®] [3] were used as a surrogate for the neat ionomer nanofibers. MEA inks were prepared with standard 20%Pt-XC72 catalysts, surrogate Nafion[®]/MWCNT fibers, and either low or high solubilized Nafion[®] levels. The fuel cell performances of 50 cm² MEAs with 0.05 mg Pt/cm² cathode loadings indicated that the high-solubilized Nafion[®] ink had a high ECSA but mediocre performance, and the low-solubilized content had a low ECSA but performance that nearly matched that of the commercial baseline MEA in side-by-side testing [4]. Improvements are expected provided stable nanofiber ionomers and improved thin film dispersions (to maximize ECSA/minimize film thickness) can be obtained.

In the side effort to improve ionomer (and catalyst) dispersions on carbon catalyst supports, phosphorus was added to nitrogen as heteroatom dopants as it increases surface energy and stability in supercapacitors [5]. Nanofibers from electrospun polyacrylonitrile + phosphoric acid (PA) solutions were pyrolyzed to obtain doped carbon supports. However, under inert pyrolysis gasses, PA suppressed N and increased O content. Using N₂ or NH₃ gas increased N but O was still high and NH₃ scavenged P at high temperatures. A combination of NH₃ at lower temperatures and N₂ at high maximized P and N content and significantly reduced O.

Returning to the main effort, approaches were pursued to increase nanofiber durability and solvent resistance. One method was to electrospin Nafion[®] solutions in the tetrabutylammonium form to impart thermoplasticity to the ionomer [6] and thus increase durability and crystallinity after thermal annealing. Indeed, post-spinning annealing substantially improves the properties, but at the risk of the fine thermoplastic fibers fusing into coarse structures. Annealing temperature is consequently critical. A more forgiving and higher temperature approach under development capitalizes upon the increased strength and insolubility imparted by high temperature casting of the ionomer [3]. Since high temperature electrospinning is impractical, the process here entails introducing a low volatility component into the electrospinning solution that is retained within the as-spun fibers (Figure 4a) and then removed in a high temperature “recasting,” resulting in some fiber fusion and cross-linking (Figure 4b). If too much agent is used, the high temperature recast again dissolves the fibers into featureless films. With the appropriate amount, fiber morphology is retained and easily handled robust veils

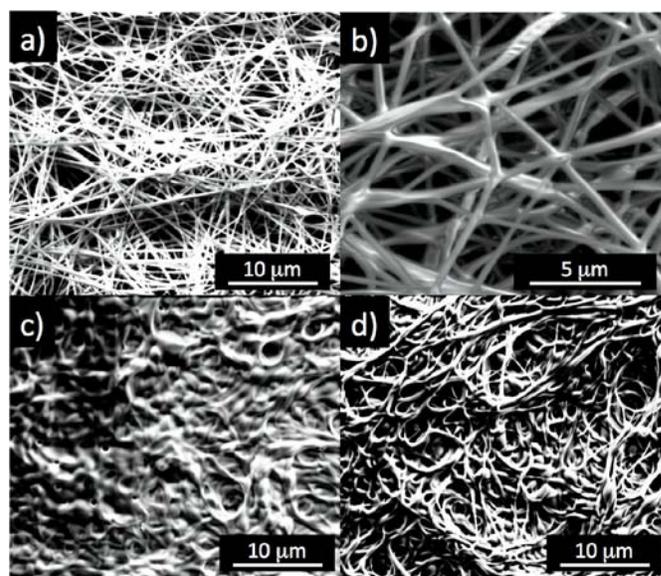


FIGURE 4. (a) As-spun ionomer nanofibers containing a recasting agent (b) Nanofibers after 250°C annealing (c) Milled and cast H⁺ nanofibers after heating in neat alcohols (d) Milled and cast H⁺ nanofibers after heating in alcohol, water, and ethylene glycol mixture

are formed. After protonation, the mats swell up in alcohols much like cross-linked superabsorbents, but dry again to pliable veils. Milling results in nanofiber suspensions for use in catalyst layer inks, however, solvents plus heating can still degrade the fibers. To test, suspensions were formed and heated in various ink solvent mixtures without catalysts so that cast films can be imaged to evaluate fiber integrity. Figure 4c of one such casting shows substantial dissolution after heating and stirring in neat alcohols, while Figure 4d depicts fibers that have remained intact using a solution also containing water and ethylene glycol (such convoluted and dense-packed morphologies are typical from casting milled suspensions).

CONCLUSIONS AND FUTURE DIRECTIONS

Modeling predicts that the engineered ionomer topology approach has the potential to significantly increase fuel cell performance. The ideal catalyst layer configurations have yet to be achieved, but even the non-ideal surrogates nearly matched commercial baseline MEAs. Success will hinge on the ability to attain the ideal ionomer topology and requisite durability. Before the end of the FY, the best ink formulations (high thin film dispersion and high rate of nanofiber survival) will be used to make a series of 50 cm² MEAs of varying nanofiber to thin film ratios to compare to commercial MEAs and the modeling results.

FY 2015 PUBLICATIONS/PRESENTATIONS

1. “Next Generation Catalyst Layers,” M.S. Wilson and H.-S. Shiau. Oral presentation to the 8th Meeting of the Transport Modeling Working Group, May 19, 2015, Lawrence Berkeley National Laboratory, Berkeley, CA.
2. “Engineered Low-Pt Catalyst Layers,” M.S. Wilson, A.Z. Weber, H.-S. Shiau, Y.S. Kim, D. Langlois, K.S. Lee, R. Mukundan, and K. More. Poster presentation at the DOE Hydrogen and Fuel Cells Program Annual Merit Review, Washington, DC, June 8–12, 2015.

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